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METODOLOGÍA BÁSICA PARA LA DETERMINACIÓN DE CONTAMINANTES PRTR-ESPAÑA EN EL SECTOR DEL REFINO DE PETROLEO

Fecha de elaboración: 29 de febrero de 2008

Fecha de actualización (Anexo 7): 31 de julio de 2014

METODOLOGÍA BÁSICA PARA LA DETERMINACIÓN DE CONTAMINANTES PRTR-ESPAÑA EN EL SECTOR DEL REFINO DE PETRÓLEO

Es el objeto del presente documento revisar, actualizar y ampliar la metodología de determinación de contaminantes que en su momento fue desarrollada para satisfacer las exigencias de información requeridas por el registro EPER. Como consecuencia de la superación de dicho registro por el nuevo E-PRTR, se procede en este documento a presentar una metodología que, partiendo como base de la anteriormente preparada, se completará para dar cumplimiento a los nuevos requisitos solicitados por PRTR-España.

La naturaleza del registro E-PRTR es en todo similar a la de EPER, aunque aporta una serie de novedades respecto a su antecesor que hacen que a pesar de seguir siendo válido el formato de la metodología inicial, ésta haya de ser parcialmente modificada y ampliada.

Por ello, la metodología que aquí se presenta ha perseguido mantener el concepto de “manejabilidad” con que se desarrolló en el caso de EPER, continuándose por tanto con la naturaleza modular del trabajo, el cual se ha estructurado en modo de ANEXOS.

Así, se han desarrollado ANEXOS independientes por cada uno de los aspectos considerados en PRTR-España de manera que en cada uno de ellos se han introducido todas aquellas herramientas necesarias para la cuantificación de los contaminantes recogidos en las sublistas E-PRTR que puedan afectar al sector del refino:

1(a) Refinerías de Petróleo y Gas (Sector de la Energía)

1(c) Centrales térmicas y otras instalaciones de combustión(1) (Sector de la Energía)

Es por esto que se ha pretendido que la presente introducción constituya un índice de contenidos que permita, de una manera concisa y clara, conocer la totalidad del documento potenciando así la funcionalidad del mismo.

Seguidamente, se relacionan los distintos ANEXOS que integran la metodología:

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(1) De más de 50 MW_{th} (potencia térmica total).

ANEXO 1: NUEVOS REQUERIMIENTOS INTRODUCIDOS POR PRTR-ESPAÑA

La finalidad de este ANEXO es definir los nuevos requerimientos que PRTR-España introduce, señalando las principales diferencias y novedades que comporta en referencia a EPER. Así, este ANEXO recoge de manera sumaria las novedades en el ámbito de aplicación, la inclusión de las emisiones al suelo, la transferencia de residuos, las emisiones accidentales y la descripción de la metodología de medición/cálculo.

ANEXO 2: CONTAMINANTES ATMOSFÉRICOS

En él se recoge la metodología específica de cuantificación de contaminantes al medio atmosférico. Consta de dos partes:

- Observaciones Generales: donde se explica el fundamento y las generalidades del sistema de Fichas adoptado para presentar la totalidad de las metodologías estudiadas.

- Fichas: donde se recoge explícitamente la descripción, cuantificación y observaciones propias de cada una de las metodologías planteadas.

ANEXO 3: CONTAMINANTES HÍDRICOS

En él se recoge la metodología específica de cuantificación de contaminantes al medio hídrico. Dada la particular naturaleza de estas emisiones (la descarga de contaminantes tiene lugar a través de muy pocos puntos, perfectamente definidos y concretados) se entiende que la metodología específica sea completamente independiente de la desarrollada para el medio atmosférico.

En concreto, la cuantificación de contaminantes se basará en determinaciones analíticas, atendiendo al hecho de lo escaso de la existencia de factores de emisión para el medio hídrico y la igualmente escasa fiabilidad de los mismos. Por otro lado, el desarrollo de programas de vigilancia ambiental sucesivamente más complejos ha dado lugar a la disponibilidad de nuevas medidas que, junto con una profundización en el estudio de aquellas sustancias que por su naturaleza pueden excluirse del reporte, ha constituido el núcleo de este ANEXO 3 que aquí se presenta.

ANEXO 4: RESIDUOS

El ANEXO 4 se dedica al análisis de otra de las novedades que PRTR-España conlleva, como es la necesidad de informar en materia de residuos. En concreto, el ANEXO se ha estructurado en dos apartados independientes en función de las nuevas necesidades. El primero de ellos se dirige a sentar las bases que permitan informar acerca de la capacidad de transferir residuos del Complejo, mientras que el segundo se presenta con el fin de desarrollar las obligaciones del titular en cuanto a su responsabilidad en materia de transferencia directa de contaminantes al suelo.

ANEXO 5: ACCIDENTES

Al igual que el anterior, éste es un ANEXO que se prepara para dar respuesta a otra de las novedades introducidas por PRTR-España, las emisiones accidentales. Así, el titular de un Complejo, siempre que disponga información de ello, tiene la responsabilidad de cuantificar las emisiones bien al medio atmosférico, bien al medio hídrico, que tengan lugar como consecuencia de situaciones no deliberadas, habituales u ocasionales.

ANEXO 6: EXCLUSIONES

En este Anexo se presentan justificadamente aquellos contaminantes que, atendiendo a su naturaleza y origen, han sido excluidos del alcance de la presente metodología a pesar de figurar en las sublistas antes mencionadas.

Estos ANEXOS contienen la metodología propiamente dicha, pero con vistas a alcanzar el máximo nivel de integración posible, se ha incluido una serie de documentos (incluidos en el CD adjunto) que han constituido una fuente de gran importancia para la generación de la metodología. Dichos documentos son:

ANEXO 7

Documentación de CONCAWE (Conservation of Clean Air and Water in Europe, asociación europea de compañías de petróleo para el medio ambiente, la salud y la seguridad en el refino y la distribución) para factores de emisión. Se incluye:

- Air pollutant emission estimation methods for E-PRTR reporting by refineries (report no. 1/09).

ANEXO 8

Documentación EEA (European Environment Agency) para factores de emisión. Se incluyen los siguientes capítulos del EMEP/CORINAIR Emission Inventory Guidebook-2006:

- Combustión in energy & transformation industries

B111	Combustion Plants as Point Sources
B111(S1)	Particulate emissions from smaller Combustion Plants (<50 MWth)
B111(S2)	Particulate emissions from large Combustion Plants (>50 MWth)
B111(S3)	Particulate emissions from gas turbines and internal combustion engines
B112	Combustion Plants as Area Sources
B114	Gas Turbines

- Petroleum and/or gas refining plants

B132	Combustion Plants ≥ 50 and < 300 MW (boilers)
	Combustion Plants < 50 MW (boilers)
	Stationary Engines
B136	Process Furnaces

- Processes in petroleum industries
  B411 Petroleum Products Processing
  Fluid Catalytic Cracking
  B414 Storage and Handling of Products in Refinery

- Waste incineration
  B923 Flaring in Oil Refinery

- Other waste treatment
  B9101 Waste Water Treatment in Industry
  Waste Water Treatment in Residential/Commercial Sectors

ANEXO 9

Documentación EPA (US Environmental Protection Agency) para factores de emisión. Se incluye:

- Aplicación FIRE (Factor Information Retrieval Data System). Versión 6.25.

- AP-42. Compilation of Air Pollutant Emission Factors. Capítulos 1.3 (combustión de fuel oil), 1.4 (combustión de gas natural), 1.5 (combustión de LPG) y 5.1 (refino de petróleo).

ANEXO 10

Documentación NPI (National Pollutant Inventory) de Australia para factores de emisión. Se incluye:

- Emission Estimation Technique Manual for Petroleum Refining.

ANEXO 11

Documentación referente a compuestos orgánicos volátiles. Se incluye:

- Metodología de estimación del número de elementos para las distintas unidades de Refinería.

  - A model for evaluation of Refinery and Synfuels VOC Emission Data. EPA Nº 68-02-3926. 1.984

  - “Locating and Estimating Air Emissions from Sources of Benzene”. EPA-454/R-98-011. 1998. Cap 6. Páginas 6-22, 6-23.

- Breve descripción de un programa LDAR (Leak Detection and Repair).

- Método 21 de US EPA para la determinación de fugas de compuestos orgánicos volátiles.

ANEXO I

NUEVOS REQUERIMIENTOS INTRODUCIDOS POR PRTR-ESPAÑA

1. INTRODUCCIÓN

La Directiva 96/61/CE del Consejo, de 24 de septiembre de 1996, relativa a la prevención y al control integrado de la contaminación (IPPC), estableció en sus Artículos 15 y 19 la exigencia a los Estados miembros de desarrollar un inventario de las principales emisiones y fuentes responsables. Dicha exigencia se concretó en la Decisión 2000/479/CE de 17 de julio de 2000, en virtud de la cual se fijó la necesidad de realizar el Inventario Europeo de Emisiones (EPER).

En enero de 2006, el Parlamento Europeo y el Consejo aprobaron el Reglamento 166/2006 relativo al establecimiento de un registro europeo de emisiones y transferencia de contaminantes (E-PRTR). Dicho registro amplía los requisitos del EPER, incorporando nuevas sustancias contaminantes, así como una serie de exigencias adicionales en cuanto al alcance de la información a suministrar.

En España el Real Decreto 508/2007, de 20 de abril, por el que se regula el suministro de información sobre emisiones del Reglamento E-PRTR, dicta normas que complementan dicho reglamento. Dicho Real Decreto se ha visto posteriormente modificado por el Real Decreto 812/2007, de 22 de junio, sobre evaluación y gestión de la calidad del aire ambiente en relación con el arsenio, cadmio, mercurio, níquel y HAP's.

2. OBJETIVOS

Se redacta el presente documento con la intención de expresar con la máxima concreción posible, las principales novedades aportadas por PRTR-España sobre las directrices previamente establecidas por la Unión Europea a través del ya superado registro europeo de emisión de contaminantes (EPER).

Por tanto, es el objeto de esta memoria señalar exclusivamente aquellos matices diferenciadores entre ambos Registros destacando las nuevas obligaciones que se derivan para los titulares de las instalaciones afectadas, sin entrar en consideraciones adicionales como las propias de las actuales necesidades derivadas de EPER.

3. ANÁLISIS DE REQUERIMIENTOS DE PRTR-ESPAÑA. NOVEDADES INTRODUCIDAS

1. Ámbito de aplicación

En primer lugar, debe comenzarse por señalar cómo las actividades afectadas que puedan estar relacionadas con el sector del Refino han visto incrementadas significativamente el número de contaminantes del que debe informarse(1), tal y como se muestra en el siguiente cuadro:

TABLA 1
NÚMERO DE SUSTANCIAS A INFORMAR

Actividad	Emisiones al aire			Emisiones al agua		
	EPER	E-PRTR	PRTR-España(1)	EPER	E-PRTR	PRTR-España(1)
Refinerías de petróleo y gas	18	22	29	17	26	44
Centrales térmicas y otras instalaciones de combustión (>50 MW_{th})	16	25	32	14	19	37

(1) En España, el Real Decreto 508/2007 amplía, respecto a E-PRTR, el número de sustancias de las que hay que informar.

Tal y como recoge la Tabla anterior, como actividades se han considerado: *1(a) Refinerías de petróleo y gas y 1(c) Centrales Térmicas y otras instalaciones de combustión*, actividades propias de los Complejos industriales y objeto del presente documento.

Cada uno de los Complejos afectados, además de informar sobre sus emisiones y operaciones de transferencia de contaminantes, debe notificar una serie de información general de la propia Refinería relativa a la identificación de actividades, producción y perfil ambiental, tal y como se explicita en el Anexo III del Real Decreto 508/2007.

2. Inclusión de las emisiones al suelo

Una de las principales novedades que introduce E-PRTR es la obligación de comunicar las emisiones al suelo, para lo cual se recoge una lista de 61 contaminantes de los que es preciso informar. Estos contaminantes se incrementan en 18 más en base al Real Decreto 508/2007. No obstante, esta obligación sólo se circunscribe a dos operaciones muy concretas como son:

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(1) Existen algunas diferencias considerando los contaminantes ya incluidos en EPER. Así, el umbral para dioxinas y furanos se ha dividido por 10, pasando de 0,001 a 0,0001).

- Tratamiento en medio terrestre de residuos (por ejemplo, biodegradación de residuos líquidos o lodos en el subsuelo, etc): Código D2 del Anejo 1 de la Orden MAM/304/2002. Como cuestión de interés se señala la exclusión del landfarming de las técnicas consideradas D2 en base a que la propia "Guía para la implantación del E-PRTR" recoge en su apartado 1.1.8.3 "Emisiones al suelo" lo siguiente: "*El extendido de fangos y estiércol se consideran operaciones de valorización, y por tanto, no deben comunicarse como emisiones al suelo".*

- Inyección en profundidad (por ejemplo, inyección de residuos bombeados en pozos, minas de sal, fallas geológicas naturales, etc.): Código D3 del Anejo 2 de la Orden MAM/304/2007.

Es obligación del titular de la instalación que da lugar al residuo (no del gestor que se encargue de ello) informar de las cantidades de los 61 contaminantes antes citados que pudiesen encontrarse en el residuo producido.

Por último, se señala que a pesar de que la Guía para la Implantación del E-PRTR excluye explícitamente las emisiones accidentales al suelo, el Real Decreto 508/2007, de 20 de abril, por el que se regula el suministro de información sobre emisiones del Reglamento E-PRTR y de las autorizaciones ambientales integradas, incluye en su Anexo III un campo para emisiones accidentales en emisiones al suelo.

3. Transferencia de residuos(1)

El titular de un Complejo tiene la obligación de informar de las salidas (y entradas en su caso) de residuos peligrosos y no peligrosos siempre que éstas superen las 2 t/a y las 2.000 t/a respectivamente. De esta notificación se excluyen las operaciones antes consideradas de eliminación mediante tratamiento de suelo o inyección profunda (D2 ó D3).

Sólo se deberá informar de la cantidad total de toneladas de residuos peligrosos y no peligrosos generada, sin especiación alguna. No obstante en el caso sólo de residuos peligrosos, sí deberá distinguirse entre aquellos residuos que son trasladados finalmente a otros países(2) y los que no superan el ámbito nacional. Adicionalmente, se distinguirá entre las cantidades dedicadas a operaciones de recuperación (código R de la Orden MAM/304/2002) o a las de eliminación (código D de la Orden MAM/304/2002) (3).

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(1) También se incluye la transferencia de contaminantes en aguas residuales destinadas a tratamiento, aunque dicha actividad no es propia del Refino.

(2) En este caso se particulariza el reporte para cada destinatario final, el cual es señalado explícitamente.

(3) En el Anexo IV, dedicado a los residuos, se detalla qué información hay que suministrar en cada caso.

4. Emisiones accidentales(1)

Otra de las principales novedades que E-PRTR comporta es la obligación de discriminar y cuantificar individualmente las emisiones accidentales de contaminantes al aire o al agua, siempre y cuando "*se disponga de dicha información*". Como se ha comentado con anterioridad, esta obligación no se hace extensiva al suelo en principio, aunque el Real Decreto 508/2007 recoge un campo para esta información en la Tabla ejemplo de presentación de resultados de su Anexo III.

Se definen las emisiones accidentales como todas aquellas no deliberadas, habituales u ocasionales generadas o resultantes de desarrollos incontrolados durante el transcurso o el funcionamiento de las actividades del Complejo. Por tanto, se excluyen de esta definición las operaciones que si bien son ocasionales o extraordinarias, se desarrollan de forma controlada (como las paradas y puestas en marcha).

Esta distinción no implica que no haya que informar de las emisiones ocasionales, sino que no hay que distinguirlas de las habituales, de manera que por cada contaminante se presenten dos valores, el correspondiente a las emisiones totales y el propio de las situaciones accidentales.

Con la intención de facilitar la comprensión de lo anterior, a continuación se presenta un **ejemplo**(2) de notificación de emisiones a la atmósfera.

TABLA 2
COMUNICACIÓN DE INFORMACIÓN SOBRE EMISIONES A LA ATMÓSFERA

Emisiones a la atmósfera					
Contaminante		**Método**		**Cantidad**	
Nº A II	**Nombre**	**M/C/E**	**Método utilizado**	**T (total) (kg/año)**	**A (accidental) (kg/año)**
1	Metano	C	IPCC	521.000	-
3	Dióxido de carbono	M	ISO 12039:2001	413.000.000	-
21	Mercurio	M	EN 13211:2001	17,0	2,00

La Tabla anterior describe ejemplos de notificación de una instalación cualquiera. En este complejo se emiten, entre otras sustancias, dióxido de carbono (CO_2), metano (CH_4) y mercurio y compuestos. Los umbrales de las emisiones a la atmósfera de los tres contaminantes (100 millones kg/año para el CO_2, 100.000 kg/año para el CH_4 y 10 kg para el mercurio y compuestos) han sido superados. Las emisiones de CO_2 se han generado en condiciones normales de funcionamiento y se han medido utilizando el método estándar internacional

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(1) En el Anexo V, dedicado a las emisiones accidentales, se presenta una metodología para estimar las emisiones al aire y al agua como consecuencia de los posibles accidentes que pueden tener lugar en un Complejo de Refino.

(2) Ejemplo extraído de la *Guía para la implantación del E-PRTR.*

indicado. Las emisiones de CH_4 se han calculado de acuerdo con las directrices IPCC. En el caso de las emisiones totales de mercurio y compuestos, éstas se generaron en condiciones normales de funcionamiento (15,0 kg/año) y también por causas accidentales (2,00 kg/año). Estas últimas deben comunicarse como emisiones accidentales e incluirse en las emisiones totales (15,0+2,00=17,0 kg/año). Por otro lado, las emisiones normales se han obtenido en base a mediciones mientras que las accidentales se han estimado. Dado que la información sobre la mayor parte de las emisiones de mercurio y compuestos (15 kg) se base en mediciones, las emisiones totales de Hg y compuestos deben consignarse como datos medidos "M" y, además, indicar la metodología o estándar internacional utilizada para su determinación (en este caso la norma EN 13211:2001).

5. Metodologías de medición/cálculo

Como es sabido, en virtud de lo exigido por EPER, las cantidades informadas de cada contaminante deben ir acompañadas por un código que indica el origen del valor reportado (medición -M-, cálculo -C- o estimación -E-). De conformidad con PRTR-España, en caso de datos medidos o calculados, deberá indicarse además la metodología de medición o de cálculo, incorporándose así nuevos requisitos en relación a la gestión de datos y la garantía de calidad de la información suministrada. Por cada contaminante, sólo se indicará la metodología que ha dado lugar a la mayor cantidad de contaminante obtenida, en el supuesto de que se haya recurrido a diversos métodos para la cuantificación.

En el caso concreto de las mediciones, la *Guía para la Implantación del E-PRTR* recoge en su Apéndice 3 una lista de métodos de medición de emisiones a la atmósfera y al agua reconocidos a escala internacional.

En el caso de los métodos de cálculo, la citada Guía señala una serie de métodos igualmente reconocidos a escala internacional, así como otras metodologías válidas con su propio código (IPCC, PER, NRB, MAB,...) que pueden emplearse a la hora de calcular aquellas emisiones de contaminantes para los cuales no existen mediciones ni métodos de estimación fiables.

ANEXO II

METODOLOGÍA PARA LA DETERMINACIÓN DE CONTAMINANTES PRTR-ESPAÑA AL MEDIO ATMOSFÉRICO

FICHAS

En el presente ANEXO se presentan las fichas que han sido preparadas como desarrollo de la metodología de determinación de contaminantes PRTR-España al medio atmosférico. Las fichas en cuestión han partido de las que en su momento se prepararon para EPER. Dichas fichas se han actualizado, utilizando para ello nuevas fuentes de información. Así, se han localizado nuevos factores de emisión, se han discriminado nuevos focos, se han introducido nuevos contaminantes, etc.

Al igual que en el caso de EPER, este ANEXO contiene una gran cantidad de metodologías susceptibles de ser empleadas a la hora de proceder a la determinación de los contaminantes en cuestión, y sólo la común utilización de las mismas por parte de los Complejos afectados podría dar lugar a la obtención de resultados directamente comparables. En cualquier caso, las metodologías empleadas (mayoritariamente factores de emisión) proceden de referencias y bibliografía internacional de reconocida solvencia. Por ello, dicha documentación de carácter general difícilmente puede recoger las particularidades de cada instalación concreta, motivo por el cual se plantea la conveniencia de que cada centro desarrolle, en la medida de lo posible, metodologías propias asentadas en bases experimentales concretadas a cada Complejo. No obstante, ante la ausencia de avances significativos en este sentido, el grueso de la información que compone este ANEXO ha seguido basándose en los principios generales recogidos en las ya citadas referencias internacionales (CONCAWE, EMEP CORINAIR, EPA, …).

A continuación se mostrará una serie de **consideraciones generales** a las fichas desarrolladas que permitirá un apropiado manejo de las mismas.

1. Descripción general de la ficha

Cada ficha está compuesta por los siguientes campos:

- Identificación de la ficha (esquina superior derecha): Describe qué contaminante, fuente y método se recogen en la ficha (ver punto 2). Bajo esta identificación se recogen las sublistas donde se ha identificado al contaminante en cuestión (1.a: Refinerías de petróleo y gas, 1.c: Grandes instalaciones de combustión o R.D. 508/2007(1)).

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(1) Se recuerda que el R.D. 508/2007 incluye nuevos contaminantes pero no los asocia a ningún sector productivo concreto.

- Indicación expresa del contaminante, valor umbral de información pública (kg) y forma de expresión del resultado (kg de qué compuesto). Dicha información se localiza en la esquina superior izquierda.

- Indicación expresa de la fuente de emisión considerada: Se recoge explícitamente en el recuadro inmediatamente inferior al encabezado de la ficha.

- Metodología propiamente dicha: Se identifica en primer lugar el número ordinal que la describe ("metodología 1", p.ej.), siguiendo a continuación el código que según la *Guía para la implantación del E-PRTR* le corresponde.

  * El código **M** se emplea cuando el método utiliza datos obtenidos por observación directa de los procesos que se evalúan, en función de mediciones reales de las concentraciones de contaminantes existentes en una determinada vía de descarga. La letra M indica que los datos proceden de sistemas de control o monitorización de los procesos, en continuo o discontinuo. Esta letra también se utiliza si el cálculo de las emisiones anuales se basa en los resultados de mediciones puntuales discontinuas y de corta duración. Como novedad, PRTR-España recoge la necesidad de describir el método de medidas empleado en el que se basa la cuantificación realizada. Por tanto se recuerda que a la hora de consignar un valor para un contaminante determinado, en el caso de utilizarse el código M **habrá que indicarse adicionalmente el método de medida concreto empleado**. A modo orientativo, la *Guía para la implantación del E-PRTR*, en su apéndice incluye una lista de métodos de medición de emisiones a la atmósfera y al agua reconocidos a escala internacional. Dicho listado se adjunta al final de este ANEXO.

    Como puede observarse en el citado listado, existen contaminantes para los que no se recoge método alguno. Para el caso del empleo de métodos de medida no incluidos en el listado anterior (bien porque el contaminante carezca de ellos en la referencia de la Guía, bien porque existiendo metodología referenciada el Complejo haya utilizado otra distinta), a la hora de reportar el valor habría que indicar, a modo orientativo, alguno de estos códigos:

    - ALT: Método alternativo que el Complejo demuestra equivalente a normas internacionales.

    - CRM: Método equivalente, lo cual se ha demostrado mediante materiales de referencia certificados conforme a ISO 17025(1)/Guía ISO 33(2), y aceptado por la autoridad competente.

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(1) Conjunto de requisitos que debe cumplir un laboratorio de análisis o calibración para demostrar su competencia y capacidad de producción de resultados técnicamente válidos.

(2) Guía sobre el uso de materiales de referencia.

* El código **C** se utiliza cuando la metodología se basa en cálculos realizados con datos de la actividad (combustible utilizado, producción, etc) y factores de emisión. La letra C también se aplica en algunos casos en los que se emplean métodos de cálculo más complicados, utilizando variables como la temperatura, la radiación global, etc. Otro caso de aplicación de este código son los cálculos realizados por balance de masas. Además, se utiliza este código si el método de cálculo de emisiones se basa en referencias publicadas. Al igual que en el caso anterior (mediciones, código M), en el caso de que la cuantificación se realice a través de cálculos (C), también se hace necesaria la identificación/descripción del método de cálculo concreto empleado. Así, la *Guía para la implantación del E-PRTR* recoge una serie de códigos que pueden emplearse a la hora de informar. En concreto se pueden citar:

- MAB: código que identifica la cuantificación a través del empleo de balances de masa.

- SCC: método de cálculo específico del sector a nivel europeo, desarrollado por expertos en el sector y notificado a la Comisión Europea y a la Agencia Europea del Medio Ambiente. Este código parece apropiado para el empleo, por ejemplo, de factores de emisión publicados por CONCAWE.

- CEPE-ONU/EMEP: El empleo de este código es preceptivo en aquellos casos en los que la cuantificación se realice en base a la utilización de factores de emisión propios del inventario EMEP/CORINAIR.

- ETS: En el caso concreto de contaminantes gaseosos con efecto invernadero, se utilizará este código si se emplea para la cuantificación de las directrices para el seguimiento y comunicación de emisiones de gases de efecto invernadero en virtud del plan de comercio de emisiones.

- IPCC: Al igual que para los contaminantes del caso anterior (gases de efecto invernadero), se aplicará el código IPCC si la cuantificación procede del empleo de los métodos desarrollados según las directrices IPCC.

- OTH: Se reserva este código para el empleo de otros métodos distintos(1) a los contenidos en la Guía para la implantación del E-PRTR, como podría ser el caso de los factores de emisión propios desarrollados por un Complejo.

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(1) Además de los códigos presentados, la Guía recoge otros códigos que no han sido incluidos aquí por su difícil aplicación práctica:

- PER: En el caso de que la Administración prescriba un método concreto en licencias o permisos.
- NRB: En el caso en el que un texto o norma legal prescribe un método para un contaminante y Complejo concreto.

* El código **E** se basa en estimaciones no normalizadas, fundamentadas en hipótesis óptimas o en opiniones o experiencias de expertos, según métodos. Esta categoría también se aplica si se utilizan previsiones por falta de metodologías de estimación reconocidas o directrices de buenas prácticas, y en especial en ausencia de estándares o normas internacionales para la estimación de emisiones.

En la Tabla que se muestra a continuación se resumen los códigos anteriores, especificando cuáles de ellos se aplican a cada método de medición o cálculo(1) empleado.

Posteriormente en la ficha, se presentan los campos que describen la metodología propiamente dicha:

Descripción: Se define concisamente cuál es la metodología empleada, incluso explicitando valores concretos de factores de emisión a considerar (cuando sean de aplicación) y detallando la fuente bibliográfica de referencia.
Cuantificación: Se explicitan aquellas fórmulas o expresiones que, en función de los datos definidos en el campo anterior, derivan en la obtención cuantitativa de los valores de emisión.

Observaciones: Se recogen comentarios generales acerca de la metodología descrita, prestando especial interés a los índices de confianza o fiabilidad del método y estableciendo las oportunas comparaciones entre factores de emisión cuando la búsqueda bibliográfica realizada ofrece diversos valores.

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(1) Cuando los datos comunicados se basen en estimaciones ("E"), de acuerdo con el Reglamento E-PRTR, no es necesario comunicar el nombre del método utilizado.

TABLA 1
DESIGNACIÓN DEL MÉTODO UTILIZADO PARA LA DETERMINACIÓN DE EMISIONES/TRANSFERENCIAS FUERA DEL EMPLAZAMIENTO

Método utilizado para la determinación de emisiones/transferencias fuera del emplazamiento	**Designación del método utilizado**
Métodos de medición	
Normas o estándares a escala internacional	Designación abreviada de la norma relevante(1)
Método de medición prescrito con anterioridad por las autoridades competentes en una licencia o un permiso de explotación de dicho complejo (PERmit)	PER
Método de medición vinculante nacional o regional prescrito por un acto legal para un contaminante y el complejo en cuestión (National or Regional Binding measurement methodology)	NRB
Método de Medición Alternativo equivalente a las normas de medición CEN/ISO existentes (ALTernative measurement method)	ALT
Método de medición cuyo rendimiento está demostrado mediante Materiales de Referencia Certificados y aceptado por las autoridades competentes (Certified Reference Materials)	CRM
Otros métodos de medición (OTHer measurement methodology)	OTH
Métodos de cálculo	
Método de cálculo reconocido a escala internacional	Designación abreviada del método utilizado
· Según las directrices para el seguimiento y la comunicación de emisiones de GEI en virtud del Plan de Comercio de Emisiones	· ETS
· Desarrollado según las directrices IPCC	· IPCC
· Procedente de EMEP/CORINAIR	· CEPE-ONU/EMEP
Método de cálculo prescrito con anterioridad por las autoridades competentes en una licencia o un permiso de explotación de dicho complejo (PERmit)	PER
Método de cálculo vinculante nacional o regional prescrito por un acto legal para un contaminante y el complejo en cuestión (National or Regional Binding calculation methodology)	NRB
Método de balance de materia aceptado por las autoridades competentes (MAss Balance method)	MAB
Método de cálculo específico del sector a nivel europeo (Sector Specific Calculation) · CONCAWE	SSC
Otros métodos de cálculo (OTHer calculation methodology) · EPA · NPI (Australia)	OTH

(1) Ver APÉNDICE.

2. Numeración

Con la intención de desarrollar una sistemática de aplicación lo más general posible, se ha creado un conjunto de fichas para todos y cada uno de los contaminantes señalados en PRTR-España para los apartados correspondientes a refinerías de petróleo y gas, grandes instalaciones de combustión además de los nuevos contaminantes aportados por el R.D. 508/2007. La generación de fichas no se ha hecho extensiva a aquellos contaminantes que, por su origen o naturaleza, han sido justificadamente excluidos del alcance de este estudio conforme al análisis contenido en el Anexo VI.

Para la identificación de las fichas, se ha utilizado un sistema de tres valores separados por barras, situado en la esquina superior derecha de cada ficha. El primer valor hace referencia al contaminante en cuestión siguiendo el orden del Real Decreto 508/2007 (ej.: 1 para metano, 2 para monóxido de carbono, etc). El segundo valor hace referencia a la fuente de emisión considerada como origen (ej.: en el metano, el 1 es para la combustión en hornos y calderas, el 2 para turbinas, el 3 para motores, etc). Por último, el tercer valor identifica la metodología concreta propuesta en esa ficha para cuantificar el contaminante señalado por el primer valor y emitido por la fuente identificada a través del segundo.

3. Ordenación de las metodologías. Preferencias

Debe aclararse que ni el orden con el que se han presentado las diversas metodologías (para un mismo contaminante y fuente de emisión) ni el código que las acompaña hacen referencia a la precisión del método, al no existir una relación uniforme entre la metodología y la precisión de la cifra de emisiones resultantes. Es exclusivamente en el campo “observaciones” donde se muestra el índice de confianza del método propuesto o las precauciones a tener en cuenta para que el resultado de la metodología a aplicar sea de la máxima fiabilidad.

En cuanto a los criterios a seguir a la hora de elegir entre las metodologías propuestas (en aquellos casos en los que para un mismo contaminante y una misma fuente haya más de una), seguidamente se prioriza el criterio general que a juicio del equipo redactor de esta metodología debería seguirse de cara a conseguir unos resultados con la máxima exactitud. Así, con la finalidad anteriormente expresada se entiende que la jerarquía a tener en cuenta sería:

- Empleo de datos obtenidos de monitorización en continuo.

- Empleo de medidas puntuales.

- Empleo de balances de materia. Este tipo de metodología, para casos como el SO_2 procedente del empleo de combustibles cuyo consumo y composición se conoce con garantías, puede incluso considerarse como más apropiada que los resultados derivados de la monitorización.

- Empleo de factores de emisión propios, basados en la experiencia de cada Complejo.

- Empleo de factores de emisión[1] propios del sector del refino: Factores avalados por CONCAWE. A pesar de que CONCAWE no aporta índices de confianza para los factores que recoge en su documentación, es de entender que el estar incluidos en las referencias de la sociedad que agrupa a las principales Compañías del sector a nivel europeo es una garantía más que suficiente para las metodologías propuestas.

- Empleo de factores de emisión EMEP/CORINAIR. Dado el ámbito europeo de aplicación del registro E-PRTR, se considera en el siguiente nivel de esta clasificación el empleo de los factores propuestos por la European Environment Agency a través de su conocido Emission Inventory Guidebook[2].

- Empleo de factores de emisión EPA. Considerando la tradición de la agencia estadounidense del medio ambiente en el desarrollo de este tipo de información (información en la que en no pocas ocasiones se asientan las demás fuentes de consulta), se entiende razonable considerar este tipo de información como alternativa en la cuantificación de emisiones.

- Resto de metodologías.

4. Naturaleza de las metodologías

Es muy importante destacar que las metodologías aquí presentadas no son únicas ni excluyentes. Respecto a lo primero, dada la propia concepción del trabajo, la posibilidad de que aparezcan nuevas tecnologías o nuevos estudios que permitan desarrollar metodologías distintas a las aquí contenidas (o incluso corregir las ya existentes) es una variable real que está presente en este trabajo, siempre abierto a cualquier mejora razonada que pudiese surgir. En este sentido, la estructuración modular en base al sistema de fichas es una solución óptima al permitir integrar nuevas metodologías. De hecho, esta concepción ha sido la que ha permitido, partiendo de la base que en su momento se preparó para EPER, actualizar las fichas existentes e incorporar las correspondientes a los nuevos contaminantes.

En cuanto al concepto de exclusión, los diversos métodos preparados para un mismo contaminante y origen de emisión no han de entenderse necesariamente como alternativas incompatibles sino que en muchas ocasiones se podrán combinar entre sí para cubrir la totalidad de focos con un origen común.

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(1) En general, se prefiere el empleo de factores de emisión basados en el combustible empleado a los que conllevan la utilización de corrientes de proceso, por entenderse que los primeros se hallan más directamente relacionados, al menos en los procesos de combustión, con la emisión de contaminantes.

(2) De hecho, la “UNECE CORINAIR Guidance” se está revisando en la actualidad en base al report nº. 3/07 (“Air pollutant emission estimation methods for E-PRTR reporting by refineries”) de CONCAWE.

5. Referencias a cálculos de caudales

Existen diversas metodologías (aquellas que se centran en la medición en continuo) en cuyo campo “descripción” se hace referencia al cálculo del volumen de humos, citándose:

A. Combustión: “Orden de 26 de diciembre de 1995”(1).

B. Cracking catalítico: “el caudal de humos (Q, Nm^3/h) se determina mediante el empleo de correlaciones”.

En ambos casos, la determinación del volumen de humos se realiza a través de unos cálculos que se han querido obviar de las fichas (para dotarlas de mayor manejabilidad) y que seguidamente se reproducen:

A. Orden de 26 de diciembre de 1995

$V_{eh} = 0{,}314396 \cdot \%H + 0{,}088931 \cdot \%C + 0{,}033172 \cdot \%S + 0{,}007997 \cdot \%N -$
$- \quad 0{,}026424 \cdot \%O + 0{,}012113 \cdot \%H_2O$

$V_{es} = 0{,}209723 \cdot \%H + 0{,}088931 \cdot \%C + 0{,}033172 \cdot \%S + 0{,}007997 \cdot \%N -$
$- \quad 0{,}026424 \cdot \%O$

$h_D = 1 – 1/20{,}92 \text{ x } [V_{es}/V_{eh} \text{ x } (20{,}9 (1 – ha) - \% O_{seco} + \% O_{seco}]$

$V_g = V_{es} \text{ x } 20{,}9 / (20{,}9 - \% O_{seco})$

$V_{gh} = V_{es} \text{ x } 20{,}9/(20{,}9 - \% O_{seco}) \text{ x } 1/(1 – h_D)$

donde:

V_{eh} = volumen estequiómétrico de gases húmedos (Nm^3/kg combustible)

V_{es} = volumen estequiométrico de gases secos (Nm^3/kg combustible)

h_D = humedad media de los gases (tanto por 1)

h_a = humedad absoluta del aire (moles agua/moles aire seco, tanto por 1)

% O_{seco}= porcentaje de oxígeno (seco)

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(1) Esta Orden va a ser derogada por la que actualmente está en preparación para el desarrollo del Real Decreto 430/2004. No obstante, puesto que el cálculo que aparece en la Orden actualmente vigente no es más que un cálculo teórico para determinar el volumen estequiométrico de los gases, es previsible que la futura Orden, en lo que a dicho cálculo se refiere, se limite a reproducir el contenido de la actual.

%H, %C, %N, %O, %H_2O = porcentajes en peso, sobre bruto, de la composición del combustible consumido.

V_g= volumen de gases secos (Nm^3/kg) para las condiciones % O_{seco}

V_{gh} = volumen de gases reales (Nm^3/kg) para las condiciones % O_{seco} y h_D

B. Determinación de caudal de humos en cracking catalítico

$$Q = \frac{0{,}79 \times Q_1}{100 - \%O_2 - \%CO - \%CO_2 - \%SO_2}$$

donde:

Q = caudal de humos efluentes de la unidad, en base seca (Nm^3/h).

Q_1 = caudal de aire a la entrada de la unidad, en base seca (Nm^3/h). Se asume una composición del 79% (V) de N_2 y 21% (V) de O_2.

%O_2 = Porcentaje de O_2 en volumen en humos efluentes de la unidad.

%CO = Porcentaje de CO en volumen en humos efluentes de la unidad.

%CO_2 = Porcentaje de CO_2 en volumen en humos efluentes de la unidad.

%SO_2 = Porcentaje de SO_2 en volumen en humos efluentes de la unidad.

NOTA: Todos los parámetros en las mismas condiciones de referencia.

6. Índices de confianza. Análisis de la Incertidumbre

En muchas ocasiones, en el campo “observaciones” aparece una letra que representa el índice de confianza o fiabilidad para el empleo del factor de emisión propuesto. En concreto, para los factores procedentes de EPA AP-42, el significado de los índices es el siguiente:

TABLA 2
ÍNDICES DE CONFIANZA PARA FACTORES EPA

INDICE	CALIDAD	DESCRIPCIÓN
A	Excelente	El factor se desarrolla en base a estudios(1) (A y B) realizados en numerosas instalaciones del sector.
B	Sobre la media	El factor se desarrolla en base a un razonable número de estudios (A y B) en instalaciones. No se constata si las instalaciones estudiadas representan una muestra aleatoria del sector
C	Media	El factor se desarrolla en base a un razonable número de estudios (A, B y/o C) en instalaciones. No se constata si las instalaciones estudiadas representan una muestra aleatoria del sector.
D	Bajo la media	El factor se desarrolla en base a una pequeña cantidad de estudios (A, B y/o C) en instalaciones. Posiblemente, las instalaciones estudiadas no constituyen una muestra aleatoria del sector.
E	Pobre	El factor se desarrolla en base a estudios C y D. Posiblemente, las instalaciones estudiadas no constituyen una muestra aleatoria del sector.
U(*)	Sin determinar	El factor se desarrolla a partir de hipótesis no apoyadas en documentación que permita adjudicar un índice de los vistos anteriormente.

Fuente: Capítulo 4. Evaluating the Uncertainty of Emission Estimates. Emission Inventory Improvement Program (US EPA 1996)

(1) El tipo de estudio (tests) también lleva un índice de confianza aparejado. Ver Tabla 3.

(*) No aparece en la referencia anterior, pero sí en numerosas publicaciones EPA, como en los documentos “Locating and Estimating” o FIRE (Factor Information Retrieval Data System).

En la Tabla anterior se mencionan índices para el tipo de estudio realizado para el desarrollo del factor. En la Tabla 3 se presenta el significado de los mismos.

TABLA 3
ÍNDICES DE CONFIANZA PARA ESTUDIOS PARA DESARROLLOS DE FACTORES DE EMISIÓN (EPA)

INDICE	DESCRIPCIÓN
A	Tests desarrollados a través de metodologías bien fundadas y suficientemente detalladas para una adecuada validación
B	Tests desarrollados a través de metodologías generales, pero sin suficiente detalle para una adecuada validación
C	Tests desarrollados en base a metodologías nuevas o no contrastadas, o con carencias significativas de información
D	Tests desarrollados en base a métodos generalmente no aceptados, pero que sí pueden proporcionar un orden de magnitud para la emisión considerada

Fuente: Capítulo 4. Evaluating the Uncertainty of Emission Estimates.
Emission Inventory Improvement Program (US EPA 1996)

En cuanto a los factores de emisión cuya fuente bibliográfica ha sido “Libro Guía EMEP/CORINAIR”, no se han encontrado índices de confianza salvo para determinados contaminantes, tal y como se muestra en la Tabla 4, donde sólo se han mantenido las categorías SNAP más relacionadas con el trabajo aquí presentado.

TABLA 4
ÍNDICES DE CONFIANZA PARA FACTORES EMEP/CORINAIR

Categoría SNAP	SO_2	NO_x	VOC	CO	NH_3	HM/POP*
Instalaciones de combustión de Centrales térmicas, Cogeneración…	A	B	C	B	-	D
Combustión industrial	A	B	C	B	-	D
Procesos industriales	B	C	C	C	E	E

* Metales pesados y contaminantes orgánicos persistentes

Fuente: Apartado 4.3.3. “Default uncertainty ranges”. Good Practice Guidance for CLRTAP Emission Inventories 2004.
Part B General Methodology Chapters. EMEP/CORINAIR Emission Inventory Guidebook 2006.

Por último, en la Tabla 5 se definen por defecto los rangos de incertidumbre asociados a cada rango cualitativo (letra). Los rangos de incertidumbre se han obtenido de la “EU Guidance Report on Supplementory Assessment under EC Air Quality Directives”, en donde se han definido para aplicaciones en métodos de calidad del aire.

TABLA 5
DEFINICIÓN ÍNDICES DE CONFIANZA EMEP/CORINAIR

Puntuación	Definición	Rango de error típico
A	Estimación basada en un gran número de mediciones hechas a lo largo de un gran número de instalaciones, de forma que son totalmente representativas del sector.	10-30%
B	Estimación basada en un gran número de mediciones efectuadas a un gran número de instalaciones, de forma que representan a una gran parte del sector.	20-60%
C	Estimación basada en las mediciones efectuadas a un número reducido de instalaciones representativas, o juicio de ingenieros expertos basados en un número de hechos relevantes.	50-150%
D	Estimación basada en mediciones individuales o en cálculos de ingeniería derivados de un número de hechos relevantes.	100-300%
E	Estimación basada en círculos de ingeniería derivados simplemente de una serie de hipótesis.	Otro orden de magnitud

Fuente: Apartado 4.3.3. “Default uncertainty ranges”. Good Practice Guidance for CLRTAP Emission Inventories 2004.
Part B General Methodology Chapters. EMEP/CORINAIR Emission Inventory Guidebook 2006.

APÉNDICE

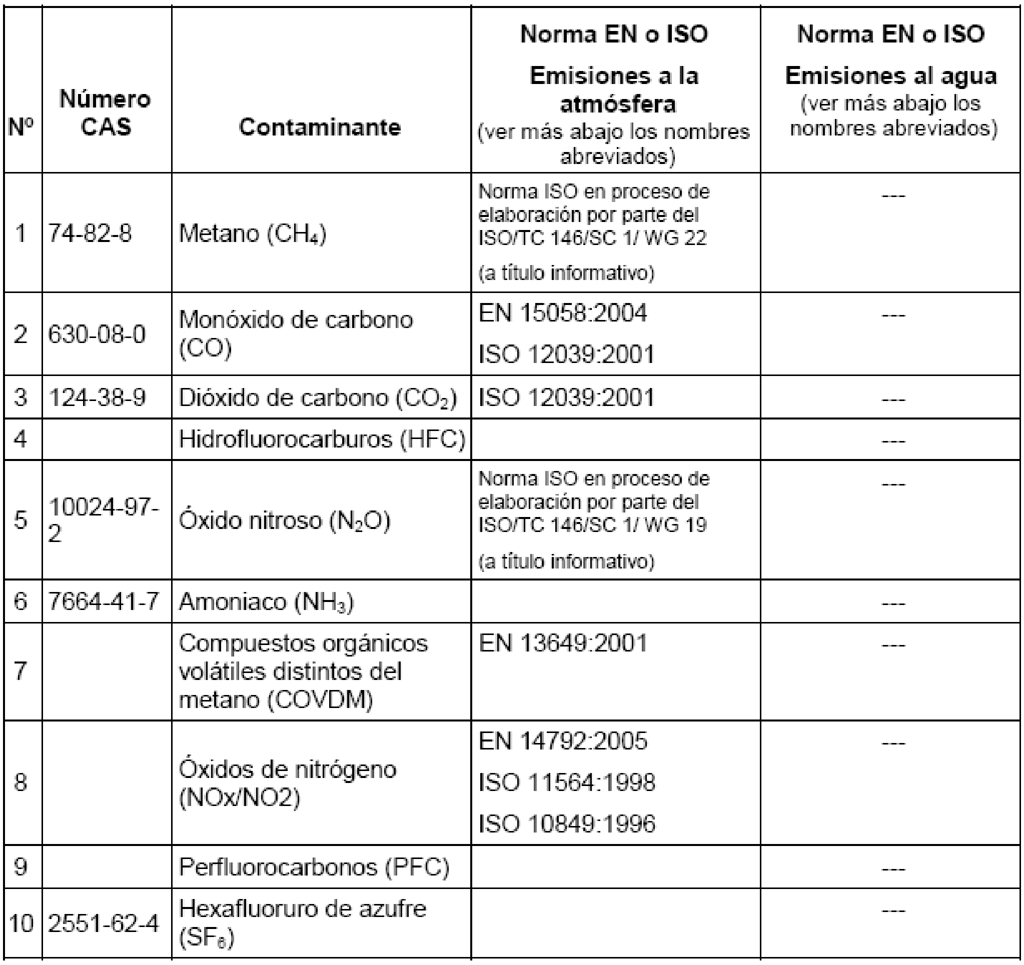
LISTADO DE MÉTODOS DE MEDICIÓN DE EMISIONES A LA ATMÓSFERA Y AL AGUA RECONOCIDOS A ESCALA INTERNACIONAL

(extraídos de la *Guía para la implantación del E-PRTR*)

Apéndice: Lista de de métodos de medición de emisiones a la atmósfera y al agua reconocidos a escala internacional*

A continuación se reproduce la Tabla recogida en el Apéndice 3 de la "*Guía para la implantación del E-PRTR*". En esta tabla se recogen los métodos analíticos recomendados para la **totalidad** de los contaminantes PRTR (no sólo los del Refino o Grandes Instalaciones de Combustión), no incluyéndose los contaminantes aportados por el RD 508/2007.

NOTA – Los distintos pasos de estos métodos de medición (muestreo, transporte y almacenamiento, pre-tratamiento, extracción, análisis y cuantificación, comunicación de información) están normalizados en una o varias normas. Para las emisiones a la atmósfera, las normas citadas generalmente cubren todos los pasos de los métodos de medición. Para las emisiones al agua, las normas citadas generalmente cubren el paso de cuantificación y análisis. Las "normas generales (G1- G7)" listadas al final de esta tabla facilitan directrices sobre los demás pasos. Asimismo, entre estas normas se incluyen normas (G6, G7) sobre cuestiones como la competencia de laboratorios, incertidumbres, etc. La ausencia de normas CEN o ISO en esta tabla no siempre significa que no existan procedimientos relevantes, de hecho es posible que ya se esté trabajando en esos temas en CEN o ISO.



Nº	Número CAS	Contaminante	**Norma EN o ISO** **Emisiones a la atmósfera** (ver más abajo los nombres abreviados)	**Norma EN o ISO** **Emisiones al agua** (ver más abajo los nombres abreviados)
1	74-82-8	Metano (CH_4)	Norma ISO en proceso de elaboración por parte del ISO/TC 146/SC 1/ WG 22 (a título informativo)	---
2	630-08-0	Monóxido de carbono (CO)	EN 15058:2004 ISO 12039:2001	---
3	124-38-9	Dióxido de carbono (CO_2)	ISO 12039:2001	---
4		Hidrofluorocarburos (HFC)		---
5	10024-97-2	Óxido nitroso (N_2O)	Norma ISO en proceso de elaboración por parte del ISO/TC 146/SC 1/ WG 19 (a título informativo)	---
6	7664-41-7	Amoniaco (NH_3)		---
7		Compuestos orgánicos volátiles distintos del metano (COVDM)	EN 13649:2001	---
8		Óxidos de nitrógeno (NOx/NO2)	EN 14792:2005 ISO 11564:1998 ISO 10849:1996	---
9		Perfluorocarbonos (PFC)		---
10	2551-62-4	Hexafluoruro de azufre (SF_6)		---

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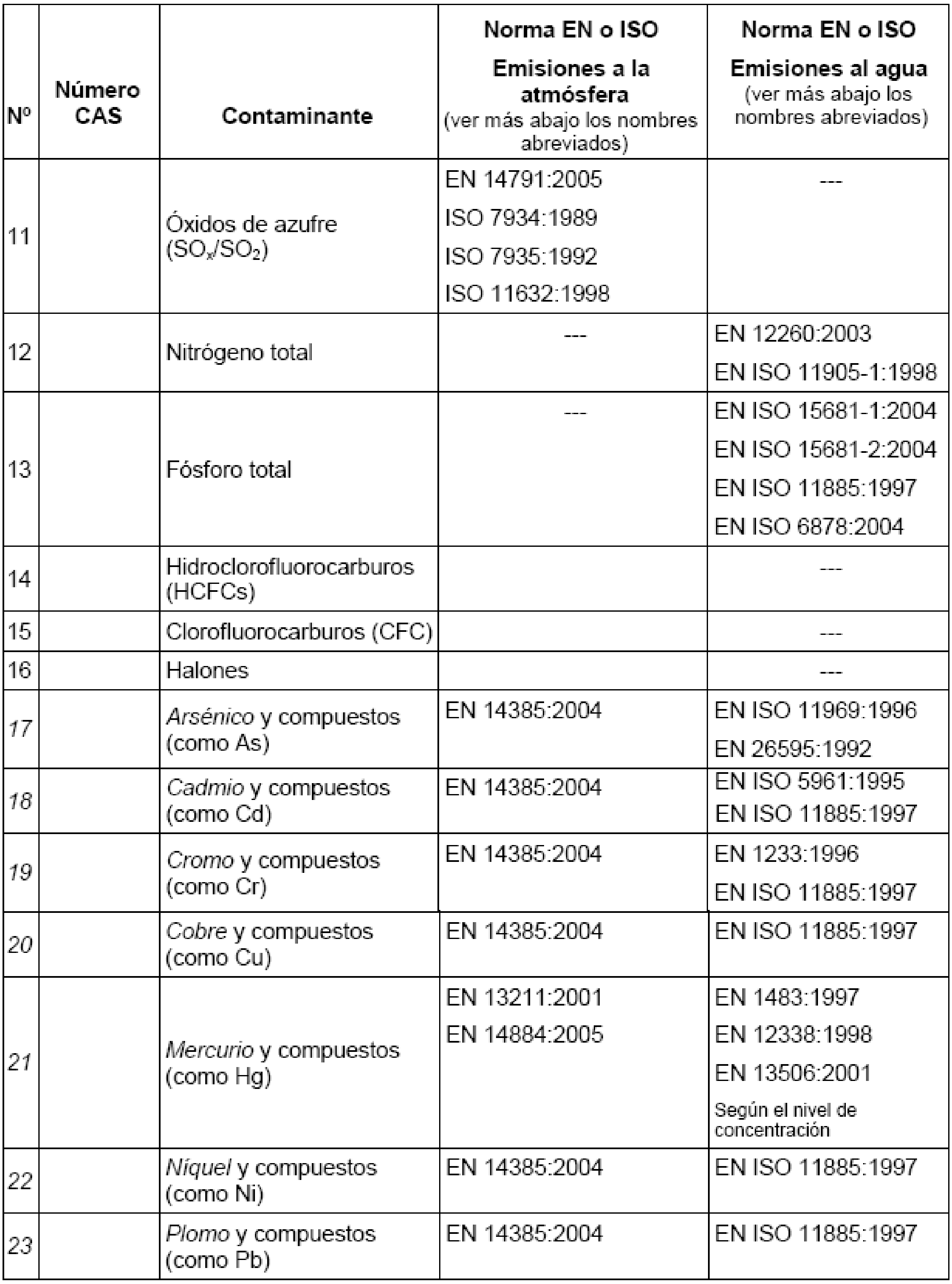
[*] *En el caso de emisiones de contaminantes incluidas en varias categorías de contaminantes, deberá facilitarse información sobre cada una de estas categorías.*



Nº	Número CAS	Contaminante	Norma EN o ISO Emisiones a la atmósfera (ver más abajo los nombres abreviados)	Norma EN o ISO Emisiones al agua (ver más abajo los nombres abreviados)
11		Óxidos de azufre (SO_x/SO_2)	EN 14791:2005 ISO 7934:1989 ISO 7935:1992 ISO 11632:1998	---
12		Nitrógeno total	---	EN 12260:2003 EN ISO 11905-1:1998
13		Fósforo total	---	EN ISO 15681-1:2004 EN ISO 15681-2:2004 EN ISO 11885:1997 EN ISO 6878:2004
14		Hidroclorofluorocarburos (HCFCs)		---
15		Clorofluorocarburos (CFC)		---
16		Halones		---
17		*Arsénico* y compuestos (como As)	EN 14385:2004	EN ISO 11969:1996 EN 26595:1992
18		*Cadmio* y compuestos (como Cd)	EN 14385:2004	EN ISO 5961:1995 EN ISO 11885:1997
19		*Cromo* y compuestos (como Cr)	EN 14385:2004	EN 1233:1996 EN ISO 11885:1997
20		*Cobre* y compuestos (como Cu)	EN 14385:2004	EN ISO 11885:1997
21		*Mercurio* y compuestos (como Hg)	EN 13211:2001 EN 14884:2005	EN 1483:1997 EN 12338:1998 EN 13506:2001 Según el nivel de concentración
22		*Níquel* y compuestos (como Ni)	EN 14385:2004	EN ISO 11885:1997
23		*Plomo* y compuestos (como Pb)	EN 14385:2004	EN ISO 11885:1997

Nº	Número CAS	Contaminante	**Norma EN o ISO** **Emisiones a la atmósfera** (ver más abajo los nombres abreviados)	**Norma EN o ISO** **Emisiones al agua** (ver más abajo los nombres abreviados)
24		*Zinc* y compuestos (como Zn)		EN ISO 11885:1997
25	15972-60-8	Alaclor	---	
26	309-00-2	Aldrina		EN ISO 6468:1996
27	1912-24-9	Atrazina	---	EN ISO 10695:2000
28	57-74-9	Clordano		
29	143-50-0	Clordecona		
30	470-90-6	Clorfenvinfos	---	
31	85535-84-8	Cloroalcanos, C_{10}-C_{13}	---	
32	2921-88-2	Clorfenvinfós	---	
33	50-29-3	DDT		EN ISO 6468:1996
34	107-06-2	1,2-dicloroetano (DCE)		EN ISO 10301:1997 EN ISO 15680:2003
35	75-09-2	Diclorometano (DCM)		EN ISO 10301:1997 EN ISO 15680:2003
36	60-57-1	Dieldrina		EN ISO 6468:1996
37	330-54-1	Diurón	---	EN ISO 11369:1997
38	115-29-7	Endosulfán	---	EN ISO 6468:1996
39	72-20-8	Endrina		EN ISO 6468:1996
40		Compuestos orgánicos halogenados (como AOX)	---	EN ISO 9562:2004
41	76-44-8	Heptacloro		EN ISO 6468:1996
42	118-74-1	Hexaclorobenceno (HCB)		EN ISO 6468:1996
43	87-68-3	Hexaclorobutadieno (HCBD)	---	
44	608-73-1	1,2,3,4,5, 6 -hexaclorociclohexano (HCH)		EN ISO 6468:1996
45	58-89-9	Lindano		EN ISO 6468:1996

Nº	Número CAS	Contaminante	Norma EN o ISO **Emisiones a la atmósfera** (ver más abajo los nombres abreviados)	Norma EN o ISO **Emisiones al agua** (ver más abajo los nombres abreviados)
46	2385-85-5	Mirex		
47		PCDD +PCDF (dioxinas +furanos) (como Teq)	EN 1948-1 a -3:2006	ISO 18073:2004
48	608-93-5	Pentaclorobenceno		EN ISO 6468:1996
49	87-86-5	Pentaclorofenol (PCP)		
50	1336-36-3	Policlorobifenilos (PCB)	(prCEN/TS 1948-4) (a título informativo)	EN ISO 6468:1996
51	122-34-9	Simazina	---	EN ISO 11369:1997 EN ISO 10695:2000
52	127-18-4	Tetracloroetileno (PER)		EN ISO 15680:2003 EN ISO 10301:1997
53	56-23-5	Tetraclorometano (TCM)		EN ISO 10301:1997
54	12002-48-1	Triclorobencenos (TCB) *(todos los isómeros)*		EN ISO 15680:2003
55	71-55-6	1,1,1-tricloroetano		---
56	79-34-5	1,1,2,2-tetracloroetano		---
57	79-01-6	Tricloroetileno		EN ISO 15680:2003 EN ISO 10301:1997
58	67-66-3	Triclorometano		EN ISO 15680:2003 EN ISO 10301:1997
59	8001-35-2	Toxafeno		
60	75-01-4	Cloruro de vinilo		EN ISO 15680:2003
61	120-12-7	Antraceno	ISO 11338-1 a -2:2003	EN ISO 17993:2003
62	71-43-2	Benceno	EN 13649:2001	ISO 11423-1:1997 ISO 11423-2:1997 EN ISO 15680:2003
63		Bromodifeniléteres (PBDE)	---	ISO/DIS 22032:2004
64		Nonilfenol y etoxilatos de *Nonilfenol (NP/NPE)*	---	
65	100-41-4	Etilbenceno	---	EN ISO 15680:2003

Nº	Número CAS	Contaminante	Norma EN o ISO Emisiones a la atmósfera (ver más abajo los nombres abreviados)	Norma EN o ISO Emisiones al agua (ver más abajo los nombres abreviados)
66	75-21-8	Óxido de etileno		
67	34123-59-6	Isoproturón	---	
68	91-20-3	Naftaleno		EN ISO 15680:2003 EN ISO 17993:2003
69		Compuestos organoestánnicos (como Sn total)	---	EN ISO 17353:2005
70	117-81-7	Ftalato de bis (2-etilhexilo) (DEHP)		EN ISO 18856:2005
71	108-95-2	Fenoles (como C total)	---	ISO 18857-1:2005
72		Hidrocarburos aromáticos policíclicos (HAP)	ISO 11338-1 a -2:2003	EN ISO 17993:2003 ISO 7981-1:2005 ISO 7981-2:2005
73	108-88-3	Tolueno	---	EN ISO 15680:2003
74		Tribultiestaño y compuestos	---	EN ISO 17353:2005
75		Trifenilestaño y compuestos	---	EN ISO 17353:2005
76		Carbono orgánico total (COT) (como C total o DQO/3)	---	EN 1484:1997
77	1582-09-8	Trifluralina	---	
78	1330-20-7	Xilenos	---	EN ISO 15680:2003
79		Cloruros (como Cl total)	---	EN ISO 10304-1:1995 EN ISO 10304-2:1996 EN ISO 10304-4:1999 EN ISO 15682:2001
80		Cloro y compuestos inorgánicos (como HCl)	EN 1911-1 a -3:2003	---
81	1332-21-4	Amianto	ISO 10397:1993	
82		Cianuros (como CN total)	---	EN ISO 14403:2002

Nº	Número CAS	Contaminante	**Norma EN o ISO** **Emisiones a la atmósfera** (ver más abajo los nombres abreviados)	**Norma EN o ISO** **Emisiones al agua** (ver más abajo los nombres abreviados)
83		Fluoruros (como F total)	---	EN ISO 10304-1:1995
84		Flúor y compuestos inorgánicos (como HF)	ISO/DIS 15713:2004	---
85	74-90-8	Cianuro de hidrógeno (HCN)		---
86		Partículas (PM10)	Norma ISO en proceso de elaboración por parte del ISO/TC 146/SC 1/ WG 20 (disponible como proyecto de norma de Comité CD 23210) (a título informativo)	---
87	1806-26-4	Octilfenoles y etoxilatos de octilfenol	---	
88	206-44-0	Fluoranteno	ISO 11338-1 a -2:2003	EN ISO 17993:2003
89	465-73-6	Isodrina	---	
90	36355-1-8	Hexabromobifenilo		
91	191-24-2	Benzo(g,h,i)perileno	---	EN ISO 17993:2003
NORMAS GENERALES PARA EMISIONES A LA ATMÓSFERA Y/O AL AGUA				
G1	Muestreo – Parte 1 Guía para el diseño de programas de muestreo			EN ISO 5667-1:1996
G2	Muestreo – Parte 10 Guía para el muestreo de aguas residuales			EN ISO 5667-10:1992
G3	Muestreo – Parte 3 Guía para la conservación y la manipulación de muestras			EN ISO 5667-3:1994
G4	Guía del control de calidad analítica para el análisis del agua			CEN/ISO TR 13530:1998

G5	Fuente de emisión fija – Procedimiento de validación interlaboratorio de un método alternativo frente a un método de referencia	CEN/TS 14793	
G6	Requisitos generales para la competencia de laboratorios de prueba y calibración	EN ISO 17025: 2005	
G7	GUM = Guía para la expresión de la incertidumbre (1995) publicada por BIPM, ICE, IFCC, ISO, IUPAC, IUPAP, OIML	CEN TS 13005 : 2000	

Abreviaturas:

EN	Norma europea
CEN/TS	Especificación técnica CEN
CEN/TR	Informe técnico CEN
ISO	Norma internacional
ISO/CD	Proyecto de norma de Comité ISO
ISO/TS	Especificación técnica ISO
ISO/TR	Informe técnico ISO
ISO/DIS	Proyecto de norma ISO sujeto a consulta pública
ISO/FDIS	Proyecto de norma ISO sujeto a adopción por votación formal
PrXXX	Proyecto de norma (a título informativo)
“---“	no obligatoriedad de comunicar información según el E-PRTR

Nombres de Normas

Normas EN (ISO)

EN 1233:1996: *Water quality - Determination of chromium - Atomic absorption spectrometric methods*

EN 1483:1997: *Water quality - Determination of mercury*

EN 1484:1997: *Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*

EN 1911-1:1998: *Stationary source emissions - Manual method of determination of HCl - Part 1: Sampling of gases*

EN 1911-2:1998: *Stationary source emissions - Manual method of determination of HCl - Part 2: Gaseous compounds absorption*

EN 1911-3:1998: *Stationary source emissions - Manual method of determination of HCl - Part 3: Absorption solutions analysis and calculation*

EN 1948-1:2006: *Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling of PCDDs/PCDFs*

EN 1948-2:2006: *Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 2: Extraction and clean-up of PCDDs/PCDFs*

EN 1948-3:2006: *Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 3: Identification and quantification of PCDDs/PCDFs*

prCEN/TS 1948-4:xxxx: *Stationary source emissions -- Determination of the mass concentration of PCDD/PCDF and dioxin-like PCBs - Part 4: Sampling and analysis of dioxin-like PCBs*

EN 12260:2003: *Water quality – Determination of nitrogen – Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides*

EN 12338:1998: *Water quality – Determination of mercury – Methods after enrichment by amalgamation*

ENV 13005:1999: *Guide to the expression of uncertainty in measurement*

EN 13211:2001: *Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury*

EN 13506:2001*: Water quality - Determination of mercury by atomic fluorescence spectrometry*

EN 13649:2001: *Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Activated carbon and solvent desorption method*

EN 14385:2004: *Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V*

EN 14791:2005: *Stationary source emissions - Determination of mass concentration of sulphur dioxide - Reference method*

EN 14792:2005: *Stationary source emissions – Determination of mass concentration of nitrogen oxides (NO2) – Reference method: chemiluminescence*

CEN/TS 14793:2005: *Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method*

EN 14884:2005: *Air quality - Stationary source emissions - Determination of total mercury: Automated measuring systems*

EN 15058:2004: *Stationary source emissions - Reference method for the determination of carbon monoxide in emission by means of the non-dispersive infrared method*

EN 26595:1992/AC:1992: *Water quality; determination of total arsenic; silver diethyldithiocarbamate spectrophotometric method (ISO 6595:1982)*

EN ISO 5667-1:2005: *Calidad del agua. Muestreo. Parte 1: Guía de diseño de los programas de muestreo y técnicas de toma de muestra (revisión de ISO 5667-1:1980 e ISO 5667-2:1991)*

EN ISO 5667-3:2003: *Calidad del agua. Muestreo. Parte 3: Directrices para la preservación y manejo de las muestras de agua*

EN ISO 5667-10:1992: *Calidad del agua. Muestreo. Parte 10: Guía para el muestreo de aguas residuales*

EN ISO 5961:1995: *Calidad del agua. Determinación de cadmio por espectrometría de absorción atómica*

EN ISO 6468:1996: *Calidad del agua. Determinación de ciertos insecticidas organoclorados, bifenilos policlorados y clorobencenos. Método por cromatografía de gases con extracción líquido-líquido*

EN ISO 6878:2004: *Calidad de agua. Determinación del fósforo. Método espectro-métrico con molibdato amónico*

EN ISO 9562:2004: *Calidad del agua. Determinación de compuestos orgánicos halogenados. absorbibles (AOX)*

EN ISO 10301:1997: *Calidad del agua. Determinación de hidrocarburos halogenados altamente volátiles. Métodos por cromatografía de gases*

EN ISO 10304-1:1995: *Calidad del agua. Determinación de iones fluoruro, cloruro, nitrito, ortofosfato, bromuro, nitrato y sulfato disueltos, por cromatografía en fase líquida. Parte 1: Método aplicable a aguas débilmente contaminadas*

EN ISO 10304-2:1996: *Calidad del agua. Determinación de aniones disueltos por cromatografía iónica en fase líquida. Parte 2: Determinación de bromuro, cloruro, nitrato, nitrito, ortofosfato y sulfato en aguas residuales*

EN ISO 10304-4:1999: *Calidad del agua. Determinación de aniones disueltos por cromatografía iónica en fase líquida. Parte 4: Determinación de clorato, cloruro y clorito en aguas débilmente contaminadas*

EN ISO 10695:2000: *Calidad del agua. Determinación de ciertos compuestos orgánicos nitrogenados y fosforados seleccionados. Métodos por cromatografía de gases*

EN ISO 11369:1997: *Calidad del agua. Determinación de ciertos agentes para el tratamiento de las plantas. Método por cromatografía líquida de alta resolución (HPLC) con detección UV tras extracción sólido-líquido*

EN ISO 11885:1997: *Calidad del agua. Determinación de 33 elementos por espectroscopía de emisión atómica con plasma acoplado inductivamente*

EN ISO 11905-1:1998: *Calidad del agua. Determinación de nitrógeno. Parte 1: Método por mineralización oxidante con peroxidisulfato*

EN ISO 11969:1996: *Calidad del agua. Determinación de arsénico. Método de espectrometría de absorción atómica (técnica de generación de hidruros)*

ENV/ISO 13530:1998: *Calidad del agua. Guía para el control de la calidad analítica en el análisis del agua*

EN ISO 14403:2002: *Calidad de agua. Determinación del cianuro libre y del cianuro total por análisis de flujo continuo*

EN ISO 15680:2003: *Calidad del agua. Determinación de ciertos hidrocarburos aromáticos monicíclicos, naftaleno, y algunos compuestos clorados utilizando purga y trampa y desorción térmica*

EN ISO 15681-1:2004: *Calidad del agua. Determinación de ortofosfato y fósforo total por análisis en flujo (FIA y. CFA). Parte 1: Método por análisis de inyección en flujo (FIA)*

EN ISO 15681-2:2004: *Calidad del agua. Determinación de ortofosfato y fósforo total por análisis en flujo (FIA y. CFA). Parte 1: Método por análisis en flujo continuo (CFA)*

EN ISO 15682:2001: *Calidad del agua. Determinación de cloruro por análisis en flujo (FIA y CFA) y detección fotométrica o potenciométrica*

EN ISO/IEC 17025:2005: *Requisitos Generales para la Competencia de Laboratorios de Prueba y Calibración*

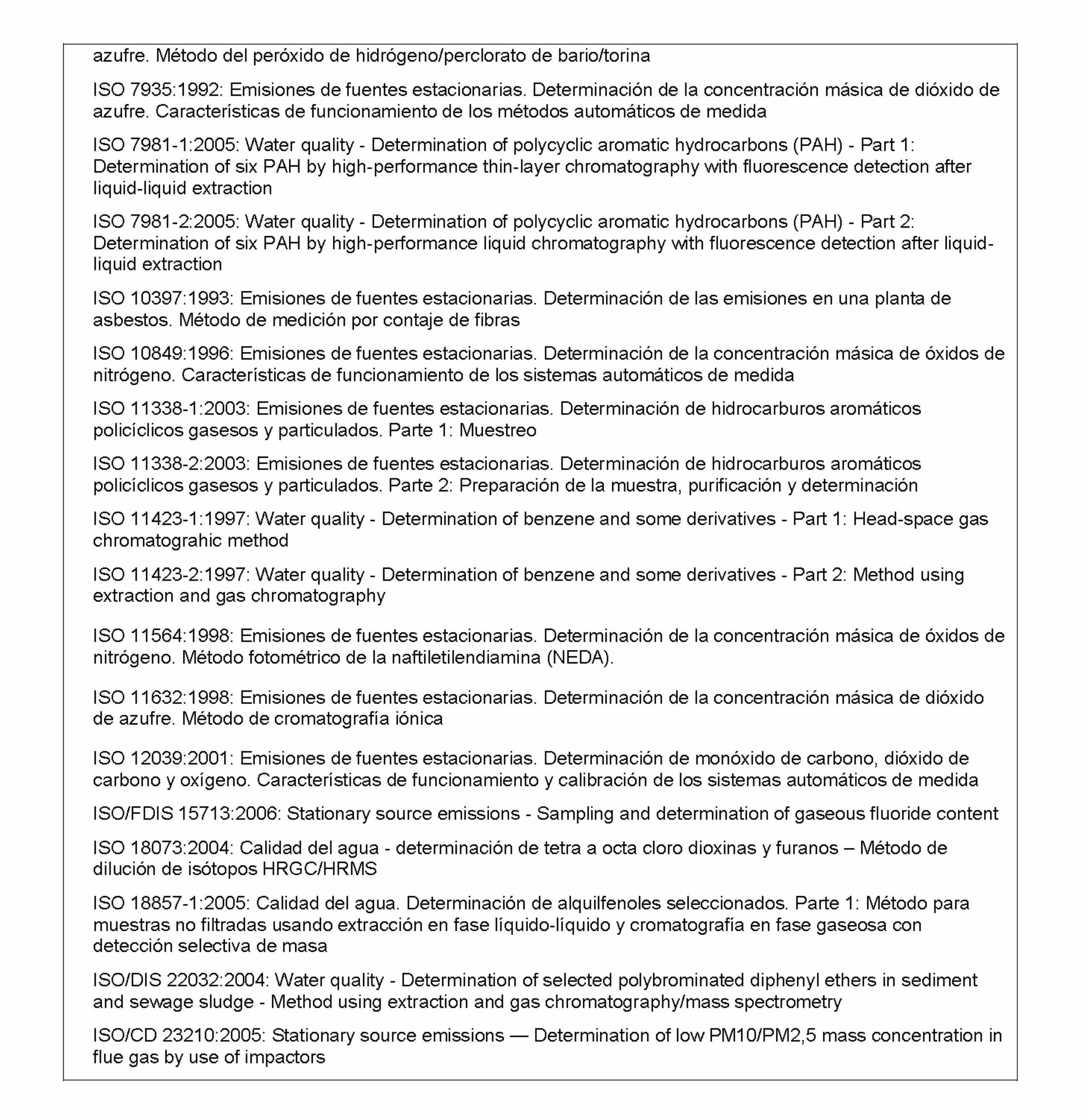
EN ISO 17353:2005: *Calidad del agua. Determinación de compuestos orgánicos seleccionados. Método por cromatografía de gases*

EN ISO 17993:2003: *Calidad del agua. Determinación de 15 hidrocarburos policíclicos aromáticos (PAH) en agua mediante. HPLC con detección fluorescente después de extracción líquido-líquido*

EN ISO 18856:2005: Calidad del agua. Determinación de determinados ftalatos mediante cromatografía de gases/espectroscopia de masas

Normas ISO

ISO 7934:1989: Emisiones de fuentes estacionarias. Determinación de la concentración másica de dióxido de



azufre. Método del peróxido de hidrógeno/perclorato de bario/torina

ISO 7935:1992: Emisiones de fuentes estacionarias. Determinación de la concentración másica de dióxido de azufre. Características de funcionamiento de los métodos automáticos de medida

ISO 7981-1:2005: Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) - Part 1: Determination of six PAH by high-performance thin-layer chromatography with fluorescence detection after liquid-liquid extraction

ISO 7981-2:2005: Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) - Part 2: Determination of six PAH by high-performance liquid chromatography with fluorescence detection after liquid-liquid extraction

ISO 10397:1993: Emisiones de fuentes estacionarias. Determinación de las emisiones en una planta de asbestos. Método de medición por contaje de fibras

ISO 10849:1996: Emisiones de fuentes estacionarias. Determinación de la concentración másica de óxidos de nitrógeno. Características de funcionamiento de los sistemas automáticos de medida

ISO 11338-1:2003: Emisiones de fuentes estacionarias. Determinación de hidrocarburos aromáticos policíclicos gasesos y particulados. Parte 1: Muestreo

ISO 11338-2:2003: Emisiones de fuentes estacionarias. Determinación de hidrocarburos aromáticos policíclicos gasesos y particulados. Parte 2: Preparación de la muestra, purificación y determinación

ISO 11423-1:1997: Water quality - Determination of benzene and some derivatives - Part 1: Head-space gas chromatograhic method

ISO 11423-2:1997: Water quality - Determination of benzene and some derivatives - Part 2: Method using extraction and gas chromatography

ISO 11564:1998: Emisiones de fuentes estacionarias. Determinación de la concentración másica de óxidos de nitrógeno. Método fotométrico de la naftiletilendiamina (NEDA).

ISO 11632:1998: Emisiones de fuentes estacionarias. Determinación de la concentración másica de dióxido de azufre. Método de cromatografía iónica

ISO 12039:2001: Emisiones de fuentes estacionarias. Determinación de monóxido de carbono, dióxido de carbono y oxígeno. Características de funcionamiento y calibración de los sistemas automáticos de medida

ISO/FDIS 15713:2006: Stationary source emissions - Sampling and determination of gaseous fluoride content

ISO 18073:2004: Calidad del agua - determinación de tetra a octa cloro dioxinas y furanos – Método de dilución de isótopos HRGC/HRMS

ISO 18857-1:2005: Calidad del agua. Determinación de alquilfenoles seleccionados. Parte 1: Método para muestras no filtradas usando extracción en fase líquido-líquido y cromatografía en fase gaseosa con detección selectiva de masa

ISO/DIS 22032:2004: Water quality - Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry

ISO/CD 23210:2005: Stationary source emissions — Determination of low PM10/PM2,5 mass concentration in flue gas by use of impactors

Además de las “normas generales (G1-G7)” listadas anteriormente, para el caso de monitorización en continuo merece mención especial la norma UNE-EN 14181 *Emisiones de fuentes estacionarias. Aseguramiento de la calidad de los sistemas automáticos de medidas*, versión oficial en español de la Norma Europea EN 14181:2004, elaborada por el Comité Europeo de Normalización (CEN).

A continuación se reproduce parte del contenido de la misma:

INTRODUCCIÓN

Esta norma describe los procedimientos de garantía de calidad necesarios para asegurar que un Sistema Automático de Medida (SAM), instalado para medir emisiones al aire, es capaz de cumplir los requisitos de incertidumbre de los valores medidos establecidos en la reglamentación, por ejemplo Directivas europeas 2000/76/CE, 2001/80/CE o legislación nacional, y de forma más general por las autoridades competentes.

Para conseguir este objetivo se definen tres Niveles diferentes de Garantía de Calidad (NGC1, NGC2 y NGC3). Estos Niveles de Garantías de Calidad cubren la aptitud de un SAM para su función de medida (por ejemplo, antes o durante el período de compra del SAM), la validación del SAM después de su instalación, y el control del SAM durante su operación en funcionamiento en una planta industrial. También se define un Ensayo Anual de Seguimiento (EAS).

La evolución de la aptitud del SAM y su procedimiento de medida se describen en la Norma EN ISO 14956 (NGC1), donde se da una metodología para calcular la incertidumbre total de los valores medidos del SAM. Esta incertidumbre total se calcula a partir de la evaluación de todos los componentes de la incertidumbre de las características de su funcionamiento individual.

1. OBJETO Y CAMPO DE APLICACIÓN

Esta norma europea especifica los procedimientos para el establecimiento de los Niveles de Garantía de Calidad (NGC) para los Sistemas Automáticos de Medida (SAM) instalados en plantas industriales, para la determinación de los componentes y otros parámetros del gas efluente.

Esta norma especifica:

- *un procedimiento (NGC2) para calibrar el SAM y determinar la variabilidad de los valores medidos, obtenidos por él, de manera que se demuestre la aptitud del SAM para su aplicación, después de su instalación;*
- *un procedimiento (NGC3) para mantener y demostrar la calidad requerida de los resultados de medición durante la operación normal de un SAM, verificando que las características del cero y rango son consistentes con las determinadas durante el NGC1;*
- *un procedimiento para los Ensayos Anuales de Seguimiento (EAS) del SAM a fin de evaluar (i) que funciona correctamente y su funcionamiento permanece válido y (ii)*

que su función de calibración y variabilidad se mantiene como se determinó anteriormente.

Esta norma se diseñó para usarse después de que el SAM ha sido aceptado de acuerdo con los procedimientos especificados en la Norma EN ISO 14956 (NGC1).

Esta norma se restringe a la Garantía de Calidad (GC) del SAM y no incluye la GC de la captación de datos y sistemas de registro de la planta.

ANEXO III

METODOLOGÍA PARA LA DETERMINACIÓN DE CONTAMINANTES HÍDRICOS

Atendiendo a la naturaleza del vertido al medio hídrico, caracterizada fundamentalmente por llevarse a cabo a través de muy pocos puntos (completamente determinados y concretos), se entiende que la metodología a considerar para este medio sea totalmente distinta al sistema de fichas empleadas para el medio atmosférico.

El hecho de que el vertido se produzca a través de emisarios o conducciones de desagüe posibilita en gran medida el empleo de determinaciones analíticas a la hora de cuantificar la carga de contaminantes en el vertido.

Éste es el motivo de que la determinación de contaminantes al medio hídrico se centre en la obtención de valores empíricos medidos en el efluente final.

No obstante lo anterior, se recuerda que el registro E-PRTR, en comparación con EPER, ha multiplicado notablemente el número de contaminantes a considerar, al menos en teoría:

TABLA 1
CONTAMINANTES A REPORTAR AL MEDIO HÍDRICO

ACTIVIDAD	EPER	E-PRTR	PRTR-España(1)
Refino	17	26	44
Grandes instalaciones de combustión	14	19	37

(1) En España, el Real Decreto 508/2007 amplía, respecto a E-PRTR, el número de sustancias de las que hay que informar.

Otra cuestión de interés a considerar es el actual desarrollo de medidas analíticas para multitud de parámetros que antes no eran determinados. En efecto, como consecuencia de los reportes a EPER así como de la entrada en vigor de las Autorizaciones Ambientales Integradas, los programas de vigilancia ambiental, por lo que a los efluentes se refiere, han ganado notablemente en complejidad, motivo por el cual en la actualidad se dispone de analíticas mucho más extensas que unos años atrás.

En base a estas consideraciones, los contaminantes al medio hídrico se tratarán en tres grandes grupos:

A) Contaminantes presentes de un modo significativo en los efluentes.

Estas sustancias incluyen a aquellos contaminantes que, en base a determinaciones realizadas en los diversos Complejos analizados **se encuentran o pueden encontrase por encima de los límites de detección** de métodos de medida de reconocido prestigio.

B) Contaminantes no detectados en el efluente.

Este segundo grupo de sustancias estaría integrado por aquellas para las cuales no existe una bibliografía que permita excluirlas con claridad de las sustancias relacionadas con los procesos que se desarrollan en un Complejo de Refino. No obstante, en base a las distintas campañas de medida que han sido realizadas en los diversos Centros analizados, **se consideran excluidas de las necesidades de información** al no haberse encontrado en los efluentes analizados (por debajo de límites de detección de métodos internacionalmente aceptados).

C) Contaminantes ajenos al proceso productivo.

En este último grupo se encuentran aquellas sustancias que por su propia naturaleza, origen o aplicación **no se encuentran relacionadas directa o indirectamente con los procesos que tienen lugar en una Refinería y por lo tanto se consideran excluidos de las obligaciones de información**. Dichas sustancias han sido identificadas generalmente mediante el empleo de bibliografía técnica monográficamente dedicada a los contaminantes en cuestión, habiéndose incluso realizado determinaciones analíticas en alguno de los Complejos analizados para un numeroso grupo de estas sustancias que han venido a ratificar lo apropiado de la exclusión realizada.

En las Tablas siguientes se muestran los contaminantes considerados en este documento (presentes en la sublista del Refino(1), o aportados por el R.D. 508/2007) clasificados según la tipología anterior: A, B o C.

CONTAMINANTES GRUPO A
(POTENCIALMENTE PRESENTES EN VERTIDO)

Nitrógeno total	HAP
Fósforo total	COT
Zinc	Cloruros
AOX	Cianuros
Dioxinas y furanos	Fluoruros
Benceno	DQO(*)
Fenoles	

(*) Incluidos en R.D. 508/2007

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(1) La sublista de Grandes Instalaciones de Combustión no aporta nuevos contaminantes.

CONTAMINANTES GRUPO B
(NO DETECTADOS EN EFLUENTE)

Arsénico	Tolueno
Cadmio	Xileno (e isómeros(*))
Cromo	Fluoranteno
Cobre	Benzo(ghi)perileno
Mercurio	Benzo(a)pireno(*)
Níquel	Benzo(b)fluoranteno(*)
Plomo	Benzo(k)fluoranteno(*)
Etilbenceno	Indeno (123cd)pireno(*)

(*) Incluidos en R.D. 508/2007

CONTAMINANTES GRUPO C
(AJENOS AL PROCESOPRODUCTIVO)

Diclorometano	Isómeros del triclorobenceno(*)
Pentaclorobenceno	Isómeros de bromodifenilétores(*)
Isómeros del DDT(*)	

(*) Incluidos en R.D. 508/2007

ANEXO IV

CONSIDERACIÓN DE RESIDUOS EN PRTR-ESPAÑA

Como es sabido, uno de los aspectos novedosos que recoge el nuevo registro PRTR-España es la obligatoriedad de informar acerca de la capacidad de generación de residuos de las instalaciones afectadas por la nueva normativa, o más concretamente, de la transferencia de residuos que origina la actividad de los establecimientos incluidos en el ámbito de aplicación.

En referencia a la citada transferencia de residuos, deben considerarse dos aspectos a diferenciar:

- Residuos transferidos

- Residuos gestionados

Ambos tipos responden a una filosofía y a unas exigencias distintas en cuanto a la naturaleza de la información a presentar, por lo que seguidamente se pasa a analizar de forma independiente cada uno de los grupos anteriores.

1. RESIDUOS TRANSFERIDOS

El titular de un Complejo tiene la obligación de informar de las salidas de residuos (residuos transferidos hacia otras instalaciones sean o no de tratamiento final(1)) que tienen lugar en su instalación.

Estas necesidades de información han de cumplirse, para los residuos catalogados como peligrosos, siempre y cuando se rebasen las 2 toneladas/año, y en el caso de los no peligrosos, cuando se superen las 2.000 toneladas/año. Ambas cantidades, y en especial la correspondiente a residuos peligrosos, se entienden como susceptibles de ser superadas con relativa facilidad por parte de los Complejos afectados.

a) Residuos peligrosos

En referencia a los residuos peligrosos, tan sólo se deberá informar de las toneladas(2) que anualmente abandonan el Complejo, sin necesidad de especiación alguna. No obstante, habrá que distinguir entre residuos destinados a recuperación (Código R según orden MAM/304/2007) o a eliminación (Código D según la citada orden), indicando el método mayoritariamente empleado para su cuantificación. En caso de

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(1) A excepción, como se verá después, de las operaciones de eliminación de “tratamiento de suelo” o “inyección profunda”.

(2) Residuos expresados en toneladas y con tres cifras significativas, como en la totalidad de la información a suministrar en el campo de la transferencia de residuos, sean o no peligrosos.

aquellos residuos destinados a tratamientos que puedan contemplar operaciones tanto de recuperación como de eliminación, se consignará el código R o D al que se destine más del 50% de los residuos, y en caso de duda, se utilizará el código D.

Por otro lado habrá que distinguir aquellos residuos que sean transferidos más allá del ámbito del territorio nacional. En tal caso, habrá que informar de manera individual para cada destinatario final, el cual ha de quedar perfectamente identificado a través de su nombre y dirección.

b) Residuos no peligrosos

En referencia a los residuos no peligrosos, la información a suministrar será en todo igual a la del caso de no peligrosos, salvo en lo tocante a transferencias transfronterizas, que no habrán de ser especificadas.

Así, habrá que consignar, para los residuos destinados a su eliminación por un lado (código D) y los destinados a recuperación por otro (código R), las toneladas (con tres cifras significativas) transferidas, así como el método utilizado para la cuantificación.

Para mayor claridad, se adjunta seguidamente una Tabla en la que se representa la información que ha de consignarse en el caso de la transferencia de residuos.

TABLA 1

COMUNICACIÓN DE INFORMACIÓN SOBRE TRANSFERENCIA DE RESIDUOS

Transferencias fuera del emplazamiento	Destino Eliminación (D) Recuperación (R)	Cantidad t/a (3 cifras significativas)	Origen Información M/C/E	Método utilizado	Entidad Responsable Eliminación o Recuperación	Dirección Entidad Responsable Eliminación o Recuperación	Dirección Centro Responsable Eliminación o Recuperación
Residuos no peligrosos (dentro o fuera del país)	D	X	M	Determinación por pesada	-	-	-
	R	X	M	Determinación por pesada	-	-	-
Residuos peligrosos (dentro del país)	D	X	M	Determinación por pesada	-	-	-
	R	X	M	Determinación por pesada	-	-	-
Residuo peligroso “i” (fuera del país)	D o R	X	M	Determinación por pesada	X	X	X

En la tabla anterior se ha presentado de manera resumida la información que un Complejo debe aportar en lo que a transferencia de residuos se refiere. Respecto a la misma, señalar:

- La X indica campo que ha de ser rellenado, el guión (-) campo que no lo debe ser.

- En el origen de la información (M/C/E) y método utilizado se ha consignado el origen habitual de la determinación de residuos, esto es, la pesada de los mismos, por lo que se utiliza el código de medida (M). En caso de recurrirse mayoritariamente al empleo de cálculos (C) o estimaciones (E) habría que indicarlo, especificando el método utilizado.

- Por cada grupo de residuos peligrosos transferido a un mismo gestor fuera del país habrá que consignar una fila distinta.

En relación a la Tabla anterior es de interés hacer dos observaciones:

- El *Real Decreto 508/2007, de 20 de abril, por el que se regula el suministro de información sobre emisiones del Reglamento E-PRTR y de las Autorizaciones Ambientales Integradas* aporta en su Anexo II un cuadro acerca de qué información debe consignarse en el caso de la transferencia de residuos. En este cuadro no aparece la necesidad de indicar el "método utilizado" para la cuantificación de los residuos, a pesar de que este requisito es claramente indicado por la *Guía para la implantación del E-PRTR* de la Dirección General del Medio Ambiente de la Comisión Europea.

- Atendiendo al Anexo III del citado Real Decreto 508/2007, también es necesario aportar el código de la Lista Europea de Residuos (LER) para cada una de las cantidades de residuos de las que se informa.

  Por ello, es de entender que en la práctica **no será posible informar de los residuos de manera agrupada como la Guía Europea establece** (diferenciando sólo entre los destinados a recuperación -código R- y los destinados a eliminación -código D-), de manera que **cada Centro deberá informar de las cantidades individualizadas de cada residuo particular generado.**

A continuación se expone un ejemplo que muestra cómo debe informarse sobre los datos de transferencia de residuos fuera del emplazamiento(1).

TABLA 2. EJEMPLO DE NOTIFICACIÓN DE RESIDUOS

RESIDUOS PELIGROSOS	CANTIDAD (t/año)	LER	MÉTODO	DESTINO
Residuo 1 (filtros)	1,20	150202	Pesada (M)	D
residuo 2 (carbón activo)	5,26	190110	Pesada (M)	D
Residuo 3 (disolventes orgánicos no halogenados)	0,820	140603	Pesada (M)	R
Residuo "i"				
RESIDUOS PELIGROSOS	**CANTIDAD (t/año)**	**LER**	**MÉTODO**	**DESTINO**
Residuo 1 (lodos efluente)	227	070112	Pesada (M)	D
Residuo 2 (chatarra)	15,2	170407	Pesada (M)	R
Residuo "i"				

En el caso de los residuos peligrosos transferidos al extranjero, la información se amplía con los datos propios del gestor final del residuo, tal y como se muestra en la Tabla 3.

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(1) Ejemplos extraídos de la *Guía para la implantación del E-PRTR.*

TABLA 3

COMUNICACIÓN DE INFORMACIÓN SOBRE TRANSFERENCIAS FUERA DEL EMPLAZAMIENTO DE RESIDUOS PELIGROSOS A OTROS PAÍSES

LER	***Cantidad (t/año)***	***Operación de tratamiento de residuos***	***M/C/E***	***Método utilizado***	***Nombre del responsable de la recuperación/ eliminación***	***Dirección del responsable de la recuperación/ eliminación***	***Dirección del centro de recuperación/ eliminación en cuestión***
130205	*15*	*R*	*M*	*Por peso*	*Sunshine Components Ltd.*	*Sun Street, Flowertown south, PP12 8TS, Reino Unido*	*Sun Street, Flowertown south, PP12 8TS, Reino Unido*
070101	*4*	*D*	*M*	*Por peso*	*BEST Environmental Ltd.*	*Kings Street, Kingstown, Highlands, AB2 1CD, Reino Unido*	*Planta de residuos energéticos de Kingstown, Kinas Street, Kingstown, Highlands, AB2 1CD, Reino Unido*
070199	*30*	*D*	*M*	*Por peso*	*BEST Environmental Ltd.*	*Kings Street, Kingstown, Highlands, AB2 1CD, Reino Unido*	*Planta de incineración de Queens, Crown Street, Queenstown, EF3 4GH, Reino Unido*

En base a las necesidades informativas que el registro PRTR-España exige en referencia a los residuos, **la metodología a seguir para el reporte de dicha información** debe basarse necesariamente en el empleo de documentación como la Declaración Anual de Productor de Residuos o información equivalente. Este tipo de documentación (ya disponible en Refinerías) recoge las toneladas de cada residuo peligroso generadas, particularizando por código LER, indicando los datos del gestor (por lo que es fácilmente discriminable una posible transferencia al extranjero).

Además, recoge la identificación del residuo según las Tablas del Anexo I del *Real Decreto 952/1997, de 20 de junio, por el que se modifica el Reglamente para la Ejecución de la Ley 20/1986, de 14 de mayo, Básica de Residuos Tóxicos y Peligrosos, aprobado mediante Real Decreto 833/1988, de 20 de julio*. Se recuerda que la Tabla 2 de dicho Real Decreto recoge los códigos D o R que corresponden a la operación que se realizará sobre el residuo, códigos coincidentes con los contenidos en la Orden MAM/304/2002.

Por tanto, la información a aportar en materia de residuos peligrosos será fácilmente extraíble de las Declaraciones Anuales (una vez diferenciadas las transferencias transfronterizas, caso de haberlas) sin más que considerar cada residuo individual, su código LER, y su código D o R.

En el caso de residuos no peligrosos, dado que éstos no suelen aparecer en esta documentación (salvo en el caso de Cataluña, como se verá posteriormente) habrá de recurrirse a otro tipo de registros que a nivel particular pueda llevar cada Refinería, bien para cumplimentación de Declaraciones Medioambientales, bien para seguimiento de gestores, del propio municipio, etc.

Por último, se cita el caso de Cataluña por disponer de una aplicación propia para la cumplimentación de los residuos anuales generados. Dicha aplicación recoge tanto los residuos peligrosos ("especiales") como los no peligrosos ("no especiales"), señalando el gestor que los recibe, por lo que no se hace necesario recurrir a información adicional para cumplimentar el registro PRTR-España. Como particularidad, en esta aplicación aparece el método de gestión (para discriminar si es una operación de eliminación D o recuperación R), pero no conforme a la Orden MAM/304/2002, sino en base al *Decreto 92/1999, de 26 abril, de modificación del Decreto 34/1996, de 9 de enero, por el que se aprueba el Catálogo de Residuos de Cataluña*. La nomenclatura de este Decreto (apartados 2B y 2C de su Anexo) recoge una serie de códigos T para las operaciones de eliminación y códigos V para las de recuperación. A pesar de que las operaciones concretas no coinciden con las de la Orden MAM/304/2002, dado que PRTR-España tan sólo precisa distinguir si el residuo es eliminado o recuperado, la información contenida en este tipo de documentación es totalmente válida para los fines perseguidos, sin más que considerar por un lado los residuos con código T (equivalente a D) y por otro los de código V (equivalente a R), previa segregación de residuos especiales (peligrosos) y no especiales (no peligrosos).

2. EMISIONES AL SUELO

Como una de las novedades más destacables del nuevo registro, se encuentra la necesidad de informar de las emisiones al suelo que puedan darse, explicitando la especiación correspondiente para un total de 79 sustancias(1).

No obstante, tal comunicación sólo es preceptiva a los contaminantes en residuos que son sometidos a dos operaciones de eliminación muy concretas, **ninguna de las cuales se desarrolla en el sector del Refino:**

A) Tratamiento en medio terrestre (por ejemplo, biodegradación de residuos líquidos o lodos en el suelo, etc): Código D2 de la Orden MAM/304/2002. Tal y como se indicó con anterioridad, se excluye de estas técnicas el landfarming, atendiendo como se citó en su momento a que la propia "*Guía para la Implantación del E-PRTR*" recoge en su apartado 1.1.8.3 dedicado a las emisiones al suelo que "el extendido de fangos y estiércol se consideran operaciones de valorización, y por tanto, no deben comunicarse como emisiones al suelo".

B) Inyección en profundidad (por ejemplo, inyección de residuos bombeables en pozos, minas de sal, fallos geológicos naturales, etc): Código D3 de la Orden MAM/304/2002.

En los casos anteriores, habría que informar de las cantidades anuales (expresadas en kg, con tres cifras significativas) de las 79 sustancias que se pudiesen encontrar en el residuo en cuestión, señalando adicionalmente si se han medido, calculado o estimado y detallando el método concreto utilizado.

No obstante, hay dos cuestiones particulares que deben señalarse:

- En principio, no deberían comunicarse las emisiones accidentales de contaminantes al suelo (como por ejemplo, los derrames), a diferencia de lo que ocurre con los contaminantes al medio atmosférico y al medio hídrico. En este punto se señala que aunque la "*Guía para la implantación del E-PRTR"* recoge explícitamente tal circunstancia, la Tabla ejemplo de emisiones al suelo del Anexo III del Real Decreto 508/2007 dispone de un campo para "emisiones accidentales", por lo que se entiende que en caso de que haya habido situaciones episódicas de contaminación de suelos derivadas de accidentes, el Complejo afectado debería informar de la hipotética presencia de aquellos de los 79 contaminantes que habrían sido susceptibles de ser emitidos al suelo.

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(1) E-PRTR contempla 61 sustancias de las que hay que informar respecto a emisiones al suelo. Sin embargo, el *Real Decreto 508/2007, de 20 de abril, por el que se regula el suministro de información sobre emisiones del Reglamento E-PRTR y de las autorizaciones ambientales integrales*, añade 18 nuevos contaminantes al suelo de los que sería preciso informar.

- No existen sublistas para las actividades particulares en el caso de las emisiones al suelo, de manera que no hay una “preselección” de entre todos los contaminantes, de aquellos que puedan ser más propios del Refino de Petróleo.

Para el supuesto considerado en el que hubiese que informar de contaminación al suelo por accidente es de entender que **la única metodología fiable sería proceder a la determinación analítica de las especies a notificar.**

No obstante, como se ha visto con anterioridad el listado es desmesurado, con un total de 79 substancias (18 aportadas por el Real Decreto 508/2007), de las que no se realiza ninguna particularización en función de cada actividad concreta. Una gran cantidad de estas sustancias, pueden considerarse como no asociadas a los procesos de refino, por lo que a priori podrían no considerarse a la hora de realizar una determinación analítica en una muestra de suelo.

ANEXO V

EMISIONES ACCIDENTALES

Tal y como se ha visto con anterioridad, una de las novedades que PRTR-España introduce respecto a EPER es la necesidad de informar acerca de las emisiones accidentales, las cuales se definen como “aquellas emisiones que no son deliberadas, habituales u ocasionales generadas o resultantes de desarrollos incontrolados durante el transcurso o el funcionamiento de las actividades que se realicen en el emplazamiento del Complejo”.

Dado lo complejo de la problemática, la *Guía para la implantación del E-PRTR* recoge que “Los titulares de Complejos están obligados a especificar cualquier información relacionada con emisiones accidentales cuando **se disponga de dicha información** (…)”. La propia Guía recoge cómo en casos particulares, “podrá ser imposible obtener información sobre todos los contaminantes relevantes en base a estimaciones”, aunque ofrece como posibilidad general de cálculo trabajar sobre la base de la determinación de cantidades residuales en conducciones o recipientes o considerando la duración de una emisión accidental y asociándola a los índices de flujo asumidos.

Una vez hecho este planteamiento inicial, se pretende en este ANEXO establecer una metodología que permita estimar (realmente, en base a la terminología de PRTR-España sería calcular), las emisiones que al aire o al agua puedan tener lugar en un Complejo de Refino como consecuencia de la ocurrencia de accidentes.

Para ello, es de entender que las herramientas a emplear coincidan en mayor o menor medida con las que se utilizan en el desarrollo de la documentación relacionada con el ámbito de los Accidentes Graves (SEVESO). No obstante, existe una gran diferencia y es que en relación a la notificación PRTR-España, los accidentes que habría que evaluar se corresponden a situaciones reales que han ocurrido durante el periodo del que se quiere informar, por lo que la evolución del escenario que ha dado lugar al accidente es totalmente conocida.

Así, debe empezar por señalarse cómo en la práctica se pueden limitar los escenarios susceptibles de ocurrir en un Complejo de Refino a tres, entendiendo por escenario aquella situación que puede dar lugar a un accidente. Los escenarios concretos serían:

- Fuga de gas inflamable y/o tóxico

- Fuga de líquido inflamable y/o tóxico

- Condiciones explosivas en un ambiente confinado

De los tres escenarios anteriores, los dos primeros desembocarán en un tipo u otro de accidente en función de las diversas evoluciones que pueden tener. El tercer escenario sólo puede dar lugar a un tipo de accidente, conocido como VCE (vapour cloud explosion), es decir la deflagración explosiva de una nube de gas inflamable que se halla en un espacio confinado.

Respecto a los dos escenarios correspondientes a fugas (bien de líquidos, bien de gases), se procede a definir completamente las evoluciones que pueden tener lugar para cada accidente ocurrido, aplicando la técnica del árbol de sucesos, independientemente de la gran diversidad de parámetros que afectan al posible desarrollo de un accidente.

Así, en las Figuras que a continuación se muestran, se presentan los árboles de sucesos para las fugas de gases inflamables y/o tóxicos (Figura 1) y para las fugas de líquidos inflamables y/o tóxicos (Figura 2). A partir de estas figuras se puede ver cómo a partir del escenario inicial se pueden tener distintas evoluciones, llegándose a un accidente final único, cuyas emisiones serán las que se evalúen finalmente.

FIGURA 1
ÁRBOL DE SUCESOS DE FUGA DE GAS TÓXICO Y/O INFLAMABLE

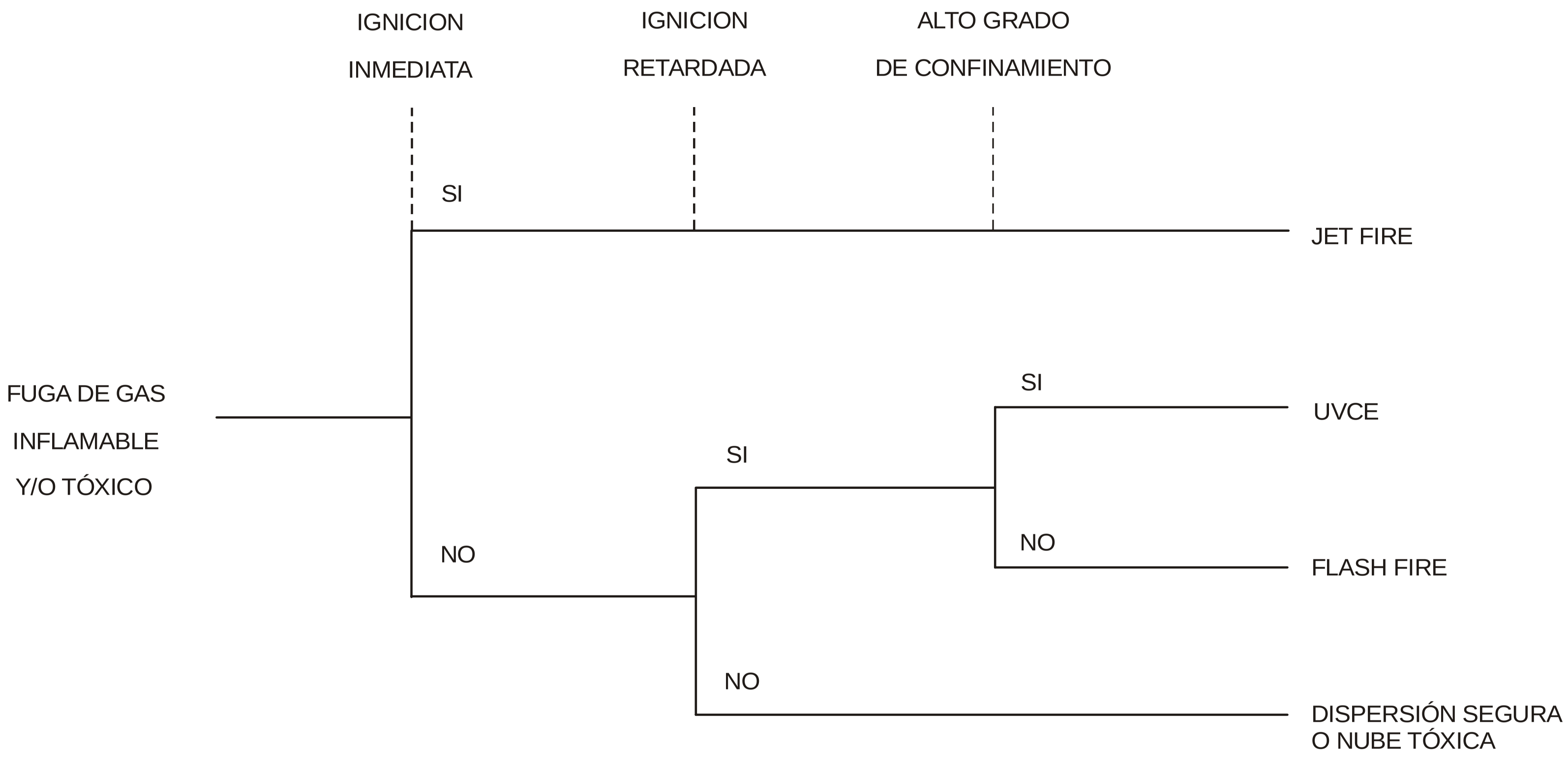
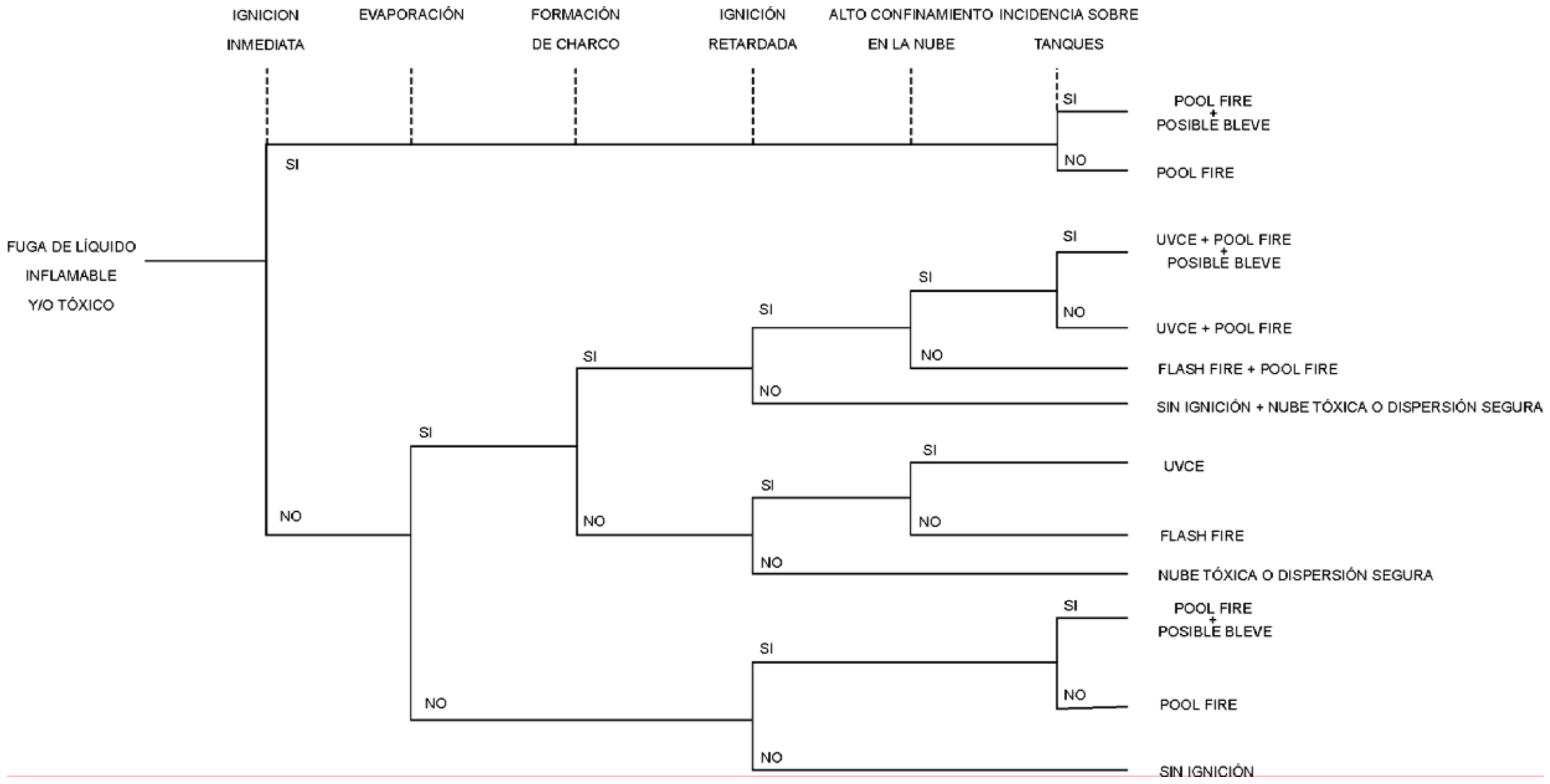


FIGURA 2
ÁRBOL DE SUCESOS DE FUGA DE LÍQUIDO INFLAMABLE Y/O TÓXICO



De la observación de la evolución de los escenarios de las figuras anteriores se deduce que en general, los accidentes que pueden tener lugar en una Refinería son:

A) Jet fire (dardo o lengua de fuego, llama estacionaria de difusión de gran longitud y poca anchura, como la producida por un soplete oxiacetilénico. Es provocada por la ignición de chorros turbulentos).

B) UVCE (unconfined vapour cloud explosion, deflagración explosiva de una nube de gas inflamable que se halla en un espacio amplio, cuya onda de presión alcanza una sobrepresión máxima del orden de 1 bar en la zona de ignición).

C) Flash fire (llamarada, llama progresiva de difusión premezclada con baja velocidad de llama que no produce onda de presión).

D) Pool fire (incendio de charcos, se aplica a una combustión estacionaria con llama de difusión de un líquido en un recinto descubierto de dimensiones dadas).

E) BLEVE (boiling liquid expanding vapour explosion, estadillo producido por el calentamiento externo de un recipiente que contiene un líquido a presión, al perder resistencia mecánica el material de la pared y estanqueidad bruscamente).

F) VCE (vapour cloud explosion, como UVCE, pero en este caso la deflagración ocurre en un gas inflamable que se halla confinado).

G) Dispersión segura o nube tóxica (cuando el gas fugado o evaporado no deflagra y se dispersa en la atmósfera).

Una vez presentados los distintos accidentes que en general pueden tener lugar en un Complejo, se analizarán los mismos bajo el punto de vista PRTR-España, es decir, para conocer cómo cada uno de ellos puede derivar en incremento de emisiones al medio atmosférico o al medio hídrico.

1. MEDIO ATMOSFÉRICO

Desde el punto de vista de la emisión de contaminantes a la atmósfera, los accidentes pueden organizarse a su vez en dos grupos, por un lado los que implican combustión (jet fire, UVCE, flash fire, pool fire, BLEVE y VCE) y por otro, los que no la conllevan (dispersión segura o nube tóxica).

1) Jet fire, UVCE, flash fire, pool fire, BLEVE y VCE.

En el primer caso, dado que de un modo u otro el gas involucrado en el accidente experimenta una combustión, parece lógico suponer que los contaminantes a considerar sean los típicos de combustión.

Para evaluar la emisión concreta de contaminantes se recomienda el empleo de modelos de cálculo, entre los que se puede citar EFFECTS.

Effects ("Modelling the effect of accidental release of hazardous substance"), es un software desarrollado por TNO y basado en los fundamentos incluidos en el Manual de consecuencias de fugas de productos peligrosos denominado "Methods for the calculation of the physical effects of the scape of dangerous material –liquids and gases-", conocido como Yellow Book. En el programa EFFECTS se encuentran implementados los siguientes modelos:

- Modelos de fugas.
  - Fuga de gas.
    - Fuga desde un depósito/línea.
    - Fuga desde una línea de gran longitud.
  - Fuga de gas licuado.
    - Fuga desde un depósito o línea.
    - Fuga bifásica.
    - Fuga de gas licuado.
    - Fuga en forma de spray de un gas licuado a presión.
    - Fuga con flash instantánea.
  - Fuga de líquido.
    - Fuga desde un depósito o línea.
- Modelos de evaporación desde charco.
  - Evaporación desde suelo.
    - Líquido en ebullición.
    - Líquido sin ebullición.
  - Evaporación desde agua.
    - Líquido soluble sin ebullición.
    - Líquido insoluble sin ebullición con flotación.
    - Líquido insoluble en ebullición con flotación.
    - Líquido insoluble en ebullición sin flotación.

- Modelos de dispersión.

    - Dispersión gas neutro.
        - Fuga instantánea.
        - Fuga semicontinua.
        - Fuga continua.

    - Dispersión gas denso.
        - Fuga instantánea.
        - Evaporación desde charco.
        - Dispersión desde un jet.

    - Dispersión con chorro libre turbulento.

- Modelo de explosiones Multi Energy.

- Modelos de radiación desde fuegos.

    - BLEVE.
    - Charco.
    - Dardo de fuego de una fuga de gas.
    - Dardo de fuego de una fuga bifásica.

En el caso concreto que se analiza, es decir, la generación de contaminantes típicos de combustión, los únicos parámetros que se necesita conocer son los siguientes:

- Sustancia fugada: para los fines perseguidos, basta conocer la composición elemental de la misma

- Caudal de sustancia fugada (kg/s)

- Tiempo de ocurrencia de la fuga

En caso de no conocerse el caudal y el tiempo de la fuga, podría aportarse directamente la masa total fugada, lo cual implicaría considerar que toda la masa fugada habría explotado (situación más desfavorable). Por el contrario, si se aportasen los dos parámetros anteriores (caudal y tiempo), podría calcularse la cantidad estimada de sustancia que se ha encontrado entre los límites de inflamabilidad, ya que debe decirse que es usual que no toda la sustancia involucrada en el proceso termine finalmente explotando. Como es natural, de llegarse a conocer la cantidad fugada que no ha participado en el proceso de combustión, debería reportarse la cantidad de sustancias (incluidas en las sublistas) presentes en el gas, ya que éstas habrían sido directamente emitidas al aire (ver caso de dispersión segura o nube tóxica).

2) Dispersión segura o nube tóxica.

En el caso de la dispersión segura o nube tóxica parece evidente considerar que la totalidad del gas fugado debe considerarse como contaminante emitido al medio atmosférico. Para cuantificar la emisión basta con conocer el caudal fugado, el tiempo de duración de la fuga y naturalmente, la sustancia fugada, datos todos ellos de los que es de entender deben disponerse, al menos a posteriori. Así, conocida la composición de la fuga y los kg de gas fugados, la determinación de las sustancias a reportar sería inmediata.

Es necesario señalar que en este caso, al no existir ningún tipo de reacción química, los únicos contaminantes que podrían estar presentes en un accidente de este tipo son los que por sí mismos pueden formar parte del proceso productivo de Refinería y por tanto encontrarse en las corrientes manipuladas. De entre la sublista de contaminantes el medio atmosférico para el sector del refino, las principales sustancias susceptibles de estar presentes en este tipo de accidentes podrían ser:

- CH_4
- CO_2 (en caso de existir unidades de recuperación de CO_2)
- NH_3
- COVDM
- C_6H_6
- PCB’s (en caso de accidente en equipos eléctricos que los contengan. VER FICHA 50/2/01)

2. MEDIO HÍDRICO

En el caso de los accidentes con repercusiones al medio hídrico, la metodología es mucho más directa, ya que los accidentes que dan lugar a un vertido que alcance el medio receptor (cauce, mar) se computan directamente.

Nótese que en caso de vertidos accidentales al suelo, no hay obligación de reportar (en cuanto a transferencia de contaminantes al suelo), tal y como recoge la *Guía para implantación del E-PRTR*, por lo que este hipotético vector no debería en principio ser considerado, salvo en el caso de que el vertido percolase a través del suelo y alcanzase un flujo de agua subterránea. No obstante, a pesar de lo que la citada Guía recoge, se señala que el Real Decreto 508/2007, de 20 de abril, por el que se regula el suministro de información sobre emisiones del Reglamento E-PRTR y las autorizaciones ambientales integradas, en su Anexo III, apartado 5, recoge un campo para la notificación de emisiones accidentales al suelo.

De todos modos, incluso la afección sobre flujos subterráneos sería muy discutible. Tal afirmación se basa en el empleo de software como por ejemplo VLEACH (desarrollado por la EPA), modelo unidimensional de diferencias finitas que permite estimar el impacto en aguas subterráneas debido a la movilización y migración de contaminantes orgánicos en suelos porosos.

Pues bien, el empleo de este tipo de software permite comprobar cómo las escalas temporales (años) que se manejan son tales que se puede considerar que un derrame puntual, sobre el que se actúa en un corto plazo de tiempo mediante la retirada del propio vertido y de las capas superficiales del terreno que hayan podido verse afectadas, no tiene efecto sobre la transferencia de contaminación a cursos de aguas subterráneas.

En cualquier caso, las actuaciones anteriores podrían dar lugar a un fenómeno de transferencia de contaminación al suelo, cuestión ésta que quedaría sobradamente cubierta en base al contenido del Anexo IV (se recuerda que el concepto “tierras contaminadas por hidrocarburos” es un integrante típico de las declaraciones de productor de residuos de Refinerías).

Una vez hechas las puntualizaciones anteriores, los accidentes resultantes con vertido al medio hídrico podrían ser:

1) Vertido directo a cauce o al mar.

   En este caso, conocida la sustancia y la cantidad fugada (caudal y tiempo de fuga), bastaría con aplicar el porcentaje másico del contaminante a reportar (es de entender que la sustancia vertida es conocida) sobre la emisión másica total de la sustancia fugada. Entre los contaminantes que podrían estar presentes en el vertido, destacar como el más típico, el COT, atendiendo a que la práctica totalidad de las corrientes involucradas en los trasiegos o procesos productivos de una Refinería son de naturaleza hidrocarburada.

2) Agua Contraincendios.

   En el caso de que haya habido un incendio, éste habrá dado lugar a un efluente líquido altamente contaminado ya sea por las propias sustancias que hayan originado el accidente como por los propios medios empleados en la extinción.

ANEXO VI

EXCLUSIONES

Se presenta el siguiente ANEXO con la finalidad de excluir del alcance de este trabajo determinados contaminantes que en base a su propia naturaleza pueden considerarse ajenos a los procesos productivos que tienen lugar en un Complejo de Refino.

Dichos contaminantes son:

- Isómeros del DDT (incluidos por R.D. 508/2007, agua)
- Isómeros del triclorobenceno (incluidos por R.D. 508/2007, agua)
- Isómeros del bromodifeniléter (incluidos por R.D. 508/2007, agua)
- Diclorometano (incluido en sublista del refino, agua)
- Pentaclorobenceno (incluido en sublista del refino, agua)
- Hidroclorofluorocarburos (incluido en sublista del refino, aire)
- Hidrofluorocarburos (incluido en sublista del refino, aire)
- Tricloroetileno (incluido en sublista de G.I.C., aire)
- Hexafluoruro de azufre (incluido en sublista de G.I.C., aire)
- Talio (incluido por R.D. 508/2007 aire)

El objetivo de este ANEXO es identificar en base a bibliografía especializada el origen de las emisiones de los compuestos en cuestión, comprobándose adicionalmente cómo estas fuentes de emisión no se hallan presentes en las unidades que integran las Refinerías españolas.

Para configurar este ANEXO, se han preparado tantos informes como sustancias se han considerado, estando constituido cada uno de ellos por una breve descripción del contaminante, indicación de cómo se produce y a qué uso se destina**, análisis exhaustivo de las fuente de emisión** y por último, las referencias bibliográficas que sustentan toda la información anterior.

Air pollutant emission estimation methods for E-PRTR reporting by refineries

2009 edition

Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-69)

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ABSTRACT

This report is the first revision of CONCAWE Report 3/07, which itself replaced Report No. 9/05R *Air Pollutant Emission Estimation Methods for EPER and PRTR Reporting by Refineries*. It provides algorithms to permit emission estimates to be made by refineries to meet the reporting requirements of the European Pollutant Release and Transfer Register (E-PRTR) regarding pollutant emissions to air.

KEYWORDS

Air pollution, refineries, E-PRTR, emission factors, sources.

INTERNET

The controlled version of this report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org) and the latter should be checked for updates. New and updated information provided in this version is summarised in Appendix 2.

CONTENTS

SUMMARY

With the introduction of the public domain databases of pollutant releases - EPER (European Pollutant Emission Register) and its successor E-PRTR (European Pollutant Release and Transfer Register) - there is a need for reliable and consistent emissions data in the oil industry sector.

The E-PRTR Regulation requires that annual emissions of key species are reported where those emissions exceed a minimum threshold.

This Report provides the estimation algorithms and emission factors for uncontrolled releases of air pollutants from stationary sources at oil refineries which CONCAWE recommends for E-PRTR reporting purposes, where measurements have not been undertaken. The emission estimation algorithms are fully referenced and the emission factors provided in a consistent metric unit base.

CONCAWE has previously published Report No. 9/05 (and a revised version 9/05R) *Air Pollutant Emission Estimation Methods for EPER and PRTR Reporting by Refineries.*

Report No. 9/05R was submitted to the European Commission and the European Environment Agency and is referenced as a source of sector specific calculation methods in the EU (2006) *Guidance Document for the Implementation of the European PRTR.*

It was updated in 2007 by Report No. 3/07 *Air Pollutant Emission Estimation Methods E-PRTR Reporting by Refineries.* This provided new and revised factors and algorithms and focused on the reporting requirements of the E-PRTR Regulations.

This current report updates Report No. 3/07 and contains some additional algorithms and new and updated emission factors. A change log is presented in Appendix 2.

It is expected that future refinements to the emission factor database will be made. This document is therefore a "snapshot" of the present knowledge. Before using this report, the version number should be compared with the control copy which is posted as an electronic document on the CONCAWE web-site (www.concawe.org).

1. INTRODUCTION

The European Directive 96/61/EC on integrated pollution prevention and control (IPPC) [1] mandated the publication of a regularly updated pollutant inventory. The European Pollutant Emission Register (EPER) required the reporting of a number of pollutants, both to air and water, from all facilities listed in Annex 1 of the IPPC Directive.

The EPER requirements have been succeeded by those of the European Pollutant Release and Transfer Register (E-PRTR) Regulation [2]. This implements at EU level the UNECE PRTR Protocol which was signed in 2003 in Kiev [3]. The first report of the E-PRTR will be for the year 2007 and reporting will be annually thereafter. The E-PRTR is more extensive than EPER in a number of respects. For example, the list of pollutants is enlarged and the amount of information required to be reported concerning emissions and transfers of pollutants has increased. Guidance on the implementation of the E-PRTR has been provided by the European Commission [4]. The list of air pollutants and their threshold values above which emissions must be reported are given in **Appendix 1**.

With regard to the data submissions for these Registers, CONCAWE identified three issues that require attention by the oil refining sector:

1. The data submitted should be reliable, in the sense that they represent as accurately as possible the actual pollutant emissions. Over-estimation of emissions is clearly to be avoided. Moreover, under-estimation can give a false impression of what pollution emissions levels can be reached under realistic circumstances.
2. Data should be consistent between comparable sources within the industry.
3. The sharing of best practices in terms of emission factors is important in order to improve the quality of the reporting.

To address these issues the CONCAWE Air Quality Management Group initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the reporting threshold values from stationary sources found at the majority of European refineries.

It was noted that there were no emission estimation guidelines for each and every one of the pollutants to air from refineries which may possibly require reporting under the regulations. Although guidance is provided in the European Environment Agency Emission Inventory Guidebook [5] for the major air pollutants, estimation methodologies are not available for all of the E-PRTR listed pollutants.

On the other hand, for some pollutants such as non-methane volatile organic compounds (NMVOCs) there are a number of different estimation methodologies being used by European refineries e.g. protocols produced by the US EPA [6] and a number of nationally agreed methods such as that published by the UK Energy Institute [7].

CONCAWE, therefore, published Report No. 9/05 and its first revision No. 9/05R [8] which comprised a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants. The compendium could not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considered this to be the most appropriate set of emissions factors for the refining sector.

Report No. 9/05R was replaced by Report No. 3/07 [9], which focused on the requirements of the E-PRTR and contained additional algorithms and updated emission factors.

This current report is the first revision of Report No. 3/07. It provides the estimation algorithms which CONCAWE recommends for E-PRTR reporting purposes where measurements have not been undertaken.

The report does not consider the estimation of accidental or non-routine (e.g. due to maintenance) releases to air. Guidance in reference [4] recommends that emissions from such releases should be estimated by sites on an ad-hoc basis using whatever data are available and the most appropriate methods considered for the circumstances. Nor does it provide guidance on estimating emissions from mobile sources.

The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc.

Where emission factors are available, algorithms are provided for sources found in the majority of European refineries. There are some emission sources for which estimation algorithms are not provided in this report e.g. coke calciners. Refineries should review all of the sources of air pollutants on-site and establish if there are any additional sources from those listed in this report which may require emission estimates to be made for E-PRTR reports.

CONCAWE has previously published reports on non-methane volatile organic compound (NMVOC) emissions from refineries and other downstream oil industry sources. However Report No. 85/54 [10] which was widely used by Industry is now out of date and is no longer available. Although marketing terminals and service stations are not subject to E-PRTR reporting requirements, for completeness this current report provides NMVOC emission estimation algorithms which are applicable to gasoline storage and handling at these facilities.

A summary of the changes to the algorithms and emission factors given in Report No. 3/07 is provided in **Appendix 2**.

2. EMISSION ESTIMATION METHODOLOGIES

There are a number of sources of emission estimation methodologies:

- Oil industry associations e.g. CONCAWE, API, etc.
- Oil companies that have published methods in the professional press
- National and international environmental authorities e.g. US EPA, European Environment Agency, etc.
- International organisations e.g. IPCC, etc.
- European Commission.

Methodologies published by the national and international organisations may be non oil-industry sector specific.

Only those estimation methods which are currently in the public domain were considered for inclusion in this report. The methodologies were considered in the following order of preference to determine those most representative for oil industry sources:

- Methods published by the oil industry
- Sector specific methods published by national and international authorities
- Non-sector specific methods.

Reported E-PRTR emission data must include a code to identify the type of estimation methodology used. The classification codes are simple letters:

> Class M: emission data are based on measurements. Additional calculations are needed to convert the results of measurements into annual emission data. Emissions can be derived from continuous or discontinuous measurements of pollutant concentrations. Alternatively, they can be determined based on the results of short term or spot measurements.
>
> Class C: emission data are based on calculations using activity data (e.g. fuel used, production rate) and emission factors or mass balances.
>
> Class E: emission data are based on non-standardised estimations derived from best assumptions or expert guesses that are not based on publicly available references or good practice guidelines.

Where data are measured or calculated, the method of measurement and/or the calculation method must also be provided in the E-PRTR data submission.

The EU Guidance document [4] provides a list of the internationally approved or "equivalent" methodologies that should be used and the method names to be included in the E-PRTR submission. One of the accepted equivalent methodologies is a "European-wide sector specific calculation method, developed by industry experts, which has been delivered to the European Commission, to the European Environment Agency and the relevant international organisations". The EU Guidance document [4] references CONCAWE Report No. 9/05R [8] which has been submitted to the EC and EEA. This current report is a replacement for Report No. 9/05R and hence use of the algorithms in this report can be considered to be an approved calculation methodology: data could then be reported using the letters "C" and method name acronym "SSC" (sector specific calculation).

3. POLLUTANTS

There are sixty air pollutants which must be reported under the E-PRTR requirements if their respective annual emission threshold values are exceeded at a facility. All of these are shown in **Appendix 1,** with their threshold values.

The EU Guidance Document on E-PRTR Implementation [4] provides indicative lists of the pollutants likely to be emitted on a sector specific “activity” basis. In addition to having its own specific sectoral activity of “mineral oil and gas refineries”, the Oil Industry also uses combustion units with ratings in excess of 50 MW. These are included in the sectoral activity classified within the PRTR Regulation [2] as “thermal power stations and other combustion installations”.

Those pollutants on the sector specific indicative lists within the EU Guidance Document for these two activities are listed in **Appendix 1**.

Information was requested from the CONCAWE member companies in 2002 concerning the emissions of air pollutants from refineries reported either internally or externally. **Appendix 1** lists those pollutants which had been estimated, by at least one of the nine companies who responded, to exceed the E-PRTR reporting thresholds.

Appendix 1 indicates that the pollutants included on the two EU indicative lists are almost identical to those on the oil industry list. The difference is the addition of two pollutants on the combustion installation list: dioxins/furans and trichloroethylene.

Trichloroethylene (TRI) is not a product of combustion; its major use is as an organic solvent for industrial degreasing. The inclusion of this pollutant on the sector specific indicative list for combustion installations appears to be due to an anomaly in the EPER database. Only one facility classified as "Combustion installation > 50 MW" reported emissions of TRI, but these would appear to be from the process of manufacturing rubber tyres and tubing at the site and not as a by-product of combustion. This report, therefore, does not consider this pollutant further.

This report provides algorithms to estimate the emissions of all of the other pollutants on the indicative lists in the EU Guidance for refineries and combustion installations rated in excess of 50 MW.

Anthracene and naphthalene are two pollutants that are known to be emitted by refineries, but are not on the sector specific indicative lists. A review of the emissions of these pollutants is provided in **Appendix 3.** It is shown that, even for the largest refineries, neither anthracene nor naphthalene emissions are likely to exceed their E-PRTR reporting threshold values.

Sites should review their processes and emission sources to establish if there is the potential for any of the other E-PRTR air pollutants to be released in excess of their reporting thresholds.

4. EMISSION SOURCES

4.1. REFINERIES

This report divides the sources found within the majority of refineries, for which emission factors are available in the public domain, into the following categories:

- Combustion
- Process vents
- Storage
- Loading
- Miscellaneous

Combustion sources considered comprise:

- Boilers
- Furnaces
- Fired waste heat boilers
- CO boilers
- Gas turbines
- Gas engines
- Diesel engines
- Incinerators
- Flares

Process sources included are:

- Hydrogen plants
- Fluid coking units
- Fluidised catalytic cracking units
- Catalytic reforming units

Miscellaneous sources included are:

- Process drains
- Oil-water separators
- Fugitive emissions from pressurised pipe work and components
- Refrigeration systems
- Use of SF_6

There are some sources which are only found in a limited number of refineries for which algorithms are not given in this report. One example for which emission factors are available [11] is coke calcining.

4.2. GASOLINE MARKETING FACILITIES

Neither marketing distribution terminals nor service stations are regulated under the terms of the IPPC Directive [1] and hence are not required to submit E-PRTR reports.

Emission estimates for distribution terminals and service stations may, however, be made by oil companies for their own environmental reporting purposes.

Emissions from distribution terminals are primarily NMVOCs due to the storage and loading of refined products, in particular gasolines. Emission estimation methods for sources of NMVOCs at terminals are provided in **Appendix 4.1**.

Some terminals have small steam raising boilers e.g. to heat heavy oil storage tanks. The algorithms provided in this report can be used to estimate combustion emissions from these facilities.

Unlike refineries and terminals, storage at service stations is in underground horizontal tanks. Emissions occur from these due to the displacement of vapours during filling and the evaporation of the stored gasoline. Emissions also occur due to the filling of automobile fuel tanks and from minor drips and spills during those operations. Estimation methods for NMVOC emissions from these sources are provided in **Appendix 4.2**.

5. EMISSION ESTIMATION ALGORITHMS

5.1. INTRODUCTION

Algorithms are provided for the E-PRTR air pollutants which may exceed their emissions reporting thresholds. The level of emissions depends upon the refinery crude throughput, the process units installed, fuels consumed, type of equipment in use, procedures in place, etc.

Algorithms are given on a pollutant by pollutant basis in **Sections 7** to **30**, in the order of the pollutant list in **Appendix 1**.

Algorithms are also provided in **Appendix 3** for two additional pollutants (anthracene and naphthalene). It is demonstrated that the emissions of neither of these pollutants are likely to exceed their E-PRTR reporting thresholds.

Estimation algorithms are given for the sources of each pollutant. A reference is provided for each method, with additional details where considered appropriate.

If no pollutant algorithm is provided for a source, it is because:

- emissions of the pollutant do not occur from that source;
- emissions are considered negligible; or
- no published algorithm has been found or considered appropriate for sources at refineries.

Table 1 indicates those sources for which pollutant algorithms are provided in this report.

Emission factors are given in scientific units to 3 significant figures i.e. 5.67E+03 is equivalent to 5670.

It should be noted that data submitted in E-PRTR reports should be expressed in kg/year and with three significant digits, e.g. 123 000, 17.9, 2.10.

Table 1 Sources for which pollutant emission estimation methodologies are provided in this report

	CH_4	CO	CO_2	HFC	N_2O	NH_3	NMVOC	NO_X	SF_6	SO_X	HCFC	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Dioxins	C_6H_6	PAH	Cl	PM_{10}
Boiler	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×	×	×	×		×
Furnace	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×	×	×	×		×
Gas turbine	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×		×
Gas engine	×	×	×		×		×	×		×											×	×		×
Diesel engine	×	×	×		×		×	×		×											×	×		×
Pilot or support fuel	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×		×
Incinerator	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×		×
Flare	×	×	×				×	×		×											×			×
Hydrogen plant			×				×																	
Fluid coking unit			×				×					×			×	×	×	×	×		×			×
Catalytic cracking unit		×	×			×	×	×		×		×	×		×	×	×	×	×		×	×		×
Catalytic reforming unit		×	×							×										×			×	
Process drainage							×																	
Oil-water separator							×																	
Process fugitives	×						×														×			
Loading							×																	
Storage							×																	
SCR/SNCR						×																		
Refrigeration				×		×					×													
Lab/test/HV switch gear									×															

5.2. EMISSION FACTORS DERIVED FROM MEASUREMENTS WITH DATA BELOW THE LIMIT OF DETECTION

A few emission factors were originally derived from measurements where, if the values measured were all below the limit of detection, those data points were set at the limit of detection level. Where possible, in this report these factors have been identified and the following rule used to adjust them:

- Where all data points were below the measurement detection limit, the emissions factor has been set to zero (i.e. it is considered that the source is not proven).

Where both the averages of data points above and below the limit of detection (the ‘detect’ and ‘non-detect’ values) are provided in a reference, along with the number of data points used to derive these, a weighted value as calculated below has been used in this report.

- Weighted factor = [(average detect value × number of detect samples) + (average non-detect value × number of non-detect samples × detect ratio)] / total number of samples

where detect ratio = number of detect samples / total number of samples.

Reference: [12], Section 7.4.7

Where only the average of the detect and non-detect values and the detect ratio is provided in a reference, a weighted value as calculated below has been used in this report.

- Weighted factor = [(average value × detect ratio) + {(average value / 2) × (1 - detect ratio)}]

All algorithms where these adjustments have been made are identified in the text.

5.3. TREATMENT OF DATA WHERE MEAN AND MEDIAN VALUES AVAILABLE

In references [11], [13] and [14], both the mean and median values of pollutant emission data sets are provided. A small number of the data sets used to determine emission factors are highly skewed, resulting in mean values dominated by a few very high values that are not representative of the majority of readings. Where the mean value exceeds the median value by more than a factor of ten, the median has been considered a more realistic value and has been used in this report. In all other cases the mean value has been used.

All algorithms where the median value has been used are identified in the text.

5.4. OVERVIEW OF COMBUSTION ALGORITHMS

For many of the pollutants arising from combustion sources the published emission factors are one of the following types:

a) Mass per unit volume combusted (EF_{VOL})
b) Mass per energy consumed (EF_{NCV})

To provide a consistent approach within this report, algorithms using emissions factors based on EF_{NCV} are provided. This type of factor enables emissions to be calculated for fuels which are widely different in composition to those for which EF_{VOL} was originally determined. Where published factors are only in the form of EF_{VOL}, the values of EF_{NCV} have been calculated using default values for the fuels. Where appropriate, this is noted within the text. Details, along with the default fuel heating values used in this report, are provided in **Appendix 5**.

5.4.1. Heating Values

In the USA, the norm is to use Higher Heating Value (HHV) (or Gross Calorific Value) for a fuel, whilst in Europe the Net Calorific Value (NCV) (or Lower Heating Value - LHV) is usually quoted. In this report all heating values quoted are NCVs and all emission factors involving heat energy require the use of the corresponding fuel NCV, unless otherwise quoted.

NCV = HHV x Correction Factor for heat of vaporisation of water in the fuel

For liquid fuels:

$$NCV = HHV \times 0.95$$

For gaseous fuels:

$$NCV = HHV \times 0.9$$

Reference: [15], Section 3.6.3

6. EMISSION CONTROLS

6.1. OVERVIEW

The algorithms provided in this report (with the exceptions identified in **Sections 6.2** and **6.3**) assume that no emission reduction control equipment (e.g. flue gas desulphurisation system, vapour recovery unit, etc.) is installed in vent lines, stacks or flues.

Calculated emissions must, therefore, take account of any emission controls. The algorithm to be used is:

Emissions reported = Uncontrolled emissions × (1 – [EFF x ONTIME] / 10 000)

where:
EFF = Average percentage efficiency of emission reduction control equipment over reporting period.
ONTIME = Percentage of the time that the emission reduction equipment is operational when required during the reporting period.

Where there are two or more emission control devices in series impacting a particular pollutant (e.g. for particulates: cyclone plus electrostatic precipitator) then the effect of each device on the pollutant emissions must be taken into account. For example, if two devices are installed, with respective efficiencies of EFF_1 and EFF_2 and operating times of $ONTIME_1$ and $ONTIME_2$, then the algorithm is:

Emissions reported = Uncontrolled emissions × {(1 – [EFF_1 x $ONTIME_1$] / 10 000) × (1 – [EFF_2 x $ONTIME_2$] / 10 000)}

For vapour recovery units (VRUs) designed to reduce NMVOC emissions from loading operations, algorithms are also provided where the average vent emission concentration is known but not the overall VRU efficiency.

6.2. PARTICULATE EMISSIONS FROM CATALYTIC CRACKING UNITS

The algorithms for particulate (PM_{10}) and metals emissions from these units assume that there are cyclone systems installed inside the regenerator vessel to separate the catalyst particles from the hydrocarbon vapours. If additional cyclones or other emission abatement devices such as electrostatic precipitators are installed external to the regenerator then the effect of these additional controls to reduce emissions must be taken into account in the reported emission level.

6.3. EMISSIONS FROM CATALYTIC REFORMING UNITS

There are limited references to emissions from catalytic reforming units (CRUs). The emission factors quoted in this report for CO and SO_X are from reference [14]. This paper uses combined emissions data from a number of units. As some of these units may have emission abatement controls installed, the factors may not truly represent uncontrolled emissions.

A review of the emissions for particulates and metals using the factors in reference [14] for a very high throughput CRU indicated that the estimated emissions were very small relative to other sources of these pollutants in a large refinery. No factors for these pollutants have therefore been provided.

7. METHANE (CH_4)

Estimation methods are provided for emissions due to:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Venting to atmosphere of uncontrolled blowdown systems

7.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 2**.

Table 2 CH_4 Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	6.98E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Oil	1.43E+00	[15] Section 4, Table 4.4a
	LPG	9.63E-01	[15] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[15] Section 4, Table 4.4a
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	1.68E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Oil	3.02E+00	[15] Section 4, Table 4.4a
	LPG	9.63E-01	[15] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[15] Section 4, Table 4.4a

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[15] Section 4, Table 4.4a
Boilers and Furnaces > 100 MW	Distillate (gas oil)	9.05E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Oil	8.45E-01	[15] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[15] Section 4, Table 4.4a
Gas Turbine[1]	Natural Gas	4.11E+00	[15] Section 4, Table 4.5
Gas Engine 4-stroke, Lean Burn	Natural Gas	5.97E+02	[15] Section 4, Table 4.5
Diesel Engine[2] Large, Stationary	Diesel Fuel	3.67E+00	[15] Section 4, Table 4.5
Incinerator Support Fuel or Flare Pilot Fuel	LPG	9.63E-01	[15] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[15] Section 4, Table 4.4a

Notes:
1. Factor derived from turbines operating at high (≥ 80%) loads.
2. Factor is derived from data from one engine with 9% CH_4 by weight in the exhaust gas.

7.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 2**.

7.2. DESTRUCTION OF GASEOUS STREAMS

7.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithms in **Section 7.1**.

7.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 5.00E-00 × M × MF_{CH4}

where:
M = total mass of gas flared (in tonnes)
MF_{CH4} = mass fraction of methane in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in “well designed and operated flares, such as in refineries”.

Reference: [15], Section 4.4, Figure 4-2.

7.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 2.28E-05 × Refinery Feed (in m^3)

Reference: [15], Section 4.4, Table 4-7.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

7.2.2. Incinerators

For all incinerator gas streams, use the algorithm in **Section 7.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 7.1**.

7.3. FUEL GAS SYSTEMS

Fugitive emissions can occur from the components e.g. valves, flanges, etc., in fuel gas lines containing methane. Emissions may be determined from leak monitoring surveys where CH_4 concentrations are measured, or calculated using equipment component counts (see **Section 13.5**). Where neither of these is available, a conservative emissions estimate can be obtained from:

Mass emitted (kg) = 3.00E-01 × M × MF_{CH4}

where:
M = total mass of fuel gas combusted (in tonnes)
MF_{CH4} = mass fraction of methane in fuel gas

Reference: [16], Appendix E.

7.4. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the total hydrocarbons emissions can be conservatively estimated using the factor provided in reference [6], Table 5.1-1. This reference states that methane comprises less than 1% by mass of the total hydrocarbon emissions.

8. CARBON MONOXIDE (CO)

Estimation methods are provided for emissions due to:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Partial burn regeneration of fluidised catalytic cracking units (FCCUs)
- Regeneration of catalytic reforming units

8.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 3**.

Table 3 CO Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)[1]	1.62E+01	[17] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1]	1.51E+01	[17] Section 1.3, Table 1.3-1
	LPG[2]	3.71E+01	[17] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[17] Section 1.4, Table 1.4-1
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)[1]	1.62E+01	[17] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1]	1.51E+01	[17] Section 1.3, Table 1.3-1
	LPG[2]	3.71E+01	[17] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[17] Section 1.4, Table 1.4-1
Boilers and Furnaces > 100 MW	Distillate (gas oil)[1]	1.62E+01	[17] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1]	1.51E+01	[17] Section 1.3, Table 1.3-1
	LPG[2]	3.47E+01	[18] SCC 10101002
	Natural Gas	3.93E+01	[17] Section 1.4, Table 1.4-1

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Gas Turbine[3]	Distillate (gas oil)[4]	1.49E+00	[19] Section 3.1, Table 3.1-1
	Natural Gas	3.92E+01	[19] Section 3.1, Table 3.1-1
Gas Engine[5] 4-stroke, Lean Burn	Natural Gas	2.66E+02	[19] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	3.85E+02	[19] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG[2]	3.71E+01	[17] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[17] Section 1.4, Table 1.4-1

Notes:

1. Reference [17], Table 1.3-1, note *e* states that CO emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.
2. Factor is for propane combustion.
3. Factor derived from turbines operating at high (≥ 80%) loads.
4. Factor provided in reference [19] was derived using HHV of 139 MBtu/10^3 US gal.
5. Factor derived from engines operating at < 90% load.

8.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 3**.

8.2. DESTRUCTION OF GASEOUS STREAMS

8.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithms in **Section 8.1**.

8.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 1.77E-01 × M × NCV

where:
M = mass of flare gas combusted (in tonnes)
NCV = net calorific value of the flare gas combusted (in MJ/kg)

Reference: [20], Section 4.2.1, Table 8.

8.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 1.20E-02 × Refinery Feed (in m^3)

Reference: [21], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

8.2.2. Incinerators

For all incinerator gas streams, use the algorithm in **Section 8.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 8.1**.

8.3. CATALYTIC CRACKING UNIT REGENERATORS

CO is produced during the regeneration process and depends upon its severity. Emissions from partial burn regeneration are normally controlled with a CO boiler.

It is anticipated that EU refineries will estimate CO_2 emissions from FCCUs using the algorithm in **Section 9.3**. In this case, the CO emissions will be determined from measurements of flue gas flow and CO concentration.

Where the method in **Section 9.3** is not used, CO emissions can be estimated using the following:

8.3.1. Full Burn Regeneration

CO emissions are deemed to be negligible.

8.3.2. Partial Burn with CO Boiler

CO emissions are deemed to be negligible.

Reference: [6], Table 5.1-1.

8.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 3.92E+01 × Volume of fresh feed to unit (in m^3)

Reference: [6], Table 5.1-1.

8.4. CATALYTIC REFORMING UNITS

Mass emitted (kg) = 4.16E-02 × Volume of feed to unit (in m^3)

Reference: [14], Table 1. This reference uses data from a number of units with varying degrees of abatement equipment installed – see **Section 6.3**. It also provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

9. CARBON DIOXIDE (CO_2)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Other catalyst regeneration e.g. in catalytic reforming units
- Fluid and Flexi-cokers
- Hydrogen plants

European refineries must estimate their CO_2 emissions under the terms of the EU greenhouse gas emission allowance trading scheme [22]. Reference [23] sets out detailed guidelines for the monitoring and reporting of CO_2 emissions.

9.1. COMBUSTION

Reference [23] specifies that CO_2 emissions from combustion installations be calculated by multiplying the energy content of each fuel used by an emission factor and an oxidation factor (default value equal to one). This requires the NCV of each fuel to be determined along with activity-specific emission factors.

The algorithm provided below applies the fundamental principle of complete stoichiometric combustion using the value of carbon content of the fuel. This approach reduces the emission calculation uncertainty as only carbon content has to be determined instead of values for both NCV and emission factor,

Mass emitted (kg) = $1000 \times M \times MF_{CARBON} \times CFC_{MW}$

where:
M = mass of fuel burnt (in tonnes)
MF_{CARBON} = mass fraction of carbon in fuel
CFC_{MW} = Molecular weight conversion from C to CO_2 = (44.01/12.01) = 3.664

Thus for refinery oil and gaseous fuels:

Mass emitted (kg) = 3.664E+03 × M × MF_{CARBON}

9.2. DESTRUCTION OF GASEOUS STREAMS

9.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 9.1**.

9.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known, use algorithm in **Section 9.1**, where:
M = mass of flare gas burnt (in tonnes)
MF_{CARBON} = mass fraction of carbon in flare gas

[23] specifies this methodology for CO_2 reporting purposes by European refineries.

9.2.1.2. Flare Stream Composition Unknown

If the composition of the flare gas stream is not known, a conservative factor based on the combustion of ethane can be used:

Mass emitted (kg) = 3.93E+00 × Volume of gas flared (in m^3)

Reference: [23], Annex II, Section 2.1.1.3 (b).

9.2.1.3. Flare Stream Details Unknown

If both the mass and the composition of the flare gas stream are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 3.14E+00 × Refinery Feed (in tonne)

Reference: [24], Section 3, Table 5.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

9.2.2. Incinerators

Use algorithm in **Section 9.1**, where:
M = mass of gas incinerated (in tonnes)
MF_{CARBON} = mass fraction of carbon in gas incinerated

9.3. CATALYTIC CRACKING UNIT REGENERATORS

Reference [23] requires that emissions shall be calculated by a material balance approach, taking into account the state of the input air and the flue gas. Note that for CO_2 reporting, all CO in the flue gas shall be reported as CO_2.

[25] provides the following algorithm:

Mass emitted (kg) = $(AR + SR) \times (VF_{CO2} + VF_{CO}) \times CON_{VOL} \times TIME$

where:

AR = Air blower capacity (in m^3/minute)
SR = Supplemental oxygen addition rate (in m^3/minute)
VF_{CO2} = Volume fraction of CO_2 in flue gas
VF_{CO} = Volume fraction of CO in flue gas (prior to CO boiler if installed)
CON_{VOL} = Volume conversion factor at 15 C = 44 / MCF
MCF = Molar conversion factor at 15 C = (22.4 × 288 / 273) = 23.631 m^3/kgmole
TIME = time blower operated (in minutes)

Thus:

Mass emitted (kg) = 1.86E+00 × (AR + SR) × (VF_{CO2} + VF_{CO}) × TIME

Reference: [15], Section 5.2.1, equation 5-4.

9.3.1. FCCU With CO Boiler

Mass emitted (kg) = 1.86E+00 × (AR + SR) × (VF_{CO2} + VF_{CO}) × TIME

9.3.2. FCCU Without CO Boiler

Mass emitted (kg) = 1.86E+00 × (AR + SR) × VF_{CO2} × TIME

9.4. OTHER CATALYST REGENERATION

CO_2 is produced during the catalyst regeneration in reforming and hydro-processing units.

9.4.1. Flue Gas Flow and Composition Known

Reference [23] specifies that the method provided in **Section 9.3** should be used.

9.4.2. Flue Gas Details Unknown

The following algorithm conservatively assumes complete stoichiometric combustion of the carbon in the coke deposited on the catalyst. In practice there will be small emissions of CO (see **Section 8.4**).

Mass emitted (in kg) = 3.66E+03 × CR × MF_{CARB} × Feed

where:
CR = Mass ratio of coke produced per feed
MF_{CARB} = Mass fraction of carbon in coke
Feed = Feed to unit (in tonnes)

Reference: [15], Section 5.2.4.

9.5. COKERS

There are several varieties of cokers in use in refineries, including delayed cokers, fluid cokers, and flexi-cokers.

Delayed cokers will not have CO_2 emissions, other than from their process heaters [15]. These should be calculated using the fuel combustion algorithm in **Section 9.1**.

Fluid cokers and flexi-cokers may have a CO_2 vent resulting from the coke burner.

Reference [23] specifies that the method provided in **Section 9.3** should be used for flexi-cokers.

For cokers where flue gas flow and composition are unknown:

Mass emitted (in kg) = 3.66E+03 × CR × MF_{CARB} × Feed

where:
CR = Mass ratio of coke produced per feed
MF_{CARB} = Mass fraction of carbon in coke
Feed = Feed to unit (in tonnes)

Reference: [15], Section 5.2.3.

If the burner off-gas is burned as a low joule gas fuel, the subsequent emissions should be calculated using the fuel combustion algorithm in **Section 9.1**.

9.6. HYDROGEN PLANTS

CO_2 is produced during the hydrogen production process.

9.6.1. Feed Composition Data Known

Reference [23] specifies that emissions should be calculated from the carbon content of the feed gas.

Mass emitted (kg) = 3.66E+03 × MF_{CARB} × Feed

where:
MF_{CARB} = mass fraction of carbon in feed gas
Feed = Feed to unit (in tonnes)

9.6.2. Feed Composition Data Unknown

If the composition of the feed gas is not known, a conservative factor based on an ethane feed can be used:

Mass emitted (kg) = 2.90E+03 × Feed to unit (in tonnes)

Reference: [23], Annex III, Section 2.1.2.2 (b).

10. HYDROFLUOROCARBONS (HFC)

Hydrofluorocarbons (HFCs) may be used as refrigerants in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

11. NITROUS OXIDE (N_2O)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators

11.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 4**.

Table 4 N_2O Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	8.40E-01	[15] Section 4, Table 4.4a
	Refinery Fuel Oil	1.60E+00	[15] Section 4, Table 4.4a
	LPG	4.33E+00	[15] Section 4, Table 4.4a
	Natural Gas	1.03E+00	[15] Section 4, Table 4.4a
	Natural Gas (where low NO_X burners fitted)	3.00E-01	[15] Section 4, Table 4.4a
Gas Turbine[1]	Natural Gas	1.43E+00	[15] Section 4, Table 4.5
Gas Engine 4-stroke, Lean Burn	Natural Gas	Not Detected[2]	[15] Section 4, Table 4.5
Diesel Engine Large, Stationary	Diesel Fuel	2.21E+00	[15] Section 4, Table 4.5
Incinerator Support Fuel or Flare Pilot Fuel	LPG	4.33E+00	[15] Section 4, Table 4.4a
	Natural Gas	1.03E+00	[15] Section 4, Table 4.4a

Notes:

1. Factor based on limited source tests on a single turbine with water-steam injection and operating at high (≥ 80%) loads.

2. Compound was not detected. The emission factor stated in reference [15] represents the detection limit. For the purposes of this report the emission factor is considered to be zero as source not proven (See **Section 5.2** of this report).

11.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 4**.

11.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 11.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 11.1**.

12. AMMONIA (NH_3)

Estimation methods are provided for emissions from:

- Selective Non-Catalytic NO_X Reduction (SNCR) systems
- Selective Catalytic NO_X Reduction (SCR) systems
- Refrigeration systems
- Catalytic Cracking Unit Regenerators

12.1. NO_X REDUCTION SYSTEMS

Ammonia is produced as a by-product by SCR and SNCR systems installed in flues to reduce NO_X emissions.

12.1.1. SNCR

The emission algorithms are:

Mass emitted (kg) = 3.50E-01 × V_{OIL}

or

Mass emitted (kg) = 2.88E+02 x V_{GAS}

where:
V_{OIL} = Volume of oil combusted in device connected to SNCR (in m^3)
V_{GAS} = Volume of gas combusted in device connected to SNCR (in million m^3)

Reference: [26], Section 5.4, Table 5-5.

12.1.2. SCR

The emission algorithms are:

Mass emitted (kg) = 1.70E-01 × V_{OIL}

or

Mass emitted (kg) = 1.46E+02 x V_{GAS}

where:
V_{OIL} = Volume of oil combusted in device connected to SCR (in m^3)
V_{GAS} = Volume of gas combusted in device connected to SCR (in million m^3)

Reference: [26], Section 5.4, Table 5-5.

12.2. REFRIGERATION SYSTEMS

Ammonia may be used as a refrigerant in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

12.3. CATALYTIC CRACKING UNIT REGENERATORS

NH_3 is produced during the regeneration process and depends upon its severity. Emissions from partial burn regeneration are normally controlled by a CO boiler.

12.3.1. Full Burn Regeneration

Emissions are deemed to be negligible

Reference: [27], Section 9.3.4.

12.3.2. Partial Burn with CO Boiler

Emissions are deemed to be negligible

Reference: [27], Section 9.3.4.

12.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 1.55E-01 × Volume of fresh feed to unit (in m^3)

Reference: [26], Section 4, Table 4.1.

13. NON-METHANE VOLATILE ORGANIC COMPOUNDS (NMVOC)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Fluid cokers
- Components under pressure e.g. pumps and valves ("fugitives")
- Process drains
- Oil-water separators
- Loading of mobile containers (rail-cars, road tankers, ships and barges)
- Storage tanks
- Venting to atmosphere of uncontrolled blowdown systems
- Uncontrolled bitumen blowing

The driver for reporting VOC emissions is photochemical production of ozone. Methane has a negligible photochemical reactivity. In Europe this compound is therefore excluded from the "basket" of reactive VOCs which are collectively referred to as non-methane volatile organic compounds (NMVOC). The US EPA also considers ethane to have a significantly low reactivity. A number of emission factors developed by the EPA, therefore, are for non-(methane and ethane) VOCs. Those NMVOC emission factors provided in this section which exclude ethane emissions are identified.

13.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 5**.

Table 5 NMVOC Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.10E+00	[17] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	3.41E+00	[17] Section 1.3, Table 1.3-3
	LPG[1]	3.96E+00	[17] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[17] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	6.47E-01	[17] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	8.45E-01	[17] Section 1.3, Table 1.3-3
	LPG[1]	3.96E+00	[17] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[17] Section 1.4, Table 1.4-2
Boilers and Furnaces > 100 MW	Distillate (gas oil)	2.46E+00	[17] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	2.29E+00	[17] Section 1.3, Table 1.3-3
	LPG[2]	2.27E+00	[18] SCC 10101002
	Natural Gas[2]	2.58E+00	[17] Section 1.4, Table 1.4-2
Gas Turbine[2, 3]	Distillate (gas oil)[4]	1.86E-01	[19] Section 3.1, Table 3.1-2a
	Natural Gas	1.00E+00	[19] Section 3.1, Table 3.1-2a
Gas Engine[2] 4-stroke, Lean Burn	Natural Gas	5.64E+01	[19] Section 3.2, Table 3.2-2
Diesel Engine[5] Large, Stationary	Diesel Fuel	3.71E+01	[19] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG[1]	3.96E+00	[17] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[17] Section 1.4, Table 1.4-2

Notes:

1. Factor is for propane combustion. Derived by subtracting the emissions factor for methane from that for total organic compounds.
2. Factor excludes ethane emissions.
3. Factor derived from turbines operating at high (≥ 80%) loads
4. Factor provided in reference [19] was derived using HHV of 139 MBtu/10^3 US gal.
5. Based on data from one engine with exhaust gas TOC composition by weight of 91% NMVOCs.

13.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 5**.

13.2. DESTRUCTION OF GASEOUS STREAMS

13.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 13.1**.

13.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 5.00E-00 × M × MF_{NMVOC}

where:
M = total mass of gas flared (in tonnes)
MF_{NMVOC} = mass fraction of NMVOC in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in "well designed and operated flares, such as in refineries".

Reference: [15], Section 4.4.

13.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 2.00E-03 × Refinery Feed (in m^3)

This factor is for total unburned hydrocarbons. Comparison with the emission factor for methane (**Section 7.2.1.2**) indicates that methane is assumed to constitute about 1% by mass of the total unburned hydrocarbons.

Reference: [21], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

13.2.2. Incinerators

For all incinerator gas streams, use the algorithm in **Section 13.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 13.1**.

13.3. CATALYTIC CRACKING UNIT REGENERATORS

NMVOCs are produced during the regeneration process. Emissions from units operating with partial burn regeneration are normally controlled with a CO boiler.

13.3.1. Full Burn Regeneration

Emissions are deemed to be negligible

13.3.2. Partial Burn with CO Boiler

Emissions are deemed to be negligible

Reference: [6], Table 5.1-1.

13.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 6.30E-01 × Volume of fresh feed to unit (in m^3)

This factor is for total hydrocarbons (THC). Reference [6] states that, overall, less than 1% by mass of THC emissions is methane.

Reference: [6], Table 5.1-1.

13.4. FLUID COKERS

If the off-gas is not fed to a CO boiler, or it is not in operation:

Mass emitted (kg) = 4.60E-02 × Feed to unit (in m^3)

Reference: [20], Section 4.2.1, Table 8.

13.5. FUGITIVE EMISSIONS FROM PRESSURISED COMPONENTS

Emissions can occur due to leakage past seals on components installed in pressurised pipework or process plant e.g. valves, pumps, flanges, etc.

Emission estimates can be made by:

- Measuring the VOC concentration adjacent to potential leak points and estimating the emission flux using correlation equations or emission factors.
- Detecting leaks using optical gas imaging.
- Using average emission factors for individual types of components and their process service, where the number of components is known.
- Using a conservative overall emission factor based on refinery throughput.

Note that this Section does not deal with emissions from low pressure equipment such as drains, oil-water separators, loading systems and product storage tanks. Emission estimation methodologies for these sources are provided separately – see **Sections 13.6**, **13.8** and **13.9**.

13.5.1. Leak Detection Surveys Undertaken

Leaking components can be identified either using a conventional hydrocarbon monitor to measure the VOC concentration adjacent to potential leak points or an optical gas imaging (OGI) camera can be used to visualise gas leaks remotely.

This report does not provide details of the measurement methods. A CONCAWE Report [28] provides a comparative review of conventional and OGI techniques for leak detection.

13.5.1.1. Conventional Hydrocarbon Monitor

This method requires the “screening” of leak sources by measuring the concentration of VOCs at the surface of each potential source using a conventional hydrocarbon monitor. The local VOC concentration (“screening value”) at the surface of a leak source is converted into an emission flux using a correlation equation or emission factors.

Details of the methodologies and the calculation of emissions are provided by the US EPA [29] and in the European CEN Standard on fugitive emission estimation [30].

13.5.1.2. Optical Gas Imaging Camera

In this method emissions are estimated using a “leak” / “no-leak” criterion where the emission factor used depends on the "leak" detection sensitivity of the camera. The emission factors for each equipment type for specified camera detection limits are provided in **Table 6.**

The emissions can be calculated for each equipment type and service using:

$$\textbf{Mass emitted (kg)} = [(F_{LEAK} \times N_{LEAK}) + (F_{NO\text{-}LEAK} \times N_{NO\text{-}LEAK})] \times \textbf{TIME}$$

where:
F_{LEAK} = Emission factor for leaking components according to the detection limit of the camera
N_{LEAK} = Number of components identified as leaking
$F_{NO\text{-}LEAK}$ = Emission factor for non-leaking components according to the detection limit of the camera
$N_{NO\text{-}LEAK}$ = Number of components identified as not leaking
TIME = Time that the equipment is in operation and pressurised (in hours).

Details of the methodology and the calculation of emissions are provided in Concawe report 6/08 [28] and in reference [31].

Table 6 Leak/No-Leak Emission Factors where optical gas imaging (OGI) is used to detect leaks

Equipment Type	Factor Type	Emission Factor for Specified OGI Leak Definition for different camera sensitivity settings kg/hr/source			
		3 g/hr	6 g/hr	30 g/hr	60 g/hr
Valves	Leak	5.50E-02	7.30E-02	1.40E-01	2.00E-01
	No-Leak	1.90E-05	4.30E-05	1.70E-04	2.70E-04
Pumps	Leak	1.40E-01	1.60E-01	3.10E-01	3.50E-01
	No-Leak	9.60E-05	1.30E-04	5.90E-04	7.50E-04
Flanges	Leak	2.90E-02	4.50E-02	8.80E-02	1.20E-01
	No-Leak	2.60E-06	4.10E-06	1.00E-05	1.40E-05
All other components	Leak	5.60E-02	7.50E-02	1.50E-01	2.10E-01
	No-Leak	7.00E-06	1.40E-05	5.10E-05	8.10E-05

Reference: [31]

Definitions of "Service"

Reference [30] provides the following definitions for "service":

- Gas service: equipment which in use contains process fluid that is in the gaseous state at operating conditions.
- Light liquid service: equipment which in use contains hydrocarbon streams of which at least 20% wt has a vapour pressure in excess of 0.3 kPa at 20ºC. For example, this includes automotive and aviation gasolines and crude oil. It excludes products such as kerosenes and gasoils.

13.5.2. Leak Detection Surveys Not Undertaken

13.5.2.1. Component Data Available

Where no monitoring (or only a partial survey) has been undertaken, the emissions from un-surveyed equipment can be calculated using:

Mass emitted (kg) = F_{COMP} × N × TIME

where:
F_{COMP} = Average emission factor for the particular equipment type as in **Table 7**.
N = Number of pieces of equipment grouped in the relevant category according to the equipment type, service and operation.
TIME = Time that the equipment group is in operation and pressurised (in hours).

This algorithm is conservatively high as it assumes that the product contained within the equipment components wholly comprises NMVOCs i.e. it does not account for non-NMVOC components contained within the fugitive emission. However, the non-

NMVOC emissions will mainly be methane e.g. from fuel gas, and this has the lowest density of the hydrocarbons emitted. For fuel gas systems this can be compensated for; see **Section 7.3** for methane emission estimation. Moreover, the number of equipment components in pipelines containing low concentration NMVOC streams (e.g. low joule gas) is generally a very small percentage of the total components on a refinery.

Table 7 Average Emission Factors for Components

Equipment Type	Service	Emission Factor kg/hr/source
Valves	Gas	2.68E-02
	Light Liquid	1.09E-02
Pump seals	Light Liquid	1.14E-01
Compressor seals	Gas	6.36E-01
Pressure relief valves	Gas	1.60E-01
Flanges and non-flanged connectors	All	2.50E-04
Open-ended lines	All	2.30E-03
Sampling connections	All	1.50E-02

Reference: [30]

<u>Component counts</u>

The count can be based on up-to-date piping and instrumentation diagrams, equipment lists, operating manuals or physical component counts. The count should include spare components if these are filled with process fluid and are pressurised.

If actual counts are not available, an extrapolation can be made from published information. Reference [32] cites an example of a US refinery of 52 500 m^3/day capacity having 11 500 valves, 46 500 flanges, 350 pump seals, 70 compressor seals and 100 relief valves.

Alternatively, reference [27], Section 3.4.1, Table 3-1, provides the following "average" refinery data:

Emission Source Component	Gas	Liquid
Valves per pump or compressor	133	41
Flanges per valve	4.1	4.1
Mixer seals per mixer	-	1
Pump seals per pump	-	1.35
Compressor seals per compressor	2	-

13.5.2.2. No Component Data Available

A conservative emission factor can be used if no data on components are available:

Mass emitted (kg) = 2.00E-01 × Refinery feed (in tonnes)

Reference: [5], Chapter 1.B.2.a.iv, Table 3-6.

13.6. OILY-WATER COLLECTION AND TREATMENT SYSTEMS

Contaminated waste water systems principally comprise process drains and a water treatment facility, such as a gravity separator. The emissions from oily-water systems vary significantly with time, depending, for example, on the amount and volatility of the entrained oil, waste water temperature, flow, etc.

Emissions can be estimated for the entire system using complex models available as software packages (see **Section 13.6.1**).

Alternatively, the emissions from the process drains and the separator systems can be estimated separately (see **Sections 13.6.2** and **13.6.3**).

13.6.1. Emission Estimation Models For Entire System

There are a number of complex estimation models available to calculate emissions from waste water systems. They aim to estimate average emission rates of individual species for each of the system components, collectively permitting the determination of the overall emissions from a refinery wastewater collection and treatment system.

The US EPA has developed a freely available computer program model called WATER9 [33]. This is Windows based and consists of analytical expressions for estimating air emissions of individual waste constituents in waste water collection, storage, treatment, and disposal facilities. Reference [34] provides the mathematical equations used in this model.

It should be noted that the input data demands of the model are large and require considerable sampling and analyses to be undertaken. However, it is likely that the increased level of characterisation of the hydrocarbons present in the refinery's waste water will lead to more accurate estimation of emissions than the more simple emission factor approach.

13.6.2. Process Drains

The following algorithm provides an estimate for emissions from the entire refinery process drain system in oily-water service. Note that drain systems on clean water (with minimal potential for contact with oil) and storm water are excluded.

Process drains and junction boxes are normally fitted with an emission control device such as a water seal or sealed cover. An assessment needs to be made to establish how many of the drain covers are unsealed and vent directly to atmosphere.

Mass emitted (kg) = 3.20E-02 × N × TIME

where:
N = number of <u>unsealed</u> drain openings in the refinery process drain system.
TIME = period of emission estimate in hours (for E-PRTR annual reports = 8760)

This factor excludes ethane emissions.

Reference: [27], Section 7.5, Table 7-3.

13.6.3. Oil-Water Separators

Emissions from separators can be determined using simple emission factors which are known to give conservatively high estimates. Alternatively, an algorithm can be used for uncovered gravity separators which requires, as a minimum, data on separator inlet flow and entrained oil concentration. Sampling and analysis thus have to be undertaken and due to the temporal variability of the input parameters the estimation accuracy will depend on the frequency of testing.

13.6.3.1. Gravity Separator - where separator inlet monitoring data available

An estimate for the emissions from uncovered API type separators is provided by:

Mass emitted (kg) = $1.00E\text{-}04 \times D \times V \times (5.74 \times T_{AMB} - 5.15 \times T_{DP} + 38.6 \times T_{WW} + 33.6) \times TIME$

where:
D = liquid density of evaporated hydrocarbons (kg/m^3). If unknown, [36] provides a default average value of 660 kg/m^3
V = flow rate of hydrocarbons entering the separator (m^3/h). Calculated from data on waste water flow and concentration of hydrocarbons in the waste water.
T_{AMB} = ambient water temperature (°C)
T_{DP} = 10% distillation point (°C). If unknown, [36] provides a default average value of 150°C
T_{WW} = Waste water temperature (°C)
TIME = period of emission estimate in hours (for E-PRTR annual reports = 8760)

Reference: [35], developed in reference [36], Section 5.2.

Where a cover is fitted to a gravity separator, the emissions abatement efficiency can be assumed to be 97% [27].

13.6.3.2. Simple Algorithms

These algorithms assume emissions to be dependent solely on the type of separator installed.

Mass emitted (kg) = $EF_{SEP} \times VOL_{WATER}$

where:
EF_{SEP} = Emission factor for the type of separator given in **Table 8**.
VOL_{WATER} = Volume of waste water treated by the separator (in m^3).

Table 8 Emission Factors for Oil-Water Separators

SEPARATOR TYPE	EMISSION FACTOR (EF_{SEP})[1] kg/m^3 waste water treated
Gravity type – uncovered[2]	1.11E-01
Gravity type – covered	3.30E-03
Gravity type – covered and connected to flare	0
DAF[3] or IAF[4] – uncovered[5]	4.00E-03
DAF or IAF – covered[5]	1.20E-04
DAF or IAF – covered and connected to flare	0

Notes:

1. These factors exclude ethane emissions
2. Measurements on uncovered gravity type waste water treatment plants at two Canadian refineries varied by two orders of magnitude [27]. The factor provided here was confirmed by the greater of these measurements
3. DAF = Dissolved air floatation type
4. IAF = Induced air floatation type
5. The emission factors for these types of separator apply where they are installed as secondary treatment systems.

Reference: [27], Section 7.5, Table 7-3.

Emissions from basins and ponds that handle clean water or storm water are considered negligible.

For ponds temporarily storing oily-water, use the emission factor for an uncovered, gravity type separator from **Table 8**.

13.7. COOLING WATER TOWERS

Emissions from cooling water towers are considered negligible as sound refinery engineering practice ensures that oil is prevented from entering these systems.

Guidance on estimating emissions if a heat exchanger oil leak has occurred and monitoring data are unavailable is provided in reference [27], Section 7.7.5.

13.8. LOADING OF MOBILE CONTAINERS

Emissions from the loading of mobile containers (i.e. road tankers, rail tank cars, barges and marine tankers) depend upon the type of container being loaded and the degree of saturation of the vapour in the cargo tank. For example, uncontrolled emissions from road tankers depend upon the mode of loading (i.e. top loading with a drop pipe through an open hatch or bottom loading through pipework connected on the tanker) and if the tanker delivers product to a facility with a “vapour balancing” system installed. In this type of system, the vapours displaced from the storage tank being filled by the tanker are fed back into the tanker compartment to “balance” the off-loaded product. The tanker thus returns to the loading facility with the compartments filled with vapour.

Emissions from loading can be controlled with a vapour recovery unit (VRU) or thermal oxidiser. Algorithms for VRUs are given below. Emissions from thermal oxidisers can be calculated using the algorithms listed in this report for incinerators.

13.8.1. Uncontrolled Emissions

$$\textbf{Mass emitted (kg)} = EF_{LOAD} \times VOL_{LOAD} \times TVP$$

where:
EF_{LOAD} = Emission Factor from **Table 9**, depending on loading mode.
VOL_{LOAD} = Volume of product loaded (in m^3).
TVP = True Vapour Pressure of product at loading temperature (in kPa).

Reference: [7], Section 3.

For gasolines, TVP can be calculated from:

$$TVP = RVP \times 10^{[(7.047E\text{-}06 \times RVP + 1.392E\text{-}02) \times TEMP + (2.311E\text{-}04 \times RVP - 5.236E\text{-}01)]}$$

where:
RVP = Reid Vapour Pressure (in kPa)
TEMP = product loading temperature (in degrees Centigrade)

Reference: [7], Appendix 1.

Table 9 NMVOC Emission Factors for Loading of Mobile Containers

LOADING MODE	EMISSION FACTOR EF_{LOAD} kg/m^3/kPa
Road Tanker, Bottom Loading No Vapour Balancing during Previous Off-Loading	8.60E-03
Road Tanker, Top Loading No Vapour Balancing during Previous Off-Loading	9.40E-03
Road Tanker, Bottom or Top Loading Vapour Balancing during Previous Off-Loading	2.28E-02
Rail Tanker, Top Loading	1.08E-02
Rail Tanker, Bottom Loading[1]	1.05E-02
Marine tanker - typical cargo tank condition[2,3]	3.91E-03
Barge - typical cargo tank condition[2,3]	7.45E-03

Notes:

1. During the top loading of rail tankers emissions occur from the open loading hatch both before and after loading [7]. As there is no open hatch during bottom loading of a rail tanker, this factor assumes no pre- or post-loading emissions.
2. Value corrected from that published in [7].
3. These factors are for typical cargo tank vapour conditions. For other situations (e.g. tank gas freed or ballasted, previous cargo non-volatile, etc.) specific emission factors are provided in reference [6], Table 5.2-2 for the loading of gasoline with a TVP of 55 kPa. These factors should be prorated for the value of the TVP of the product loaded.

13.8.2. Emissions Controlled with a Vapour Recovery Unit (VRU)

VRUs may be fitted with a continuous emissions monitor (CEM) or the recovery efficiency may be known from tests.

13.8.2.1. VRU Fitted with a CEM

Mass emitted (kg) = 1.00E-03 × $\mathbf{MEAS_{CONC}}$ × $\mathbf{VOL_{LOAD}}$ × (1 – TVP / 100)

where:
$MEAS_{CONC}$ = Measured VRU vent concentration (in g/m^3)
VOL_{LOAD} = Volume of product loaded (in m^3)
TVP = True Vapour Pressure of product at loading temperature (in kPa)

Reference: [7], Section 3.2.

13.8.2.2. VRU Efficiency Known

Emissions should be calculated using the algorithm in **Section 6.1**.

13.9. STORAGE TANKS

Emissions from storage tanks comprise two components:

- Working loss; emissions due to the tank being filled (displacing vapours above the product stored) or emptied (evaporation of product “clingage” on tank internal walls)
- Standing losses: emissions due to the expansion of the vapour space in fixed roof tanks due to vapour temperature or pressure changes and leakage past equipment (e.g. seals, still wells, etc.) fitted to floating roofs.

13.9.1. Floating Roof Tanks

Floating roof tanks can be of the following types:

- External floating roof (EFR)
- EFR fitted with domed cover
- Internal floating roof (IFR)
  - fitted with open vents in the fixed roof
  - fitted with vents in the fixed roof which can be closed e.g. pressure/vacuum valves, connected to a vapour recovery unit, etc.

For all of these tank types except IFR tanks which are not freely vented, use the latest edition of reference [37]. For IFR tanks fitted with vents which can be closed, guidance is provided in reference [38] which shows that emissions from closed-vent internal floating roof tanks are approximately 5% less than emissions from internal floating roof tanks with open vents determined in accordance with [37].

Methodologies to estimate the emissions when the roof has landed on its legs and is no longer floating on the product are provided in reference [39].

13.9.2. Vertical Fixed Roof Tanks (VFRT)

For these tanks in normal service, use the latest edition of reference [40].

13.9.2.1. VFRTs Connected to a Vapour Holding Tank (VHT)

A vapour holding tank comprises a fixed roof tank containing a flexible diaphragm. Where connected to a storage tank, a correctly sized VHT stores any emissions from the tank due to the rise in vapour temperature during the day, and then releases these vapours back to the tank as it cools at night. The VHT, therefore, controls the "standing losses".

Emissions, therefore, can be assumed to equal only the "working losses".

13.9.3. Aboveground Horizontal Tanks

For these tanks, use the latest edition of reference [41], Section 7.1.3.1.

13.9.4. Underground Tanks

Use the algorithms for service station storage tanks provided in **Appendix 4.2**.

13.9.5. Tank Cleaning

Guidance on the estimation of evaporative emissions during tank cleaning is provided in reference [42].

13.9.6. Storage Tanks - General Comments

Reference [41] normally contains the latest versions of references [37], [39] and [40]. Emission calculation software utilising the algorithms in reference [41] is available from the US EPA via their website, http://www.epa.gov, or on a CD-ROM [43]. This CD also contains the EPA publication AP-42 *Compilation of Air Pollutant Emission Factors* and references [29], [34].

It should be noted that some options are provided in the algorithms in references [37] to [41] to cover the state of equipment; e.g. degrees of rust on tank internal shells, tightness of floating roof seals, etc. Users of the algorithms, therefore, must ensure that the factors utilised to derive emissions for a particular tank are appropriate. In particular, the API states that the algorithms are only 'applicable to properly maintained equipment under normal working conditions'

13.10. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the total hydrocarbons emissions can be conservatively estimated using the factor provided in reference [6], Table 5.1-1.

13.11. UNCONTROLLED BITUMEN BLOWING

The gaseous emissions from bitumen blowing in EU refineries are controlled, for example using scrubbers and incinerators.

Where these controls are not operational and all of the emissions are emitted to atmosphere, the emissions can be estimated using the factor in reference [21], Activities 040101 & 040102, Section 8.2.1, Table 8.2.

14. NITROGEN OXIDES (NO_X)

Estimation methods are provided for emissions of NO_X from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators

14.1. COMBUSTION IN BOILERS AND FURNACES

NO_X emissions from combustion comprise two components:

- Thermal NO_X; this is the thermal fixation of molecular nitrogen and is generally a function of flame temperature, residence time and oxygen concentration in the flame zone
- Fuel NO_X; this is the result of the direct oxidation of the nitrogen in liquid fuels or the non-inert nitrogen containing species in gaseous fuels.

The following methodology is outlined in more detail, with an example, in reference [44].

Total NO_X Emissions = Thermal NO_X + Fuel NO_X

<u>Thermal NO_X</u>

Thermal NO_X Mass emitted (kg) = 1.00E-03 × TNF × M × HHV

where:
TNF = Thermal NO_X factor (in g/GJ)
M = Mass of fuel combusted (in tonnes)
HHV = Higher heating value of the fuel combusted (in MJ/kg)
For liquid fuels
HHV = 1.05 × NCV
For gaseous fuels
HHV = 1.11 × NCV
where NCV = Net calorific value (in MJ/kg)

$$\mathbf{TNF = F_{BASE} \times F_{H2} \times F_{CONTROL} \times F_{PREHEAT} \times F_{H_2O} \times F_{LOAD} \times F_{BURN}}$$

F_{BASE} is the base fuel factor. This accounts for differences in flame temperature due to fuel composition and is therefore dependent on the type of fuel burnt. Values for different fuels are given in **Table 10**.

Table 10 Values for F_{BASE}

FUEL	F_{BASE} (g/GJ) (HHV)
Methane, Natural Gas, LPG	56
Refinery Fuel Gas	69
Low Joule Gas	30
Refinery Fuel Oil, Distillates	56

F_{H2} is the adjustment factor for the amount of hydrogen gas in the fuel.

For all liquid fuels, methane, natural gas and LPG: $F_{H2} = 1.0$

For other refinery gaseous fuels, values for F_{H2} are given for some hydrogen concentrations in **Table 11**. These can be used to extrapolate for other compositions.

Table 11 Values for F_{H2}

FUEL	H_2 CONCENTRATION % v/v	F_{H2}
Refinery Fuel Gas	0 - 23	1.00
	33	1.04
	43	1.09
	63	1.25
	83	1.46
Low Joule Gas	0 - 14.7	1.00
	24.7	1.04
	34.7	1.09
	54.7	1.25
	74.7	1.46

$F_{CONTROL}$ is the adjustment factor for at-the-source control technologies, including burner type. Values are given in **Table 12**.

Table 12 Values for $F_{CONTROL}$

CONTROL TECHNOLOGY		$F_{CONTROL}$
None		1.00
Low NOX burner, staged fuel		0.33
Low NOX burner, staged air		0.60
Ultra-low NOx burner		0.30
Flue Gas Recirculation	0%	1.00
	5%	0.60
	10%	0.40
	15%	0.30
	20%	0.20

$\mathbf{F_{PREHEAT}}$ is the adjustment factor for the average air preheat temperature. Values are given in **Table 13**.

Table 13 Values of $F_{PREHEAT}$

AIR PREHEAT TEMPERATURE Degrees C	$\mathbf{F_{PREHEAT}}$
< 38	1.00
38	1.00
93	1.10
149	1.32
204	1.60
260	1.86

$\mathbf{F_{H_2O}}$ is the adjustment factor for the moisture content of the combustion air. Values are given in **Table 14**.

Table 14 Values of F_{H_2O}

MOISTURE CONTENT kg H_2O / kg dry air	$\mathbf{F_{H_2O}}$
0	1.00
0.01	0.79
0.02	0.67
0.03	0.53
0.04	0.41
0.05	0.29

$\mathbf{F_{LOAD}}$ is the adjustment factor for the loading of the combustion unit. For dual fuel firing, the load is calculated using the total thermal input. Values are given in **Table 15**.

Table 15 Values of F_{LOAD}

LOAD (% of design)	$\mathbf{F_{LOAD}}$
40	0.55
60	0.70
80	0.85
100	1.00

$\mathbf{F_{BURN}}$ is the adjustment factor for the burner intensity, a measure of the heat release per volume of burner space. There is no precise measure for burner intensity. Where no combustion unit information on intensity is available, in general high intensity burners are used for packaged boilers and pyrolysis furnaces and low intensity burners are used for all other fired heaters and boilers. Where furnace (radiant cell) volume is known, then the classification can be ascertained from:

- High intensity is > 700 KW/m^3
- Low intensity is < 30 kW/m^3

Values for F_{BURN} are given in **Table 16**.

Table 16 Values for F_{BURN}

BURNER INTENSITY	F_{BURN}
High	1.8
Low	1.0

Fuel NO_X

Fuel NO_X Mass emitted (kg) = 1.00E-03 × FNF × M × HHV

where:
FNF = Fuel NO_X factor (in g/GJ)
M = Mass of fuel combusted (in tonnes)
HHV = Higher Heating Value of the fuel combusted (in MJ/kg)

FNF = (1.00E+04 × $MP_{NITROGEN}$ × CFN_{MW} × $F_{N2CONTENT}$) / HHV

where:
$MP_{NITROGEN}$ = Mass Percentage of Nitrogen in the fuel combusted
CFN_{MW} = Molecular weight conversion from N to NO_2 = 46 / 14 = 3.286
$F_{N2CONTENT}$ = Adjustment factor for nitrogen content. Values are given in **Table 17**.

Table 17 Values for $F_{N2CONTENT}$

FUEL NITROGEN % m/m	$F_{N2CONTENT}$	
	Uncontrolled Burner	Low-NOx burner with staged air
< 0.05	1.00	1.00
0.05	0.87	0.86
0.1	0.78	0.75
0.3	0.53	0.43
0.5	0.38	0.30
1.0	0.32	0.25[1]

Notes:
1. Reference: [45] - value corrected from that published in reference [44].

Combining the above equations:

Fuel NO_X Mass emitted (kg) = 32.86 × $MP_{NITROGEN}$ × $F_{N2CONTENT}$ × M

where:
$MP_{NITROGEN}$ = Mass Percentage of Nitrogen in the fuel combusted (see note below).
$F_{N2CONTENT}$ = Adjustment factor for nitrogen content. Values are given in **Table 17**.
M = Mass of fuel combusted (in tonnes)

Note: the mass percentage of nitrogen in gaseous fuels only relates to the nitrogen bound in the combustible components in the fuel (e.g. ammonia) and does not apply to molecular nitrogen (N_2) where present as a gaseous fuel component.

Reference: [44].

14.2. GAS TURBINES

14.2.1. Natural Gas Combustion

Mass emitted (kg) = 1.53E-01 × M × NCV

where:
M = mass of fuel gas burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [19], Table 3.1-1. Factor derived from turbines operating at high loads (≥ 80%).

14.2.2. Distillate Oil Combustion

Mass emitted (kg) = 3.98E-01 × M × NCV

where:
M = mass of distillate oil burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [19], Table 3.1-1. Factor derived from turbines operating at high loads (≥ 80%).

14.3. GAS ENGINES (4 STROKE, LEAN BURN)

Mass emitted (kg) = 4.05E-01 × M × NCV

where:
M = mass of fuel gas burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [19], Table 3.2-2. Factor derived from engines operating at < 90% load.

14.4. DIESEL ENGINES (LARGE, STATIONARY)

Mass emitted (kg) = 1.45E+00 × M × NCV

where:
M = mass of diesel fuel burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [19], Table 3.4-1.

14.5. COMBUSTION OF AUXILIARY AND PILOT FUELS

Auxiliary fuels are used to support combustion in, for example, CO boilers and incinerators. Pilots are used to initiate combustion in flares.

Mass emitted (kg) = 6.22E-02 × M × NCV

where:
M = mass of auxiliary/pilot fuel burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

This assumes emissions are equivalent to burning natural gas with dry combustion air in an uncontrolled furnace – see **Section 14.1**.

Reference: [44].

14.6. DESTRUCTION OF GASEOUS STREAMS

14.6.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 14.5**.

14.6.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 3.22E-02 × M × NCV

where:
M = mass of flare gas burnt (in tonnes)
NCV = net calorific value of the flare gas burnt (in MJ/kg)

Reference: [20], Section 4.2.1, Table 8.

14.6.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 5.40E-02 × Refinery Feed (in m^3)

Reference: [21], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

14.6.2. Incinerators

For all incinerator streams use the algorithms in **Section 14.1**, assuming that the 'fuel' is low joule gas and that $F_{CONTROL}$, $F_{PREHEAT}$, F_{LOAD} and F_{BURN} all have a value of 1.00

For emissions from the combustion of the auxiliary gas fuel used to support incinerator combustion, use the algorithm in **Section 14.5**.

14.7. CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, both with and without CO boilers:

Mass emitted (kg) = 2.04E-01 × Volume of fresh feed to unit (in m^3)

Reference: [6], Section 5.1, Table 5.1-1.

15. SULPHUR HEXAFLUORIDE (SF_6)

Emissions of sulphur hexafluoride (SF_6) may occur due to its use as a tracer gas or from leaks from high voltage electrical equipment where this gas is used as an insulator.

Emissions are assumed to equal the amount used and not recovered during test procedures and/or the mass used to top-up or refill equipment.

Mass emitted (kg) = Mass used (in kg)

16. OXIDES OF SULPHUR (SO_X)

The E-PRTR requires estimates of the total oxides of sulphur (SO_2 and SO_3) reported as SO_2.

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Catalytic reforming units

16.1. COMBUSTION

For all fuel combustion, the following algorithm applies:

Mass emitted (kg) = $1000 \times M \times MF_S \times SF_{MW}$

where:
M = mass of fuel burnt (in tonnes)
MF_S = mass fraction of sulphur in fuel
SF_{MW} = Molecular weight conversion from S to SO_2 = 64/32

This assumes that all the sulphur in the fuel is converted to SO_2.

For refinery oil and gaseous fuels:

Mass emitted (kg) = 2.00E+03 × M × MF_S

Reference: [20], Section 4.1.1.1.

16.2. DESTRUCTION OF GASEOUS STREAMS

16.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 16.1**.

16.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known, use algorithm in **Section 16.1**, where:
M = mass of flare gas burnt (in tonnes)
MF_S = mass fraction of sulphur in flare gas

16.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used. This assumes that a flare gas recovery system is not installed:

Mass emitted (kg) = 7.70E-02 × Refinery Feed (in m^3)

Reference: [21], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

16.2.2. Incinerators

For all incinerator gas streams, including that from a sulphur plant if the gas composition is known, use the algorithm in **Section 16.1**, where:
M = mass of gas incinerated
MF_S = mass fraction of sulphur in gas incinerated

For emissions from the combustion of the auxiliary gas fuel used to support incinerator combustion, also use the algorithm in **Section 16.1**.

16.2.2.1. Sulphur Plant Tail Gas Incinerator

For a sulphur plant, if the composition of the gas stream is unknown, emissions can be determined from the sulphur balance across the plant.

Mass emitted (kg) = [(100 - ERC_{EFF}) / ERC_{EFF}] × PROD × SF_{MW} × 1000

where:
ERC_{EFF} = recovery efficiency (in %)
PROD = sulphur production (in tonnes)
SF_{MW} = Molecular weight conversion from S to SO_2 = 64/32

Reference: [46], Section 8.13, Table 8.13-1.

16.3. CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, the emissions can be determined using coke sulphur content data. If these are not available, a less accurate emission factor can be used.

Where $DeSO_X$ catalyst additive is used, the abatement effect of this on the emissions should be taken into account using the algorithm in **Section 6.1** with the value of EFF being the SO_X percentage removal efficiency.

The following emission estimation algorithms are applicable both with and without CO boilers.

16.3.1. Sulphur retention on coke known

Mass emitted (kg) = 2.00E+03 × M × $\mathbf{MF_{SFEED}}$ × $\mathbf{MF_{SCOKE}}$

where:
M = mass of feed to unit (in tonnes)
MF_{SFEED} = mass fraction of sulphur in feed
MF_{SCOKE} = mass fraction of MF_{SFEED} contained in coke

Reference: [27], Section 15.3.1.4.

16.3.2. Sulphur retention on coke not known

Mass emitted (kg) = 1.41E+00 × Volume of fresh feed to unit (in $\mathbf{m^3}$)

Reference: [6], Section 5.1, Table 5.1-1.

16.4. CATALYTIC REFORMING UNITS

Mass emitted (kg) = 3.63E-03 × Volume of feed to unit (in $\mathbf{m^3}$)

Reference: [14], Table 1. This reference uses data from a number of units with varying degrees of abatement equipment installed – see **Section 6.3**.

17. HYDROCHLOROFLUOROCARBONS (HCFC)

Hydrochlorofluorocarbons (HCFCs) may be used as refrigerants in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

18. ARSENIC (As)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

18.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 18**.

Table 18 As Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.81E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	3.98E-03	[17] Section 1.3, Table 1.3-11
	Natural Gas	9.37E-05	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	3.43E-04	[11], [47][1]
Gas Turbine	Distillate (gas oil)	Not detected[2]	[19] Section 3.1, Table 3.1-5
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	9.37E-05	[17] Section 1.4, Table 1.4-4

Notes:
1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. Compound was not detected. The emission factor stated in reference [19] is based on one half of the detection limit. For the purposes of this report the emission factor is considered to be zero as source not proven (See **Section 5.2** of this report).

18.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 18.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 18.1**.

18.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.39E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

18.4. FLUID COKERS

Mass emitted (kg) = 2.16E-03 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

19. CADMIUM (Cd)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators

19.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 19**.

Table 19 Cd Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.20E-03	[17] Section 1.3, Table 1.3-11
	Natural Gas	5.16E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	7.12E-04	[11], [47][1]
Gas Turbine	Distillate (gas oil)[2]	2.17E-03	[19] Section 3.1, Table 3.1-5
	Natural Gas[3]	3.31E-03	[18] SCC 20200201
	Refinery Fuel Gas[4]	2.52E-03	[11], [47][1]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	5.16E-04	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. Factor derived from turbines operating at high (≥ 80%) loads. Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
3. Factor has an EPA quality rating of "U" (unrated).
4. Factor derived from gas turbines without duct burners.

19.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 19.1**, with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 19.1**.

19.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.25E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

20. CHROMIUM (Cr)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators

20.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 20**.

Table 20 Cr Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.48E-02	[11], [47][1]
	Natural Gas	6.55E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	2.74E-03	[11], [47][1,2]
Gas Turbine	Distillate (gas oil)[3]	4.98E-03	[19] Section 3.1, Table 3.1-5
	Natural Gas[4]	6.35E-03	[18] SCC 20200201
	Refinery Fuel Gas[5]	6.26E-03	[11], [47][1,2]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	6.55E-04	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.
3. Factor derived from turbines operating at high (≥ 80%) loads.
   Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
4. Factor has an EPA quality rating of “U” (unrated).
5. Factor derived from gas turbines without duct burners.

20.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 20.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 20.1**.

21. COPPER (Cu)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

21.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 21**.

Table 21 Cu Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	2.72E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.19E-02	[11], [47][1]
	Natural Gas	3.98E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	2.22E-03	[11], [47][1]
Gas Turbine	Natural Gas[2]	3.31E-02	[18] SCC 20200201
	Refinery Fuel Gas[3]	1.97E-02	[11], [47][1]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	3.98E-04	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. Factor has an EPA quality rating of "U" (unrated).
3. Factor derived from gas turbines without duct burners.

21.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 21.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 21.1**.

21.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.39E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

21.4. FLUID COKERS

Mass emitted (kg) = 1.50E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

22. MERCURY (Hg)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

22.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 22**.

Table 22 Hg Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	Not Detected[1]	[11], [47][2]
	Natural Gas	1.22E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	8.60E-05	[11], [47][2,3]
Gas Turbine	Distillate (gas oil)[4]	5.43E-04	[19] Section 3.1, Table 3.1-5
	Natural Gas[5]	3.17E-03	[18] SCC 20200201
	Refinery Fuel Gas[6]	7.31E-03	[11], [47][2]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.22E-04	[17] Section 1.4, Table 1.4-4

Notes:
1. Compound was not detected. Emission factor stated in reference [11] represents the detection limit. For the purposes of this report the emission factor is considered to be zero as the source is not proven (See **Section 5.2** of this report).
2. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
3. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.
4. Factor derived from turbines operating at high (≥ 80%) loads.
   Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
5. Factor has an EPA quality rating of “U” (unrated).
6. Factor derived from gas turbines without duct burners

22.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 22.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 22.1**.

22.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.95E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

22.4. FLUID COKERS

Mass emitted (kg) = 3.00E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

23. NICKEL (Ni)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

23.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 23**.

Table 23 Ni Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1,03E+00	[11], [47][1]
	Natural Gas	9.85E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	3.60E-03	[11], [47][1,2]
Gas Turbine	Distillate (gas oil)	Not detected[3]	[19] Section 3.1, Table 3.1-5
	Natural Gas[4]	5.48E-02	[18] SCC 20200201
	Refinery Fuel Gas[5]	7.93E-02	[11], [47][1]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	9.85E-04	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.
3. Compound was not detected. The emission factor stated in reference [19] is based on one half of the detection limit. For the purposes of this report the emission factor is considered to be zero as the source is not proven (See **Section 5.2** of this report).
4. Factor has an EPA quality rating of "U" (unrated).
5. Factor derived from gas turbines without duct burners.

23.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 23.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 23.1**.

23.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.12E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

23.4. FLUID COKERS

Mass emitted (kg) = 5.70E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

24. LEAD (Pb)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

24.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 24**.

Table 24 Pb Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	4.07E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	4.56E-03	[17] Section 1.3, Table 1.3-11
	Natural Gas	2.34E-04	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas	1.79E-03	[11], [47][1]
Gas Turbine	Distillate (gas oil)[2]	6.34E-03	[19] Section 3.1, Table 3.1-5
	Refinery Fuel Gas[3]	1.36E-02	[11], [47][1,4]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.34E-04	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. Factor derived from turbines operating at high (≥ 80%) loads. Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
3. Factor derived from gas turbines without duct burners.
4. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

24.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 24.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 24.1**.

24.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 3.20E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

24.4. FLUID COKERS

Mass emitted (kg) = 4.50E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

25. ZINC (Zn)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

25.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 25**.

Table 25 Zn Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.81E-03	[17] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	4.93E-02	[11], [47][1]
	Natural Gas	1.36E-02	[17] Section 1.4, Table 1.4-4
	Refinery Fuel Gas[2]	2.55E-02	[11]
Gas Turbine	Refinery Fuel Gas[3]	2.38E+00	[11], [47][1]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.36E-02	[17] Section 1.4, Table 1.4-4

Notes:

1. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures.
2. Factor represents median value as the ratio of mean to median value > 10. See **Section 5.3**.
3. Factor derived from gas turbines without duct burners.

25.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 25.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 25.1**.

25.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.18E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in CCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [20], Section 4.2.3, Tables 10 and 11.

25.4. FLUID COKERS

Mass emitted (kg) = 4.50E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [20], Section 4.2.3, Tables 10 and 11.

26. DIOXINS AND FURANS (PCDD AND PCDF)

Dioxins and furans are only produced during combustion processes under specific conditions and where chlorine is present. Estimation methods are provided for emissions from:

- Combustion of fuel oil
- Catalytic reforming units

The emission factors for each of the 17 isomers of PCDD and PCDF have been multiplied by the Toxic Equivalence Factor (TEF) in **Table 26** to give the emission factor in g **I**-TEQ (Toxic Equivalent to the most toxic isomer 2,3,7,8-CDD).

26.1. COMBUSTION OF FUEL OIL

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g **I**-TEQ/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 26**

Table 26 Emission Factors for PCDD and PCDF from Fuel Oil Combustion

ISOMER	I-TEF	Emission Factor lb/MMBtu (HHV)	Emission Factor g I-TEQ/GJ (NCV)
Dioxin 4D 2378	1	Not detected	0[1]
Dioxin 5D 12378	0.5	Not detected	0[1]
Dioxin 6D 123478	0.1	Not detected	0[1]
Dioxin 6D 123678	0.1	2.50E-12	1.13E-10
Dioxin 6D 123789	0.1	2.50E-12	1.13E-10
Dioxin 7D 1234678	0.01	2.12E-11	9.59E-11
Dioxin 8D	0.001	5.10E-10	2.31E-10
Furan 4F 2378	0.1	5.54E-12	2.51E-10
Furan 5F 12378	0.05	Not detected	0[1]
Furan 5F 23478	0.5	Not detected	0[1]
Furan 6F 123478	0.1	2.48E-12	1.12E-10
Furan 6F 123678	0.1	1.86E-12	8.42E-11
Furan 6F 123789	0.1	Not detected	0[1]
Furan 6F 234678	0.1	3.74E-12	1.69E-10
Furan 7F 1234678	0.01	9.79E-12	4.43E-11
Furan 7F 1234789	0.01	Not detected	0[1]
Furan 8F	0.001	4.86E-11	2.20E-11
TOTAL			**1.24E-09**

Notes:

1. Compound was not detected. The emission factor stated in reference [11] is based on the detection limit. For the purposes of this report, the emission factor is considered to be zero as the source was not proven (See **Section 5.2** of this report).

Reference: [11].

26.2. CATALYTIC REFORMING UNIT REGENERATORS

There are very few data available for the emissions from these units. The US EPA [48] provides emission factors derived from tests on two units with different modes of catalyst regeneration – continuous and semi-regenerative.

Continuous Regeneration Mode

Mass emitted (kg I-TEQ) = 1.91E-11 × Volume of feed to unit (in m^3)

Semi-Regenerative Mode

Mass emitted (kg I-TEQ) = 6.35E-15 × Volume of feed to unit (in m^3)

Reference: [48], Section 5.4.

27. BENZENE (C_6H_6)

Benzene is emitted as a constituent of VOC evaporative or leakage (fugitive) emissions and from the combustion of flare streams, fuels e.g. in boilers and furnaces, and coke in FCCU regenerators and cokers.

Combustion emissions are typically negligible compared to fugitive emissions.

Fugitive emissions are diffuse in a large facility like a refinery. Although those from pressurised equipment can be determined from speciation data for each stream in the refinery and leak monitoring surveys, this requires considerable effort and does not cover emissions from systems such as tanks, drains, oil-water separators, etc. One measurement technique is to monitor occasionally the composition of NMVOCs in the ambient air at the fence line to determine the average benzene mass fraction.

Where this technique is not undertaken, an estimation method for fugitives is provided using a default value for the mass fraction of benzene. For completeness, algorithms are also provided for the minor sources.

27.1. SPECIATED FENCELINE NMVOC DATA AVAILABLE

In general, VOC fugitive sources are numerous but individually small e.g. from valves, drain systems, etc. To determine the benzene emitted by a facility, one approach is to take occasional ambient air samples at regular points around the boundary fence and establish the average benzene mass fraction of the NMVOCs measured. Care must be taken in the positioning of the samplers to ensure that they are not located near to local emission sources that may skew the results. Full details of a methodology are given in reference [49].

The mass of benzene emitted by the facility is then calculated from:

Mass emitted (kg) = $\text{SUMCALC}_{\text{NMVOC}} \times \text{MF}_{\text{BENZENE}}$

where:
$\text{SUMCALC}_{\text{NMVOC}}$ = sum of the individual calculated masses of NMVOCs emitted (in kg) within the facility, as per **Section 13**.
$\text{MF}_{\text{BENZENE}}$ = Mass fraction of benzene (from fence line monitoring survey).

27.2. NO SPECIATED FENCELINE NMVOC DATA AVAILABLE

Where fence line monitoring is not undertaken, a value of $\text{MF}_{\text{BENZENE}}$ = 1.72% mass can be used.

Mass emitted (kg) = 1.72E-02 × $\text{SUMCALC}_{\text{NMVOC}}$

where:
$\text{SUMCALC}_{\text{NMVOC}}$ = sum of the individual calculated masses of NMVOCs emitted (in kg) within the facility, as per **Section 13**.

Reference: [27], Section 15.5.3, Table 15-7.

27.3. ESTIMATION BY SOURCE

For completeness, algorithms are provided below for combustion sources and uncontrolled blowdown systems. The emission from the following combustion sources are typically negligible compared to fugitive sources:

- Combustion of fuels
- Destruction of gaseous streams in flares
- Catalytic cracking unit regenerators
- Fluid cokers

If some or all of the following algorithms are used, then the emissions are:

Mass emitted (kg) = Sum of emissions using algorithms below + Sum of emissions from all other sources using algorithms in Section 27.1 or 27.2

27.3.1. Combustion of Fuels

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 27**.

Table 27 Benzene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Refinery Fuel Oil	6.47E-04	[17] Section 1.3, Table 1.3-9
	Natural Gas	9.84E-04	[17] Section 1.3, Table 1.3-9
	Refinery Fuel Gas	2.13E-03	[11][1,2]
Gas Turbine[3]	Distillate (Gas Oil)[4]	2.49E-02	[19] Section 3.1, Table 3.1-4
	Natural Gas	5.73E-03	[19] Section 3.1, Table 3.1-3
Gas Engine 4-stroke, Lean Burn	Natural Gas	2.10E-01	[19] Section 3.2, Table 3.2-2
	Refinery Fuel Gas	6.21E-01	[11], [47][5]
Diesel Engine Large, Stationary	Distillate (Gas Oil)	3.22E-01	[11], [47][5]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	9.84E-04	[17] Section 1.3, Table 1.3-9

Notes:
1. Factor represents the median value as the ratio of mean to median value > 10. See **Section 5.3**.

2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.
3. Factor derived from turbines operating at high (≥ 80%) loads.
4. Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
5. Reference [11] is base document, but reference [47] provides the same emission factors to more significant figures

27.3.2. Destruction of Flare Streams

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 27.3.1**.

27.3.2.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 5.00E-00 × M × $\mathbf{MF_{BENZ}}$

where:
M = total mass of gas flared (in tonnes)
MF_{BENZ}= mass fraction of benzene in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in "well designed and operated flares, such as in refineries".

Reference: [15], Section 4.4.

27.3.2.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 1.66E-06 × Refinery Feed (in $\mathbf{m^3}$)

Reference: Derived from [21], Activity 090203, Section 8, Table 2, and [20], Section 4.22, Table 9.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

27.3.3. Catalytic Cracking Unit Regenerators

27.3.3.1. Full Burn Regeneration

Emissions of NMVOCs, and hence benzene, are considered negligible.

27.3.3.2. Partial Burn with CO Boiler

Emissions of NMVOCs, and hence benzene, are considered negligible.

Reference: [6], Table 5.1-1.

27.3.3.3. Partial Burn without CO Boiler

If the off-gas is not fed to a CO boiler, or it is not in operation:

Mass emitted (in kg) = 8.04E-04 × Mass of coke burnt (in tonnes)

Reference: [13], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

27.3.4. Fluid Cokers

27.3.4.1. Emissions Controlled with CO or Fired Waste Heat Boiler

Emissions of NMVOCs, and hence benzene, are considered negligible.

Reference: [6], Table 5.1-1.

27.3.4.2. Non-Controlled Emissions

If the off-gas is not fed to a CO or fired waste heat boiler, or it is not in operation:

Mass emitted (in kg) = 1.75E-04 × Feed to unit (in m^3)

This assumes that benzene makes up 0.38% by mass of the VOCs in the vented gas.

Reference: [20], Section 4.2.1, Table 8 and Section 4.2.2, Table 9.

27.3.5. Uncontrolled Blowdown System

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the benzene emissions can be conservatively estimated using the factor provided in reference [6], Table 5.1-1 to determine total hydrocarbon (THC) emissions and assuming that benzene makes up 0.38% by mass of the THCs in the blowdown gas (reference [20], Section 4.2.2, Table 9).

28. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

The E-PRTR requires the total emissions of the four PAHs listed below:

- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Indeno(1,2,3-cd)pyrene

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators

Speciated values are provided for the four individual PAHs in addition to the summation of the emission factors.

Emission factors for <u>total</u> PAH emissions are available for the combustion of distillate fuel in gas turbines (reference [19], Section 3.1, Table 3.1-15) and for flare gas (reference [20], Section 4.2.2, Table 9). These factors are not reproduced in this report as E-PRTR requires the emissions to be reported of only a limited number of the total PAH compounds.

28.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Sections 28.1.1** to **28.1.5**.

28.1.1. Refinery Fuel Oil Combustion in Boilers and Furnaces

Table 28 PAH Emission Factors for Fuel Oil Combustion

PAH	**EF_{NCV} g/GJ**
Benzo(a)pyrene	0[1]
Benzo(b)fluoranthene	3.670E-06[2]
Benzo(k)fluoranthene	0[1]
Indeno(1,2,3-cd)pyrene	0[1]
Total	3.67E-06

Notes:

1. Compound was not detected. The emission factor stated in reference [11] represents the detection limit. The emission factor is thus considered to be zero as the source is not proven (See **Section 5.2** of this report).

2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

For CO boilers and fired waste heat boilers, the algorithm should only be applied to the support fuel fired.

Reference: [11], [47].

28.1.2. Gas Combustion in Boilers and Furnaces

28.1.2.1. Natural Gas

The emission factors for all four of the PAHs stated in reference [17], Table 1.4-3 represent detection limit values. The emission factors are thus considered to be zero as the source is not proven (See **Section 5.2** of this report).

28.1.2.2. Refinery Fuel Gas

Table 29 PAH Emission Factors for Refinery Fuel Gas Combustion in Boilers and Furnaces

PAH	**EF_{NCV} g/GJ**
Benzo(a)pyrene	6.688E-07[1,2]
Benzo(b)fluoranthene	1.137E-06[1,2]
Benzo(k)fluoranthene	6.306E-07[1,2]
Indeno(1,2,3-cd)pyrene	6.306E-07[1,2]
Total	3.07E-06

Notes:
1. Ratio of mean to median value > 10. Median value used. See **Section 5.3**.
2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

For CO boilers and fired waste heat boilers, the algorithm should only be applied to the support fuel fired.

Reference: [11], [47].

28.1.3. Gas Combustion in Gas Turbines

Table 30 PAH Emission Factors for Gas Combustion in Gas Turbines

PAH	**EF_{NCV} g/GJ**[1]
Benzo(a)pyrene	0[2]
Benzo(b)fluoranthene	1.576E-06[3]
Benzo(k)fluoranthene	1.113E-06[3]
Indeno(1,2,3-cd)pyrene	8.360E-07[3]
Total	3.53E-06

Notes:
1. Emission factors for gas turbine without duct burners.
2. No data available.
3. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

Reference: [11], [47].

28.1.4. Gas Combustion in Gas Engines

Table 31 PAH Emission Factors for Gas Combustion in Gas Engines

PAH	**EF_{NCV} g/GJ**[1]
Benzo(a)pyrene	1.615E-05[2]
Benzo(b)fluoranthene	1.486E-04[2]
Benzo(k)fluoranthene	2.408E-04[2]
Indeno(1,2,3-cd)pyrene	5.446E-05
Total	4.60E-04

Notes:
1. Emission factors for 4-stroke, lean-burn gas engine.
2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

Reference: [11], [47].

28.1.5. Distillate Oil Combustion in Diesel Engines

Table 32 PAH Emission Factors for Distillate Oil Combustion in Diesel Engines

PAH	**EF_{NCV} g/GJ**[1]
Benzo(a)pyrene	1.127E-04[2]
Benzo(b)fluoranthene	4.888E-04[2]
Benzo(k)fluoranthene	9.640E-05[2]
Indeno(1,2,3-cd)pyrene	1.815E-04[2]
Total	8.79E-04

Notes:
1. Emission factors for large stationary engine with stack gas oxygen concentration < 13%.
2. The detect ratio reported in [11] is < 1.0. This emission factor is a weighted value using the value of the detect ratio – see **Section 5.2** of this report.

Reference: [11], [47].

28.1.6. Incinerator Support Fuel and Flare Pilot Fuel

Use values of EF_{NCV} provided in **Section 28.1.2**.

28.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

For all incinerator gas streams, use the algorithm in **Section 28.1**, with values of EF_{NCV} provided in **Section 28.1.2.2**.

28.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = EF_{FCC} × Mass of coke burned (in tonnes)

where:
EF_{FCC} = emission factor from **Table 33**

Table 33 PAH Emission Factors for CCU Regenerators

PAH	**EF_{FCC}**
Benzo(a)pyrene	7.072E-07
Benzo(b)fluoranthene	1.223E-06
Benzo(k)fluoranthene	8.212E-07
Indeno(1,2,3-cd)pyrene	6.238E-07
Total	3.38E-06

Reference: [13], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

29. CHLORINE AND INORGANIC CHLORINE COMPOUNDS

The E-PRTR requires estimates of the emissions of chlorine and inorganic chlorine compounds reported as HCl.

The major source of these pollutants is the catalytic reforming unit.

29.1. CATALYTIC REFORMING UNITS

The source of these compounds is the reactivation of the catalyst in the catalytic reforming unit. The catalyst is reactivated, following the burning off of coke deposits, using chlorine, chlorinated compounds or a chlorinated solvent. The emissions can be abated, for example using a caustic or water wash system, chloride trap or driers where HCl is present in water vapour.

A review of data from units without flue gas abatement systems installed indicate that for very high throughput units the emissions may be greater than the E-PRTR reporting threshold of 10 000 kg/year. For units with abatement systems the emissions were below the threshold value.

There are emission factors related to reformer feed rate for both chlorine and HCl available in reference [14], Table 1. This reference uses combined data from reformer units both with and without flue gas abatement systems installed. Due to the corresponding very wide scatter of emissions data, the emission factor for HCl has a variance between the median and average values of four orders of magnitude.

It is not possible, therefore, to provide reliable emission factors for uncontrolled emissions from the reformer catalyst reactivation process.

The uncontrolled emissions could be estimated from knowledge of the mass of chlorine or chlorinated compound injected, the efficiency of the reactivation process and any conversion of the compound that takes place during the activation process.

For reporting purposes, the calculated mass emitted needs to be converted to equivalent mass of HCl. This is obtained by multiplying the mass of chlorinated compound emitted by the ratio of the molecular weight of HCl to the molecular weight of the compound.

30. PARTICULATE MATTER WITH DIAMETER <10 µm (PM_{10})

Estimation methods are provided for emissions of PM_{10} due to:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Fluid cokers

PM_{10} is defined by the UNECE Task Force on Emission Inventories and Projections as particulate matter which is measured after passing through a size selective inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter. Emission factors derived from US EPA reference sources are for 'filterable' particulate matter i.e. collected on or prior to a filter of an EPA Method 5 (or equivalent) sampling train.

30.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 34**.

Table 34 PM_{10} Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	3.49E+00	[17] Section 1.3, Table 1.3-7
	Refinery Fuel Oil	Alg. A - see below	[17] Section 1.3, Table 1.3-7
	LPG[1]	9.89E-01	[17] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[17] Section 1.4, Table 1.4-2
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	3.23E+00	[17] Section 1.3, Table 1.3-6
	Refinery Fuel Oil	Alg. B - see below	[17] Section 1.3, Table 1.3-5
	LPG[1]	9.89E-01	[17] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[17] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces > 100 MW	Distillate (gas oil)	3.23E+00	[18] SCC 10100501
	Refinery Fuel Oil	Alg. C - see below	[17] Section 1.3, Table 1.3-4
	LPG[2]	7.84E-01	[18] SCC 10101002
	Natural Gas	8.90E-01	[17] Section 1.4, Table 1.4-2
Gas Turbine[3]	Distillate (gas oil)[4]	1.95E+00	[19] Section 3.1, Table 3.1-2a
	Natural Gas	9.08E-01	[19] Section 3.1, Table 3.1-2a
Gas Engine 4-stroke, Lean Burn	Natural Gas	3.68E-02	[19] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	2.24E+01	[19] Section 3.4, Table 3.4-2
Incinerator Support Fuel or Flare Pilot Fuel	LPG[1]	9.89E-01	[17] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[17] Section 1.4 Table 1.4-2

Notes:

1. Factor is for both butane and propane combustion
2. Factor is for propane combustion
3. Factors based on combustion turbines using water-steam injection.
4. Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.

Algorithms for refinery fuel oil

A. $EF_{NCV} = (17.47 \times MASS\%S) + 5.772$

B. $EF_{NCV} = (24.229 \times MASS\%S) + 8.004$

C. $EF_{NCV} = (19.937 \times MASS\%S) + 6.586$

where:

MASS%S = Percentage mass of sulphur in fuel oil (%)

(i.e. if the fuel contains 1.2% sulphur, then MASS%S = 1.2)

30.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 34**.

30.2. DESTRUCTION OF GASEOUS STREAMS

30.2.1. Flares

For a non-smoking flare, the emissions of PM_{10} can be assumed to be negligible.

Reference: [20], Section 4.2.1, Table 8.

30.2.2. Incinerators

For all incinerator gas streams, use the algorithm in **Section 30.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 30.1**.

30.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (in kg) = 5.49E-01 × Feed to unit (in m^3)

Reference: [20], Section 4.2.1, Table 8.

This algorithm is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

30.4. FLUID COKERS

Mass emitted (in kg) = 7.65E-01 × Feed to unit (in m^3)

Reference: [20], Section 4.2.1, Table 8.

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APPENDIX 1 E-PRTR AIR POLLUTANTS

Table A1.1 lists the air pollutants that must be reported under the E-PRTR Regulation if annual emissions exceed the threshold values shown. It indicates those pollutants on the sector specific indicative lists in the EU Guidance Document [4] which are considered "likely" to be emitted by refineries and combustion installations (> 50 MW). It also shows those pollutants which have been estimated by at least one refinery to exceed the E-PRTR reporting threshold.

Table A1.1 List of E-PRTR Air Pollutants

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [4], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Methane (CH_4)	100 000	X	X	X
Carbon monoxide (CO)	500 000	X	X	X
Carbon dioxide (CO_2)	100 000 000	X	X	X
Hydrofluorocarbons (HFCs)	100	X	X	X
Nitrous oxide (N_2O)	10 000	X	X	X
Ammonia (NH_3)	10 000	X	X	X
Non-methane volatile organic compounds (NMVOCs)	100,000	X	X	X
Nitrogen oxides (NO_X)	100 000	X	X	X
Perfluorocarbons (PFCs)	100	-	-	-
Sulphur hexafluoride (SF_6)	50	-	X	X
Sulphur oxides (SO_X)	150 000	X	X	X
Hydrochlorofluorocarbons (HCFCs)	1	X	X	X
Chlorofluorocarbons (CFCs)	1	-	-	-[1]
Halons	1	-	-	-[1]
Arsenic + compounds	20	X	X	X
Cadmium + compounds	10	X	X	X
Chromium + compounds	100	X	X	X
Copper + compounds	100	X	X	X
Mercury + compounds	10	X	X	X
Nickel + compounds	50	X	X	X
Lead + compounds	200	X	X	X
Zinc + compounds	200	X	X	X

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [4], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Aldrin	1	-	-	-
Chlordane	1	-	-	-
Chlordecone	1	-	-	-
DDT	1	-	-	-
1,2-dichloroethane	1000	-	-	-
Dichloromethane	1000	-	-	-
Dieldrin	1	-	-	-
Endrin	1	-	-	-
Heptachlor	1	-	-	-
Hexachlorobenzene	10	-	-	-
1,2,3,4,5,6-hexachlorocyclohexane	10			
Lindane	1	-	-	-
Mirex	1	-	-	-
PCDD + PCDF (dioxins and furans) (as TEQ)	0.0001	-	X	-
Pentachlorobenzene	1	-	-	-
Pentachlorophenol	10	-	-	-
Polychlorinated biphenyls (PCBs)	0.1	-	-	-
Tetrachloroethylene	2000	-	-	-
Tetrachloromethane	100	-	-	-
Trichlorobenzenes	10	-	-	-
1,1,1-trichloroethane	100	-	-	-
1,1,2,2-tetrachloroethane	50	-	-	-
Trichloroethylene	2000	-	X [2]	-
Trichloromethane	500	-	-	-
Toxaphene	1	-	-	-
Vinyl chloride	1000	-	-	-
Anthracene	50	-	-	- [3]
Benzene	1000	X	X	X
Ethylene oxide	1000	-	-	-
Naphthalene	100	-	-	- [3]

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [4], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Di-(2-ethyly hexyl) phthalate	10	-	-	-
Polycyclic aromatic hydrocarbons (PAHs) [4]	50	X	X	X
Chlorine + inorganic compounds (as HCl)	10 000	X	X	X
Asbestos	1	-	-	-
Fluorine + inorganic compounds (as HF)	5000	-	-	-
Hydrogen cyanide (HCN)	200	-	-	-
Particulate matter < 10 micron diameter (PM_{10})	50 000	X	X	X
Hexabromobiphenyl	0.1	-	-	-
TOTALS of 60 E-PRTR air pollutants		*22*	*25*	*23*

Notes:

1. These halocarbons have been banned under EU Regulations [50] and would not be used to top-up existing equipment.
2. Trichloroethylene is not a product of combustion. The inclusion of this pollutant in the indicative sector specific list of air pollutants for thermal power stations and other combustion installations in reference [4] appears to be due to an anomaly in the EPER database.
3. The possible magnitude of emissions of anthracene and naphthalene are reviewed in **Appendix 3**.
4. Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

APPENDIX 2 UPDATES IN EMISSION ALGORITHMS AND FACTORS

The following changes in emission algorithms and factors have been made from the predecessor CONCAWE report No. 3/07 [9].

Carbon Monoxide

Updated emission factors:
- LPG combustion in boilers and furnaces rated < 10 MW and between 10 and 100 MW.

Carbon Dioxide

Updated oxidation factor:
- All fuel combustion.

New algorithms:
- Flare gas combustion where stream composition is unknown.
- Hydrogen plant where composition of feed is known.

Revised algorithm:
- Hydrogen plant where composition of feed is unknown.

Non-Methane Volatile Organic Compounds

New emission factors
- for optical gas imaging systems used for detection of leaks from pressurised components.

Updated emission factors:
- LPG combustion in boilers and furnaces rated < 10 MW and between 10 and 100 MW.
- fugitive emissions from pressurised components where component counts are not available.
- loading of marine tankers and barges.

New algorithms:
- emissions from pressurised components using optical gas imaging.
- emissions from uncovered gravity separators.

References to new methodologies:
- emissions from waste water treatment systems.
- emissions from internal floating roof tanks with vents that can be closed.
- emissions from tank cleaning.

Nitrogen Oxides

Updated emission factors:
- adjustment factor for amount of hydrogen in the fuel.

Oxides of Sulphur

New algorithm:
- catalytic cracking unit regenerators where the sulphur content in the coke is known.

Arsenic

Updated emission factor:
- natural gas combustion in all sizes of boilers and furnaces.

Cadmium

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas turbines.

Chromium

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas turbines.

Copper

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas turbines.

Mercury

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas turbines.

Nickel

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas turbines.

Lead

Updated emission factor:
- natural gas combustion in all sizes of boilers and furnaces.

Amended emission factor (deleted):
- natural gas combustion in gas turbines.

Zinc

Updated emission factor:
- natural gas combustion in all sizes of boilers and furnaces.

Amended emission factor (deleted):
- natural gas combustion in gas turbines.

Benzene

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- natural gas combustion in gas engines.
- catalytic cracking unit regenerators: partial burn without CO boiler.

PAHs

Updated emission factors:
- natural gas combustion in all sizes of boilers and furnaces.
- catalytic cracking unit regenerators.

Particulate Matter

New emission factors:
- LPG combustion in all sizes of boilers and furnaces.

Anthracene (Appendix 3)

Updated emission factors:
- catalytic cracking unit regenerators.

Naphthalene (Appendix 3)

Updated emission factors:
- catalytic cracking unit regenerators.

APPENDIX 3 ANTHRACENE AND NAPHTHALENE

Anthracene and naphthalene are pollutants known to be emitted by refineries, but neither is included on the sector specific indicative lists in the EU E-PRTR Guidance [4]. Emission estimation methods for these two pollutants are provided in this Appendix. It is demonstrated that emissions of neither pollutant are likely to exceed their respective E-PRTR reporting threshold, even at the largest of refineries.

A3.1 ANTHRACENE

Estimation methods are provided for emissions from:

- Combustion of fuels
- Fluidised catalytic cracking units

A3.1.1 Combustion of Fuels

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table A3.1**.

Reference: [11].

Table A3.1 Anthracene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Furnaces and Boilers	Refinery Fuel Oil	9.37E-07	[11], [47][1]
	Gas	2.26E-06	[11], [47][1]
Gas Turbine[2]	Gas	1.64E-05	[11], [47][1]
Gas Engine 4-Stroke, Lean-Burn	Refinery Fuel Gas	1.17E-04	[11], [47][1]
Diesel Engine Large, Stationary[3]	Distillate (Gas Oil)	5.43E-04	[11], [47][1]

Notes:
1. Reference [11] is base document, but reference [47] provides emission factors to more significant figures.
2. Factor derived from gas turbines without duct burners.
3. Factor for stack oxygen concentration < 13%

A3.1.2 Catalytic Cracking Unit Regenerator

Mass emitted (kg) = 3.06E-06 × Mass of coke burned (in tonnes)

Reference: [13], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

A3.1.3 Emissions from a Very Large Refinery

To establish if anthracene could be emitted in excess of the E-PRTR reporting threshold, emissions have been calculated for a very large refinery. A survey by CONCAWE identified that the most fuel consumed at a European refinery was 8.4E+07 GJ/year, of which 3.6E+07 GJ was due to fuel oil use. The same refinery has a FCCU with a capacity of 2.9E+06 m^3/year, with a resultant coke burn of about 140 000 t/year.

- Fuel oil combusted = 3.6E+07 GJ/year
- Fuel gas combusted = 4.8E+07 GJ/year
- FCCU coke combusted = 1.4E+05 tonnes/year

The emissions from this very large refinery would be:

Emissions from oil and gas combustion
= [(9.37E-07 × 3.6E+07) + (2.26E-06 × 4.8E+07)] × 1.0E-03 = 1.42E-01 kg
Emissions from coke burn = 3.06E-06 × 1.4E+05 = 4.28E-01 kg

Total emissions = 0.57 kg/year

These emissions are significantly less than the E-PRTR reporting threshold of 50 kg/year.

A3.2 NAPHTHALENE

Estimation methods are provided for emissions from:

- Combustion of fuels
- Fluidised catalytic cracking units

A3.2.1 Combustion of Fuels

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table A3.2**.

Reference: [11].

Table A3.2 Naphthalene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Furnaces and Boilers	Refinery Fuel Oil	1.83E-04	[11], [47][1]
	Gas	1.86E-04	[11], [47][1]
Gas Turbine	Distillate (Gas Oil)[2]	1.58E-02	[19], Section 3.1, Table 3.1-4
	Gas[3]	3.48E-04	[11], [47][1]
Gas Engine 4-Stroke, Lean-Burn	Refinery Fuel Gas	5.54E-02	[11], [47][1]
Diesel Engine Large, Stationary[4]	Distillate (Gas Oil)	5.75E-02	[11], [47][1]

Notes:

1. Reference [11] is base document, but reference [47] provides emission factors to more significant figures.
2. Factor derived from turbines operating at high (≥ 80%) loads.
   Factor provided in reference [19] derived using HHV of 139 MBtu/10^3 US gal.
3. Factor derived from gas turbines without duct burners.
4. Factor for stack oxygen concentration < 13%

A3.2.2 Catalytic Cracking Unit Regenerator

Mass emitted (kg) = 5.59E-05 × Mass of coke burned (in tonnes)

Reference: [13]], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

A3.2.3 Emissions from a Very Large Refinery

To establish if naphthalene could be emitted in excess of the E-PRTR reporting threshold, emissions have been estimated for the very large refinery described in **Section A3.1.3**.

- Fuel oil combusted = 3.6E+07 GJ/year
- Fuel gas combusted = 4.8E+07 GJ/year
- FCCU coke combusted = 1.4E+05 tonnes/year

The emissions from this very large refinery would be:

Emissions from combustion
= [(1.83E-04 × 3.6E+07) + (1.86E-04 × 4.8E+07)] × 1.0E-03 = 1.55E+01 kg
Emissions from FCCU coke burn = 5.59E-05 × 1.4E+05 = 7.83E+00 kg

Total emissions = 23.3 kg/year

These emissions are less than the E-PRTR reporting threshold of 100 kg/year.

APPENDIX 4 NMVOC EMISSIONS FROM GASOLINE MARKETING FACILITIES

Neither marketing distribution terminals (i.e. road tanker gasoline loading facilities which are not located on a refinery site) nor service stations are regulated under the terms of the IPPC Directive [1] and hence are not required to submit E-PRTR reports.

Algorithms are provided in this Appendix, however, as emission estimates for distribution terminals and service stations may be made by oil companies for their own environmental reporting purposes.

A 4.1 DISTRIBUTION TERMINALS

The major sources of emissions at terminals are the storage and loading of gasolines. As there is negligible methane in refined transport fuels, it can be assumed that there are no emissions of CH_4.

A 4.1.1 Storage Tanks

Use the methodologies provided in **Section 13.9**.

A 4.1.2 Loading of Mobile Containers

Use the methodologies provided in **Section 13.8**.

A 4.1.3 Fugitive Emissions from Components

Emissions can occur due to leakage past seals, flanges, etc., on components installed in product pipelines and loading systems e.g. pump seals, connectors.

The emissions from fugitives at terminals are very much lower than at refineries because the systems do not operate at such high pressures. The emission factors provided in **Section 13.5**, which were derived from measurements on refinery process plants, should therefore not be used to estimate fugitive emissions at distribution terminals. Equivalent emission factors for terminal equipment are provided in reference [29], Table 2-3. Emissions from this source are typically less than 1 tonne/year for high throughput terminals.

A 4.1.4 Oil-Water Separators

The emission factors provided in **Section 13.6** have been derived from measurements on oil-water separators at refineries and are not appropriate for facilities at distribution terminals due to the differences in inlet conditions.

Emissions can be considered to be negligible if good maintenance and operating procedures are in place.

A 4.2 SERVICE STATIONS

Algorithms are provided for the following sources:

- Storage tanks
- Automobile refuelling

Gasoline vapour emissions at service stations can be controlled using "vapour balancing" techniques:-

> Storage tank filling: When the storage tank is filled the vapours normally vented to atmosphere can be fed back into the tanker cargo tank (compartment) from which the gasoline is being off-loaded. This technique is called "Stage 1b" vapour balancing.
>
> Automobile Refuelling: When an automobile is being refuelled, the vapours normally vented to atmosphere from the fuel tank can be fed back to the service station storage tank from which the gasoline was dispensed. This technique has been mandated in the majority of EU countries and is called "Stage 2" vapour balancing. An alternative, which has been mandated in the USA, is to enlarge the carbon canister fitted on the automobile to control fuel system hot-soak emissions so that refuelling emissions can also be captured.

Other emissions comprise storage tank "breathing" due to evaporation of the gasoline in the tank, and drips and minor spillage during automobile refuelling.

The emissions can be estimated from:

Mass emitted (kg) = EF × $\mathbf{VOL_{DISP}}$ × TVP

where:
EF = Emission Factor from **Table A4.3** depending on source and activity.
VOL_{DISP} = Volume of gasoline dispensed (in m^3).
TVP = True Vapour Pressure of gasoline at storage temperature (in kPa).

Reference: [7], Section 4.

Table A4.3 NMVOC Emission Factors for Service Stations

SOURCE / ACTIVITY		**EMISSION FACTOR (EF)** **$kg/m^3/kPa$**
Storage Tank	Filling without Stage 1b	2.44E-02
	Filling with Stage 1b in operation	1.10E-03
	Breathing	3.30E-03
Automobile Refuelling	Refuelling with no emission controls in operation	3.67E-02
	Refuelling with Stage 2 in operation	3.70E-03
	Drips and minor spillage	2.20E-03

Gasoline TVP can be calculated from:

$$\mathbf{TVP = RVP \times 10^{[(7.047E\text{-}06 \times RVP + 1.392E\text{-}02) \times TEMP + (2.311E\text{-}04 \times RVP - 5.236E\text{-}01)]}}$$

where:
RVP = Reid Vapour Pressure (in kPa)
TEMP = Gasoline storage temperature (in degrees Centigrade)

If the storage tank temperature is unknown, for the estimation of annual emissions TEMP can be assumed to equal the average annual ambient temperature.

Reference: [7], Appendix 1.

APPENDIX 5 CONVERSION FACTORS AND DEFAULT FUEL VALUES

To convert from Higher Heating Value (HHV) to Net Calorific Value (NCV), the following approach, as used in reference [15], was taken.

NCV = HHV x Correction Factor for heat of vaporisation of water in the fuel (CF_{H_2O})

For Liquid Fuels, Correction Factor (CF_{H_2O}) = 0.95
For Gaseous Fuels, Correction Factor (CF_{H_2O}) = 0.9

Reference: [15], Section 3.6.3, Table 3-5.

To convert Emission Factor from lb/MBtu$_{(HHV)}$ to g/GJ$_{(NCV)}$

$$EF\ g/GJ_{(NCV)} = (EF\ lb/MBtu_{(HHV)} / CF_{H_2O}) \times (g / lb) \times (MBtu / GJ)$$

To convert Emission Factor from lb/10^3 gal to g/GJ$_{(NCV)}$

$$EF\ g/GJ_{(NCV)} = EF\ lb/10^3\ gal \times (10^3\ gal / MBtu_{(NCV)}) \times (g / lb) \times (MBtu / GJ)$$

To convert Emission Factor from lb/10^6 scf to g/GJ$_{(NCV)}$

$$EF\ g/GJ_{(NCV)} = EF\ lb/10^6\ scf \times (10^6\ scf / MBtu_{(NCV)}) \times (g / lb) \times (MBtu / GJ)$$

Unless otherwise stated, emission factors were calculated using the following heating values expressed in their original units.

FUEL	HIGHER HEATING VALUE (HHV)	REFERENCE
Distillate (gas oil)	140 MBtu / 10^3 gal	[51]
Diesel Fuel	137 MBtu / 10^3 gal	[51]
Refinery Fuel Oil	150 MBtu / 10^3 gal	[51]
LPG	94 MBtu / 10^3 gal	[51]
Propane	91.5 MBtu / 10^3 gal	[17] Section 1.5.3.1
Natural Gas	1020 MBtu / 10^6 scf	[17] Section 1.4.1

Some useful conversion factors

Refinery Fuel Oil

1 lb/10^3 US gal = 3.017 g/GJ$_{(NCV)}$
1 lb/10^6 Btu$_{(HHV)}$ = 453 g/GJ$_{(NCV)}$

Distillate (Gas Oil)

1 lb/10^3 US gal = 3.233 g/$GJ_{(NCV)}$
1 lb/10^6 $Btu_{(HHV)}$ = 453 g/$GJ_{(NCV)}$

LPG

1 lb/10^3 US gal = 4.815 g/$GJ_{(NCV)}$

Propane

1 lb/10^3 US gal = 4.946 g/$GJ_{(NCV)}$

Natural Gas

1 lb/10^6 scf = 0.468 g/$GJ_{(NCV)}$
1 lb/10^6 $Btu_{(HHV)}$ = 478 g/$GJ_{(NCV)}$

SNAP CODE:	**010103** **010203** **020103** **020202** **020302** **030103**
SOURCE ACTIVITY TITLE:	**COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES** ***Particulate emissions from smaller Combustion Plants (<50MWth)***
NOSE CODE:	**101.03**
NFR CODE:	**1 A 1 a-c** **1 A 2 a-f** **1 A 4 a, bi, ci**
ISIC	**3510**

1 ACTIVITIES INCLUDED

This chapter covers emissions of particulate matter released from smaller combustion installations within the energy and transformation industries in boilers and furnaces with a thermal capacity $\leq 50\ MW_{th}$. Emissions of other pollutants from these sources can be found in chapter B111. Note that Chapter B216 also includes some combustion technologies relevant to the energy and transformation industries.

2 CONTRIBUTION TO TOTAL EMISSION

The contributions of PM_{10} and $PM_{2.5}$ emissions released from combustion in small combustion installations to total emissions in countries of the CORINAIR90 inventory is presented in Table 2.1.

Table 2.1 Contribution to total particulate matter emissions from 2004 EMEP database (WEBDAB)

NFR Sector	Data	PM_{10}	$PM_{2.5}$	TSP
1 A 1 a - Public Electricity and Heat Production[a]	No. of countries reporting	26	26	27
	Lowest Value	0.2%	0.2%	0.2%
	Typical Contribution	11.7%	10.1%	12.8%
	Highest Value	48.8%	47.8%	48.4%
1 A 2 - Manufacturing Industries and Construction[b]	No. of countries reporting	26	26	26
	Lowest Value	0.7%	0.6%	0.6%
	Typical Contribution	9.0%	9.5%	7.9%
	Highest Value	20.7%	22.1%	25.7%
1 A 4 a - Commercial / Institutional[c]	No. of countries reporting	23	23	23
	Lowest Value	0.1%	0.1%	0.1%
	Typical Contribution	3.9%	3.4%	4.5%
	Highest Value	19.3%	22.2%	29.5%
1 A 4 b - Residential[d]	No. of countries reporting	3	2	3
	Lowest Value	2.0%	6.5%	3.7%
	Typical Contribution	14.9%	26.2%	10.8%
	Highest Value	36.6%	45.8%	15.4%
1 A 4 b i - Residential plants[e]	No. of countries reporting	23	23	23
	Lowest Value	2.7%	5.8%	0.8%
	Typical Contribution	28.3%	33.1%	22.0%
	Highest Value	67.1%	74.6%	53.2%
1 A 5 a - Other, Stationary (including Military)[f]	No. of countries reporting	7	7	7
	Lowest Value	0.0%	0.0%	0.0%
	Typical Contribution	0.1%	0.1%	0.1%
	Highest Value	0.5%	0.4%	0.6%

[a] Includes contribution from Chapter 112

[b] Includes contributions from Chapter 112 and 316 (SNAP 030106)

[c] Includes contribution from Chapter 112 and 216 (SNAP 020205)

[d] Includes contribution from Chapter 810

[e] Includes contribution from Chapter 112

[f] Includes contribution from Chapter 112 and 216 (SNAP 020106)

3 GENERAL

3.1 Description

This chapter considers emissions of PM generated by boilers smaller than 50 MWth, this chapter covers the energy and transformation industries use of combustion plant and the devices in use are generally larger than 1 MW_{th}. Information on smaller units can be found in Chapter B216. Other emissions from this source category are considered in B111.

3.2 Definitions

See B111.

3.3 Techniques

See B111 for information on boiler types and fuels. Combustion of coal and other solid fuels present the main source for primary PM emissions.

3.4 Emissions

Particulate emissions from small combustion installations burning solid fuels are often greater than emissions from larger plants (per unit of energy input); the physical and chemical characteristics of the PM also differ. This is because different combustion and abatement techniques are applied.

Combustion of fuels will generate solid residues which may be deposited in the combustion chamber (furnace bottom ash), within the furnace, boiler surfaces or ducting (fly ash). Coal and other fuels with a significant ash content have the highest potential to emit PM. Suspended ash material in exhaust gases will be retained by particulate abatement or other emission abatement equipment (abatement residues). Material which remains in the flue gases beyond the abatement equipment and passes to the atmosphere is primary PM. Secondary PM is formed by chemical and physical processes after discharge to atmosphere and is NOT considered here.

3.5 Controls

Particulate emission reduction for smaller boilers is usually obtained applying abatement equipment. It is unlikely that solid-fuel boilers or furnaces in the size range considered in this chapter would be unabated however; some may have comparatively low technology abatement measures. Settling Chambers use gravity separation to remove particles, but the collection efficiency is low. Cyclone separators can be used or, more commonly, units with multiple cyclones are applied to improve the collection efficiency. More efficient abatement measures are electrostatic precipitators and fabric filters, although use of these on the smallest boilers may be limited due to comparatively high capital and operating costs.

Other measures to prevent or reduce particle emissions can also be implemented, such as replacing coal with other fuels, or replacing old appliances with newer, more efficient equipment.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the Tier 1 simpler methodology, where limited information is available, a default emission factor can be used together with production capacity information for the country or region of interest without further specification on the type of industrial technology or the type and efficiency of control equipment. For a Tier 2 approach an approximation to the most appropriate technology factors can be adopted with potential, if more detailed activity data are available, for use of default sector or technology factors.

Consequently the simplest methodology (Tier 1) is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR x EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

The Tier 2 methodology is a modified version of this basic equation :

$$\text{Emission} = \sum((AR_1 \text{ x } EF_1) + (AR_2 \text{ x } EF_2) + \ldots.(AR_n \text{ x } EF_n))$$

Default emission factors for this purpose are provided in Sections 8.1 and 8.2.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3) to estimate emissions of pollutants from combustion plant <50 MW_{th} is based on measurements or estimations using plant specific emission factors for the types of plant and technologies used within the country - guidance on determining plant specific emission factors is given in the Measurement Protocol Annex.

The recommended detailed methodology to estimate emissions of PM from combustion activities is based on measurements and/or estimations using technology-specific emission factors.

Information on the type of the process and activity data, for example combustion and abatement technologies, is required to assign appropriate emission factors.

Reference emission factors for comparison with users' own data are provided in Section 8.2.

6 ACTIVITY STATISTICS

Activity statistics for fuel consumption in industry sectors for estimating emissions using the simpler estimation methodology (Tiers 1 and 2) are usually derived from national statistics. However, data on fuel use by smaller combustion plant within industry sectors may not be readily available. However, fuel suppliers, regulators and individual operators may be able to provide some data and other information may be available through relevant surveys, energy modelling and other studies.

The detailed methodology (Tier 3) requires more detailed information such as the amount and types of fuel consumed and the type of installation it is used in. However, the large number of plant in most countries will be a constraint on a Tier 3 approach and these data are not always easily available.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 2 on energy, Chapter 1.

7 POINT SOURCE CRITERIA

The largest boilers may be considered point sources if plant specific data are available however; in general, this chapter covers area sources only.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors For Use With Simpler Methodology (Tier 1)

Table 8.1 Default emission factors for the simple methodology for small combustion installations

Fuel	**Emission factor, g GJ^{-1}**			**Notes**[2]
	TSP	**PM_{10}**	**$PM_{2.5}$**	
Hard coal, brown coal, other solid fuels	80	60	60	From Chapter B216
Natural gas	0.9	0.9	0.9	US EPA
Derived gases	5	5	5	CEPMEIP worst case for derived gases
Heavy fuel oil	50	40	30	From chapter B216
Other liquid fuels	50	40	30	From Chapter B216
Biomass	50	40	40	From Chapter B216

8.2 Reference Emission Factors For Use With Tier 2 Methodology

Tables 8.2a-z contain reference particulate emission factors for fuel combustion in various technologies with different types of abatement. These are suitable for use with the Tier 2 methodology.

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[2] Source: US EPA AP 42 (1996); CEPMEIP (2006)

Table 8.2a Emission factors for combustion processes burning hard coal.

Fuel	**NAPFUE**	**NFR Codes**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
Hard coal					**TSP**	**PM_{10}**	**$PM_{2.5}$**	
Bit. Coal	101	Various	Electricity, CHP, heat	FF <20 mg.Nm^{-3}	6	6	5	CEPMEIP ‘BAT’
				ESP (or FF) <50 mg.Nm^{-3}	15	12	6	Scaled from CEPMEIP ESP factor. TSP scaled to a nominal 100 mg.Nm^{-3} limit
				ESP <100 mg.Nm^{-3}	30	25	12	From CEPMEIP sub-bit coal ‘high efficiency ESP’, TSP scaled to a nominal 100 mg.Nm^{-3} limit
				ESP Old/conventional <500 mg. Nm^{-3}	140	70	17	CEPMEIP
				Unit with multicyclone	100	60	35	CEPMEIP
				Unit, uncontrolled or cyclone	500	250	100	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
Sub-bituminous coal	103	Various	Electricity, CHP, heat plant	FF <20 mg.Nm^{-3}	6	6	5	CEPMEIP ‘BAT’
				ESP (or FF) <50 mg.Nm^{-3}	15	12	6	Scaled from CEPMEIP ESP factor (TSP scaled to a nominal 100 mg.Nm^{-3} limit)
				ESP <100 mg.Nm^{-3}	30	25	12	From CEPMEIP sub-bit coal ‘high efficiency ESP’, TSP scaled to a nominal 100 mg.Nm^{-3} limit
				ESP Old/conventional	140	70	17	CEPMEIP

Fuel	**NAPFUE**	**NFR Codes**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
				<500 mg. Nm^{-3}				
				Unit with multicyclone	100	60	35	CEPMEIP
				Unit, uncontrolled or cyclone	500	250	100	CEPMEIP (the lower of the two TSP factors, the 800 g GJ-1 for small uncontrolled plant is such a high emission concentration that would apply to few if any plant)
Coke	107	1 A 1 b	Oil refineries	Uncontrolled	500	250	100	Coke is unlikely to be burned as primary fuel, when co-fired use the factor for the principal fuel.

Table 8.2b Emission factors for combustion processes burning brown coal.

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Brown coal	105	Various	Electricity plant, CHP plant, heat plant	Modern FF <20 $mg.Nm^{-3}$	9	8	6	CEPMEIP 'BAT'
				High efficiency ESP (or FF)	40	30	14	CEPMEIP
				Conventional large unit with multicyclone	100	60	35	CEPMEIP
Peat	113	Various	Electricity plant, CHP plant, heat plant	Modern abatement (FF) <30 mg.Nm3	9	8	6	CEPMEIP
				Efficient abatement, <50 mg.Nm3	20	15	10	TSP Scaled from emission limit of 50 $mg.Nm^{-3}$
				Efficient abatement, <100mg.Nm3	40	30	20	TSP Scaled from emission limit of 100 $mg.Nm^{-3}$
				Conventional technology	120	40	20	CEPMEIP
				Conventional smaller, multicyclone	300	40	20	CEPMEIP

Table 8.2c Emission factors for combustion processes burning other solid fuels

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM$_{10}$**	**PM$_{2.5}$**	
Municipal solid waste	114	Various	Electricity plant, CHP plant, heating plant	Effective emission control (BAT)	15	13	10	CEPMEIP, (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
				Conventional emission control	100	70	55	CEPMEIP (uncontrolled. optimised combustion), (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
Ind. waste	115	Various	Electricity, CHP, heating plant	Effective emission control (BAT)	15	13	10	CEPMEIP, (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
				Conventional emission control	100	70	55	CEPMEIP (uncontrolled, optimised combustion), (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
				Older small uncontrolled	600	350	210	CEPMEIP (uncontrolled, optimised combustion), (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)

Table 8.2d Emission factors for combustion processes burning natural gas.

Fuel	NAPFUE	NFR Code	Activity description	Activity detail	Emission factor			Notes
					TSP	PM_{10}	$PM_{2.5}$	
Natural gas	301	Various	Electricity, CHP and heating plant	Burner with optimised combustion	0.1	0.1	0.1	CEPMEIP
				Conventional installation	0.2	0.2	0.2	CEPMEIP
				Conventional installation	0.9	0.9	0.9	USEPA Filterable

Table 8.2e Emission factors for combustion of derived gases.

Fuel	NAPFUE	NFR Code	Activity description	Activity detail	Emission factor			Notes
					TSP	PM_{10}	$PM_{2.5}$	
Gas works gas	311	Various	Electricity, CHP and heating plant	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, Conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP (High PM due to fuel quality)
Other gaseous fuel	314	Various	Electricity, CHP and heating plant	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Conventional installation	5	5	5	CEPMEIP

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
Coke oven gas	304	Various	Electricity, CHP heating plant, coke ovens	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP
Blast furnace gas	305	Various	Electricity, CHP and heating plant, coke ovens	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, Conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP

Table 8.2f Emission factors for combustion of heavy fuel oil.

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	PM_{10}	$PM_{2.5}$	
Residual fuel oil	203	Various	Electricity, CHP and heating plant	Low S fuel with optimised burner and abatement	3	3	2.5	CEPMEIP. (About 10 mg.Nm^{-3} or BAT)
				Low S fuel, efficient combustion	14	12	10	CEPMEIP (About 50 mg. Nm^{-3})
				Low-Medium S fuel, conventional installation	20	15	9	CEPMEIP (about 70 mg. Nm^{-3})
				Low-Medium S fuel, conventional installation	60	50	40	CEPMEIP (higher of two entries used. about 200 mg.N Nm^{-3})
				High S fuel	210	190	130	CEPMEIP (lower of two entries for high S used (higher entry 240 g GJ-1 for TSP). Very high emission concentration (about 750 mg. Nm^{-3})
Petroleum coke	110	1 A 1 b	Oil refineries	Conventional, multicyclone	100	60	35	CEPMEIP, *Bit. Coal factors more appropriate.*

Table 8.2g Emission factors for combustion of other liquid fuels.

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Gas/Diesel oil	205	Various	Electricity, CHP, heating plant	Optimised burner	2	2	2	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Naphtha	210	1 A 1 b	Oil refineries	All units	5	5	5	CEPMEIP
Liquefied Petroleum gas	303	Various	Electricity, CHP, heating plant	Optimised burner	0.1	0.1	0.1	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Refinery gas	308	Various	Electricity, CHP, heating plant	Optimised burner	0.1	0.1	0.1	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Other oil	224	Various	Electricity, CHP, heating plant	Low S fuel, optimised burner	3	3	2.5	CEPMEIP
				Low S fuel, efficient combustion	14	12	10	CEPMEIP for residual oil. (About 50 mg. Nm^{-3} (LCPD limit for existing plant)
				Low-Medium S fuel, conventional installation	20	15	9	CEPMEIP. (about 70 mg. Nm^{-3})
				Low-Medium S fuel, conventional installation	60	50	40	CEPMEIP, (highest of similar entries with TSP of 35, 40, 50 and 60 used. About 200 mg.N Nm^{-3})
				High S fuel	210	190	130	CEPMEIP, lower of two entries for high S used.

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
								(This is a very high emission concentration (about 750 mg.N Nm^{-3})

Table 8.2h Emission factors for combustion of biomass

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Wood	111	Various	Electricity, CHP, heating plant	Modern unit with FF, <20 mg.Nm3 TSP	7	7	6	TSP scaled from BAT benchmark, fractions applied based on Bit coal
				Older unit, <100 mg.Nm3 TSP	35	25	12	TSP scaled from emission concentration, fractions based on bit coal
				Uncontrolled conventional	100	70	55	CEPMEIP (Uncontrolled Multicyclone)
				Conventional minimal control	160	150	150	CEPMEIP for conventional installation
Charcoal	112	1 A 2 c	Chemicals	Conventional large unit with multicyclone	100	60	35	CEPMEIP, the use of charcoal is likely to be very rare.
					400	100	35	CEPMEIP, the use of charcoal is likely to be very rare. .
Black liquour	215	1 A 2 f	Textile & leather (Pulp and Paper)	Conventional installation	160	150	150	CEPMEIP (N.B. such a high emission concentration would apply to few if any

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Notes**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
								plant)
Biogas	309	Various	Electricity, CHP, heating plant	Modern optimised large installation	3	3	2.5	(CEPMEIP, clean fuel)
				Conventional burner	5	5	5	CEPMEIP
				Modern, optimised	20	15	10	CEPMEIP (gasification plant),

9 SPECIES PROFILES

The US EPA (2003) undertook a review of species profiles within $PM_{2.5}$ and reports particle size distribution data for a variety of fuels and combustion and abatement technologies. Some of these data are dated and have high uncertainty ratings. Profiles of other materials are not available.

Table 9-1 US EPA $PM_{2.5}$ species profile for combustion activities

Profile ref	Profile name	Component				
		POA	PEC	GSO4	PNO3	Other
22002	Residual Oil Combustion	0.1075	0.0869	0.5504	0.0005	0.2547
22003	Distillate Oil Combustion	0.0384	0.0770	0.3217	0.0024	0.5605
22004	Natural Gas Combustion	0.6000	0.0000	0.2000	0.0055	0.1945
22007	Liquid Waste Combustion	0.0540	0.1050	0.0680	0.0000	0.7730
22009	Solid Waste Combustion	0.0068	0.0350	0.0680	0.0000	0.8902
NCOAL	Coal Combustion	0.20	0.01	0.16	0.005	0.625
NWWAS	Wood Waste Boiler	0.39	0.14	0.08	0	0.39

Notes:
POA - Primary organic aerosol derived from organic carbon
PEC Elemental Carbon
GSO4 - Sulphate
PNO3 - Nitrate
Other – Remainder of $PM_{2.5}$ material emitted.

Note that the data for the coal combustion and some other profiles are derived from dilution tunnel measurements on large combustion plant and may not be directly comparable with primary $PM_{2.5}$ from sub-50 MW_{th} boilers.

10 UNCERTAINTY ESTIMATES

The overall 'Uncertainty' in national emission inventories may be significant – as illustrated in Table 9.1.

Table 9.1 Uncertainty estimate for selected pollutants in the UK air emission inventory (NAEI, 2005).

Pollutant	Estimated Uncertainty (%)
PM_{10}	-20 to +50
$PM_{2.5}$	-20 to +30
$PM_{1.0}$	-10 to +20
$PM_{0.1}$	+/- 10
Sulphur Dioxide	+/- 3
Oxides of Nitrogen	+/- 8
NMVOCs	+/- 10
Ammonia	+/- 20

There is uncertainty in both the aggregated emission factors and activity data used to estimate emissions i.e. the imprecision and error to be expected from the application of an 'average' emission factor or activity statistic to estimate emissions from a specific sector - an artificial grouping of 'similar' sources.

The uncertainty is partly the result of how emission factors are developed and applied. In the case of primary particulate matter, the expanded statistical uncertainty is made up of: between plant variance, within plant variance, and uncertainties associated with the measurement methodology used and the aggregation of data. The measurement data in Annex 1 illustrates the variability in emission factors that occurs from between plant variance.

Process measurements, from which emission factors are developed at individual facility level, are subject to both systematic and random errors in the determination of mass concentration, mass emission, size distribution, and analytical errors etc.

In addition bias may exist in emission factors arising from:

1. Assumptions made about the abatement used on 'typical' industrial installations. For example emission factors 'age', the factors widely used in the Guidebook and hence by many countries as default emission factors in their national inventories become out of date. Recent measurement work suggests that they may overestimate emissions from the industrial processes subject to more modern industrial emissions regulation. They may, however, still be fully representative for older plant, small plant, or for poorer fuels;
2. Assumptions about the relationship between TSP and PM10/$PM_{2.5}$. The technical literature is comprehensive for TSP and the data quality can be good if measurements

have been made using the international standard methods that are available (typically the 95% confidence limit ~10%). But a variety of methods are used for particle size fractionation and as yet there are no harmonised international standards to ensure comparability. Published measurement data for PM10 is sparse, that for $PM_{2.5}$ emissions more so. An added complication is that the methodology for the determination of TSP differs from that of PM10 and $PM_{2.5}$ and so the two need not correlate directly.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Knowledge of combustion and abatement techniques, dust removal efficiencies and operating techniques is limited.

Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges. Emission factors also need to be generated, which specifically relate to different levels of abatement on different types of plant.

The stack emission factors described in the Guidebook, and all the PM_{10} emission factors, are based whenever possible on measurements. Particle measurements have often been made on the mass of total particulate matter and then converted to PM_{10} based either on the size distribution of the sample collected or, more usually, on size distributions given in the literature. There may be secondary sources of particulate matter, that are diffuse or fugitive in nature e.g. emissions from coke ovens, stockpiles, ash handling etc. These emissions are difficult to measure and in some cases it is likely that no entirely satisfactory measurements have ever been made, in many cases estimates of emissions from such sources are missing.

There is very little published data suitable for emission inventory compilation. I.e. representative data of known quality relating a) quantities of (particulate) material released to b) the activity associated with the release of that pollutant. Suitable data and associated information would record the determination of mass emissions rates using standardized measurement methods or calculation-based methods. Ideally such methods would cover the planning and execution of the data collection programme including: the selection of sampling methodology, choice of equipment, suitable working procedures, the calculation of representative emissions rates, the selection of matching activity data, the determination of sampling/measurement uncertainty, and the reporting of information in a form that is suitable for calculating emissions factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Combustion plants should be considered as point sources if plant specific data are available. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment, population or other relevant statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Combustion processes in most industrial sectors can be considered as a continuous process however; district and agricultural heating plants will tend to have an operational profile determined by the season. Individual combustion plant may have daily and/or seasonal temporal profiles.

14 ADDITIONAL COMMENTS

See chapters B111 and B216.

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCESSES

17 REFERENCES

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18 BIBLIOGRAPHY

For a detailed bibliography the primary literature mentioned in AP 42 can be used.

19 RELEASE VERSION, DATE AND SOURCE

Version: 1

Date: Aug 2006

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20 POINT OF ENQUIRY

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SNAP CODE:
010101 & 010102
010201 & 010202
010301
010401
010501 & 010502
020101 & 020102
020201
020301
020302
030101 & 030102

SOURCE ACTIVITY TITLE: **COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES**
Particulate emissions from large Combustion Plants (>50MWth)

NOSE CODE:
101.01
101.02

NFR CODE:
1 A 1 a,b,c
1 A 2 a-f
1 A 4 b,c,i

ISIC **3510**

1 ACTIVITIES INCLUDED

This Supplement, to be read in conjunction with the existing Chapter B111, covers emissions of particulate matter (PM) released from combustion processes within the energy and transformation industries in boilers and furnaces larger than 50 MWth. This Supplement includes guidance on estimating total PM (TSP), PM_{10} and $PM_{2.5}$ emissions from these sources. Emissions of other pollutants from this sector are provided in chapter B111.

2 CONTRIBUTION TO TOTAL EMISSION

The contributions of PM_{10} and $PM_{2.5}$ emissions released from combustion in large combustion plant to total emissions in countries of the CORINAIR90 inventory is presented in Table 2.1.

Table 2.1 Contribution to total particulate matter emissions from 2004 EMEP database (WEBDAB)

NFR Sector	Data	PM_{10}	$PM_{2.5}$	TSP
1 A 1 a - Public Electricity and Heat Production[a]	No. of countries reporting	26	26	27
	Lowest Value	0.2%	0.2%	0.2%
	Typical Contribution	11.7%	10.1%	12.8%
	Highest Value	48.8%	47.8%	48.4%
1 A 2 - Manufacturing Industries and Construction[b]	No. of countries reporting	26	26	26
	Lowest Value	0.7%	0.6%	0.6%
	Typical Contribution	9.0%	9.5%	7.9%
	Highest Value	20.7%	22.1%	25.7%
1 A 4 a - Commercial / Institutional[c]	No. of countries reporting	23	23	23
	Lowest Value	0.1%	0.1%	0.1%
	Typical Contribution	3.9%	3.4%	4.5%
	Highest Value	19.3%	22.2%	29.5%
1 A 4 b - Residential[d]	No. of countries reporting	3	2	3
	Lowest Value	2.0%	6.5%	3.7%
	Typical Contribution	14.9%	26.2%	10.8%
	Highest Value	36.6%	45.8%	15.4%
1 A 4 b i - Residential plants[e]	No. of countries reporting	23	23	23
	Lowest Value	2.7%	5.8%	0.8%
	Typical Contribution	28.3%	33.1%	22.0%
	Highest Value	67.1%	74.6%	53.2%
1 A 5 a - Other, Stationary (including Military)[f]	No. of countries reporting	7	7	7
	Lowest Value	0.0%	0.0%	0.0%
	Typical Contribution	0.1%	0.1%	0.1%
	Highest Value	0.5%	0.4%	0.6%

[a] Includes contribution from Chapter 112

[b] Includes contributions from Chapter 112 and 316 (SNAP 030106)

[c] Includes contribution from Chapter 112 and 216 (SNAP 020205)

[d] Includes contribution from Chapter 810

[e] Includes contribution from Chapter 112

[f] Includes contribution from Chapter 112 and 216 (SNAP 020106)

3 GENERAL

3.1 Description

This chapter considers emissions of PM generated by boilers larger than 50 MWth. Other emissions from this source category are considered in B111.

3.2 Definitions

See B111.

3.3 Techniques

See B111 for information on boiler types and fuels. Combustion of coal and other solid fuels present the main source for primary PM emissions.

3.4 Emissions

Particulate emissions result from activities such as storage of fuels; on site transportation of solid fuel; combustion of fuels, transport, storage and disposal of combustion residues including furnace bottom ash, fly ash and, abatement residues.

Combustion of fuels will generate solid residues which may be deposited in the combustion chamber (furnace bottom ash), within the furnace, boiler surfaces or ducting (fly ash). Coal and other fuels with a significant ash content have the highest potential to emit PM. Suspended ash material in exhaust gases will be retained by particulate abatement or other emission abatement equipment (abatement residues). Material which remains in the flue gases beyond the abatement equipment and passes to the atmosphere is primary PM. Secondary PM is formed by chemical and physical processes after discharge to atmosphere and is NOT considered here.

3.5 Controls

Particulate emission reduction is usually achieved using abatement equipment. Electrostatic precipitators (ESPs) and fabric filters (FFs) are widely used on boilers. Cyclones (particularly multicyclones) can be found on smaller grate-fired boilers. Most pulverised coal fired power station boilers use ESPs although fabric filters are becoming more common. Flue gas desulphurisation (FGD) plant can also help reduce particulate emissions from pulverised coal-fired boilers. Wet limestone FGD systems retrofitted to existing plant are generally located downstream of existing ESPs and can provide a further stage of PM reduction. Dry lime injection FGD systems incorporate a FF for sorbent capture and PM removal.

Fabric filters are capable of achieving higher emission reductions than electrostatic precipitators but both are suitable[1] for the sector and can achieve PM emission concentrations of 5 - 30 mg/m^3.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[2]:

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[1] Either technology is considered part of Best Available Techniques (BAT) under EU Integrated Pollution Prevention and Control regulations.

[2] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.

Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.

Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

The Tier 1 simpler methodology, where limited information is available, uses a restricted set of default emission factors together with production capacity information specific to the country or region of interest; there is little or no specification of the type of industrial technologies or the type and efficiency of control equipment in place. The Tier 2 approach, in addition, requires an approximation of the mix of technologies in place, and more detailed activity data, but still allows the use of default sector or technology factors.

Consequently the simplest methodology (Tier 1) is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR x EF}$$

In the energy sector, for example, fuel consumption would be the measure of activity and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

The Tier 2 methodology is a modified version of this basic equation:

$$\text{Emission} = \sum((AR_1 \text{ x } EF_1) + (AR_2 \text{ x } EF_2) + \ldots.(AR_n \text{ x } EF_n))$$

Default emission factors for this purpose are provided in Sections 8.1 and 8.2.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3) to estimate emissions of pollutants from combustion plant >50 MW_{th} is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

In many countries, operators of combustion plant >50MWth will report emissions to comply with regulatory requirements and this data can be used to help compile the national inventory.

The recommended detailed methodology to estimate emissions of PM from combustion activities is based on measurements and/or estimations using technology-specific emission factors.

Information on the type of the process and activity data, for example combustion and abatement technologies, is required to assign appropriate emission factors.

Reference emission factors for comparison with users' own data are provided in Section 8.2.

6 ACTIVITY STATISTICS

Activity statistics for energy consumption or other relevant national activity data for estimating emissions using the simpler estimation methodology (Tiers 1 and 2) are available from national statistics.

The detailed methodology (Tier 3) requires more detailed information such as the amount and types of fuel consumed within individual combustion plant or industry sectors. These data are not always easily available although in many countries operators do report fuel use for emission trading or other legislative requirements.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 2 on energy, Chapter 1.

7 POINT SOURCE CRITERIA

Large combustion plants are regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors For Use With Simpler Methodology (Tier 1)

Fuel	**Technology**	**Emission factor, g GJ^{-1}**			**Notes**[3]
		TSP	**PM_{10}**	**$PM_{2.5}$**	
Hard coal, (assumes 20% ash) Brown coal, Other solid fuels	Pulverised coal, ESP	30	20	9	Based on AP 42 - assumes 20% ash content and PM emissions from solid mineral fuels generally similar to coal
	Pulverised coal, fluid bed, other FF	7.4	7.4	3.7	
	Cyclone furnace, ESP	6.1	4.2	2.3	
	Stoker with multicyclone	330	230	27	
	Pulverised coal ESP + wet limestone FGD	6	6	5	From CEPMEIP data (US EPA default factors for wet scrubbers are very high)
Natural gas		0.9	0.9	0.9	AP-42 filterable PM factor
Derived gases		5	5	5	CEPMEIP data, worst case for derived gases.
Heavy fuel oil (1% S)	No control	25	18	13	Assumes 1% sulphur as specified in the EU Sulphur content of liquid fuels Directive
	FGD	1.5	1.5	1.5	
Heavy fuel oil (3% S)	No control	64	45	33	Assumes 3% sulphur (maximum permitted in EU countries)
	FGD	3.8	3.8	3.7	
Other liquid fuels	LPG	2.0	2.0	2.0	
Biomass	FF	51	38	33	AP 42 Wood waste
	ESP	28	21	18	

The information provided in Section 8.2 provides further information for selection of more appropriate emission factors.

8.2 Reference Emission Factors For Use With Tier 2 Methodology

Tables 8.2a-z contain reference particulate emission factors for fuel combustion in various technologies with different types of abatement.

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[3] Source: R. Stewart (2006); US EPA AP 42 (1996); CEPMEIP (2006)

Table 8.2a Emission factors for combustion processes burning hard coal.

Fuel	**NAPFUE**	**NFR Codes**	**Activity description**	**Activity detail**[4]	**Emission factor $g.GJ^{-1}$**			**Notes**[5]
Hard coal					**TSP**	**PM_{10}**	**$PM_{2.5}$**	
Bit. Coal	101	Various	Electricity plant, CHP plant	FGD, ESP or FF <20 $mg.Nm^{-3}$ (BAT)	6	6	5	CEPMEIP
				ESP (or FF) <50 $mg.Nm^{-3}$ (LCPD)	15	12	6	Scaled from CEPMEIP ESP factor
				ESP <100 $mg.Nm^{-3}$ (LCPD)	30	25	12	From CEPMEIP sub-bit coal 'high efficiency ESP', TSP scaled to the EU LCP Directive existing plant sub $100MW_{th}$ limit
				ESP Old/conventional <500 $mg. Nm^{-3}$	140	70	17	CEPMEIP
				Large unit with multicyclone	100	60	35	CEPMEIP
				Large unit, uncontrolled or cyclone	500	250	100	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
Sub-bituminous coal	103	Various	Electricity plant, CHP plant, heat plant	FGD, ESP or FF <20 $mg.Nm^{-3}$ (BAT)	6	6	5	CEPMEIP
				ESP (or FF) <50 $mg.Nm^{-3}$ (LCPD)	15	12	6	Scaled from CEPMEIP ESP factor
				ESP <100 $mg.Nm^{-3}$ (LCPD)	30	25	12	From CEPMEIP sub-bit coal 'high efficiency ESP', TSP scaled to LCPD existing plant sub $100MW_{th}$ limit

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[4] KEY: FGD: Flue gas desulphurisation, ESP: Electrostatic Precipitator, FF: Fabric Filter, BAT: Best Available Techniques, LCPD: Large Combustion Plant Data

[5] Sources: R. Stewart (2006); US EPA AP 42 (1996); CEPMEIP (2006)

Fuel	NAPFUE	NFR Codes	Activity description	Activity detail[4]	Emission factor $g.GJ^{-1}$			Notes[5]
				ESP Old/conventional <500 $mg. Nm^{-3}$	140	70	17	CEPMEIP
				Conventional large unit with multicyclone	100	60	35	CEPMEIP
				Conventional unit, uncontrolled or cyclone	500	250	100	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
Coke	107							Coke is unlikely to be burned as primary fuel, when co-fired use the factor for the principal fuel.

Table 8.2b Emission factors for combustion processes burning brown coal.

Fuel	NAPFUE	NFR Code	Activity description	Activity detail	Emission factor			Reference/Comments
					TSP	PM_{10}	$PM_{2.5}$	
Brown coal	105	Various	Electricity plant, CHP plant, heat plant	FGD, ESP or FF <20 $mg.Nm^{-3}$ (BAT)	9	8	6	CEPMEIP
				High efficiency ESP (or FF)	40	30	14	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
				Conventional large unit with multicyclone	100	60	35	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
				Older ESP	160	80	20	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)
				Older installation	500	250	100	CEPMEIP (N.B. such a high

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference/Comments**
				uncontrolled or cyclone				emission concentration would apply to few if any plant)
Peat	113	Various	Electricity plant, CHP plant, heat plant	BAT/new LCPD, Modern end-of-pipe abatement FGD, ESP or FF. <30 mg.Nm3	9	8	6	CEPMEIP
				Efficient abatement LCP larger facility, <50 mg.Nm3	20	15	10	TSP Scaled from LCP emission limit of 50 mg.Nm^{-3}
				Efficient abatement LCP <100 MW$_{th}$, <100mg.Nm3	40	30	20	TSP Scaled from LCP emission limit of 50 mg.Nm^{-3}
				Conventional technology	120	40	20	CEPMEIP
				Conventional smaller, multicyclone	300	40	20	CEPMEIP

Table 8.2c Emission factors for combustion processes burning other solid fuels

Fuel	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Municipal solid waste	114	Various	Electricity plant, CHP plant, heating plant	Effective emission control (BAT)	15	13	10	CEPMEIP, (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
(Solid)				Conventional emission control	100	70	55	CEPMEIP (uncontrolled. optimised combustion), (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
Ind. waste	115	Various	Electricity, CHP, heating plant	Effective emission control (BAT)	15	13	10	CEPMEIP, (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)
				Conventional emission control	100	70	55	CEPMEIP (uncontrolled, optimised combustion), (N.B. care should be taken using this factor as waste burning is often controlled under national/international regulation to a more stringent specification)

Table 8.2d Emission factors for combustion processes burning natural gas.

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Natural gas	301	Various	Electricity, CHP and heating plant	Burner with optimised combustion	0.1	0.1	0.1	CEPMEIP
				Conventional installation	0.2	0.2	0.2	CEPMEIP
				Conventional installation	0.9	0.9	0.9	USEPA AP-42 filterable PM (all PM stated to be PM_1)

Table 8.2e Emission factors for combustion of derived gases.

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Gas works gas	311	Various	Electricity, CHP and heating plant	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, Conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP. (N.B. High PM due to fuel quality)
Other gaseous	314	Various	Electricity, CHP and heating plant	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
fuel								
				Conventional installation	5	5	5	CEPMEIP
Coke oven gas	304	Various	Electricity, CHP heating plant, coke ovens	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP.
Blast furnace gas	305	Various	Electricity, CHP and heating plant, coke ovens	Clean fuel, efficient combustion	0.1	0.1	0.1	CEPMEIP
				Clean fuel, Conventional installation	0.2	0.2	0.2	CEPMEIP (conventional installation)
				Conventional installation	5	5	5	CEPMEIP.

Table 8.2f Emission factors for combustion of heavy fuel oil.

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Residual fuel oil	203	Various	Electricity, CHP and heating plant	Low S fuel with optimised burner or abatement	3	3	2.5	CEPMEIP (equivalent to about 10 mg.Nm3 or BAT)
				Low S fuel, efficient combustion	14	12	10	CEPMEIP. About 50 mg.Nm3 (EU LCPD limit for existing plant)
				Low-Medium S fuel, conventional installation	20	15	9	CEPMEIP (equivalent. to about 70 mg.Nm3.
				Low-Medium S fuel, conventional installation	60	50	40	CEPMEIP, the higher of two entries used about 200 mg.Nm3
				High S fuel	210	190	130	CEPMEIP, the lower of two entries for high S used. (N.B. such a high emission concentration 750 mg.Nm3 would apply to few if any plant)
Petroleum coke	110	1 A 1 b	Oil refineries	Conventional, multicyclone	100	60	35	CEPMEIP, N.B the factor is very high compared to the EU LCP Directive ELVs and BAT for large furnaces. Bit Coal factors more appropriate.

Table 8.2g Emission factors for combustion of other liquid fuels.

Fuel (IPCC Cat)	NAPFUE	NFR Code	Activity description	Activity detail	Emission factor			Reference
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Gas/Diesel oil	205	Various	Electricity, CHP, heating plant	Optimised burner	2	2	2	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Naphtha	210	1 A 1 b	Oil refineries	All units	5	5	5	CEPMEIP
Liquefied Petroleum gas	303	Various	Electricity, CHP, heating plant	Optimised burner	0.1	0.1	0.1	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Refinery gas	308	Various	Electricity, CHP, heating plant	Optimised burner	0.1	0.1	0.1	CEPMEIP
				Conventional burner	5	5	5	CEPMEIP
Other oil	224	Various	Electricity, CHP, heating plant	Low S fuel, optimised burner	3	3	2.5	CEPMEIP
				Low S fuel, efficient combustion	14	12	10	CEPMEIP for residual oil. About 50 mg.Nm3 (LCPD limit for existing plant)
				Low-Medium S fuel, conventional installation	20	15	9	CEPMEIP (equiv. to about 70 mg.Nm3.
				Low-Medium S fuel, conventional installation	60	50	40	CEPMEIP (highest of similar entries with TSP of 35, 40, 50 and 60 used. About 200 mg.Nm^{-3})

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
				High S fuel	210	190	130	CEPMEIP, lower of two entries for high S used. (N.B. this is a very high emission concentration ~750 mg.Nm3)

Table 8.2h Emission factors for combustion of biomass

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Wood	111	Various	Electricity, CHP, heating plant	Modern, BAT unit <20 mg.Nm3 TSP	7	7	6	TSP scaled from BAT benchmark, fractions applied based on Bit coal
				Older unit, <100 mg.Nm3 TSP	35	25	12	TSP scaled from emission concentration, fractions based on bit coal
				Uncontrolled conventional	100	70	55	CEPMEIP (equiv. To an uncontrolled multicyclone)
Charcoal	112	1 A 2 c	Chemicals	Conventional large unit with multicyclone	100	60	35	CEPMEIP (N.B. the use of charcoal in LCP is likely to be rare.
Black liquour	215	1 A 2 f	Textile & leather (Pulp and Paper ?)	Conventional installation	160	150	150	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)

Fuel (IPCC Cat)	**NAPFUE**	**NFR Code**	**Activity description**	**Activity detail**	**Emission factor**			**Reference**
					TSP	**PM_{10}**	**$PM_{2.5}$**	
Biogas	309	Various	Electricity, CHP, heating plant	Modern optimised large installation	3	3	2.5	CEPMEIP (cleaned fuel)
				Conventional burner	5	5	5	CEPMEIP
				Modern, optimised	20	15	10	CEPMEIP (gasification plant), *seems high for gaseous fuel*
				Conventional installation	*160*	*150*	*150*	CEPMEIP (N.B. such a high emission concentration would apply to few if any plant)

8.3 Measured Emission Factors for consideration in Tier 3 Methodology

Annex 1 lists measurement derived PM emission factor data typical of that required for a tier 3 approach for large combustion plant – see also Section 15.

9 SPECIES PROFILES

The US EPA (2003) undertook a review of species profiles within $PM_{2.5}$ and reports particle size distribution data for a variety of fuels and combustion and abatement technologies. Some of these data are dated and have high uncertainty ratings. Profiles of other materials are not available.

Table 8.2j US EPA (2003) $PM_{2.5}$ species profiles

Profile ref	Profile name	Component				
		POA	PEC	GSO4	PNO3	Other
22002	Residual Oil Combustion	0.1075	0.0869	0.5504	0.0005	0.2547
22003	Distillate Oil Combustion	0.0384	0.0770	0.3217	0.0024	0.5605
22004	Natural Gas Combustion	0.6000	0.0000	0.2000	0.0055	0.1945
22007	Liquid Waste Combustion	0.0540	0.1050	0.0680	0.0000	0.7730
22009	Solid Waste Combustion	0.0068	0.0350	0.0680	0.0000	0.8902
NCOAL	Coal Combustion	0.20	0.01	0.16	0.005	0.625
NWWAS	Wood Waste Boiler	0.39	0.14	0.08	0	0.39

Notes:
POA - Primary organic aerosol derived from organic carbon
PEC - Elemental Carbon
GSO4 - Sulphate
PNO3 - Nitrate
Other – Remainder of $PM_{2.5}$ material emitted.

Note that the data for the coal combustion and other profiles are derived from dilution tunnel measurements and may not be directly comparable with primary $PM_{2.5}$.

10 UNCERTAINTY ESTIMATES

The overall ‘Uncertainty’ in national emission inventories may be significant – as illustrated in Table 9.1.

Table 9.1 Uncertainty estimate for selected pollutants in the UK air emission inventory (NAEI, 2005).

Pollutant	Estimated Uncertainty (%)
PM_{10}	-20 to +50
$PM_{2.5}$	-20 to +30
$PM_{1.0}$	-10 to +20
$PM_{0.1}$	+/- 10
Sulphur Dioxide	+/- 3
Oxides of Nitrogen	+/- 8
NMVOCs	+/- 10
Ammonia	+/- 20

There is uncertainty in both the aggregated emission factors and activity data used to estimate emissions i.e. the imprecision and error to be expected from the application of an ‘average’ emission factor or activity statistic to estimate emissions from a specific sector - an artificial grouping of ‘similar’ sources.

The uncertainty is partly the result of how emission factors are developed and applied. In the case of primary particulate matter, the expanded statistical uncertainty is made up of: between plant variance, within plant variance, and uncertainties associated with the measurement methodology used and the aggregation of data. The measurement data in Annex 1 illustrates the variability in emission factors that occurs from between plant variance.

Process measurements, from which emission factors are developed at individual facility level, are subject to both systematic and random errors in the determination of mass concentration, mass emission, size distribution, and analytical errors etc.

In addition bias may exist in emission factors arising from:

1. Assumptions made about the abatement used on ‘typical’ industrial installations. For example emission factors ‘age’, the factors widely used in the Guidebook and hence by many countries as default emission factors in their national inventories become out of date. Recent measurement work suggests that they may overestimate emissions from the industrial processes subject to more modern industrial emissions regulation. They may, however, still be fully representative for older plant, small plant, or for poorer fuels;
2. Assumptions about the relationship between TSP and PM10/$PM_{2.5}$. The technical literature is comprehensive for TSP and the data quality can be good if measurements have been made using the international standard methods that are available (typically the 95% confidence limit ~10%). But a variety of methods are used for particle size fractionation and as yet there are no harmonised international standards to ensure comparability. Published measurement data for PM10 is sparse, that for $PM_{2.5}$ emissions more so. An added complication is that the methodology for the

determination of TSP differs from that of PM10 and $PM_{2.5}$ and so the two need not correlate directly.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The stack emission factors described in the Guidebook, and all the PM_{10} emission factors, are based whenever possible on measurements. Particle measurements have often been made on the mass of total particulate matter and then converted to PM_{10} based either on the size distribution of the sample collected or, more usually, on size distributions given in the literature. There may be secondary sources of particulate matter, that are diffuse or fugitive in nature e.g. emissions from coke ovens, stockpiles, ash handling etc. These emissions are difficult to measure and in some cases it is likely that no entirely satisfactory measurements have ever been made, in many cases estimates of emissions from such sources are missing.

There is very little published data suitable for emission inventory compilation. I.e. representative data of known quality relating a) quantities of (particulate) material released to b) the activity associated with the release of that pollutant. Suitable data and associated information would record the determination of mass emissions rates using standardized measurement methods or calculation-based methods. Ideally such methods would cover the planning and execution of the data collection programme including: the selection of sampling methodology, choice of equipment, suitable working procedures, the calculation of representative emissions rates, the selection of matching activity data, the determination of sampling/measurement uncertainty, and the reporting of information in a form that is suitable for calculating emissions factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Combustion plants should be considered as point sources if plant specific data are available. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Combustion processes can be considered as a continuous process however individual combustion plant may have daily and/or seasonal temporal profiles.

14 ADDITIONAL COMMENTS

See chapter B111.

15 SUPPLEMENTARY DOCUMENTS

Digest of UK Energy Statistics

Recommendations for the Update and Improvement of Existing $PM_{2.5}$ Split Factors – Note from Pacific Environmental Services to US EPA 29 September 2003

IIASA RAINS data

16 VERIFICATION PROCESSES

The applicability of the emission factors quoted, in Section 8 above, for use with highly regulated plant may be verified using the measurement data listed in Annex 1.

17 REFERENCES

EMEP/CORINAIR Emission Inventory Guidebook – 2005, EEA (European Environment Agency) Chapter B111

IPPC Best Available Techniques Reference Document on the Production of Iron and Steel, December 2001, http://eippcb.jrc.es

IPPC Best Available Techniques Reference Document on Large Combustion Plants, December 2001, http://eippcb.jrc.es

IPPC Best Available Techniques Reference Document on the Production of Pulp and Paper, December 2001, http://eippcb.jrc.es

NAEI (2005) UK National Atmospheric Emissions Inventory: UK Emissions of Air Pollutants 1970 to 2003, October 2005

US EPA (1996) Compilation of Air Pollutant Emission Factors Vol.1 Report AP-42 (5th ed.)

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19 RELEASE VERSION, DATE AND SOURCE

Version: 1

Date: Aug 2006

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ANNEX 1A – SUMMARY OF RECENT MEASURED PM_{10} DATA ON COMBUSTION SOURCES

Combustion Type	Process	Size indication	Fuel	Abatement Measures	PM_{10} Emission Factor or concentration	Units	Source[6]	CEPMEIP Factor	CEPMEIP Units
Coal	Combustion Plant	180 MW	dry brown coal	ESP horizontal, scrubber	1.44	g/GJ	LAU	30.00	g/GJ
		146 MW	brown coal briquette, Limestone	ESP horizontal, drying desulphurisation	1.35	g/GJ	LAU		g/GJ
		119 MW	raw brown coal	ESP horizontal, desulph., NOx removal	6.13	g/GJ	LAU	30.00	g/GJ
		1000MW	hard coal	ESP, desulphurisation, NOx removal	0.33	g/GJ	LAU	25.00	g/GJ
		1000MW	hard coal	ESP, desulphurisation, NOx removal	0.30	g/GJ	LAU	25.00	g/GJ
		-	sub-bituminous coal	ESP	11.00	mg/MJ	NRCAN	25.00	g/GJ
		-	lignite	ESP	1.80	mg/MJ	NRCAN	30.00	g/GJ
		-	75% lignite/25% bituminous	ESP	1.10	mg/MJ	NRCAN		
		120 MW	Powdercoal	ESP	51.30	mg/Nm3	VITO	70.00	g/GJ
		-	lignite	Fabric filter, desulphurisation	0.1	mg/m3	TESO	8.00	g/GJ

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Combustion Type	**Process**	**Size indication**	**Fuel**	**Abatement Measures**	**PM_{10} Emission Factor or concentration**	**Units**	**Source**[6]	**CEPMEIP Factor**	**CEPMEIP Units**
				system					
		-	lignite	ESP, desulphurisation system	1.3	mg/m3	TESO	30.00	g/GJ
		-	hard coal	Fabric filter	7.5	mg/m3	TESO	6.00	g/GJ
		-	lignite	ESP, desulphurisation system	0.4	mg/m3	TESO	30.00	g/GJ
	Dry Bottom Ash Furnace	-	hard coal	ESP	24.4	mg/m3	TESO	25.00	
		-	lignite	ESP, desulphurisation system	1.5	mg/m3	TESO	30.00	g/GJ
		-	lignite, heavy fuel oil	ESP, desulphurisation system, fabric filter	0.2	mg/m3	TESO		
		-	lignite	ESP, desulphurisation system	14.9	mg/m3	TESO	80.00	g/GJ
		-	hard coal	ESP	0.2	mg/m3	TESO	25.00	g/GJ
		-	hard coal	Fabric filter	0.8	mg/m3	TESO	6.00	g/GJ
		-	hard coal	Fabric filter	0.2	mg/m3	TESO	6.00	g/GJ
		-	coal	ESP	1.5	mg/m3	TESO	25.00	g/GJ
	Grate and Dry Bottom Ash Furnace	-	lignite	ESP, desulphurisation system	1.2	mg/m3	TESO	80.00	g/GJ
	Grate Boiler	-	hard coal	Fabric Filter	0.7	mg/m3	TESO	6.00	g/GJ
	Grate Firing	-	lignite	ESP	6.8	mg/m3	TESO	30.00	g/GJ
	Boiler for Pulverised Solid Fuel	-	hard coal, light fuel oil	ESP	22.8	mg/m3	TESO		
		-	hard coal, lignite	ESP, desulphurisation	6.3	mg/m3	TESO	25.00	g/GJ

Combustion Type	Process	Size indication	Fuel	Abatement Measures	PM_{10} Emission Factor or concentration	Units	Source[6]	CEPMEIP Factor	CEPMEIP Units
				system					
		-	lignite	ESP, desulphurisation system	1.9	mg/m3	TESO	30.00	g/GJ
		-	lignite	ESP, desulphurisation system	4.2	mg/m3	TESO	30.00	g/GJ
		-	hard coal	Fabric filter	0.1	mg/m3	TESO	6.00	g/GJ
	Fluidised bed boiler	-	lignite	ESP, desulphurisation system, fabric filter	2.5	mg/m3	TESO	8.00	g/GJ
		-	lignite	Fabric filter, desulphurisation system	0.9	mg/m3	TESO	8.00	g/GJ
		-	hard coal, blast furnace gas	ESP	0.2	mg/m3	TESO		
		-	hard coal, blast furnace gas	ESP	0.4	mg/m3	TESO		
		-	hard coal, coke oven gas, blast furnace gas	ESP	4.3	mg/m3	TESO		
	Combustion Plant	10 MW	heavy oil	additive	12.33	g/GJ	LAU	15.00	g/GJ
		10 MW	heavy oil	additive	12.95	g/GJ	LAU	15.00	g/GJ
		10 MW	heavy oil, urea	additive, SNCR	15.29	g/GJ	LAU	15.00	g/GJ
		10 MW	heavy oil, urea	additive, SNCR	18.04	g/GJ	LAU	15.00	g/GJ
		20 t/h steam	heavy oil	SNCR	1.86	g/GJ	LAU	3.00	g/GJ
		270 MW	heavy oil	NOx removal	5.75	g/GJ	LAU	3.00	g/GJ
		270 MW	heavy oil	additive, NOx removal	4.49	g/GJ	LAU	3.00	g/GJ
		270 MW	heavy oil	NOx removal	4.79	g/GJ	LAU	3.00	g/GJ
		270 MW	heavy oil	additive, NOx removal	4.65	g/GJ	LAU	3.00	g/GJ

Combustion Type	**Process**	**Size indication**	**Fuel**	**Abatement Measures**	**PM_{10} Emission Factor or concentration**	**Units**	**Source**[6]	**CEPMEIP Factor**	**CEPMEIP Units**
		-	residual oil	-	29.00	mg/MJ	NRCAN	20.00	g/GJ
		-	heavy fuel oil, natural gas	-	6.80	mg/m3	TESO		
		-	heavy fuel oil, gas fuels	-	15.30	mg/m3	TESO		
	Combustion Plant	1.4 MW	saw chips, saw dust	cyclone	100.37	g/GJ	LAU	70.00	g/GJ
		1.4 MW	saw chips, saw dust	cyclone	75.87	g/GJ	LAU	70.00	g/GJ
		0.8 MW	saw chips, saw dust	cyclone	102.81	g/GJ	LAU	70.00	g/GJ
		3 MW	hogged wood	cyclone	96.32	g/GJ	LAU	70.00	g/GJ
		2.3 MW	rest of chipboards	multicyclone	119.09	g/GJ	LAU	70.00	g/GJ
		1.1 MW	piece of wood, saw chips	cyclone	131.93	g/GJ	LAU	70.00	g/GJ
		2 MW	hogged wood, wood waste	ESP	21.41	g/GJ	LAU	70.00	g/GJ
		7.9-9.5 MW	wood, wood chips	ESP	7.53	g/GJ	LAU	70.00	g/GJ
		7.9-9.5 MW	natural gas, wood, wood chips	ESP	7.41	g/GJ	LAU	70.00	g/GJ
		15 MW	hogged wood, rest wood, wood chips	ESP	3.22	g/GJ	LAU	70.00	g/GJ
		1.5 MW	hogged wood	chimney gas condensation, multi-cyclone	17.30	g/GJ	LAU	70.00	g/GJ
		1.5 MW	hogged wood	chimney gas condensation, multi-cyclone	21.05	g/GJ	LAU	70.00	g/GJ
		31 t/h steam	matured wood	cyclone, fabric	4.72	g/GJ	LAU	70.00	g/GJ

Combustion Type	Process	Size indication	Fuel	Abatement Measures	PM_{10} Emission Factor or concentration	Units	Source[6]	CEPMEIP Factor	CEPMEIP Units
				filter, NO_x removal					
	Grate Boiler		bark, natural gas	ESP	4.90	mg/m3	TESO		
Waste	hazardous waste incineration plant	-	hazardous waste	fabric filter, desulphurisation system	10.30	mg/m3	TESO		
	waste incineration plant	-	municipal solid waste	ESP, desulphurisation system	0.90	mg/m3	TESO	100.00	g/tonne
	home heating boiler	-	mixture of fuels and household waste	-	39.90	mg/m3	TESO		
	old growth , shredder	30 t/h	lumber, demolition wood, timber waste	fabric filter	2.71	g/tonne	LAU		

ANNEX 1B – SUMMARY OF RECENT MEASURED $PM_{2.5}$ DATA ON COMBUSTION SOURCES

Combustion Type	Process	Size indication	Fuel	Abatement Measures	$PM_{2.5}$ Emission Factor or concentration	Units	Source	CEPMEIP Factor	CEPMEIP Units
Coal	Combustion Plant	180 MW	dry brown coal	ESP horizontal, scrubber	1.20	g/GJ	LAU	14.00	g/GJ
		146 MW	brown coal briquette, Limestone	ESP horizontal, drying desulphurisation	1.09	g/GJ	LAU		g/GJ
		119 MW	raw brown coal	ESP horizontal, desulph., NOx removal	4.15	g/GJ	LAU	14.00	g/GJ
		1000MW	hard coal	ESP, desulphurisation,	0.26	g/GJ	LAU	12.00	g/GJ

Combustion Type	Process	Size indication	Fuel	Abatement Measures	$PM_{2.5}$ Emission Factor or concentration	Units	Source	CEPMEIP Factor	CEPMEIP Units
				NOx removal					
		1000MW	hard coal	ESP, desulphurisation, NOx removal	0.23	g/GJ	LAU	12.00	g/GJ
		-	sub-bituminous coal	ESP	8.30	mg/MJ	NRCAN	3.00	g/GJ
		-	lignite	ESP	1.20	mg/MJ	NRCAN	3.00	g/GJ
		-	75% lignite/25% bituminous	ESP	28.10	mg/MJ	NRCAN		
		120 MW	Powdercoal	ESP	30.24	mg/Nm3	VITO	17.00	g/GJ
		-	lignite	Fabric filter, desulphurisation system	0.1	mg/m3	TESO	6.00	g/GJ
		-	lignite	ESP, desulphurisation system	1.3	mg/m3	TESO	14.00	g/GJ
		-	hard coal	Fabric filter	7.4	mg/m3	TESO	5.00	
		-	lignite	ESP, desulphurisation system	0.4	mg/m3	TESO	14.00	g/GJ
	Dry Bottom Ash Furnace	-	hard coal	ESP	9.6	mg/m3	TESO	12.00	
		-	lignite	ESP, desulphurisation system	1.3	mg/m3	TESO	14.00	g/GJ
		-	lignite, heavy fuel oil	ESP, desulphurisation system, fabric filter	0.2	mg/m3	TESO		
		-	lignite	ESP, desulphurisation system	12.3	mg/m3	TESO	20.00	g/GJ
		-	hard coal	ESP	0.2	mg/m3	TESO	12.00	
		-	hard coal	Fabric filter	0.6	mg/m3	TESO	5.00	

Combustion Type	**Process**	**Size indication**	**Fuel**	**Abatement Measures**	**$PM_{2.5}$ Emission Factor or concentration**	**Units**	**Source**	**CEPMEIP Factor**	**CEPMEIP Units**
		-	hard coal	Fabric filter	0.2	mg/m3	TESO	5.00	
		-	coal	ESP	1.4	mg/m3	TESO	12.00	g/GJ
	Grate and Dry Bottom Ash Furnace	-	lignite	ESP, desulphurisation system	0.5	mg/m3	TESO	20.00	g/GJ
	Grate Boiler	-	hard coal	Fabric Filter	0.6	mg/m3	TESO	5.00	g/GJ
	Grate Firing	-	lignite	ESP	6	mg/m3	TESO	14.00	g/GJ
	Boiler for Pulverised Solid Fuel	-	hard coal, light fuel oil	ESP	20.8	mg/m3	TESO		
		-	hard coal, lignite	ESP, desulphurisation system	5.9	mg/m3	TESO		
		-	lignite	ESP, desulphurisation system	1.9	mg/m3	TESO	14.00	g/GJ
		-	lignite	ESP, desulphurisation system	4.1	mg/m3	TESO	14.00	g/GJ
		-	hard coal	Fabric filter	0.1	mg/m3	TESO	5.00	g/GJ
	Fluidised bed boiler	-	lignite	ESP, desulphurisation system, fabric filter	1.2	mg/m3	TESO	6.00	g/GJ
		-	lignite	Fabric filter, desulphurisation system	0.8	mg/m3	TESO	6.00	g/GJ
		-	hard coal, blast furnace gas	ESP	0.4	mg/m3	TESO		
		-	hard coal, blast furnace gas	ESP	0.1	mg/m3	TESO		
		-	hard coal, coke oven gas, blast furnace gas	ESP	4.1	mg/m3	TESO		

Combustion Type	**Process**	**Size indication**	**Fuel**	**Abatement Measures**	**$PM_{2.5}$ Emission Factor or concentration**	**Units**	**Source**	**CEPMEIP Factor**	**CEPMEIP Units**
Oil	Combustion Plant	10 MW	heavy oil	additive	10.30	g/GJ	LAU	10.00	g/GJ
		10 MW	heavy oil	additive	9.18	g/GJ	LAU	10.00	g/GJ
		10 MW	heavy oil, urea	additive, SNCR	12.21	g/GJ	LAU	10.00	g/GJ
		10 MW	heavy oil, urea	additive, SNCR	13.12	g/GJ	LAU	10.00	g/GJ
		20 t/h steam	heavy oil	SNCR	1.38	g/GJ	LAU	11.00	g/GJ
		270 MW	heavy oil	NOx removal	4.69	g/GJ	LAU	2.50	g/GJ
		270 MW	heavy oil	additive, NOx removal	4.15	g/GJ	LAU	2.50	g/GJ
		270 MW	heavy oil	NOx removal	4.41	g/GJ	LAU	2.50	g/GJ
		270 MW	heavy oil	additive, NOx removal	4.23	g/GJ	LAU	2.50	g/GJ
		-	residual oil	-	28.10	mg/MJ	NRCAN	10.00	g/GJ
		-	heavy fuel oil, natural gas	-	6.70	mg/m3	TESO		
		-	heavy fuel oil, gas fuels	-	15.20	mg/m3	TESO		
Waste	Combustion Plant	1.4 MW	saw chips, saw dust	cyclone	71.66	g/GJ	LAU	55.00	g/GJ
		1.4 MW	saw chips, saw dust	cyclone	52.25	g/GJ	LAU	55.00	g/GJ
		0.8 MW	saw chips, saw dust	cyclone	65.47	g/GJ	LAU	55.00	g/GJ
		3 MW	hogged wood	cyclone	90.13	g/GJ	LAU	55.00	g/GJ
		2.3 MW	rest of chipboards	multi-cyclone	91.92	g/GJ	LAU	55.00	g/GJ
		1.1 MW	piece of wood, saw chips	cyclone	80.80	g/GJ	LAU	55.00	g/GJ
		2 MW	hogged wood, wood waste	ESP	16.10	g/GJ	LAU	55.00	g/GJ
		7.9-9.5 MW	wood, wood chips	ESP	5.49	g/GJ	LAU	55.00	g/GJ

COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES

Activities: Large Combustion Installations

Combustion Type	**Process**	**Size indication**	**Fuel**	**Abatement Measures**	**$PM_{2.5}$ Emission Factor or concentration**	**Units**	**Source**	**CEPMEIP Factor**	**CEPMEIP Units**
		7.9-9.5 MW	natural gas, wood, wood chips	ESP	5.21	g/GJ	LAU	55.00	g/GJ
		15 MW	hogged wood, rest wood, wood chips	ESP	1.95	g/GJ	LAU	55.00	g/GJ
		1.5 MW	hogged wood	chimney gas condensation, multi-cyclone	17.25	g/GJ	LAU	55.00	g/GJ
		1.5 MW	hogged wood	chimney gas condensation, multi-cyclone	20.46	g/GJ	LAU	55.00	g/GJ
		31 t/h steam	matured wood	cyclone, fabric filter, NO_x removal	1.85	g/GJ	LAU	55.00	g/GJ
		-	wooden briquettes	-	12.10	mg/m3	TESO	135.00	g/GJ
	Grate Boiler		bark, natural gas	ESP	4.80	mg/m3	TESO		
Waste	hazardous waste incineration plant	-	hazardous waste	fabric filter, desulphurisation system	8.80	mg/m3	TESO		
	waste incineration plant	-	municipal solid waste	ESP, desulphurisation system	0.80	mg/m3	TESO	100.00	g/tonne
			municipal solid waste	ESP	1.80	ng/Nm3	VITO	101.00	g/tonne
	home heating boiler	-	mixture of fuels and household waste	-	34.60	mg/m3	TESO		
	old growth , shredder	30 t/h	lumber, demolition wood, timber waste	fabric filter	0.49	g/tonne	LAU		

SNAP CODE:	**010104 & 010105** **010204 & 010205** **010404 & 010405** **020104 & 020105** **020203 & 020204** **020303 & 020304** **030104 & 030105**

SOURCE ACTIVITY TITLE: **COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES**
Particulate emissions from gas turbines and internal combustion engines

NOSE CODE:	**101.01** **101.02**
NFR CODE:	**1 A 1 a,b,c** **1 A 2 a-f** **1 A 4 b,c,i**
ISIC	**3510**

1 ACTIVITIES INCLUDED

This supplement covers emissions of particulate matter (PM) released from combustion processes within the energy and transformation industries by internal combustion engines - gas turbines and reciprocating engines . This supplement includes guidance on estimating total PM (TSP), PM_{10} and $PM_{2.5}$ emissions from these sources. Information related to the estimation of emissions of other pollutants from this sector is given in chapter B111.

2 CONTRIBUTION TO TOTAL EMISSION

The contributions of PM_{10} and $PM_{2.5}$ emissions from combustion plant to total emissions in countries according to the CORINAIR90 inventory are indicated in Table 2.1.

Table 2.1 Contribution to total particulate matter emissions from 2004 EMEP database (WEBDAB)

NFR Sector	Data	PM_{10}	$PM_{2.5}$	TSP
1 A 1 a - Public Electricity and Heat Production[a]	No. of countries reporting	26	26	27
	Lowest Value	0.2%	0.2%	0.2%
	Typical Contribution	11.7%	10.1%	12.8%
	Highest Value	48.8%	47.8%	48.4%
1 A 2 - Manufacturing Industries and Construction[b]	No. of countries reporting	26	26	26
	Lowest Value	0.7%	0.6%	0.6%
	Typical Contribution	9.0%	9.5%	7.9%
	Highest Value	20.7%	22.1%	25.7%
1 A 4 a - Commercial / Institutional[c]	No. of countries reporting	23	23	23
	Lowest Value	0.1%	0.1%	0.1%
	Typical Contribution	3.9%	3.4%	4.5%
	Highest Value	19.3%	22.2%	29.5%
1 A 4 b - Residential[d]	No. of countries reporting	3	2	3
	Lowest Value	2.0%	6.5%	3.7%
	Typical Contribution	14.9%	26.2%	10.8%
	Highest Value	36.6%	45.8%	15.4%
1 A 4 b i - Residential plants[e]	No. of countries reporting	23	23	23
	Lowest Value	2.7%	5.8%	0.8%
	Typical Contribution	28.3%	33.1%	22.0%
	Highest Value	67.1%	74.6%	53.2%
1 A 5 a - Other, Stationary (including Military)[f]	No. of countries reporting	7	7	7
	Lowest Value	0.0%	0.0%	0.0%
	Typical Contribution	0.1%	0.1%	0.1%
	Highest Value	0.5%	0.4%	0.6%

[a] Includes contribution from Chapter 112

[b] Includes contributions from Chapter 112 and 316 (SNAP 030106)

[c] Includes contribution from Chapter 112 and 216 (SNAP 020205)

[d] Includes contribution from Chapter 810

[e] Includes contribution from Chapter 112

[f] Includes contribution from Chapter 112 and 216 (SNAP 020106)

3 GENERAL

3.1 Description

This supplement considers emissions of PM generated by internal combustion engines including gas turbines and reciprocating engines. Reciprocating engines include compression ignition (CI) and spark ignition (SI) technologies. Other emissions from this source category are considered in B111.

3.2 Definitions

See B111.

3.3 Techniques

See B111 for more information on combustion plant types and fuels.

Gas turbines range in size from <100kW electrical generation (microturbines) to over 250 MW electrical generation. The most common primary fuel is natural gas but gas oil and a range of derived fuels are also used.

Diesel compression engines also range from a few kW to about 50 MW electrical generation. The most typical fuel is gas oil but, various derived fuels can be used and heavy fuel oil is used on some large units. Dual fuel engines burn natural gas or derived gases with a small quantity of gas oil.

3.4 Emissions

Internal combustion engines use liquid or gaseous fuels and particulate emissions result mainly from combustion of the fuels.

Combustion of liquid fuels can generate solid residues which may be deposited within exhaust ducts oron heat exchanger surfaces (soot and fly ash). Suspended ash material in exhaust gases may be retained by particulate abatement or other emission abatement equipment (abatement residues). Material which remains in the flue gases beyond the abatement equipment and passes to the atmosphere is primary PM. Secondary PM is formed by chemical and physical processes after discharge to atmosphere and is NOT considered here.

3.5 Controls

Particulate emission reduction is not usually associated with combustion of gaseous fuels except where derived fuels are used (in which case filtering or other treatment of the fuel gas is the preferred approach). Particulate abatement equipment may be used with oil fuels and can include, fuel pre-treatment to reduce mineral content (particularly for heavy fuel oil), diesel particle filters (on smaller units) or more traditional emission abatement equipment. . N.B. Emission concentrations of TSP from compression ignition engines associated with Best Available Techniques (BAT) as defined by EU Integrated Pollution Prevention and Control regulations are 30 mg m^{-3} for gas oil and 50 mg m^{-3} for heavy fuel oil.

4 SIMPLER METHODOLOGY

Emissions can be estimated at different levels of complexity; it is useful to think in terms of three tiers[1]:

Tier 1: a method using readily available statistical data on the intensity of processes ("activity rates") and default emission factors. These emission factors assume a linear relation between the intensity of the process and the resulting emissions. The Tier 1 default emission factors also assume an average or typical process description.
Tier 2: is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed.
Tier 3: is any method that goes beyond the above methods. These might include the use of more detailed activity information, specific abatement strategies or other relevant technical information.

By moving from a lower to a higher Tier it is expected that the resulting emission estimate will be more precise and will have a lower uncertainty. Higher Tier methods will need more input data and therefore will require more effort to implement.

For the Tier 1 simpler methodology, where limited information is available, a default emission factor can be used together with activity information for the country or region of interest with limited or no specification on the type of technology or the type and efficiency of control equipment. For a Tier 2 approach an approximation may be made of the most representative technologies, thereby allowing the use of more appropriate default factors if more detailed activity data are available.

Consequently the simplest methodology (Tier 1) is to combine an activity rate (AR) with a comparable, representative, value of the emissions per unit activity, the emission factors (EF). The basic equation is:

$$\text{Emission} = \text{AR x EF}$$

In the energy sector, for example, fuel consumption would be activity data and mass of material emitted per unit of fuel consumed would be a compatible emission factor.

NOTE: The basic equation may be modified, in some circumstances, to include emission reduction efficiency (abatement factors).

The Tier 2 methodology is a modified version of this basic equation:

$$\text{Emission} = \sum((\text{AR}_1 \text{ x } \text{EF}_1) + (\text{AR}_2 \text{ x } \text{EF}_2) + \ldots(\text{AR}_n \text{ x } \text{EF}_n))$$

Default emission factors for this purpose are provided in Sections 8.1 and 8.2.

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[1] The term "Tier" is used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and adopted here for easy reference and to promote methodological harmonization.

5 DETAILED METHODOLOGY

The detailed methodology (equivalent to Tier 3) to estimate emissions of pollutants from combustion plant >50 MW_{th} is based on measurements or estimations using plant specific emission factors - guidance on determining plant specific emission factors is given in Measurement Protocol Annex.

In many countries, operators of combustion plant >50MWth will report emissions to comply with regulatory requirements and this data can be used to help compile the national inventory.

The recommended detailed methodology to estimate emissions of PM from combustion activities is based on measurements and/or estimations using technology-specific emission factors.

Information on the type of the process and activity data, for example combustion and abatement technologies, is required to assign appropriate emission factors.

6 ACTIVITY STATISTICS

Activity statistics for energy consumption or other relevant national activity data for estimating emissions using the simpler estimation methodology (Tiers 1 and 2) are available from national statistics.

The detailed methodology (Tier 3) requires more detailed information such as the amount and types of fuel consumed within individual combustion plant or industry sectors. These data are not always easily available although in many countries operators do report fuel use for emission trading or other legislative requirements.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 2 on energy, Chapter 1.

7 POINT SOURCE CRITERIA

Large combustion plants are regarded as point sources if plant specific data are available.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Default Emission Factors For Use With Simpler Methodology (Tier 1)

Fuel	Technology	**Emission factor, $g.GJ^{-1}$**			Notes
		TSP	**PM_{10}**	**$PM_{2.5}$**	
Hard Coal		-	-	-	Not applicable
Brown Coal		-	-	-	Not applicable
Other solid fuels		-	-	-	Not applicable

Natural gas	Gas turbines	0.9	0.9	0.9	US EPA
	Spark ignition	18	18	18	US EPA 2 stroke lean burn, 4 stroke lean burn is 0.04 gGJ^{-1}.
Derived gases	Gas turbine	11	11	11	Based on US EPA Landfill gas
Heavy fuel oil	Diesel	28	23	22	US EPA factor for diesel engines
Other liquid fuels	Gas turbine	2.0	2.0	2.0	US EPA factor for PM applied to other fractions
	Diesel	28	23	22	US EPA
Biomass	Gas turbine	11	11	11	Landfill gas
	Gas turbine	5.7	5.7	5.7	Anaerobic digester gas

8.2 Reference Emission Factors For Use With Tier 2 Methodology

Tables 8.2a-z contain reference particulate emission factors for fuel combustion in various technologies with different types of abatement.

Table 8.2a Emission factors for gas turbines combustion processes

Fuel	NAPFUE	NFR Codes	Activity description	Activity detail	Emission factor, g.GJ^{-1}			Notes
					TSP	**PM$_{10}$**	**PM$_{2.5}$**	
Natural gas					0.9	0.9	0.9	Sierra (234 tests), assumes all PM2.5
Gas oil					3	3	3	Sierra (15 tests), assume all PM2.5

Table 8.2b Emission factors for compression ignition combustion processes

Fuel (IPCC Cat)	NAPFUE	NFR Code	Activity description	Activity detail	Emission factor g GJ^{-1}			Reference/Comments
					TSP	**PM$_{10}$**	**PM$_{2.5}$**	
Natural gas			Dual fuel engine, gas with HFO		11	11	11	LCP BREF, assumed all PM2.5
Heavy fuel oil			Diesel engine		50	41	39	LCP BREF, 'BAT' US EPA profile applied
			Diesel engine		<64	53	50	LCP BREF, US EPA profile applied, applicable to older equipment
Gas oil			Diesel engine	<0.02% S	<26	21	20	LCP BREF, US EPA profile
			Diesel engine		<17	14	14	Smaller unit with diesel particulate filter, US EPA profile

9 SPECIES PROFILES

The US EPA (2003) undertook a review of species profiles within $PM_{2.5}$ and reports particle size distribution data for a variety of fuels and combustion and abatement technologies. Some of these data are dated and have high uncertainty ratings. Profiles of other materials are not available.

Table

Profile ref	**Profile name**	**Component**				
		POA	**PEC**	**GSO4**	**PNO3**	**Other**
22002	Residual Oil Combustion	0.1075	0.0869	0.5504	0.0005	0.2547
22003	Distillate Oil Combustion	0.0384	0.0770	0.3217	0.0024	0.5605
22004	Natural Gas Combustion	0.6000	0.0000	0.2000	0.0055	0.1945

Notes:
POA - Primary organic aerosol derived from organic carbon
PEC Elemental Carbon
GSO4 - Sulphate
PNO3 - Nitrate
Other – Remainder of PM2.5 material emitted.

Note that the data are derived from a variety of sources including dilution tunnel measurements and may not be directly comparable with filterable $PM_{2.5}$.

10 UNCERTAINTY ESTIMATES

The overall 'Uncertainty' in national emission inventories may be significant – as illustrated in Table 9.1.

Table 9.1 Uncertainty estimate for selected pollutants in the UK air emission inventory (NAEI, 2005).

Pollutant	Estimated Uncertainty (%)
PM_{10}	-20 to +50
$PM_{2.5}$	-20 to +30
$PM_{1.0}$	-10 to +20
$PM_{0.1}$	+/- 10
Sulphur Dioxide	+/- 3
Oxides of Nitrogen	+/- 8
NMVOCs	+/- 10
Ammonia	+/- 20

There is uncertainty in both the aggregated emission factors and activity data used to estimate emissions i.e. the imprecision and error to be expected from the application of an 'average' emission factor or activity statistic to estimate emissions from a specific sector - an artificial grouping of 'similar' sources.

The uncertainty is partly the result of how emission factors are developed and applied. In the case of primary particulate matter, the expanded statistical uncertainty is made up of: between plant variance, within plant variance, and uncertainties associated with the measurement methodology used and the aggregation of data. The measurement data in Annex 1 illustrates the variability in emission factors that occurs from between plant variance.

Process measurements, from which emission factors are developed at individual facility level, are subject to both systematic and random errors in the determination of mass concentration, mass emission, size distribution, and analytical errors etc.

In addition bias may exist in emission factors arising from:

1. Assumptions made about the abatement used on 'typical' industrial installations. For example emission factors 'age', the factors widely used in the Guidebook and hence by many countries as default emission factors in their national inventories become out of date. Recent measurement work suggests that they may overestimate emissions from the industrial processes subject to more modern industrial emissions regulation. They may, however, still be fully representative for older plant, small plant, or for poorer fuels;

Assumptions about the relationship between TSP and PM_{10}/$PM_{2.5}$. The technical literature is comprehensive for TSP and the data quality can be good if measurements have been made using the international standard methods that are available (typically the 95% confidence limit ~10%). But a variety of methods are used for particle size fractionation and as yet there are no harmonised international standards to ensure comparability. Published measurement data for PM10 is sparse, that for $PM_{2.5}$ emissions more so. An added complication is that the methodology for the determination of TSP differs from that of PM10 and $PM_{2.5}$ and so the two need not correlate directly.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Published $PM_{2.5}$ emission factor information for stationary engines is sparse. It is difficult to form a representative estimate the emissions likely to arise from the range of engine/fuel combinations commonly encountered. Further work is required to develop a more complete range of emission factors.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Combustion plants should be considered as point sources if plant specific data are available. Otherwise national emissions should be disaggregated on the basis of plant capacity, employment or population statistics.

13 TEMPORAL DISAGGREGATION CRITERIA

Combustion processes can be considered as a continuous process however individual combustion plant may have daily and/or seasonal temporal profiles.

14 ADDITIONAL COMMENTS

See chapter B111 and B111 (S2) for measurement data in Annex 1.

15 SUPPLEMENTARY DOCUMENTS

None

16 VERIFICATION PROCESSES

Published $PM_{2.5}$ emission data for stationary engines is sparse.

17 REFERENCES

AEAT CCGT Measurement data

Digest of UK Energy Statistics

England, G.C., "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Final Report, 2004."

EMEP/CORINAIR Emission Inventory Guidebook – 2005, EEA (European Environment Agency) Chapter B111

IIASA RAINS data

IPPC Best Available Techniques Reference Document on Large Combustion Plants, December 2001, http://eippcb.jrc.es

IPCC Guidance document

NAEI (2005) UK National Atmospheric Emissions Inventory: UK Emissions of Air Pollutants 1970 to 2003, October 2005

US EPA (1996) Compilation of Air Pollutant Emission Factors Vol.1 Report AP-42 (5th ed.)

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Rentz, O.; Karl, U.; Peter, H. Determination and evaluation of emission factors for combustion installations in Germany for the years 1995, 2000 and 2010. French-German Institute for Environmental Research University of Karlsruhe (TH), Dec 2002.

Rubenstein, G. Gas Turbine PM Emissions – Update. Sierra Research, June 2003 Paper to ASME/IGTI Turbo-Expo, Atlanta 2003

18 BIBLIOGRAPHY

19 RELEASE VERSION, DATE AND SOURCE

Version: 1

Date: Aug 2006

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SNAP CODES: (See below)

SOURCE ACTIVITY TITLE: COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES
Combustion Plants as Point Sources

The following activities are taken into account, when treating combustion plants individually as point sources.

Combustion plants with a thermal capacity < 300 MW, gas turbines and stationary engines, which may also be considered collectively as area sources, are covered by chapter B112 “Combustion Plants as Area Sources” as well.

SNAP97 Codes	**Combustion plants as point sources** Boilers/Furnaces										
	NOSE CODE	NFR CODE	Thermal capacity [MW]	Public power and cogeneration plants	District heating	Industrial combustion and specific sector	Commercial and institutional combustion	Residential combustion	Agriculture forestry and fishing	Gas turbines	Stationary engines
01 01 01	101.01	1 A 1 a	≥ 300	x							
01 02 01	101.01	1 A 1 a			x						
01 03 01	101.01	1 A 1 b				x					
01 04 01	101.01	1 A 1 c				x					
01 05 01	101.01	1 A 1 c				x					
02 01 01	101.01	1 A 4 a					x				
03 01 01	101.01	1 A 2 a-f				x					
01 01 02	101.02	1 A 1 a	≥ 50 and < 300	x							
01 02 02	101.02	1 A 1 a			x						
01 03 02	101.02	1 A 1 b				x					
01 04 02	101.02	1 A 1 c				x					
01 05 02	101.02	1 A 1 c				x					
02 01 02	101.02	1 A 4 a					x				
02 02 01	101.02	1 A 4 b i						x			
02 03 01	101.02	1 A 4 c i							x		
03 01 02	101.02	1 A 2 a-f				x					
01 01 03	101.03	1 A 1 a	< 50	x							
01 02 03	101.03	1 A 1 a			x						
01 03 03	101.03	1 A 1 b				x					
01 04 03	101.03	1 A 1 c				x					
01 05 03	101.03	1 A 1 c				x					
02 01 03	101.03	1 A 4 a					x				
02 02 02	101.03	1 A 4 b i						x			
02 03 02	101.03	1 A 4 c i							x		
03 01 03	101.03	1 A 2 a-f				x					
01 01 04	101.04	1 A 1 a	not relevant							x	
01 02 04	101.04	1 A 1 a								x	
01 03 04	101.04	1 A 1 b								x	
01 04 04	101.04	1 A 1 c								x	
01 05 04	101.04	1 A 1 c								x	
02 01 04	101.04	1 A 4 a								x	
02 02 03	101.04	1 A 4 b i								x	
02 03 03	101.04	1 A 4 c i								x	
03 01 04	101.04	1 A 2 a-f								x	
01 01 05	101.05	1 A 1 a	not relevant								x
01 02 05	101.05	1 A 1 a									x
01 03 05	101.05	1 A 1 b									x
01 04 05	101.05	1 A 1 c									x
01 05 05	101.05	1 A 1 c									x

SNAP97 Codes	NOSE CODE	NFR CODE	**Combustion plants as point sources** Boilers/Furnaces								
			Thermal capacity [MW]	Public power and cogeneration plants	District heating	Industrial combustion and specific sector	Commercial and institutional combustion	Residential combustion	Agriculture forestry and fishing	Gas turbines	Stationary engines
02 01 05	101.05	1 A 4 a									x
02 02 04	101.05	1 A 4 b i									x
02 03 04	101.05	1 A 4 c i									x
03 01 05	101.05	1 A 2 a-f									x

x = indicates relevant combination

1 ACTIVITIES INCLUDED

This chapter covers emissions from boilers, gas turbines and stationary engines as point sources. According to CORINAIR90, combustion plants with

– a thermal capacity ≥ 300 MW
or
– emissions of SO_2 or NO_x or NMVOC > 1,000 Mg/a[1]

should be considered as point sources /41/. Within CORINAIR other combustion plants may also be considered as point sources on a voluntary basis. Different criteria are applied for the classification of combustion plants according to the Large Combustion Plant Directive (88/609/EEC)[2] /9, 42/.

Boilers, gas turbines and stationary engines need to be treated separately (see table at start of this chapter). With regard to boilers, a combustion plant may consist of one single boiler or may comprise a series of boilers of different sizes (joint plant). Therefore, whenever there is more than one boiler on a site, a decision on the aggregation of these facilities to plants has to be taken. Through this decision, an allocation to the respective SNAP categories is achieved. For aggregation criteria see Section 3.2 and Annex 1.

The subdivision of SNAP activities according to CORINAIR90 concerning combustion plants takes into account two criteria:

a) the economic sector concerning the use of energy
  - public power and co-generation,
  - district heating,
  - commercial and institutional combustion,
  - industrial combustion in boilers,
    (Note: Process furnaces are allocated separately.)

---

[1] For CO_2 a further optional criterion for point sources is the emission of > 300 Gg/a.

[2] The Large Combustion Plant Directive covers combustion plants with a thermal capacity ≥ 50 MW in the EU. Gas turbines and stationary engines are excluded. Existing plants with a thermal capacity > 300 MW have to be reported as point sources on an individual basis.

b) the technical characteristics
- with respect to boilers, the installed thermal capacity,
    - ≥ 300 MW,
    - ≥ 50 to < 300 MW,
    - ≤ 50 MW,
- other combustion technologies,
    - gas turbines,
    - stationary engines.

Emissions considered in this section are released by a controlled combustion process (boiler emissions, emissions from the combustion chamber of gas turbines or stationary engines), taking into account primary reduction measures, such as furnace optimisation inside the boiler or the combustion chamber, and secondary reduction measures downstream of the boiler or the combustion chamber. Solid, liquid or gaseous fuels are used, where solid fuels comprise coal, coke, biomass and waste (as far as waste is used to generate heat or power). In addition, a non-combustion process can be a source of ammonia emissions, namely ammonia slip in connection with several NO_x abatement techniques.

2 CONTRIBUTION TO TOTAL EMISSIONS

This section covers emissions of SO_x, NO_x, CO, CO_2, NMVOC, CH_4, N_2O, NH_3 and heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, V). The contributions of point source emissions released by combustion plants to the total emissions in countries of the CORINAIR90 inventory are given as follows in Table 1:

Table 1: Contributions of emissions from combustion plants as point sources to total emissions of the CORINAIR90 inventory reported as point sources

		Contribution to total emissions [%]							
Source category	SNAP90 code	SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
≥ 300 MW	01 01 01 01 02 01 03 01 01	85.6	81.4	10.2	5.5	16.8	79.0	35.7	2.4
50-300 MW	01 01 02 01 02 02 02 00 01 03 01 02	6.4	5.4	1.1	0.6	3.1	6.5	1.9	0.2
< 50 MW	01 01 03 01 02 03 02 00 02 03 01 03	0.2	0.3	0.1	0.05	0.1	0.2	0.1	0
Gas turbines[1)]	01 01 04 01 02 04 02 00 03	0	0.39	0.07	0.06	0.05	0.35	0.02	-

	03 01 04								
Stationary engines[1]	01 01 05 01 02 05 02 00 04 03 01 05	0.04	0.10	0.04	0	0.01	0.02	0	-

- : no emissions are reported

0 : emissions are reported, but the precise number is under the rounding limit

[1] Gas turbines and stationary engines may be reported either as point or as area sources.

In the literature concerning heavy metal emissions across Europe, point source emissions are not reported separately. Giving an order of magnitude of heavy metal emissions released from combustion plants emission data of coal-fired public power plants in Germany and Austria is presented here as an example, due to the availability of data:

Table 2: Contributions of heavy metal emissions from coal-fired public power plants to national total emissions of Germany[1] /36/

	Contribution in [wt.-%]	
Pollutant	1982	1990
As	38	27
Cd[2]	7	7
Cr	12	4
Cu	22	8
Hg[3]	11	14
Ni	5	4
Pb	8	1
Se	1	1
Zn	7	6

[1] Western part of Germany

[2] E.g. emissions of Cd in Austria in 1992 were 0,2 % /37/.

[3] E.g. emissions of Hg in Austria in 1992 were 6 % /37/.

By comparing the heavy metal emissions in 1982 (without flue gas desulphurisation (FGD) installed) to the emissions in 1990 (where most plants are equipped with FGD), it can be seen that the application of FGD technologies has lead to a significant decrease in heavy metal emissions within the last years.

For Particulate Matter:
Combustion Plants < 50 MW (boilers) are now covered in the new supplementary chapter Particulate emissions from smaller Combustion Plants (<50MWth) B111(S1).

Combustion Plants >= 50 and < 300 MW (boilers) are now covered in the new supplementary chapter Particulate emissions from large Combustion Plants (>50MWth) B111(S2).

Gas Turbines are now covered in the new supplementary chapter Particulate emissions from gas turbines and internal combustion engines B111(S3).

3 GENERAL

3.1 Description

The emissions considered in this chapter are generated either by boilers or by gas turbines and stationary engines regardless of the allocation of plants to SNAP activities. Emissions from process furnaces (combustion with contact) and from waste incineration are not included here (therefore see SNAP code 090200).

3.2 Definitions

ar	as received, a reference state of coal which determines the conditions, when coal arrives at the plant /73/.
Availability (of an abatement technology)	ratio of full load operating hours with operating emission control technology to total full load operating hours of the power plant; the availability β normally amounts to 99 %; but extreme low values of β can occur down to 95 %. By taking into account the start-up behaviour of emission reduction technologies, the availability β can decrease further down to 92 %. Default values are proposed in Tables 7 and 11.
Boiler	any technical apparatus, in which fuels are oxidised in order to generate heat for locally separate use.
Coking coal (NAPFUE 101)	subcategory of hard coal with a quality that allows the production of a coke suitable for supporting a blast furnace charge /114/.
Co-generation plant	steam production in boilers (one or more boilers) for both, power generation (in a steam turbine) and heat supply.
Combined Cycle Gas Turbine (CCGT)	gas turbine combined with a steam turbine. The boiler can also be fuelled separately.
daf	dry and ash free, a reference state of coal which is calculated with reference to a theoretical base of no moisture or ash associated with the sample (equivalent to maf - moisture and ash free) /73/.
Hard coal	refers to coal of a gross caloric value greater than 23,865 kJ/kg on an ash-free but moist basis and with a mean random

reflectance[3] of vitrinite of at least 0.6. Hard coal comprises the subcategories coking coal and steam coal[4] /114/.

---

[3] Mean random reflectance: characteristic value, which stands for a defined coal composition (modular component is e.g. vitrinite).

[4] The following coal classification codes cover those coals, which would fall into these subcategories /114/:

International classification codes (UN, Geneva, 19956)	323, 333, 334, 423, 433, 435, 523, 533, 534, 535, 623, 633, 634, 635, 723, 733, 823
USA classification	Class II Group 2 „Medium Volatile Bituminous“
British classification	Class 202, 203, 204, 301, 302, 400, 500, 600
Polish classification	Class 33, 34, 35.1, 35.2, 36, 37
Australian classification	Class 4A, 4B, 5.

Integrated Coal Gasification Combined Cycle Gas Turbine (IGCC)	gas turbine fuelled by gas, which is a product of a coal gasification process.
Lignite (NAPFUE 105)	non-agglomerating coals with a gross caloric value less than 17,435 kJ/kg and containing more than 31 % volatile matter on a dry mineral matter free basis /114/.
maf	moisture and ash free, a reference state of coal (equivalent to daf - dry and ash free) /73/.
Plant/Joint Plant	classification with respect to boilers (one or more boilers) according to the respective boiler configuration on a given site and the applied concept of aggregation. The stack-by-stack principle considers all boilers linked to the same stack as a common plant. On the other hand, according to the virtual stack principle, all boilers which, for technical and economic reasons, could be connected to a common stack, are treated as one unit. It is also possible to carry out a still broader combination following e.g. administrative aspects. Gas turbines and stationary engines are allocated separately. A typical example of different allocation possibilities of boilers to the SNAP codes is given in Annex 1.
Power plant	steam generation in boilers (one or more boilers) for power generation.
Reduction efficiency (of an abatement technology)	difference between the pollutant concentration in the raw gas (c_{raw}) and the pollutant concentration in the clean gas (c_{clean}) divided by the pollutant concentration in the raw gas (referred to full load operating hours); default values for the reduction efficiency $\eta = (c_{raw} - c_{clean})/c_{raw}$ of different emission control technologies are recommended in Tables 7 and 11 (extreme low values of η can be up to ten percent below the values given).
Start-up emission	here start-up emissions have been considered for boilers equipped with secondary measures: For SO_2 and NO_2 from the time when burners switch on up to the time when the secondary abatement facility operates under optimum conditions; for CO up to the time when the boiler operates at minimum load.
Stationary engines	spark-ignition or compression-ignition engines (2- and 4-stroke).
Steam coal (NAPFUE 102)	subcategory of hard coal used for steam raising and space heating purposes. Steam coal includes all anthracite and bituminous coals not included under coking coal /114/.

Sub-bituminous coal (NAPFUE 103)	non-agglomerating coals with a gross caloric value between 17,435 and 23,865 kJ/kg containing more than 31 % volatile matter on a dry mineral free matter basis /114/
Sulphur retention in ash	difference between the sulphur dioxide concentration calculated from the total sulphur content of fuel (c_{max}) and the sulphur dioxide concentration of the flue gas (c_{eff}) divided by the sulphur dioxide concentration calculated from the total sulphur content of the fuel. Default values for the sulphur retention in ash $\alpha_s = (c_{max} - c_{eff})/c_{max}$ are proposed in Table 8.

3.3 Techniques

3.3.1 Combustion of coal

3.3.1.1 Dry bottom boiler (DBB)

The DBB is characterised by the dry ash discharge from the combustion chamber due to combustion temperatures from 900 up to 1,200 °C. This type of boiler is mainly used for the combustion of hard coal and lignite and is applied all over Europe.

3.3.1.2 Wet bottom boiler (WBB)

Typical combustion temperatures exceeding 1,400 °C lead to a liquid slag discharge from the combustion chamber. This type of boiler is used for hard coal with a low content of volatiles and is mainly applied in Germany.

3.3.1.3 Fluidised bed combustion (FBC)

The combustion of coal takes place by injection of combustion air through the bottom of the boiler into a turbulent bed. The typical relatively low emissions are achieved by air staging, limestone addition and low combustion temperatures of about 750 - 950 °C. FBC is in particular adapted to coals rich in ash. Only few large combustion plants are equipped with the FBC technique; in the category of thermal capacities $\geq$ 300 MW mostly Circulating Fluidised Bed Combustion (CFBC) is installed.

3.3.1.4 Grate Firing (GF)

The lump fuel (coal, waste) is charged on a stationary or slowly moving grate. The combustion temperatures are mainly between 1,000 and 1,300 °C.

3.3.2 Combustion of biomass

The combustion of biomass (peat, straw, wood) is only relevant for some countries (e.g. Finland, Denmark). FBC (mostly CFBC) and DBB facilities are installed.

3.3.3 Combustion of waste

For the combustion of waste, mostly grate firing installations are in use.

3.3.4 Combustion of gas/oil

3.3.4.1 Combustion in boilers (general aspects of the combustion techniques)

For both, gas and oil combustion, the fuel and oxidising agents are gaseous under combustion conditions. The main distinctions between gas/oil combustion and pulverised coal combustion are the operation designs of the individual burners of the boiler. With respect to emissions, a principal distinction can be made between burners with and without a pre-mix of fuel and combustion air: pre-mixing burners are characterised by a homogeneous short flame and a high conversion rate of fuel bound nitrogen; non-pre-mixing burners are characterised by inhomogeneous flames with understoichiometric reaction zones and a lower conversion rate of fuel bound nitrogen.

The importance of oil and gas combustion considered as point sources (see Section 1) is low compared to coal combustion, due to the smaller total capacity of these installations. The main parameters determining emissions from oil and gas fired plants are given in Table 3.

Table 3: Main parameters determining emissions from oil and gas fired boilers /40/

Pollutant	Fuel dependent	Process dependent
	Oil-fired boiler	
SO_2	x	-
NO_x	x	x
CO	-	x
	Gas-fired boiler	
SO_2	x[1)]	-
NO_x	-	x
CO	-	x

[1)] trace amounts x : relevant - : not relevant

3.3.4.2 Gas turbines

Gas turbines are installed with a thermal capacity ranging from several hundred kW up to 500 MW. Gaseous fuels are mainly used, such as natural gas or the product of coal gasification (e.g. CCGT or IGCC installations) or other process gases. Also liquid fuels are used, such as light distillates (e.g. naphtha, kerosene or fuel oil) and in some cases other fuels (e.g. heavy fuel oil). Combustion temperatures of up to 1,300 °C in the combustion chambers may lead to considerable NO_X emissions.

Gas turbines are installed as a part of different types of combustion plants such as Combined Cycle Gas Turbine (CCGT) or Integrated Coal Gasification Combined Cycle Gas Turbine (IGCC) Plants (see also Section 3.2). For IGCC plants, the only emission relevant unit considered here is the gas turbine (combustion chamber). For CCGT, in addition to the gas turbine any installed fossil fuelled boiler should also be taken into account.

3.3.4.3 Stationary engines

Stationary engines are installed as spark-ignition engines and compression-ignition engines (2- and 4-stroke) with electrical outputs ranging from less than 100 kW to over 10 MW (e.g. in co-generation plants) /cf. 46/. Both types represent relevant emission sources.

3.4 Emissions

Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon dioxide (CO_2) and heavy metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), zinc (Zn) and in the case of heavy oil also vanadium (V)). Emissions of volatile organic compounds (non-methane VOC and methane (CH_4)), nitrous oxide (N_2O), carbon monoxide (CO) and ammonia (NH_3) are of less importance. For species profiles of selected pollutants see section 9.

The emissions are released through the stack. Fugitive emissions (from seals etc.) can be neglected for combustion plants.

The emissions of sulphur oxides (SO_x) are directly related to the sulphur content of the fuel, which for coal normally varies between 0.3 and 1.2 wt.-% (maf) (up to an extreme value of 4.5 wt.-%) and for fuel oil (including heavy fuel oil) from 0.3 up to 3.0 wt.-% /15, 16/; usually, the sulphur content of gas is negligible. Sulphur appears in coal as pyritic sulphur (FeS_2), organic sulphur, sulphur salts and elemental sulphur. A major part of the sulphur in coal comes from pyritic and organic sulphur; both types are responsible for SO_x formation. The total sulphur content of coal is usually determined by wet chemical methods; by comparison with results from the X-ray method, it has been found that standard analytical procedures may overestimate the organic sulphur content of coal /30/. The uncertainty introduced by the analytical procedures should be determined by further research.

For nitric oxide (NO, together with NO_2 normally expressed as nitrogen oxides NO_x) three different formation mechanisms have to be distinguished (see also Section 9):

-formation of "fuel-NO" from the conversion of chemically bound nitrogen in the fuel (NO_{fuel}),

-formation of "thermal-NO" from the fixation of atmospheric nitrogen coming from the combustion air ($NO_{thermal}$),

-formation of "prompt-NO".

In the temperature range considered (up to 1,700 °C) the formation of "prompt6-NO" can be neglected. The majority of NO_x emissions from coal combustion (80 to more than 90 %) is formed from fuel nitrogen. Depending on combustion temperatures, the portion of thermal-NO_x formed is lower than 20 %. The content of nitrogen in solid fuels varies: for hard coal between 0.2 and 3.5 wt.-% (maf), for lignite between 0.4 and 2.5 wt.-% (maf), for coke between 0.6 and 1.55 wt.-% (maf), for peat between 0.7 and 3.4 wt.-% (maf), for wood between 0.1 and 0.3 wt.-% (maf), and for waste between 0.3 and 1.4 wt.-% (maf) /17/. The content of nitrogen in liquid fuels varies for heavy fuel oil between 0.1 and 0.8 wt.-%, and for fuel oil between 0.005 and 0.07 wt.-% /17/. Natural gas contains no organically bound nitrogen. The content of molecular nitrogen in natural gas has no influence on the formation of fuel-NO; only thermal-NO is formed.

Emissions of non-methane volatile organic compounds (NMVOC), e.g. olefins, ketones, aldehydes, result from incomplete combustion. Furthermore, unreacted fuel compounds such as methane (CH_4) can be emitted. The relevance of NMVOC/CH_4 emissions from boilers, which are often reported together as VOC, is very low for large-sized combustion plants. VOC emissions tend to decrease as the plant size increases (cf. /24/).

Carbon monoxide (CO) appears always as an intermediate product of the combustion process and in particular under understoichiometric combustion conditions. However, the relevance of CO released from combustion plants is not very high compared to CO_2. The formation mechanisms of CO, thermal-NO and VOC are similarly influenced by combustion conditions.

Carbon dioxide (CO_2) is a main product from the combustion of all fossil fuels. The CO_2 emission is directly related to the carbon content of fuels. The content of carbon varies for hard and brown coal between 61 and 87 wt.-% (maf), for wood it is about 50 wt.-% and for gas oil and heavy fuel oil about 85 wt.-% .

The formation mechanism of nitrous oxide (N_2O) has not yet been completely clarified. There is a possible formation mechanism based on intermediate products (HCN, NH_3), which is comparable to the formation of NO /55/. It has been found, that lower combustion temperatures, particularly below 1,000 °C, cause higher N_2O emissions /13/. At lower temperatures the N_2O molecule is relatively stable; at higher temperatures the N_2O formed is reduced to N_2 /55/. Compared to emissions from conventional stationary combustion units, nitrous oxides from either bubbling, circulating or pressurised fluidised bed combustion are relatively high /13, 14/. In laboratory experiments, it has been found that nitrous oxide is formed by Selective Catalytic Reduction (SCR) processes, passing a maximum at, or close to, the optimum temperature "window" of the SCR process /13/.

Emissions of ammonia (NH_3) are not caused by a combustion process; the emissions result from incomplete reaction of NH_3 additive in the denitrification process (slip of ammonia in SCR and SNCR units).

Most of the heavy metals considered (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, V) are normally released as compounds (e.g. oxides, chlorides) in association with particulates. Only Hg and Se are at least partly present in the vapour phase. Less volatile elements tend to condense onto the surface of smaller particles in the flue gas stream. Therefore, an enrichment in the finest particle fractions is observed. The content of heavy metals in coal is normally several orders of magnitude higher than in oil (except occasionally for Ni and V in heavy fuel oil) and in natural gas. For natural gas only emissions of mercury are relevant. The concentrations are reported to be in the range of 2 - 5 $\mu g/m^3$ for natural gas /35, 63/. During the combustion of coal, particles undergo complex changes which lead to vaporisation of volatile elements. The rate of volatilisation of heavy metal compounds depends on fuel characteristics (e.g.

concentrations in coal, fraction of inorganic components, such as calcium) and on technology characteristics (e.g. type of boiler, operation mode).

From DBB, all heavy metals of concern are emitted as particulate matter, except Hg and Se. Emissions from lignite fired DBB are potentially lower than from hard coal, as the trace element content in lignite and the combustion temperatures are lower. In WBB, the recirculation of fly ash is a common operation mode, which creates an important increase in heavy metal concentrations in the raw gas. Heavy metal emissions from FBC units are expected to be lower due to the lower operating temperatures and a smaller fraction of fine particles. The addition of limestone in FBC facilities might reduce the emission of some heavy metals, corresponding to an increased retention of heavy metals in the bottom ash. This effect can be partially compensated by the increase in the fraction of fine particulates in the flue gas leading to increased emissions from particulates highly enriched by heavy metals.

High concentrations of As poison denitrification catalysts. Therefore, Selected Catalytic Reduction plants (SCR) in a high-dust configuration may require special measures (e.g. reduction of fly ash recirculation). /10, 11, 12/

3.5 Controls

Relevant abatement technologies for SO_x, NO_x and heavy metals are outlined below. Abatement techniques for gas turbines and stationary engines are treated separately. Average reduction efficiencies and availabilities of abatement technologies for SO_x and NO_x are summarised in Tables 7, 10, and 11. Due to the fact, that most published studies do not clearly distinguish between SO_x and SO_2, for the following chapters, it can be assumed that SO_2 includes SO_3, if not stated otherwise.

3.5.1 Sulphur oxides: Flue Gas Desulphurisation Processes (FGD) (Secondary measures) /cf. 18/

FGD processes are designed to remove SO_2 from the flue gas of combustion installations. Most processes, like the wet scrubbing process (WS), the spray dryer absorption (SDA), the dry sorbent injection (DSI) and the Walther process (WAP) are based on the reaction of the SO_2 with an alkaline agent added as solid or as suspension/solution of the agent in water to form the respective salts. In secondary reactions also SO_3, fluorides and chlorides are removed. In the case of the DESONOX process (see Section 3.5.4.2), the SO_2 is catalytically oxidised to SO_3 and reacts with water to form sulphuric acid. The Activated Carbon process (see Section 3.5.4.1) and the Wellman-Lord process remove the SO_2 to produce a SO_2 rich gas, which may be further processed to sulphur or sulphuric acid.

3.5.1.1 Lime/Limestone Wet Scrubbing (WS)

The pollutants are removed from the flue gas by chemical reactions with an alkaline liquid (suspension of calcium compounds in water). The main product is gypsum. The WS process represents about 90 % of the total FGD-equipped electrical capacity installed in European OECD countries. Facilities are in operation at combustion units using hard coal, lignite and oil with sulphur contents from about 0.8 to more than 3.0 wt.-%. Other fossil fuels (such as peat) are presently rarely used at combustion plants with a thermal capacity ≥ 300 MW. The SO_2 reduction efficiency is > 90 %.

3.5.1.2 Spray Dryer Absorption (SDA)

The SDA process removes the pollutant components from flue gas of fossil fired combustion units by injection of $Ca(OH)_2$. The process forms a dry by-product ($CaSO_3 \cdot 1/2\ H_2O$). This technology covers about 8 % of the total FGD-equipped electrical capacity installed in the European OECD countries. The SDA process is mostly in use at hard coal fired combustion units (sulphur content of fuel up to 3 wt.-%). Recent pilot studies have shown that this technique is also operational with other fossil fuels (oil, lignite, peat). The SO_2 reduction efficiency is > 90 %.

3.5.1.3 Dry Sorbent Injection (DSI, LIFAC Process)

The DSI process is based on a gas/solid reaction of the flue gas and a dry sorbent (e.g. lime/limestone, sodium hydrogen carbonate $NaHCO_3$) inside the boiler. There are three different process types according to the injection point of the additive into the boiler (e.g. primary or secondary air, flame front). The by-products are a dry mixture of the respective salts (mostly $CaSO_4$). Only few power plants (some 5 % of the total FGD-equipped electrical capacity installed in European OECD countries) are equipped with this technology due to its low SO_2 reduction efficiency of 40 - 50 %, which is not sufficient to meet the emission standards of some countries. DSI processes are presently in use for hard coal, lignite, oil and coal/oil fired boilers. The optimum reduction efficiency is obtained for the sulphur contents of fuel between 0.5 and 1.7 wt.-% (max. 2 wt.-%).

The LIFAC process is an advanced dry sorbent injection process using additional water injection in a separate reactor downstream of the boiler, in order to raise the reduction efficiency. Generally, the SO_2 reduction efficiency is > 50 %. At present, the LIFAC process is used in one plant in Finland with a SO_2 reduction efficiency of already 70 %.

3.5.1.4 Wellman-Lord (WL)

The WL process is a regenerable FGD process, which uses the sodium sulphite (Na_2SO_3)/ sodium bisulphite ($NaHSO_3$) equilibrium in order to remove SO_2 from the flue gas. An SO_2-rich gas is obtained, which is used for the production of sulphuric acid. At present only three installations with a total thermal capacity of 3,300 MW are in use (in Germany), due to the complexity of the process and the resulting high investments and operating costs (this technology represents about 3 % of the total thermal capacity installed in the European OECD countries). The WL process is operational with various types of fuel (e.g. hard coal, oil), especially with high sulphur contents (of about 3.5 wt.-%). The SO_2 reduction efficiency is > 97 %.

3.5.1.5 Walther Process (WAP)

The WAP process uses ammonia water in order to remove SO_2 from the flue gas. The by-product is a dry salt mixture of the respective ammonia salts (mainly ammonium sulphate ($(NH_4)_2SO_4$). One reference installation is currently operating in Germany. This process is operational with all types of fuel. However, the maximum sulphur content should be limited to 2 wt.-% (due to the increasing formation of ammonia sulphate aerosols). The SO_2 reduction efficiency is > 88 %.

3.5.2 Nitrogen oxides: Primary measures - Denitrification techniques /cf. 17, 18, 19/

3.5.2.1 Low NO_x burner (LNB)

A characteristic of LNB is the staged air to fuel ratio at the burner. Three different technical modifications are in use:

– Air-staged LNB: An understoichiometric zone is created by a fuel-air mixture and primary air. An internal recirculation zone occurs due to the swirl of primary air. A burn-out zone is created due to secondary air fed by air nozzles arranged around the primary air nozzles.

– Air-staged LNB with flue gas recirculation (FGR): The basic function is similar to air-staged LNB. The distances between the primary and secondary nozzles are greater, therefore, a flue gas layer is formed. As a result, the residence time in the reducing atmosphere increases and the oxygen concentration decreases.

– Air/Fuel staged LNB: An additional reduction zone around the primary zone is achieved by the extremely overstoichiometric addition of secondary fuel around the secondary flame.

LNB is operational with all fuels and all types of burners. The NO_x reduction efficiency for coal fired boilers varies between 10 and 30 % (see Table 10).

3.5.2.2 Staged Air Supply (SAS)

Staged air means the creation of two divided combustion zones - a primary zone with a lack of oxygen and a burn-out zone with excess air. SAS covers the low excess air (LEA), burners out of service (BOOS) and biased burner firing (BBF) techniques:

– Low excess air (LEA) means reduction of the oxygen content in the primary combustion zone of the burners. When firing hard coal, experience has shown that the general limitations are fouling and corrosion, caused by the reducing atmosphere and incomplete burn-out. When firing gas, the reduction efficiency is limited by the CO formed. LEA is more suitable for lignite and often used for retrofitting combustion plants. For oil fired boilers a reduction efficiency of 20 % has been achieved.

– Burners out of service (BOOS) means that the lower burner row(s) in the boiler operate under a lack of oxygen (fuel rich), the upper burners are not in use. This technology is in particular suitable for older installations, but the thermal capacity of the boiler decreases by about 15 - 20 %.

– Biased burner firing (BBF) means that the lower burner rows in the boiler operate under a lack of oxygen (fuel rich) and the upper burners with an excess of oxygen. The boiler efficiency is less compared to BOOS and the NO_x reduction is also lower.

The NO_x reduction efficiency for coal fired boilers varies between 10 and 40 % (see Table 10).

3.5.2.3 Overfire Air (OFA)

All burner rows in the boiler operate with a lack of oxygen. The combustion air is partly (5 - 20 %) injected through separate ports located above the top burner row in the boiler. OFA is operational with most fuels and most types of boilers. For gas fired boilers a reduction efficiency of 10 - 30 % and for oil fired boilers 10 - 40 % has been achieved. The NO_x reduction efficiency for coal fired boilers varies between 10 and 40 % (see Table 10).

3.5.2.4 Flue Gas Recirculation (FGR)

The recirculation of flue gas into the combustion air is an efficient NO_x abatement method for firing modes with high combustion temperatures, such as wet bottom boilers and especially for gas and oil fired boilers.

The recirculated flue gas can be added to the secondary or primary air. In the first case, the flame core is not affected and the only effect is a reduction of the flame temperature, which is favourable for thermal-NO_x abatement. The influence on dry bottom boilers is thus very limited, considering the fact that about 80 % of the NO_x formed originates from fuel bound nitrogen; FGR can be used as an additional measure. A more efficient method is the introduction of flue gas into the primary air of an unstaged burner. High reduction efficiencies of FGR in the primary flow (15 - 20 %) have been achieved in gas and oil fired boilers. The NO_x reduction efficiency for coal fired boilers varies between 5 and 25 % (see Table 10).

3.5.2.5 Split Primary Flow (SPF)

Split primary flow means fuel staging in the furnace. This technique involves injecting fuel into the furnace above the main combustion zone, thereby producing a second understoichiometric combustion zone. In the primary zone of the boiler the main fuel is burnt under fuel-lean conditions. This zone is followed by a secondary zone with a reducing atmosphere, into which the secondary fuel is injected. Finally, secondary air is injected into the burn-out zone of the boiler. This reburning technique can, in principle, be used for all types of fossil fuel fired boilers and in combination with low NO_x combustion techniques for the primary fuels. When nitrogen is present in the reburning fuel, a part of it will be converted into NO_x in the burn-out zone. Therefore, natural gas is the most appropriate reburning fuel. NO_x reduction efficiencies have not been yet reported.

3.5.3 Nitrogen oxides: Secondary measures - Denitrification Processes /cf. 18, 19/

3.5.3.1 Selective Non-Catalytic Reduction (SNCR)

The reduction of nitrogen oxides in the flue gas is based on the selective reaction of NO_x with injected ammonia, urea or caustic ammonia to form nitrogen and water. The SNCR process has been implemented at several installations (e.g. in Germany, in Austria and in Sweden) and has in principle proved to be operational with various types of fuels. The NO_x reduction efficiency is about 50 %, in some installations up to 80 %.

3.5.3.2 Selective Catalytic Reduction (SCR)

The reduction of nitrogen oxides is based on selective reactions with injected additives in the presence of a catalyst. The additives used are mostly gaseous ammonia, but also liquid caustic ammonia or urea. The SCR technology accounts for about 95 % of all denitrification processes. SCR is mostly used for hard coal. For brown coal, lower combustion temperatures lead to lower NO_x formation, so that primary measures fulfil the emission reduction requirements. Several heavy metals in the flue gas can cause rapid deactivation of the catalyst. The NO_x reduction efficiency varies between 70 and 90 %.

3.5.4 Nitrogen oxides and sulphur oxides: Simultaneous Processes /18, 19/

3.5.4.1 Activated Carbon Process (AC)

The AC process is a dry process for simultaneous SO_2 and NO_x removal based on the adsorption of the pollutants in a moving bed filter of activated carbon. The sulphur oxides undergo catalytic oxidation with the moisture in the flue gas to form sulphuric acid. NO_2 is completely reduced to N_2; NO reacts catalytically with the ammonia injected and forms N_2 and H_2O. The AC process has been installed at four power plants in Germany (in two cases downstream of an SDA process). The sulphur content in the fuel used should not exceed 2.3 wt.-%. The SO_2 reduction efficiency is > 95 %, the NO_x reduction efficiency is > 70 %.

3.5.4.2 DESONOX Process/SNOX Process (DESONOX)

The purification of the flue gas by the DESONOX process is based on the simultaneous catalytic reduction of nitrogen oxides (NO_x) to nitrogen (N_2) and water (H_2O) and on the catalytic oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3). The by-product is sulphuric acid. The process has been installed at one power plant in Germany, where hard coal is used with a sulphur content of about 1 wt.-%. The concentration of catalyst toxics (mainly arsenic, but also chromium, selenium etc.) has to be taken into account. The SO_2 reduction efficiency is up to 95 %, the NO_x reduction efficiency is also up to 95 %.

The SNOX process works on the same basic principle as the DESONOX process, with the main difference that reduction and oxidation take place in two separate reaction towers. The SNOX process has been applied at one Danish power plant. No reduction efficiency has been reported yet. The SNOX process is also known as a combination of the Topsøe WSA-2 process and the SCR process.

3.5.5 Heavy metals: Secondary measures /12, 20, 21, 22, 23/

Heavy metal emissions are mainly reduced by dust control equipment. Particulate control systems, which are used in coal-fired power plants, are cyclones, wet scrubbers, electrostatic precipitators (ESP), and fabric filters. In most power plants 99 % of the particulates are removed from the flue gases by using ESP or fabric filters. The latter are more efficient in controlling fine particulate matter; wet scrubbers and cyclones are less efficient.

The reduction efficiency of ESP for most elements in the solid state is > 99 %. Only for some higher volatile elements, such as Cd, Pb, Zn and Se, is the reduction efficiency less, but it remains above 90 %. The reduction efficiency of an ESP for Hg depends on the operating temperature of the ESP. A cold-side ESP operating at about 140 °C is estimated to have an average Hg reduction efficiency of about 35 %.

The influence of FGD- and $DeNO_x$-units on heavy metal emissions has been investigated mainly in the frame of mass balance studies. WS-FGD-units remove a further fraction of particulate matter in flue gas in addition to dust control. Particle bound elements are removed by FGD-units with an efficiency of about 90 %. In FGD-units, in particular WS-units, the gaseous compounds can additionally condense on particulate matter, which are mainly removed in the prescrubber. With regard to gaseous elements, various studies have shown reduction efficiencies of 30 - 50 % for Hg and 60 - 75 % for Se. Lime contributes over 90 % of the input of As, Cd, Pb and Zn to the FGD.

The abatement of Hg emissions is influenced indirectly by DeNO$_x$-units. A high dust SCR-unit improves Hg removal in a subsequent FGD-unit using a lime scrubbing system. The SCR-unit increases the share of ionic mercury ($HgCl_2$) to up to 95 %, which can be washed out in the prescrubber of the FGD-unit. A study in the Netherlands found no influence of LNB on heavy metal emissions.

3.5.6 Gas turbines /cf. 68, 69/

For gas turbines mainly NO_X emissions are of most relevance. Primary measures for NO_X reduction are the following: dry controls (e.g. overstoichiometric combustion in a dry low NO_X burner with $\eta = 0.6 - 0.8$, which is a relatively new development as a primary measure) and wet controls (injection of water and/or steam with $\eta \geq 0.6$ /114/) in order to regulate the combustion temperature. For large gas turbines secondary measures are also installed such as Selective Catalytic Reduction (SCR).

3.5.7 Stationary engines /cf. 70/

For spark-ignition engines the main pollutants emitted are NO_x, CO and unburned hydrocarbons (VOC). For diesel engines sulphur dioxide (SO_2) emissions have also to be considered. Emissions of soot also contribute to emissions of heavy metals and persistent organic pollutants, but at this stage insufficient information is available /35/.

Primary measures are installed to optimise combustion conditions (air ratio, reduced load, water injection, exhaust-gas recirculation, optimised combustion chamber etc.). Reduction efficiencies can be given e.g. for exhaust gas recirculation from 6.5 to 12 % and for internal exhaust gas recirculation from 4 to 37 %. External exhaust gas recirculation (turbo charged models) can have reductions of NO_x varying from 25 to 34 %. /cf. 114/

Secondary measures are installed, if the emission thresholds cannot be met by adjustments to the engine itself. The following methods are used depending on the air ratio λ:

$\lambda = 1$	Reduction of NO_X, CO and VOC by using a three-way catalytic converter (NSCR),
$\lambda > 1$	Reduction of NO_X by Selective Catalytic Reduction with NH_3 (SCR), Reduction of other emissions (CO, VOC) using oxidation catalytic converter (NSCR).

Typical conversion rates of NO_x range from 80 to 95 % with corresponding decreases in CO and VOC. Depending on the system design, NO_x removal of 80 up to 90 % is achievable. /114/

4 SIMPLER METHODOLOGY

4.1 General

4.1.1 General / specified emission factors

Here "simpler methodology" refers to the calculation of emissions, based on emission factors and activities. The simpler methodology should only be used in cases where no measured data is available. The simpler methodology covers all relevant pollutants (SO_2, NO_x, NMVOC, CH_4, CO, CO_2, N_2O, NH_3, heavy metals). Special emphasis is put on the pollutants SO_x, NO_x and heavy metals, due to the significant contribution of combustion plants as point sources to the total emissions of these pollutants.

A combustion plant can be treated either as a whole (irrespective of kind/size of individual boilers) or on a boiler-by-boiler level. Differences in design and operation of boilers, in fuels used and/or controls installed require different emission factors. The same applies to gas turbines and stationary engines.

The annual emission E is derived from an activity A and a factor which determines their linear relation (see Equation (1)):

$$E_i = EF_i \cdot A \tag{1}$$

E_i annual emission of pollutant i
EF_i emission factor of pollutant i
A activity rate

The activity rate A and the emission factor EF_i have to be determined on the same level of aggregation by using available data (e.g. fuel consumption) (see Section 6). For the activity rate A, the energy input in [GJ] should be used, but in principle other relations are also applicable.

Two different approaches in order to obtain the emission factor EF_i are proposed:

- General emission factor EF_{G_i}

The general emission factor is a mean value for defined categories of boilers taking into account abatement measures (primary and secondary). A general emission factor is only related to the type of fuel used and is applicable for all pollutants considered, except of SO_2[5]. It should only be used where no technique specific data are available (only as a makeshift).

- Specified emission factor EF_{R_i}

The specified emission factor is an individually determined value for boilers taking into account abatement measures (primary and secondary). A specified emission factor is related to individual fuel characteristics (e.g. sulphur content of fuel) and to technology specific

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[5] For the appropriate determination of SO_2 emissions the sulphur content of fuel is required. Therefore, the specified emission factor approach has to be applied.

parameters. The following sections provide determination procedures for suitable specified emission factors for the pollutants NO_x, SO_x and heavy metals.

In principle, plant specific data should be used, if available, for the determination of emission factors. The following Sections 4.1 to 4.8 give recommendations for the estimation and the use of general and specified emission factors as given in Table 4.

Table 4: Applicability of general emission factors EF_{G_i} and specified emission factors EF_{R_i}

Pollutant	General emission factor EF_{G_i}	Specified emission factor EF_{R_i}
SO_x	-	+
NO_x	+	++[1)]
Heavy metals	+	++[2)]
NMVOC, CH_4, CO, CO_2, N_2O, NH_3	+	*

+ : possible, but not recommended methodology; ++ : possible and recommended methodology;

- : not appropriate; * : not available

[1)] detailed calculation schemes are given for pulverised coal combustion

[2)] detailed calculation schemes are given for coal combustion

An accurate determination of full load emissions can only be obtained by using specified emission factors. For the calculation of specified SO_x and NO_x emission factors for pulverised coal combustion, a computer programme has been developed (see Annexes 2 - 6 and Annex 14).

If not stated otherwise, the general and specified emission factors presented refer to full load conditions. Start-up emissions have to be considered separately (see Section 4.1.2).

4.1.2 Start-up dependence

Start-up emissions depend on the load design of the plant and on the type of start-up (see Tables 5 and 6). A plant can be designed for:

- peak load:	to meet the short-term energy demand,
- middle load:	to meet the energy demand on working days,
- base load:	continuous operation.

Table 5: Load design and start-ups per year

Load design	Start-ups per year		Full load hours per year		Emission
	range	value	range	value	relevance[2)]
Peak load[1)]	150 - 500	200	1,000 - 2,500	2,000	x[1)]
Middle load	50 - 250	150	3,000 - 5,000	4,000	xxx
Base load	10 - 20	15	6,000 - 8,000	7,000	x

[1)] For peak load often high-quality fuels (e.g. gas, oil) and often gas turbines are used.

[2] x: low; xxx: high.

Table 6: Status of the boiler at starting time for a conventional power plant

Type of start-up	Time of stand-still [h] /65/	Status of the boiler	Frequency[2]	Emission relevance[2]
Hot-start	< 8	hot	xxx	x
Warm-start	8 - ca. 50	warm	xx	xx
Cold-start	> 50	cold	x[1]	xxx

[1] normally once a year, only for maintenance.

[2] x: low; xx: medium; xxx: high.

In order to take into consideration the relevance of start-up emissions, a detailed investigation has been carried out. There, start-up emissions and start-up emission factors have been determined for different types of boilers (DBB, WBB, gas-fired boiler, see Annex 15). Start-up emissions are only relevant if secondary measures are installed.

By taking into account boiler characteristics as given in Annex 15, the following general trends of start-up emissions of SO_x, NO_x and CO on the type of fuel and type of boiler are obtained (based on /116/).

- For the boilers considered in the detailed investigation it has been found that start-up emissions for the combustion of coal are significantly higher than for the combustion of gas.
- Start-up emissions are higher for dry bottom boilers than for wet bottom boilers and gas boilers.

In the following sections, start-up emissions and start-up emission factors derived from measured data are presented as ratios:

$$F^{EF} = EF^{A} / EF^{V} \tag{2}$$

F^{EF} ratio of start-up and full load emission factors [ ]

EF^{A} emission factor at start-up period [g/GJ]

EF^{v} emission factor at full load conditions [g/GJ]

$$F^{E} = E^{A} / E^{V} \tag{3}$$

F^{E} ratio of start-up and full load emissions [ ]

E^{A} emission during start-up period (see Section 3.2) [Mg]

E^{v} emission for full load conditions during start-up period [Mg]

Start-up emissions and full load emissions are related to comparable periods; the energy input (fuel consumption) during the start-up period is lower than during full load operation. The emission factor ratio F^{EF} is often higher than the emission ratio F^{E}. Increased specific emissions during the start-up period were found to be compensated to a high degree by the lower fuel consumption. Further pollutant specific results are given in the Sections 4.2 - 4.9.

If start-up emissions are taken into account the corresponding activity rates have to be determined as follows:

$$A = A_{\text{full load}} + A_{\text{cold}} + A_{\text{warm}} + A_{\text{hot}} \tag{4a}$$

A	activity rate within the period considered [GJ]
$A_{\text{full load}}$	activity rate for full load operation periods [GJ]
A_{cold}	activity rate for cold start periods [GJ]
A_{warm}	activity rate for warm start periods [GJ]
A_{hot}	activity rate for hot start periods [GJ]

Each sub-activity (e.g. A_{cold}) has to be determined separately by totalling the thermal energy input for the respective periods e.g. cold start periods.

Accordingly, Equation (1) becomes:

$$E = EF^{V} \cdot (A_{\text{full load}} + F^{EF}_{\text{cold}} \cdot A_{\text{cold}} + F^{EF}_{\text{warm}} \cdot A_{\text{warm}} + F^{EF}_{\text{hot}} \cdot A_{\text{hot}}) \cdot 10^{-6} \tag{4b}$$

E	emission within the period considered [Mg]
EF^{V}	emission factor at full load operation conditions [g/GJ]
$F^{EF}_{\text{cold/warm/hot}}$	ratio of start-up (cold/warm/hot start) to full load emission factor [ ]
$A_{\text{full load/cold/...}}$	activity rates at full load operation/cold start/... [GJ]

The emission factor at full load conditions EF^{V} can be approximated by using the emission factors given in Tables 24 and 25 (for NO_x) and Table 28 (for CO); SO_2 emission factors can be determined as given in Equation (5). A correction factor for the annual emission can be obtained by calculating the ratio of the annual emissions resulting from Equation (4b) to those determined without consideration of start-up emissions.

4.1.3 Load dependence

A load dependence of emissions has only been found for NO_x emissions released from older types of boiler (see Section 4.3).

4.2 SO_2 emission factors

For SO_2, only specified emission factors $EF_{R_{SO2}}$ are recommended here. For the determination of specified SO_2 emission factors the following general equation should be used (for emissions of SO_3 see Section 9):

$$EF_{R_{SO2}} = 2 \cdot C_{S_{\text{fuel}}} \cdot (1 - \alpha_S) \cdot \frac{1}{H_u} \cdot 10^{6} \cdot (1 - \eta_{\text{sec}} \cdot \beta) \tag{5}$$

$EF_{R_{SO2}}$	specified emission factor [g/GJ]
$C_{S_{\text{fuel}}}$	sulphur content in fuel [kg/kg]
α_s	sulphur retention in ash [ ]

H_u	lower heating value of fuel [MJ/kg]
η_{sec}	reduction efficiency of secondary measure [ ]
β	availability of secondary measure [ ]

Equation (5) can be used for all fuels, but not all parameters may be of relevance for certain fuels (e.g. α_s for gas). Default values for reduction efficiencies and availabilities of secondary measures installed are presented in Table 7. The technologies listed in Table 7 are mainly installed in the case of coal-fired boilers, but they can also be applied when burning other fuels.

Table 7: Default values for secondary measures for SO_2 reduction (all fuels) /18, 19/

No.	Type of secondary measure	Reduction efficiency η_{sec} [ ]	Availability β [ ]
1	WS	0.90	0.99
2	SDA	0.90	0.99
3	DSI	0.45	0.98
4	LIFAC	0.70	0.98
5	WL	0.97	0.99
6	WAP	0.88	0.99
7	AC	0.95	0.99
8	DESONOX	0.95	0.99

4.2.1 Combustion of coal

SO_2 emission factors for coal fired boilers can be calculated by using Equation (5). If some input data are not available, provided default values based on literature data can be used:

- $C_{s,fuel}$	see Annexes 7 and 8, Table 23,
- α_s	see Table 8,
- η_{sec} and β	see Table 7,
- H_u	see Annexes 7 and 8.

For further details concerning the calculation of SO_2 emission factors, see Annexes 2 (flowsheet of the computer programme) and 3 (description of the computer programme). Default values for sulphur retention in ash for coal fired boilers are presented in Table 8.

Table 8: Default values for the sulphur retention in ash (α_S) for pulverised coal fired boilers

Type of boiler	α_S [ ]	
	Hard coal	Brown coal
DBB	0.05	$0.3^{1)}$
WBB	0.01	-

$^{1)}$ average value; in practice, a range of 0.05 - 0.60 can occur (e.g. in the Czech Republic 0.05 is used)

Emission factors obtained by using Equation (5) are related to full load conditions; start-up emissions are not taken into account. If a flue gas desulphurisation unit is installed, start-up emissions should be considered as given in Section 4.1.2. The relevance of start-up emissions of SO_2 depends strongly on the following parameters:

- the type of fuel (e.g. SO_x emissions are directly related to the fuel sulphur content),
- the status of the boiler at starting time (hot, warm or cold start, see also Table 6),
- start-up of the flue gas desulphurisation unit (FGD direct or in by-pass configuration),
- limit for SO_x emissions, which has to be met (boiler specific limits can be set up below the demands of the LCP Directive).

For the combustion of coal in dry bottom boilers, the following ranges and values of F^{EF}, F^E have been obtained within the investigation outlined in Annex 15:

Table 9: Ratios of start-up to full load emission factors F^{EF} and ratios of start-up to full load emissions F^E for SO_2 for dry bottom boilers

	Ratio of start-up to full load emission factors F^{EF} [ ]	Ratio of start-up to full load emissions F^E [ ]
Range	3 - max. 16	1 - max. 4
Values for direct start-up of the FGD	F^{EF}_{cold}: 5 F^{EF}_{warm}: 5 F^{EF}_{hot}: 4	F^{E}_{cold}: 1 F^{E}_{warm}: 1 F^{E}_{hot}: 1
Values for by-pass start-up of the FGD	F^{EF}_{cold}: 8.5 - 16 F^{EF}_{warm}: 5 - 14.5 F^{EF}_{hot}: 5 - 5.5	F^{E}_{cold}: 2 - 4.5 F^{E}_{warm}: 1 - 3.5 F^{E}_{hot}: 1.5

$F^{EF}_{cold,warm,hot}$ Ratio of start-up to full load emission factors for cold, warm or hot start-ups (see also Table 6)

$F^{E}_{cold,warm,hot}$ Ratio of start-up to full load emissions for cold, warm or hot start-ups (see also Table 6)

The values from the direct start-up of the FGD show, that start-up emissions of SO_2 are not relevant (ratio F^E of ca. 1). In the case of a by-pass start-up of the FGD, start-up emissions of SO_2 are significant for hot, warm and cold starts; start-up emissions can be up to 4 times higher than emissions in a comparable full load time span (based on /116/).

4.2.2 Combustion of other fuels (biomass, waste, liquid fuels, gaseous fuels)

SO_2 emissions are directly related to the sulphur content of biomass, waste, liquid and gaseous fuels (see Equation (5)). The sulphur retention in ash α_s is not relevant. The reduction efficiency η_{sec} and the availability β of installed secondary measures have to be taken into account (in particular for the combustion of waste). Default values for η and β are given in Table 7. Sulphur contents of different fuels are given in Table 23 and in Annexes 7 and 8.

4.3 NO_x emission factors

For the determination of NO_x emissions, general as well as specified NO_x emission factors can be used. Emission factors are listed in Tables 24 and 25 depending on installed capacity, type of boiler, primary measures and type of fuel used.

4.3.1 Combustion of pulverised coal

Specified NO_x emission factors can be calculated individually for pulverised coal fired boilers. Due to the complex reaction mechanism of NO_x formation (see also Section 3.4) an estimate of specified NO_x emission factors can only be made on the basis of empirical relations as given in Equation (6). The decisive step in Equation (6) is the undisturbed NO_x formation (without primary measures) inside the boiler ($C_{NO_{2.boiler}}$). $C_{NO_{2.boiler}}$ is determined by an empirical equation depending on fuel parameters only, as described in Annex 5.

$$EF_{R_{NO_2}} = C_{NO_2,boiler} \cdot (1-\eta_{prim}) \cdot \frac{1}{H_u} \cdot 10^6 \cdot (1-\eta_{sec}\,\beta) \tag{6}$$

$EF_{R_{NO2}}$	specified emission factor [g/GJ]
$C_{NO_{2.boiler}}$	total content of nitrogen dioxide formed in the boiler without taking into account primary reduction measures (in mass NO_2/mass fuel [kg/kg])[6]
η_{prim}	reduction efficiency of primary measures [ ]
H_u	lower heating value of fuel [MJ/kg]
η_{sec}	reduction efficiency of secondary measure [ ]
β	availability of secondary measure

For further details concerning the calculation of specified NO_2 emission factors see Annexes 4 (flowsheet of the computer programme) and 5 (description of the computer programme).

If some input data are not available, default values based on literature data are provided for:

- $C_{N,\ fuel}$, content of fuel-nitrogen, see Annexes 7 and 8,
- $C_{volatiles}$, content of volatiles in the fuel, see Annexes 7 and 8,

---

[6] Note: The computer programme, which is described in Annex 5, provides $C_{NO2\ boiler}$ as (mass pollutant/mass flue gas [kg/kg]).

- η_{prim} see Table 10,
- η_{sec} and β see Table 11,
- H_u see Annexes 7 and 8.

Default values for the reduction efficiency of primary measures are presented in the following Tables 10 and 11.

Table 10: Reduction efficiencies for selected primary measures for NO_X emissions in coal fired boilers /17, 18, 19, 28, 31, 32, 33, 34, 53/ (value means recommended value)

Type of primary measure[1]	Reduction efficiency DBB η [ ]				Reduction efficiency WBB η [ ]	
	Hard coal		Lignite		Hard coal	
	range	value[3]	range	value[3]	range	value[3]
no measure[4]	0	0	0	0	0	0
LNB	0.10 - 0.30	0.20	0.10 - 0.30	0.20	0.10 - 0.30	0.20
SAS	0.10 - 0.40	0.30	0.10 - 0.40	0.30	0.10 - 0.40	0.30
OFA	0.10 - 0.40	0.30	0.10 - 0.35	0.25	0.10 - 0.35	0.25
FGR	0.05 - 0.15	0.10	0.05 - 0.20	0.15	0.10 - 0.25	0.20
LNB/SAS	0.20 - 0.60	0.45	0.20 - 0.60	0.45	0.20 - 0.60	0.45
LNB/OFA	0.20 - 0.60	0.45	0.20 - 0.55	0.40	0.20 - 0.55	0.40
LNB/FGR	0.15 - 0.40	0.30	0.15 - 0.45	0.30	0.20 - 0.50	0.35
SAS/OFA	0.20 - 0.65	0.50	0.20 - 0.60	0.40	0.20 - 0.60	0.40
SAS/FGR	0.15 - 0.50	0.40	0.15 - 0.50	0.40	0.20 - 0.55	0.45
OFA/FGR	0.15 - 0.50	0.40	0.15 - 0.50	0.35	0.20 - 0.50	0.40
LNB/SAS/OFA	0.30 - 0.75	0.60	0.30 - 0.75	0.60	0.30 - 0.75	0.60
LNB/SAS/FGR	0.25 - 0.65	0.50	0.25 - 0.70	0.50	0.30 - 0.70	0.55
LNB/OFA/FGR	0.25 - 0.65	0.50	0.25 - 0.65	0.50	0.30 - 0.65	0.50
old installation/ optimised		0.15		0.15		0.15
old installation/ retrofitted[2]		0.50		0.50		0.50
new installation[2]		0.40		0.40		0.40

[1] Selection from the DECOF database developed by and available at the Institute for Industrial Production (IIP).

[2] Recommended values, when no information concerning the type of primary measure is available.

[3] Default values used in the computer programme.

[4] No primary measures are installed. This case is mainly relevant for old installations.

Table 11: Default values for reduction efficiency and availability of secondary measures for NO_X reduction /18, 19/ (all fuels)

No.	Type of secondary measure	Reduction efficiency η_{sec} [ ]	Availability β [ ]
1	SNCR	0.50	0.99
2	SCR	0.80	0.99
3	AC	0.70	0.99
4	DESONOX	0.95	0.99

Emission factors of NO_2 for different coal compositions have been calculated by using default values as given above and are listed in Table 25.

The load dependence of NO_X emissions can be split into two different phenomena (see Sections 4.1.2 and 4.1.3):

a) Load variations during normal operation:
Load variations are discussed very controversially in the literature. Often a strong correlation of NO_X emissions and load is reported. Load corrections, e.g. as given in /66/, may be appropriate for older types of boilers.

For boilers of modern design, with optimised combustion conditions e.g. by primary measures, only a negligible load dependence has been reported /64/. This is explained by the fact that for modern boilers (with primary measures) under reduced load conditions an overstoichiometric air ratio is applied in order to achieve an acceptable burning out of the fuel, which leads to NO_x emission factors similar to those obtained under full load conditions. Therefore, for boilers of modern design no load correction is proposed.

For older boilers (without primary measures) a load dependent emission factor can be calculated according to Equation (7), which has been derived for German dry bottom boilers (combustion of hard coal) /71/:

$$EF = 1,147 + 0.47 \cdot L \tag{7}$$

EF emission factor [g/MWh][7]
L actual load [MW]

At this stage, no general approach is available for estimating the load dependence of NO_x emissions. However, a load correction factor can be obtained by using a ratio between reduced load and full load emission factors:

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[7] 1 MWh = 3.6 GJ

$$k^{load} = \frac{EF^{Reduced\ load}}{EF^{V}} = \frac{1{,}147 + 0.47 \cdot L}{1{,}147 + 0.47 \cdot L_{nominal}} \qquad (8)$$

k^{load}	ratio of reduced load to full load emission factor [ ]
$EF^{Reduced\ load}$	emission factor for reduced load conditions [g/MWh][6]
EF^{V}	emission factor for full load conditions [g/MWh][6]
L	actual load [MW]
$L_{nominal}$	nominal load [MW]

Figure 1.1 gives a graphic presentation of the results of Equation (8):

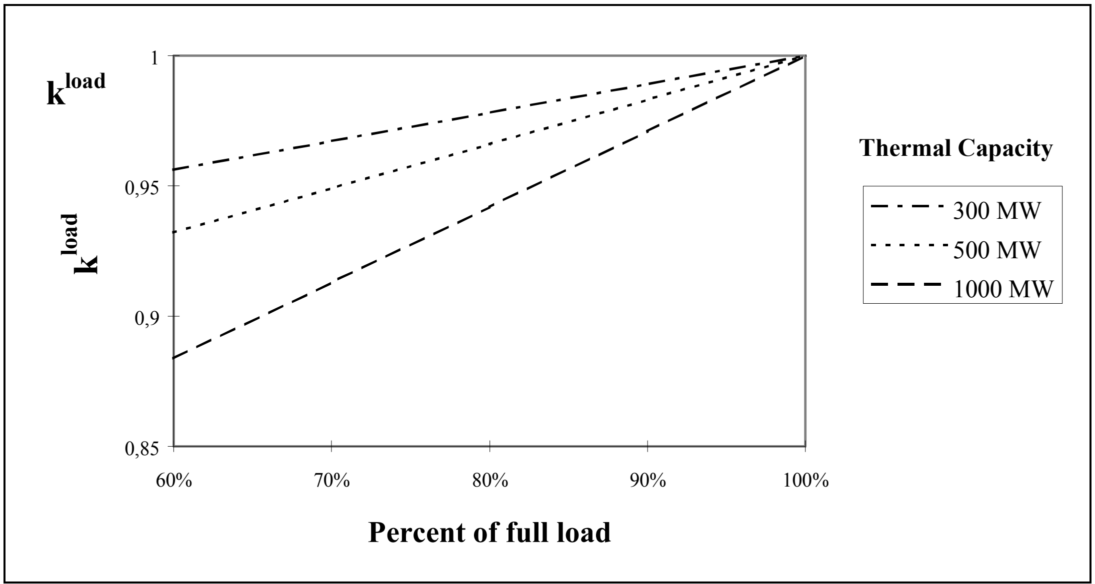


Figure 1.1: Variation of k^{load} with load

If reduced load operation is taken into account the corresponding activity rates have to be determined as follows:

$$A = A_{full\ load} + A_{load\ 1} + A_{load\ 2} + \ldots \qquad (9a)$$

A	activity rate within the period considered [GJ]
$A_{full\ load}$	activity rate for full load operation periods [GJ]
$A_{load\ i}$	activity rate for reduced load operation periods at level i [GJ]

Each sub-activity (e.g. $A_{load\ 1}$) has to be determined separately by totalling the thermal energy input for the respective periods of operation e.g. at load level 1.

Emissions are calculated according to Equation (9b):

$$E = EF^{V} \cdot (A_{\text{full load}} + k^{\text{load 1}} \cdot A_{\text{load 1}} + k^{\text{load 2}} \cdot A_{\text{load 2}} + ...) \cdot 10^{-6} \tag{9b}$$

E	emission within the period considered [Mg]
EF^{V}	emission factor at full load conditions [g/GJ]
$A_{\text{load i}}$	activity rates at load level i [GJ]
$k^{\text{load i}}$	ratio of reduced load to full load emission factor at load level i [ ]

If secondary measures are installed, no load correction for NO_X emissions has to be taken into account.

b) Load variations with respect to start-up behaviour:

Emission factors for NO_x, as given in Tables 24 and 25, are related to full load conditions; start-up emissions are not taken into account. If an SCR is installed, start-up emissions should be considered as given in Section 4.1.2. The relevance of start-up emissions of NO_x depends strongly on the following parameters:

- the type of boiler (e.g. NO_x emissions released by wet bottom boilers are always higher than those by dry bottom boilers, due to higher combustion temperatures),
- the type of fuel used (e.g. fuel nitrogen also contributes to the formation of NO_x),
- the status of the boiler at starting time (hot, warm or cold start),
- the specifications of any individual start-up, such as
    - -- the duration and the velocity of start-up,
    - -- the load level (reduced load or full load),
    - -- the configuration of secondary measures (e.g. the start-up time of the high-dust-configurations (SCR-precipitator-FGD) depends on the boiler load, due to the fact that the SCR catalyst is directly heated by the flue gas; tail-end-configurations (precipitator-FGD-SCR) can have shorter start-up times, due to the fact that the SCR catalyst can be preheated by an additional furnace),
    - -- emission standards, which have to be met (boiler-specific emission standards can be set up below the demands of the LCP Directive).

In the investigation mentioned in Annex 15 the measured data from different boilers have been analysed. For the combustion of coal the following ratios have been obtained (based on /116/):

- For the combustion of coal in dry bottom boilers the following ranges and values can be given:

Table 12: Ratios of start-up to full load emission factors F^{EF} and ratios of start-up to full load emissions F^{E} for NO_2 for dry bottom boilers

	Ratio of start-up to full load emissions factors F^{EF} [ ]	Ratio of start-up to full load emissions F^{E} [ ]
Range	2 - max. 6	1 - 2
Values for DBB	F^{EF}_{cold} : 3.5 – 6 F^{EF}_{warm} : 3 – 6.5 F^{EF}_{hot} : 2.5 – 3	F^{E}_{cold} : 1.5 – 2 F^{E}_{warm} : 1 – 2 F^{E}_{hot} : 1 – 1.5

$F^{EF}_{cold,warm,hot}$ Ratio of start-up to full load emission factors for cold, warm or hot start-ups (see also Table 6)

$F^{E}_{cold,warm,hot}$ Ratio of start-up to full load emissions for cold, warm or hot start-ups (see also Table 6)

The investigation revealed that start-up emissions of NO_2 were mostly higher than emissions under full load conditions. There is a dependence between start-up emissions (see Section 3.2) and the time of standstill of the boiler: cold starts showed emissions about 2 times higher, warm starts about 1 up to 2 times higher and hot starts about 1 up to 1.5 higher than at full load conditions. Start-up emission factors can be up to 6 times higher than full load emission factors. At the investigated boilers the SCR was installed in a high-dust configuration.

- For the combustion of coal in wet bottom boilers (SCR in tail-end configuration) it was found that start-up emissions were not higher than full load emissions (ratio of ≤1). However, this consideration is based on data of only two boilers. Measured data for hot starts was not available.

NO_x emissions, in particular for the combustion of coal in DBB, might be underestimated, if these effects are not taken into account.

4.3.2 Combustion of other fuels (biomass, waste, liquid fuels, gaseous fuels)

The emission calculation is based on Equation (1). During the combustion of solid and liquid fuels, fuel-NO and thermal-NO are formed. For gaseous fuels only thermal-NO_x is relevant, as gaseous fuels do not contain any fuel-nitrogen. For gaseous fuels the emission reduction is mainly achieved by primary measures. There are several biomass-fuelled plants with SNCR in Sweden.

The analysis of emission data from a gas fired boiler, equipped with an SCR, revealed that start-up emissions are not of relevance (ratios F^{E} were below 1) (based on /116/).

4.4 NMVOC/CH_4 emission factors

The emission calculation is based on Equation (1). Fuel and technique specific emission factors are given in Tables 26 and 27.

4.5 CO emission factors

The emission calculation is based on Equation (1). Fuel and technique specific emission factors are given in Table 28 (full load conditions); start-up emissions are not taken into account. CO emissions at starting time and under full load conditions are mainly influenced by the combustion conditions (oxygen availability, oil spraying etc.). In the detailed investigation start-up emissions for CO have only been found to be relevant for the combustion of coal. Start-up emissions for CO are determined for the time when burners switch-on up to the time when the boiler operates on minimum load.

For the combustion of coal and gas the following results have been obtained (based on /116/ see also Section 4.1.2):

- For the combustion of coal in dry bottom boilers the following ranges can be given:

Table 13: Ratios of start-up to full load emission factors F^{EF} and ratios of start-up to full load emissions F^{E} for CO for dry bottom boilers

	Ratios for start-up to full load emission factors F^{EF} [ ]	Ratios for start-up to full load emissions F^{E} [ ]
Range	0.5 - 3.5	0.1 - 0.7
Values for DBB	F^{EF}_{cold} : 1.5 – 3.5 F^{EF}_{warm} : 1 F^{EF}_{hot} : 0.5	F^{E}_{cold} : 0.4 – 0.7 F^{E}_{warm} : 0.2 – 0.7 F^{E}_{hot} : 0.1

$F^{EF}_{cold,warm,hot}$	Ratio of start-up to full load emission factors for cold, warm or hot start-ups (see also Table 6)
$F^{E}_{cold,warm,hot}$	Ratio of start-up to full load emissions for cold, warm or hot start-ups (see also Table 6)

The values in Table 13 show that start-up emissions for CO for DBB are lower than full load emissions for the boilers considered.

- Start-up emissions from wet bottom boilers can be up to 1.2 times higher than full load emissions for cold starts ($F^{EF} = 4$); they are lower for warm starts ($F^{E} = 0.3$; $F^{EF} = 0.8$).

- Start-up emissions of CO from gas boilers are also negligible.

4.6 CO_2 emission factors

The emission calculation is based on Equation (1). Fuel specific emission factors are given in Table 29. For the determination of specified CO_2 emission factors, the following general Equation (10) can be used:

$$EF_{R_{CO2}} = \frac{44}{12} \cdot C_{C_{fuel}} \cdot \varepsilon \cdot \frac{1}{H_u} \cdot 10^6 \qquad (10)$$

$EF_{R_{CO2}}$	specified emission factor [g/GJ]
$C_{C_{fuel}}$	carbon content of fuel (in mass C/mass fuel [kg/kg])
ε	fraction of carbon oxidised [ ]
H_u	lower heating value of fuel [MJ/kg]

Default values for carbon content and lower heating value of different coals, available on the world market, are given in Annexes 7 and 8. The fraction of carbon oxidised (ε) is defined as the main part of carbon which is oxidised to CO_2; small amounts of carbon may remain unoxidised. Default values for ε according to IPCC /61/ are for liquid fuels 0.99, for solid fuels 0.98 and for gaseous fuels 0.995. In this approach it is assumed that the only product of the oxidation is CO_2. Nevertheless, double counting of CO_2 has to be avoided: products of incomplete oxidation, like CO, must not be converted into CO_2.

The IPCC/OECD presented an overall model (the so-called reference approach) specially designed for the calculation of CO_2 emissions on a national level (not on a plant level) /61/. This methodology is based on national energy balances.

4.7 N_2O emission factors

The emission calculation is based on Equation (1). The fuel and technique specific emission factors are given in Table 30. At this stage, several pilot studies using measured data are described in the literature /13, 14, 25, 26, 27/. A complete list of influencing parameters has not yet been identified.

4.8 NH_3 emission factors

Emission factors referring to the energy input are not yet available. The available data for ammonia slip at SCR/SNCR installations are based on measurements and are related to the flue gas volume: SCR/SNCR installations are often designed for an ammonia slip of about 5 ppm (3.8 mg NH_3/m^3 flue gas) /45, 62/. The ammonia slip at SCR and SNCR installations increases with an increasing NH_3/NO_x ratio, but also with a decreasing catalyst activity.

4.9 Heavy metal emission factors

For heavy metals, general and specified emission factors can be used. Emission factors, depending on the fuel used and the technique installed, are given in Table 31.

The IPCC/OECD presented an overall model (the so-called reference approach) specially designed for the calculation of CO_2 emissions on a national level (not on a plant level) /61/. This methodology is based on national energy balances.

4.9.1 Combustion of coal

For an individual determination of specific heavy metal emission factors, three different methodologies can be applied, taking into account:

- fuel composition	(particle-bound and gaseous emissions),
- fly ash composition	(particle-bound emissions),
- fly ash concentration in clean gas	(particle-bound emissions).

The choice of the methodology depends on data availability.

4.9.1.1 Calculation of specified emission factors based on fuel composition /cf. 35/

Emissions of heavy metals associated with particulate matter and gaseous emissions are assessed subsequently as given in Equation (11). The enrichment behaviour of heavy metals with regard to fine particles is taken into account as an enrichment factor (see also Section 3.4). Gaseous emissions have to be taken into account additionally in the case of arsenic, mercury and selenium.

$$EF_{R_{HM}} = C_{HM_{coal}} \cdot f_a \cdot f_e \cdot 10^{-2} \cdot (1-\eta_p) + C_{HM_{coal}} \cdot f_g \cdot 10^{-2} \cdot (1-\eta_g) \qquad (11)$$

$EF_{R_{HM}}$	specified emission factor of heavy metal (in mass pollutant/mass coal [g/Mg])
$C_{HM_{coal}}$	concentration of heavy metal in coal [mg/kg]
f_a	fraction of ash leaving the combustion chamber as particulate matter [wt.-%]
f_e	enrichment factor [ ]
f_g	fraction of heavy metal emitted in gaseous form [wt.-%]
η_p	efficiency of the dust control equipment [ ]
η_g	efficiency of the emission control equipment with regard to gaseous heavy metals [ ]

The characteristics of fuel and technology are taken into account by f_a and f_e and the following default values are proposed:

Table 14: Default values for f_a for different combustion technologies (based on /35/)

Type of boiler	f_a [wt.-%]
DBB (Pulverised coal)	80
Grate firing	50
Fluidised bed	15

Table 15: Default values for f_e for different heavy metals released by the combustion of coal (based on /35/)

Heavy metal	f_e [ ]	
	range	value[1)]
Arsenic	4.5 - 7.5	5.5
Cadmium	6 - 9	7
Copper	1.5 - 3	2.3
Chromium	0.8 - 1.3	1.0
Nickel	1.5 - 5	3.3
Lead	4 - 10	6
Selenium	4 - 12	7.5
Zinc	5 - 9	7

[1)] Recommended value, if no other information is available.

Gaseous emissions (arsenic, mercury and selenium) are calculated from the heavy metal content in coal; the fraction emitted in gaseous form is given in Table 16. The efficiency of emission control devices with regard to these elements is outlined in Section 3.5.5.

Table 16: Fractions of heavy metals emitted in gaseous form (f_g) released by the combustion of coal /35/

Heavy metal	f_g [wt.-%]
Arsenic	0.5
Mercury	90
Selenium	15

4.9.1.2 Calculation of specified emission factors based on fly ash composition /cf. 39/

If the concentration of heavy metals in raw gas fly ash is known, emission factors of heavy metals can be assessed by Equation (12). Gaseous emissions have to be taken into account separately as outlined in Section 4.9.1.1.

$$EF_{R_{HM,P}} = EF_f \cdot C_{HM_{FA,raw}} \cdot 10^{-3} \cdot (1 - \eta_p) \tag{12}$$

$EF_{R_{HM,P}}$	specified emission factor of heavy metal in particulate matter (in mass pollutant/mass coal [g/Mg])
EF_f	fly ash emission factor of raw gas (in mass particulate matter/mass coal [kg/Mg])
$C_{HM_{FA,raw}}$	heavy metal concentration in raw gas fly ash (in mass pollutant/mass particulate matter [g/Mg])
η_p	efficiency of dust control equipment [ ]

Values of EF_f can be calculated in a technology specific way using default parameters, as given in Table 17 depending on the content of ash in coal (a) in [wt.-%].

Table 17: Fly ash emission factor for raw gas (EF_f) as function of the ash content in coal (a) [wt.-%] /cf. 39/

Technology	EF_f (in mass particulate matter / mass coal) [kg/Mg]
Cyclone	$1.4 \cdot a$
Stoker	$5.9 \cdot a$
Pulverised coal combustion	$7.3 \cdot a$

The emission factors calculated by taking into account the fuel or the fly ash composition mainly depend on the estimation of the efficiency of dust control equipment.

4.9.1.3 Calculation of specified emission factors based on fly ash concentration in clean flue gas /cf. 36/

If the concentration of heavy metals in fly ash in clean flue gas is known, emission factors of heavy metals can be assessed by Equation (13). Gaseous emissions have to be taken into account separately, as outlined in Section 4.9.1.1.

$$EF_{R_{HM,P}} = C_{HM_{FA,clean}} \cdot C_{FG} \cdot V_{FG} \cdot 10^{-9} \tag{13}$$

$EF_{R_{HM,P}}$	specified emission factor of heavy metal in particulate matter (in mass pollutant/mass coal [g/Mg])
$C_{HM_{FA,clean}}$	concentration of heavy metal in fly ash in clean flue gas (in mass pollutant/mass fly ash [g/Mg])
C_{FG}	concentration of fly ash in clean flue gas (in mass fly ash/volume flue gas [mg/m^3])
V_{FG}	specific flue gas volume (in volume flue gas/ mass coal [m^3/Mg])

Fuel and technology specific heavy metal concentrations in fly ash in clean flue gas ($C_{HM_{FA.clean}}$) are given in Table 18 /36/:

Table 18: Concentration of heavy metals in fly ash in clean flue gas /36/

$C_{HM_{FA,clean}}$ Heavy metal	DBB/hc [g/Mg]		WBB/hc [g/Mg]		DBB/hc [g/Mg]	
	range	value	range	value	range	value
As	61 - 528	300	171 - 1,378	690	70 - 120	100
Cd	0.5 - 18	10	18 - 117	80	7 - 12	10
Cr	73 - 291	210	84 - 651	310	10 - 250	70
Cu	25 - 791	290	223 - 971	480	13 - 76	50
Ni	58 - 691	410	438 - 866	650	n. a.	90
Pb	31 - 2,063	560	474 - 5,249	2,210	10 - 202	90
Se1)	18 - 58	45	7 - 8	7	n. a.	n. a.
Zn	61 - 2,405	970	855 - 7,071	3,350	50 - 765	240

1) does not include gaseous Se

n. a.: not available

Default values of particulate matter concentrations downstream of FGD (C_{FG}) are given in Table 19.

Table 19: Particulate matter concentrations downstream of FGD (C_{FG}) released by the combustion of coal based on /18/

Type of FGD	C_{FG} [mg/m^3]	
	range	value1)
WS	20 - 30	25
SDA	20 - 30	25
WL	5 - 10	8
WAP	5 - 10	8
AC	< 40	20
DESONOX	< 40	20

1) Recommended value, if no other information is available.

The concentration of fly ash in flue gas is often monitored continuously. In this case the total annual fly ash emissions can be derived from measured data (see Section 5.2).

4.9.2 Combustion of other fuels

General emission factors for oil and gas combustion can be found in Table 31. Among the other fuels, only waste is relevant for heavy metal emissions. Emission factors for the combustion of waste are currently not available (reported emission factors within the literature mainly refer to the incineration of waste).

5 DETAILED METHODOLOGY

The detailed methodology refers to the handling of measured data in order to determine annual emissions or in order to verify emission factors (for comparison purposes). Annual emissions from major contributors should only be obtained by using continuously measured data which are normally available if secondary abatement technologies are installed. Furthermore, the detailed methodology should be used whenever measured data are available; e.g. for medium and small sized combustion installations periodically measured data are often available.

Measurements are carried out downstream of the boiler or at the stack; measured values obtained by both variants are usable.

National monitoring programmes should include guidelines for quality assurance of measurements (measuring places, methods, reporting procedures, etc.).

The pollutants normally measured at power plants are SO_2, NO_x, CO, and particulate matter. Gaseous emissions of SO_2, NO_x, and CO are treated in Section 5.1. Continuously measured particulate matter emission data can be used to estimate heavy metal emissions (see Section 5.2).

5.1 Gaseous emissions

It is desirable to obtain annual emissions in [Mg]. The annual emission as a function of time is normally given by the following Equation (14):

$$E = \int_T e(t) \qquad dt \tag{14}$$

E emission within the period T [Mg]
e (t) emission per unit of time in the periods of operation [Mg/h]
t time [h]
T annual time period (see also Figure 1)

Usually, the emission e(t) cannot be or is not directly measured. Therefore, for practical reasons, the concentration of pollutants and the flue gas volume are used for the determination of e(t), as described by Equation (15):

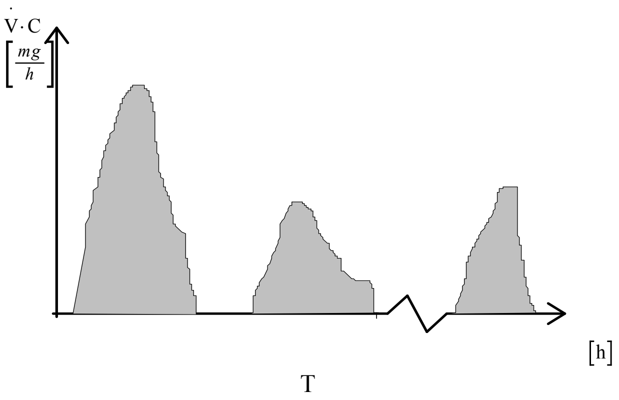
$$e(t) = \dot{V}(t) \cdot C(t) \tag{15}$$

e (t) emission in the periods of operation [Mg/h]
$\dot{V}(t)$ flue gas volume flow rate [m^3/h]

C (t)	flue gas concentration of a pollutant [mg/m^3]

Usually, emission fluctuations occur within a year (see Figure 1) as:

- periodical fluctuations (e.g. daily, weekly, seasonally), due to load management depending on the demand of e.g. district heat or electricity,
- operational fluctuations (e.g. start-ups/shut downs, raw material properties, working conditions/reaction conditions).



$\dot{V}$	flue gas volume flow rate [m^3/h]
C	flue gas concentration of a pollutant (abatement techniques installed are included) [mg/m^3]
t	time [h]
t_{bn}	beginning of operation (e.g. start-up of boiler) [h]
t_{en}	ending of operation (e.g. shut down of boiler) [h]
T	annual time period

Figure 1: Periods of operation of a combustion installation

The following approaches can be used to determine annual emissions depending on the level of detail of measured data available.

– First approach:

The flue gas volume and the concentration of a pollutant are measured continuously (e.g. in Finland). Then, the annual emission is given exactly by the following Equation (16):

$$E = 10^{-9} \int_T V(t) \cdot C(t) dt \tag{16}$$

E	emission within the period T [Mg]
$\dot{V}(t)$	flue gas volume flow rate [m^3/h]
C (t)	flue gas concentration of a pollutant (abatement techniques installed are included) [mg/m^3]
t	time [h]
T	annual time period (see also Figure 1)

The precision of measurements of $\dot{V}(t)$ and C(t) depends on the performance of the analytical methods (e.g. state-of-the-art) used. In particular, the regular calibration of measuring instruments is very important. Analytical methods commonly used for NO$_x$ detect only NO and those used for SO_x detect only SO_2. It is implicitly assumed that NO_2 in the flue gas is normally below 5 %, and that SO_3 in the flue gas is negligible. Nevertheless, for some combustion plants the amounts of NO_2 and/or SO_3 formed can be significant and have to be detected by appropriate analytical methods. The measured values have to be specified with regard to dry/wet flue gas conditions and standard oxygen concentrations[8].

For the annual time period T considered, a case distinction has to be made:

- calendar year T_1 (e.g. including time out of operation),
- real operating time T_2 of boiler/plant (e.g. start-ups are reported when „burner on/off"),
- official reporting time T_3 determined by legislation (e.g. start-ups are reported, as soon as the oxygen content in the flue gas goes below 16 %),

where $T_3 \subset T_2 \subset T_1$. If C(t) is only available for T_3, adequate corrections have to be provided.

– Second approach:

Due to the difficulty in measuring V(t) continuously in large diameter stacks, in most cases the flue gas volume flow rate V(t) is not measured. Then the annual emission can be determined by Equation (17):

$$E = 10^{-9}\bar{\dot{V}}\int_{T} C(t)dt \qquad (17)$$

E	emission within the period T [Mg]
$\bar{\dot{V}}$	average flue gas volume flow rate [m^3/h]
C(t)	flue gas concentration of a pollutant (abatement techniques installed are included) [mg/m^3]
t	time [h]
T	annual time period (see also Figure 1)

The average flue gas volume flow rate $\bar{\dot{V}}$ (dry conditions) can be determined according to the following Equations (18) and (19):

$$\bar{\dot{V}} = V_{FG} \cdot \dot{m}_{fuel} \qquad (18)$$

$\bar{\dot{V}}$	average flue gas volume flow rate [m^3/h]
V_{FG}	dry flue gas volume per mass fuel [m^3/kg]
$\dot{m}_{fuel}$	fuel consumption rate [kg/h]

$$V_{FG} \approx 1.852\left[\tfrac{m^3}{kg}\right] \cdot C_c + 0.682\left[\tfrac{m^3}{kg}\right] \cdot C_s + 0.800\left[\tfrac{m^3}{kg}\right] \cdot C_N + V_{N_{air}} \qquad (19)$$

V_{FG}	dry flue gas volume per mass fuel [m^3/kg]
C_c	concentration of carbon in fuel [kg/kg]
C_s	concentration of sulphur in fuel [kg/kg]

---

[8] In some countries the measured values obtained are automatically converted into values under standard oxygen concentrations (e.g. in Germany).

C_N	concentration of nitrogen in fuel [kg/kg]
$V_{N_{air}}$	specific volume of air nitrogen (in volume/mass fuel [m^3/kg])

This calculation of V according to Equation (19) can be performed by the computer programme (see Annex 6) by using default values for C_C, C_S, C_N and $V_{N_{air}}$.

- Third approach:
  In some countries the term $\int_T C(t)dt$ is available as an annual density function P(C) (histogram). In this case Equation (17) can be simplified to:

$$E = \overline{\dot{V}} \cdot \overline{C} \cdot t_{op} \cdot 10^{-9} \tag{20}$$

$$\text{where} \quad \overline{C} = \int_0^\infty P(C) \cdot C \cdot dC \tag{21}$$

E	emission within the period T [Mg]
$\overline{\dot{V}}$	average flue gas volume flow rate [m^3/h]
$\overline{C}$	expected value (mean value) of the flue gas concentration for each pollutant (abatement techniques installed are included) [mg/m^3]
t_{op}	annual operating time [h]
P(C)	density function [ ]
C	flue gas concentration per pollutant as given in the histogram [mg/m^3]

The variable t_{op} has to be introduced consistently with $\overline{\dot{V}}$ and $\overline{C}$ according to periods T_1, T_2 or T_3 mentioned above. If e.g. start-ups are not included, they should be taken into account as given in Sections 4.1, 4.2 and 4.4.

- Fourth approach:
  If neither T_2 nor T_3 are available, the annual full load operating hours can also be used. Then Equation (20) becomes:

$$E = \overline{\dot{V}}_{normed} \cdot \overline{C} \cdot t_{op}^{full\,load} \cdot 10^{-9} \tag{22}$$

E	emission within the period considered [Mg]
$\overline{\dot{V}}_{normed}$	average flue gas volume flow rate related to full load operation [m^3/h]
$\overline{C}$	mean value of the flue gas concentration for each pollutant (abatement techniques installed are included) [mg/m^3]
$t_{op}^{full\,load}$	annual operating time expressed as full load operating hours [h]

From here, emission factors, based on measured values, can be derived e.g. for verification purposes:

$$EF = \frac{E}{A} \cdot 10^6 \tag{23}$$

EF emission factor [g/GJ]

E emission within the period considered [Mg]
A activity rate within the time period considered [GJ]

5.2 Heavy metal emissions

Continuously measured values for the total heavy metal emissions (particle-bound and gaseous) are not available for the combustion of fossil fuels. National legislation can require periodical measurements, e.g. weekly measurements of heavy metal emissions [mg/m^3] in the case of waste incineration/combustion.

The emissions of particle-bound heavy metals depend on the emission of particulate matter which is normally periodically or continuously monitored. Therefore, the particle-bound heavy metal emissions can be derived from the element content in particulate matter. The heavy metal emission factor can be back-calculated as follows:

$$EF = \frac{\overline{\dot{m}}_{FA} \cdot \overline{C}_{HM_{FA.clean}}}{A} \tag{24}$$

EF emission factor [g/GJ]
$\overline{\dot{m}}_{FA}$ mass of fly ash within the period considered [Mg]
$\overline{C}_{HM_{FA.clean}}$ average concentration of heavy metal in fly ash (in mass pollutant/mass fly ash [g/Mg])
A activity rate within the period considered [GJ]

Measured data should also be used to replace the default values of Equation (13) for $C_{HM_{FA.clean}}$ and C_{FG}.

6 RELEVANT ACTIVITY STATISTICS

In general, the published statistics do not include point sources individually. Information on this level should be obtained directly from each plant operator.

On a national level, statistics can be used for the determination of fuel consumption, installed capacity and/or types of boilers mainly used. The following statistical publications can be recommended:

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg 1992
- Commission of the European Communities (ed.): Energy in Europe - Annual Energy Review; Brussels 1991
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank, 1993
- OECD (ed.): Environmental Data, Données OCDE sur l’environnement; compendium 1993
- Commission of the European Communities (ed.): Energy in Europe; 1993 - Annual Energy Review; Special Issue; Brussels 1994

– EUROSTAT (ed.): Panorama of EU Industry'94; Office for official publications of the European Communities; Luxembourg 1994

7 POINT SOURCE CRITERIA

Point source criteria for a combustion plant according to CORINAIR are given in chapter AINT and in /41/.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Tables 23 - 31 list emission factors for all pollutants considered, except for SO_2. For SO_2 emission factors have to be calculated individually (see Equation (5)). Sulphur contents of different fuels are given. The emission factors have been derived from the literature, from the calculations presented here (see also Section 4) and from recommendations from expert panel members. All emission factor tables have been designed in a homogenous structure: Table 20 contains the allocation of SNAP activities used related to combustion installations, where three classes are distinguished according to the thermal capacity installed. Table 21 includes the main types of fuel used within the CORINAIR90 inventory. Table 22 provides a split of combustion techniques (types of boilers, etc.); this standard table has been used for all pollutants. The sequence of the emission factor tables is:

Table 20:	SNAP code and SNAP activity related to the thermal capacities installed in combustion plants
Table 21:	Selection of relevant fuels from NAPFUE and lower heating values for boilers, gas turbines and stationary engines
Table 22:	Standard table for emission factors for the relevant pollutants
Table 23:	S-contents of selected fuels
Table 24:	NO_x emission factors [g/GJ] for combustion plants
Table 25:	NO_x emission factors [g/GJ] for coal combustion according to the model description (see Annexes 4 and 5)
Table 26:	NMVOC emission factors [g/GJ] for combustion plants (coal combustion)
Table 27:	CH_4 emission factors [g/GJ] for combustion plants
Table 28:	CO emission factors [g/GJ] for combustion plants
Table 29:	CO_2 emission factors [kg/GJ] for combustion plants
Table 30:	N_2O emission factors [g/GJ] for combustion plants
Table 31:	Heavy metal emission factors [g/Mg] for combustion plants

References of the emission factors listed are given in footnotes of the following tables. Quality codes are not available in the literature.

Table 20: SNAP code and SNAP activity related to the thermal capacities installed in combustion plants

Thermal capacity [MW]	SNAP code	SNAP activity
>= 300	010101	Public power and co-generation combustion plants
	010201	District heating combustion plants
	010301	Petroleum and/or gas refining plants
	010401	Solid fuel transformation plants
	010501	Coal mining, oil, gas extraction/distribution plants
	020101	Commercial and institutional plants
	030101	Industrial combustion plants
>=50 up to < 300	010102	Public power and co-generation combustion plants
	010202	District heating combustion plants
	020102	Commercial and institutional plants
	020201	Residential combustion plants
	020301	Plants in agriculture, forestry and fishing
	030102	Industrial combustion plants
< 50	010103	Public power and co-generation combustion plants
	010203	District heating combustion plants
	020103	Commercial and institutional plants
	020202	Residential combustion plants
	020302	Plants in agriculture, forestry and fishing
	030103	Industrial combustion plants

Table 21: Selection of relevant fuels from NAPFUE and lower heating values for boilers, gas turbines and stationary engines

Type of fuel according to NAPFUE					NAPFUE code	H_u [MJ/kg][2]
s	coal	hc	coking [1]	GHV[11] > 23,865 kJ/kg	101	29.3[4]
s	coal	hc	steam [1]	GHV[11] > 23,865 kJ/kg	102	29.3[4]
s	coal	hc	sub-bituminous	17,435 kJ/kg < GHV[11] < 23,865 kJ/kg	103	20.6
s	coal	hc/bc	patent fuels	from hard/sub-bituminous coal	104	
s	coal	bc	brown coal/lignite	GHV[11] < 17,435 kJ/kg	105	12.1
s	coal	bc	briquettes		106	19.5[4]; 18.6[5]
s	coke	hc	coke oven		107	26.3[10]
s	coke	bc	coke oven		108	29.9[7]
s	coke		petroleum		110	30[10]
s	biomass		wood		111	12.4[4], 16[10]
s	biomass		charcoal		112	
s	biomass		peat		113	9.5[10]
s	waste		municipal		114	7.5[4]
s	waste		industrial		115	8.4[8]
s	waste		wood	except wastes similar to wood	116	
s	waste		agricultural	corncobs, straw etc.	117	
l	oil		residual		203	41.0[4]
l	oil		gas		204	42.7[4], 42.5[10]
l	oil		diesel	for road transport	205	
l	kerosene				206	
l	gasoline		motor		208	43.5[4]
l	naphtha				210	
l	black liquor				215	
g	gas		natural	except liquified natural gas	301	heavy 39.7 MJ/m^3 [3], light 32.5 MJ/m^3 [3]
g	gas		liquified petroleum gas		303	45.4[10]
g	gas		coke oven		304	19.8[10]
g	gas		blast furnace		305	3.0[10]
g	gas		coke oven and blast furnace gas		306	
g	gas		waste		307	
g	gas		refinery	not condensable	308	48.4[6], 87 MJ/m^3 [10]
g	gas		biogas		309	34.7[9]
g	gas		from gas works		311	

[1] A principal differentiation between coking coal and steam coal is given in section 3.2. Further differentiation between coking coal and steam coal can be made by using the content of volatiles: coking coal contains 20 - 30 wt.-% volatiles (maf), steam coal contains 9.5 - 20 wt.-% volatiles (maf) (based on official UK subdivision). This is necessary if no information concerning the mean random reflectance of vitrinite (see Section 3.2) is available.

[2] H_u = lower heating value; lower heating values for coals from different countries are given in Annexes 7 and 8 and for solid, liquid and gaseous fuels in (/88/, Table 1-2).

[3] given under standard conditions

[4] Kolar 1990 /17/

[5] /98/

[6] MWV 1992 /97/

[7] Boelitz 1993 /78/

[8] Schenkel 1990 /105/

[9] Steinmüller 1984 /107/

[10] NL-handbook 1988 /99/

[11] GHV = Gross heating value

Table 22: Standard table of emission factors for the relevant pollutants

						Thermal boiler capacity [MW][4]																				no specification
						>= 300			>= 50 and < 300						< 50											
						Type of boiler			Type of boiler						Type of boiler							GT[10]		Stat. E.[11]		CORINAIR90[12]
						DBB[5]	WBB[6]	FBC[7]	DBB	WBB	FBC[7]		GF[8]		DBB	WBB	FBC[7]			GF						
Type of fuel[1]			NAPFUE code[1]	H_u[2] [MJ/kg]	P1[3]	Primary measures[9]	Primary measures[9]	CFBC			CFBC	PFBC	ST1	ST2			AFBC	CFBC	PFBC	ST1	ST2	SC	CC	CI	SI	
s	coal	hc																								
s	coal	hc																								
s	coal	hc																								
s	coal	bc	...	...	...																					
s	coke																									
s	biomass																									
s	waste																									
l	oil																									
g	gas																									

[1] the type of fuel is based on the NAPFUE code, see table 21

[2] H_u = lower heating value, when different from table 21

[3] relevant parameter of fuel composition for SO_2: P1 = sulphur content of fuel;

[4] the corresponding SNAP-codes are listed in table 20

[5] DBB - Dry bottom boiler

[6] WBB - Wet bottom boiler

[7] FBC - Fluidised bed combustion; CFBC = Circulating FBC; PFBC = Pressurised FBC (Dense FBC); AFBC = Atmospheric FBC

[8] GF - Grate firing; ST1 and ST2 are different types of stoker (e.g. travelling stoker, spreader stoker)

[9] Primary measures are described by reduction efficiency

[10] GT = Gas turbine; SC = Simple cycle; CC = Combined cycle

[11] Stat. E. = Stationary engine; CI = Compression ignition; SI = Spark ignition

[12] CORINAIR90 data on combustion plants as point sources

Table 23: S-contents of selected fuels [1]

Type of fuel				NAPFUE code	Sulphur content of fuel value [2]	range	unit
s	coal [3]	hc	coking	101		0.4 - 6.2	wt.-% (maf)
s	coal [3]	hc	steam	102		0.4 - 6.2	wt.-% (maf)
s	coal [3]	hc	sub-bituminous	103		0.4 - 6.2	wt.-% (maf)
s	coal [3]	bc	brown coal/lignite	105		0.4 - 6.2	wt.-% (maf)
s	coal	bc	briquettes	106		0.25 - 0.45[13]	wt.-% (maf)
s	coke	hc	coke oven	107		< 1 [5]	wt.-% (maf)
s	coke	bc	coke oven	108		0.5 - 1 [5] [6]	wt.-% (maf)
s	coke		petroleum	110			
s	biomass		wood	111		< 0.03 [5]	wt.-% (maf)
s	biomass		charcoal	112		< 0.03 [5]	wt.-% (maf)
s	biomass		peat	113			
s	waste		municipal	114			
s	waste		industrial	115			
s	waste		wood	116			
s	waste		agricultural	117			
l	oil		residual	203		0.3 [8] - 3.5 [9]	wt.-%
l	oil		gas	204	0.3 [11]	0.08 - 1.0	wt.-%
l	oil		diesel	205	0.3 [11]		wt.-%
l	kerosene			206			
l	gasoline		motor	208		< 0.05[12]	wt.-%
l	naphtha			210			
l	black liquor			215			
g	gas[4]		natural	301	(0.0075) [10]		$g \cdot m^{-3}$
g	gas		liquified petroleum gas	303	-		
g	gas		coke oven	304	8		$g \cdot m^{-3}$
g	gas		blast furnace	305	$45 \cdot 10^{-3}$ [10]		$g \cdot m^{-3}$
g	gas		coke oven and blast furnace gas	306			
g	gas		waste	307			
g	gas		refinery	308		<= 8 [10]	$g \cdot m^{-3}$
g	gas		biogas	309			
g	gas		from gas works	311			

1) for emission factor calculation see Section 4.1, and Annexes 2 and 3

2) recommended value

3) for complete coal composition see Annexes 7 and 8

4) only trace amounts

5) Marutzky 1989 /94/

6) Boelitz 1993 /78/

8) Mr. Hietamäki (Finland): Personal communication

9) Referring to NL-handbook 1988 /99/ the range is 2.0 - 3.5

10) NL-handbook 1988 /99/

11) 87/219 CEE 1987 /113/

12) $\alpha_s \sim 0$

13) Davids 1986 /46/

Table 24: NO$_x$ emission factors [g/GJ] for combustion plants

Type of fuel				NAPFUE code	Thermal boiler capacity [MW]				
					>= 300[32)]			>= 50 and < 300[32)]	
					Type of boiler[43)]			Type of boiler	
					DBB/boiler[27)]	WBB	FBC CFBC	DBB/boiler[27)]	WBB
s	coal	hc	coking	101	see table 25	see table 25	70[1)]	see table 25	see table 25
s	coal	hc	steam	102	see table 25	see table 25	70[1)]	see table 25	see table 25
s	coal	hc	sub-bitumious	103	see table 25	see table 25	70[1)]	see table 25	see table 25
s	coal	bc	brown coal/lignite	105	see table 25	X	70[1)]	see table 25	X
s	coal	bc	briquettes	106					
s	coke	hc	coke oven	107					
s	coke	bc	coke oven	108					
s	coke		petroleum	110				300[1)]	
s	biomass		wood	111				200[1),15)]	
s	biomass		charcoal	112					
s	biomass		peat	113	300[1),28)]			300[1)]	
s	waste		municipal	114					
s	waste		industrial	115					
s	waste		wood	116					
s	waste		agricultural	117					
l	oil		residual	203	210[1),29)], 260[1),28)], 155 - 296[19),20)]	X	X	150[1),29)], 170[1),29)], 190[1),30)], 210[1),30)]	X
l	oil		gas	204	64 - 68[21)]			100[1)]	
l	oil		diesel	205					
l	kerosene			206					
l	gasoline		motor	208					
l	naphtha			210					
l	black liquor			215					
g	gas		natural	301	170[1)], 48 - 333[22) 23)]	X	X	125[1),25)], 150[1),26)], 48 - 333[22),23),24)]	X
g	gas		liquified petroleum gas	303	88 - 333[23),24)]			88 - 333[23),24)]	
g	gas		coke oven	304	150[1)], 88 - 333[23) 24)]			110[1),25)], 130[1),26)], 88 - 333[23),24)]	
g	gas		blast furnace	305	95[1)], 88 - 333[23) 24)]			65[1)25)], 80[1),26)], 88 - 333[23),24)]	
g	gas		coke oven and blast furnace gas	306	88 - 333[23),24)]			88 - 333[23),24)]	
g	gas		waste	307	88 - 333[23),24)]			88 - 333[23),24)]	
g	gas		refinery	308	88 - 333[23),24)]			140[1)], 88 - 333[23),24)]	
g	gas		biogas	309	88 - 333[23),24)]			88 - 333[23),24)]	
g	gas		from gas works	311					

to be continued

Table 24: continued

Thermal boiler capacity [MW]													no specification
> 50 and < 300 [32]			< 50[32]										
Type of boiler			Type of boiler						Gas turbine		Stationary engine		CORINAIR 90[44]
FBC		GF	DBB/boiler[27]	WBB	FBC			GF					
PFBC	CFBC				PFBC	CFBC	AFBC		SC	CC	CI	SI	
150[1]	70[1]	150[1]	180[1,31], 230[1,29]			70[1]		150[1]					545[44]
150[1]	70[1]	150[1]	180[1,31], 230[1,29]			70[1]		150[1]					36.5 - 761[44]
150[1]	70[1]	150[1]	180[1,31], 230[1,29]			70[1]		150[1]					20.5 - 1,683[44]
150[1]	70[1]	150[1]	180[1,31], 230[1,29]			70[1]		150[1]					180 - 380[44]
			300[1]		300[1]	300[1]							33.3 - 175[44]
		200[1], 33 - 115[15]	200[1], 33 - 115[15]					200[1,15]					50 - 200[44]
160[1]	100[1]	230[1]	280[1]		160[1]	100[1]							150 - 240[44]
		90 - 463[16,17]						90 - 463[16,17]					220[44]
		139 - 140[18]						139 - 140[18]					
													80 - 200[44]
		88[6]											160[44]
			140[1,29], 180[1,30]						250[45]		1,090-1,200[45]		24 - 370[44]
			80[1], 100[1]						120 [1,35], 350[1,33], 380[1,34], 780[1,36]		100 - 1,200[45]		50 - 269[44]
									100 - 700[45], 300[46]		600[1,37,42], 1,200[1,38]	1,000[1,40,42], 1,800[1,39,42]	
													180[44]
													20 - 440[44]
			100[1], 48 - 333[22,23,24]						150 - 360[45]		600[1,37,42], 1,200[1,38,42]	1,000[1,40,42], 1,800[1,39,42]	22 - 350[44]
									188[4,41]	187[4,41]			
			88 - 333[23,24]										35 - 100[44]
			90[1,23,24]										70 - 571[44]
			88 - 333[23,24]										6.7 - 330[44]
			88 - 333[23,24]										
			88 - 333[23,24]										35 - 327[44]
			140[1,23,24]						150-151[45]				35 - 140[44]
			88 - 333[23,24]										60[44]

[1] CORINAIR 1992 /80/, without primary measures

[2] Ratajczak 1987 /103/, Kolar 1990 /17/

[3] Lim 1982 /91/, Kolar 1990 /17/

[4] Mobley 1985 /96/, Kolar 1990 /17/

[5] LIS 1977 /92/

[6] Radian 1990 /102/, IPCC 1994 /88/, without primary measues

[7] UBA 1985 /111/, Kolar 1990 /17/

[8] Kolar 1990 /17/

[9] Bartok 1970 /75/, Kolar 1990 /17/

[10] Kremer 1979 /90/, Kolar 1990 /17/

[11] UBA 1981 /110/, Kolar 1990 /17/

[12] LIS 1987 /93/

[13] Davids 1984 /81/, Kolar 1990 /17/

[14] Ministry 1980 /95/, Kolar 1990 /17/

[15] utility boiler: 112[6], commercial boiler: 33[6], industrial boiler: 115[6]

[16] utility boiler (GF): 140[6], commercial boiler: 463[6], commercial open burning: 3[6] kg/Mg waste

[17] GF: 90 - 180[8]

[18] industrial combustion (mass burn.): 140[6], industrial combustion (small burner): 139[6]

[19] DBB (power plants): 240[11], 245[10], 296[9], 270[10]

[20] utility boiler: 201[6], commercial boiler: 155[6], industrial boiler: 161[6]

[21] utility boiler: 68[6], commercial boiler: 64[6]

[22] utility boiler: 267[6], commercial boiler: 48[6], industrial boiler: 67[6]

[23] power plant: 160[9], 170[10], 185[10], 190[11], 215[10], 333[13]

[24] industry: 88[9], 100[11]

[25] 50 - 100 MW thermal

[26] 100 - 300 MW thermal

[27] DBB for coal combustion; boiler for other fuel combustion

[28] wall firing

[29] tangential firing

[30] wall/bottom firing

[31] wall/tangential firing

[32] The emission factors [g/GJ] are given at full load operating modus.

[33] no specification

[34] with diffusion burner

[35] modern with pre-mixer

[36] derived from aero engines

[37] prechamber injection

[38] direct injection

[39] 4 stroke engines

[40] 2 stroke engines

[41] 80[1,35], 250[1,33], 160 - 480[1,34], 650[1,36]

[42] 1000[1,33]

[43] The formation of thermal-NO is much more influenced by the combustion temperature than by the burner arrangement within the boiler /64/. Therefore, no emission factors are given for different burner arrangements (e.g. tangential firing).

[44] CORINAIR90 data of combustion plants as point sources with thermal capacity of > 300, 50 - 300, <50 MW

[45] CORINAIR90 data of combustion plants as point sources

[46] AP42 /115/

Table 25: NO_x emission factors [g/GJ] for coal combustion according to the model (see Annexes 4 and 5)

Type of fuel			coal mining country	NAPFUE code	H_u [MJ/kg] (maf)	Thermal boiler capacity [MW] >= 50 [1)									
						Type of boiler									
						DBB					WBB				
						PM0[2)	PM1	PM2	PM3	PM4	PM0	PM1	PM2	PM3	PM4
						η= 0	η= 0.20	η=0.45	η=0.45	η=0.60	η= 0	η= 0.20	η=0.45	η=0.40	η=0.60
s	coal	hc	Australia	(101)	34	568	454	312	312	227	703	562	387	422	281
			Canada	(101)	33	500	405	278	278	202	627	501	345	376	251
			China	(101)	32	413	331	227	227	165	512	409	281	307	205
			Columbia	(101)	32	535	428	394	394	214	662	529	364	397	265
			Czech Republic	(101)	34	483	387	266	266	193	598	479	329	359	239
			France	101	35	374	299	205	205	149	463	370	254	278	185
			Germany RAG	102	35	384	307	211	211	154	476	381	262	285	190
			Germany others	101	30	495	396	272	272	198	613	490	337	368	245
			CIS	(101)	32	308	247	169	169	123	382	305	210	229	153
			Hungary	101	34	401	320	220	220	160	496	397	273	298	198
			India	103	30	551	441	303	303	220	682	545	375	409	273
			South Africa	(101)	32	569	456	313	313	228	705	504	388	423	282
			USA	(101)	34	563	450	310	310	225	697	558	383	418	279
			Venezuela	(101)	34	588	471	324	324	235	728	583	401	437	291
						η= 0	η= 0.20	η=0.45	η=0.40	η=0.60					
s	coal	bc	Czech Republic	105	28	506	405	278	304	202					
			Germany												
			- Rheinisch Coal	105	27	325	260	179	195	130					
			- Middle Germany	105	25	504	403	277	302	202					
			- East Germany	105	26	539	431	296	323	215					
			Hungary-1	105	36	379	303	208	227	151					
			Hungary-2	103	28	379	304	209	228	152					
			Poland	105	25	531	425	292	319	213					
			Portugal	105	25	461	369	254	277	185					
			Turkey-2	103	27	725	580	399	435	290					

[1) The emission factors [g/GJ] are given at full load operating modus.

[2) PM0 ... PM4 = most used combinations of primary measures; η = reduction efficiencies [ ]

PM0 - no primary measures
PM1 - one primary measure: LNB
PM2 - two primary measures: LNB/SAS
PM3 - two primary measures: LNB/OFA
PM4 - three primary measures: LNB/SAS/OFA

Table 26: NMVOC emission factors [g/GJ] for combustion plants

Type of fuel				NAPFUE code	Thermal boiler capacity [MW]					no specification CORINAIR90[6]
					>= 50		< 50			
					boiler	GF	boiler	Gas turbine	Stationary engine	
s	coal	hc	coking	101	3[5], 30[2]	50[2]	600[1]			3[6]
s	coal	hc	steam	102	3[5], 30[2]	50[2]	600[1]			1 - 15[6]
s	coal	hc	sub-bituminous	103	3[5], 30[2]	50[2]	600[1]			1.5 - 15[6]
s	coal	bc	brown coal/lignite	105	30[2,3]	50[2]				1.5 - 15[6]
s	coal	bc	briquettes	106			150[1]			
s	coke	hc	coke oven	107			12[1]			5 - 15[6]
s	coke	bc	coke oven	108						
s	coke		petroleum	110						1.5[6]
s	biomass		wood	111	80[2]		100[5], 150[1], 400[4]			10 - 48[6]
s	biomass		charcoal	112						
s	biomass		peat	113	30[2,3]	30[2]				3 - 48[6]
s	waste		municipal	114						10[6]
s	waste		industrial	115						
s	waste		wood	116						40 - 48[6]
s	waste		agricultural	117						50[6]
l	oil		residual	203	10[2,3]			3[7]	50[7]	1.5 - 47.6[6]
l	oil		gas	204	5[2]		15[1]	5[2], 1.5 - 2[7]	1.5 - 100[7], 100[2]	1.5 - 9.3[6]
l	oil		diesel	205						
l	kerosene			206						3[6]
l	gasoline		motor	208						
l	naphtha			210						3[6]
l	black liquor			215						3[6]
g	gas		natural	301	5[2]			5[2], 2.5 - 4[7]	200[2]	2 - 4[6]
g	gas		liquified petroleum gas	303						2 - 2.6[6]
g	gas		coke oven	304						2.5 - 167[6]
g	gas		blast furnace	305						1 - 2.5[6]
g	gas		coke oven and blast furnace gas	306						
g	gas		waste	307						2.5[6]
g	gas		refinery	308	25[2]			2.5[7]		2.1 - 10[6]
g	gas		biogas	309						2.5[6]
g	gas		from gas works	311						

[1] LIS 1977 /92/ [2] CORINAIR 1992 /80/ [3] DBB only [4] small consumers cf. /24/ [5] power plants cf. /24/

[6] CORINAIR90 data of combustion plants as point sources with a thermal capacity of > 300, 50 - 300, < 50 MW

[7] CORINAIR90 data, point sources

Table 27: CH_4 emission factors [g/GJ] for combustion plants

Tpe of fuel				NAPFUE code	Type of combustion										stat. E.	no speci- fication CORINAIR90$^{5)}$
					Utility combustion			Commercial comb.		Industrial combustion						
					DBB/WBB FBC/ boiler$^{3)}$	GF stoker		boiler	GF	boiler	GF stoker		GT			
						spreader	travell.				spreader	travell.	SC	CC		
s	coal	hc	coking	101	0.6$^{1)}$	0.7$^{1)}$		10$^{1)}$		2.4$^{1)}$						0.3 - 15$^{5)}$
s	coal	hc	steam	102	0.6$^{1)}$	0.7$^{1)}$		10$^{1)}$		2.4$^{1)}$						1.5 - 15$^{5)}$
s	coal	hc	sub-bituminous	103	0.6$^{1)}$	0.7$^{1)}$		10$^{1)}$		2.4$^{1)}$						0.3 - 15$^{5)}$
s	coal	bc	brown coal/lignite	105	0.6$^{1)}$	0.7$^{1)}$		10$^{1)}$		2.4$^{1)}$						
s	coal	bc	briquettes	106												
s	coke	hc	coke oven	107												0.2 - 15$^{5)}$
s	coke	bc	coke oven	108												
s	coke		petroleum	110												1.5$^{5)}$
s	biomass		wood	111	18$^{1)}$			15$^{1)}$		15$^{1)}$						1 - 40$^{5)}$
s	biomass		charcoal	112												
s	biomass		peat	113												1 - 39$^{5)}$
s	waste		municipal	114				6.5$^{1),4)}$								1$^{5)}$
s	waste		industrial	115												10$^{5)}$
s	waste		wood	116												4 - 40$^{5)}$
s	waste		agricultural	117				9$^{1),4)}$								32$^{5)}$
l	oil		residual	203	0.7$^{1)}$			1.6$^{1)}$		2.9$^{1)}$			3$^{5)}$		3$^{6)}$	0.1 - 10$^{5)}$
l	oil		gas	204	0.03$^{1)}$			0.6$^{1)}$					1 - 8$^{5)}$		1.5$^{6)}$	0.1 - 8$^{5)}$
l	oil		diesel	205												
l	kerosene			206												7$^{5)}$
l	gasoline		motor	208												
l	naphtha			210												3$^{5)}$
l	black liquor			215												1 - 17.7$^{5)}$
g	gas		natural	301	0.1$^{1)}$			1.2$^{1)\ 2)}$		1.4$^{1)}$			2.5 - 4$^{6)}$			0.3 - 4$^{5)}$
													5.9$^{1)}$	6.1$^{1)}$		
g	gas		liquified petroleum gas	303												1 - 2.5$^{5)}$
g	gas		coke oven	304												0.3 - 4$^{5)}$
g	gas		blast furnace	305												0.3 - 2.5$^{5)}$
g	gas		coke oven and blast furnace gas	306												
g	gas		waste	307												2.5$^{5)}$
g	gas		refinery	308												0.1 - 2.5$^{5)}$
g	gas		biogas	309									2.5$^{6)}$			0.5 - 2.5$^{5)}$
g	gas		from gas works	311												

1) Radian 1990 /102/, IPCC 1994 /88/ 2) for all types of gas 3) DBB/WBB/FBC for coal combustion; boiler for fuel combustion 4) open burning

5) CORINAIR90 data of combustion plants as point sources with thermal capacity of >300, 50 - 300 and <50 MW

6) CORINAIR90 data, point sources

Table 28: CO emission factors [g/GJ] for combustion plants

Type of fuel				NAPFUE code	Type of combustion										no specification
					Utility combustion			Commercial comb.		Industrial combustion			GT	stat. E.	CORINAIR90$^{9)}$
					DBB/WBB/ boilers$^{1)}$	GF stoker		boiler	GF	DBB/WBB/ boiler$^{1)}$	GF stoker				
						spreader	travell.				spreader	travelling			
s	coal	hc	coking	101	$14^{3)}$	$121^{3)}$		$195^{3)}$		$9.7^{2)}$, $13^{4)}$	$81^{2)}$, $115^{4)}$	$97.2^{2)}$			$15^{9)}$
s	coal	hc	steam	102	$14^{3)}$	$121^{3)}$		$195^{3)}$		$9.7^{2)}$, $13^{4)}$	$115^{4)}$	$9.7^{2)}$			$10 - 175.2^{9)}$
s	coal	hc	sub-bituminous	103	$14^{3)}$	$121^{3)}$		$195^{3)}$		$9.7^{2)}$, $13^{4)}$	$81^{2)}$, $115^{4)}$	$97.2^{2)}$			$12 - 246.9^{9)}$
s	coal	bc	brown coal/lignite	105	$14^{3)}$	$121^{3)}$		$195^{3)}$		$16^{2)}$, $13^{4)}$	$133^{2)}$, $115^{4)}$	$160^{2)}$			$9.6 - 64.4^{9)}$
s	coal	bc	briquettes	106											
s	coke	hc	coke oven	107											$102 - 121^{9)}$
s	coke	bc	coke oven	108											
s	coke		petroleum	110											$15^{9)}$
s	biomass		wood	111	$1,473^{3)}$			$199^{3)}$		$1,504^{3)}$					$30 - 300^{9)}$
s	biomass		charcoal	112											
s	biomass		peat	113											$30 - 160^{9)}$
s	waste		municipal	114		$98^{3),6)}$		$19^{3)}$			$19^{3)7)}$, $96^{3)7)}$, 42 kg/Mg$^{3),8)}$				$30^{9)}$
s	waste		industrial	115											
s	waste		wood	116											$12 - 300^{9)}$
s	waste		agricultural	117				58 kg/Mg$^{3),8)}$							$20^{9)}$
l	oil		residual	203	$15^{3)}$			$17^{3)}$		$15^{3)}$			$10 - 15^{10)}$	$100^{10)}$	$3 - 32.6^{9)}$
l	oil		gas	204	$15^{3)}$			$16^{3)}$		$12^{3)}$			$10 - 20^{10)}$ $20.6^{11)}$	$12 - 1,130^{10)}$	$10 - 46.4^{9)}$
l	oil		diesel	205											
l	kerosene			206											$12^{9)}$
l	gasoline		motor	208											
l	naphtha			210											$15^{9)}$
l	black liquor			215											$11.1 - 314^{9)}$
g	gas		natural	301	$19^{3)}$			$9.6^{3)}$		$17^{3)}$, $13^{5)}$				$10 - 20^{10)}$, $32^{3)}$	$0.05 - 60^{9)}$
g	gas		liquified petroleum gas	303											$10 - 13^{9)}$
g	gas		coke oven	304											$0.03 - 130^{9)}$
g	gas		blast furnace	305											$0.3 - 64.4^{9)}$
g	gas		coke oven and blast furnace gas	306											
g	gas		waste	307											$0.1 - 25.5^{9)}$
g	gas		refinery	308										$10^{10)}$	$2 - 15^{9)}$
g	gas		biogas	309											$13^{9)}$
g	gas		from gas works	311											

1) DBB/WBB for coal combustion; boiler for other fuel combustion
2) EPA 1987 /85/, CORINAIR 1992 /80/
3) Radian 1990 /102/, IPCC 1994 /88/, without primary measure
4) OECD 1989 /100/, CORINAIR 1992 /80/
5) CORINAIR 1992 /80/, part 8
6) grate firing without specification
7) small combustion 19 g/GJ, mass burning 96 g/GJ
8) open burning
9) CORINAIR90 data of combustion plants as point sources with a thermal capacity of > 300, 50 - 300, < 50 MW
10) CORINAIR90 data, point sources
11) AP42 /115/

Table 29: CO_2 emission factors [kg/GJ] for combustion plants

				NAPFUE	Emission factors		
Type of fuel				code	value	range	remarks
s	coal	hc	coking	101		92 - 93 5), 89.6 - 94 2)	
s	coal	hc	steam	102	93.7 3), 92 5)	92 - 93 5), 10 - 98 2)	
s	coal	hc	sub-bituminous	103	94.7 3)	91 - 115.2 2)	
s	coal	bc	brown coal/lignite	105	100.2 3)	94 - 107.9 2), 110 - 113 5)	
s	coal	bc	briquettes	106	98	97 - 99 5)	
s	coke	hc	coke oven	107	95.9 4), 108 1)	100 - 105 5), 105 - 108 2)	
s	coke	bc	coke oven	108		96 - 111 5)	
s	coke		petroleum	110	101 5), 121.2 4), 100.8 2)		
s	biomass		wood	111	100 1), 124.9 4)	92 - 100 2)	
s	biomass		charcoal	112			
s	biomass		peat	113	98 5)	102 - 115 2)	
s	waste		municipal	114	15 5), 28 2)	109 - 141 1)	
s	waste		industrial	115		13.5 - 20 5)	
s	waste		wood	116		83 - 100 2)	
s	waste		agricultural	117			
l	oil		residual	203	75.8 4), 76.6 3), 78 5)	15 - 93 2)	petroleum oil 72.6 3)
l	oil		gas	204	72.7 4), 74 5), 75 1)	73 - 74 5), 57 - 75 2)	
l	oil		diesel	205	72.7 4), 73 5)		
l	kerosene			206	73.3 2)	72 - 74 5)	
l	gasoline		motor	208	70.8 3), 71.7 4), 72.2 1)	72 - 74 5)	
l	naphtha			210	72.6 3), 74 2)		
l	black liquor			215		100 - 110 2)	
g	gas		natural	301	55.5 3), 60.8 4)	55 - 56 5), 44 - 57 2)	
g	gas		liquified petroleum gas	303		64 - 65 5), 57 - 65 2)	
g	gas		coke oven	304	44 5)	44 - 49 5), 41.6 - 90 2)	
g	gas		blast furnace	305	105 5)	100 - 105 5), 92 - 280 2)	
g	gas		coke oven and blast furnace gas	306			
g	gas		waste	307		44.4 - 57 2)	
g	gas		refinery	308	60 5)		
g	gas		biogas	309	75 2)	10.5 - 73.3 2)	
g	gas		from gas works	311	52 2)		

[1] Schenkel 1990 /105/

[2] CORINAIR90 data on combustion plants as point sources with thermal capacity of > 300, 50 - 300, < 50 MW

[3] IPCC 1993 /87/

[4] Kamm 1993 /89/

[5] BMU 1994 /77/

Table 30: N_2O emission factors [g/GJ] for combustion plants

Type of fuel				NAPFUE code	Type of boiler								GT	stat. E.	no speci-fication CORINAIR90$^{4)}$
					DBB		WBB		FBC		GF				
					value	remarks	value	remarks	value	remarks	value	remarks			
s	coal	hc	coking	101	0.8 $^{1)}$	utility, no PM$^{3)}$	0.8 $^{1)}$	utility, no PM $^{3)}$			0.8 $^{1)}$	utility, no PM $^{3)}$			14$^{4)}$
s	coal	hc	steam	102	0.8 $^{1)}$	utility, no PM$^{3)}$	0.8 $^{1)}$	utility, no PM $^{3)}$			0.8 $^{1)}$	utility, no PM $^{3)}$			2.5 - 100$^{4)}$
s	coal	hc	sub-bituminous	103	0.8 $^{1)}$	utility, no PM$^{3)}$	0.8 $^{1)}$	utility, no PM $^{3)}$			0.8 $^{1)}$	utility, no PM $^{3)}$			2.5 - 30$^{4)}$
s	coal	bc	brown coal/lignite	105	0.8 $^{1)}$	utility, no PM$^{3)}$					0.8 $^{1)}$	utility, no PM $^{3)}$			1.4 - 30$^{4)}$
s	coal	bc	briquettes	106											
s	coke	hc	coke oven	107											1.4 - 25$^{4)}$
s	coke	bc	coke oven	108											
s	coke		petroleum	110											14$^{4)}$
s	biomass		wood	111	4.3 $^{1)}$	commercial, no PM$^{3)}$			4.3 $^{1)}$	commercial, no PM$^{3)}$	4.3 $^{1)}$	commercial, no PM$^{3)}$			1.4 - 75$^{4)}$
s	biomass		charcoal	112											
s	biomass		peat	113											2 - 75$^{4)}$
s	waste		municipal	114					14 - 165 $^{2)}$	g/t waste	11 - 270 $^{2)}$	g/t waste			4$^{4)}$
s	waste		industrial	115											1.4$^{4)}$
s	waste		wood	116											2 - 6$^{4)}$
s	waste		agricultural	117											5$^{4)}$
l	oil		residual	203	46.5 $^{1)}$	commercial, no PM$^{3)}$							2.5 - 14$^{5)}$	2.5$^{5)}$	1.4 - 14.8$^{4)}$
l	oil		gas	204	15.7 $^{1)}$	commercial, no PM$^{3)}$							2 - 3$^{5)}$	2.5$^{5)}$	0.6 - 14$^{4)}$
l	oil		diesel	205											
l	kerosene			206											14$^{4)}$
l	gasoline		motor	208											
l	naphtha			210											14$^{4)}$
l	black liquor			215											1 - 21.4$^{4)}$
g	gas		natural	301	2.4 $^{1)}$	commercial, no PM$^{3)}$								1 - 3$^{5)}$	0.1 - 3$^{4)}$
g	gas		liquified petroleum gas	303											2 - 4.3$^{4)}$
g	gas		coke oven	304											1.1 - 3$^{4)}$
g	gas		blast furnace	305											1.1 - 3$^{4)}$
g	gas		coke oven and blast furnace	306											
g	gas		waste	307											1.1 - 2.5$^{4)}$
g	gas		refinery	308										2.5$^{5)}$	2.5 - 14$^{4)}$
g	gas		biogas	309											1.4 - 2.5$^{4)}$
g	gas		from gas works	311											

$^{1)}$ Radian 1990 /102/, IPCC 1994 /88/ $^{2)}$ DeSoete 1993 /83/, IPCC 1994 /88/ $^{3)}$ PM: Primary measure $^{5)}$ CORINAIR90 data, point sources

$^{4)}$ CORINAIR90 data on combustion plants as point sources with thermal capacity of > 300, 50 - 300, < 50 MW

Table 31: Heavy metal emission factors (g/Mg fuel) for combustion plants

					Thermal boiler capacity [MW]								
					>= 300				>= 50 and < 300				< 50
					Type of boiler				Type of boiler				
Type of fuel			NAPFUE code	Heavy metal element	DBB		WBB		DBB	WBB	FBC	GF	GF
					Dust control [1]	Dust control and FGD [2]	Dust control [1]	Dust control and FGD [2]					
s	coal	hc	101/102	Mercury	0.05 - 0.2	0.02 - 0.08	0.05 - 0.2	0.02 - 0.08					
				Cadmium	0.003 - 0.01	0.0001 - 0.004	0.01 - 0.07	0.004 - 0.03					
				Lead	0.02 - 1.1	0.007 - 0.5	0.3 - 3	0.1 - 1.2					
				Copper	0.01 - 0.4	0.006 - 0.2	0.05 - 0.4	0.05 - 0.2					
				Zinc	0.03 - 1.3	0.01 - 0.5	0.5 - 4	0.2 - 1.6					
				Arsenic	0.03 - 0.3	0.01 - 0.1	0.1 - 0.8	0.04 - 0.3					
				Chromium	0.04 - 0.2	0.02 - 0.06	0.05 - 0.4	0.02 - 0.2					
				Selen	0.01 - 0.03	0.004 - 0.01	-	-					
				Nickel	0.03 - 0.4	0.01 - 0.5	0.2 - 0.5	0.1 - 0.2					
s	coal	bc	105	Mercury	0.05 - 0.2	0.02 - 0.08							
				Cadmium	0.002 - 0.004	0.0008 - 0.001							
				Lead	0.003 - 0.06	0.001 - 0.02							
				Copper	0.004 - 0.02	0.002 - 0.01							
				Zinc	0.01 - 0.2	0.006 - 0.1							
				Arsenic	0.03 - 0.04	0.008 - 0.01							
				Chromium	0.003 - 0.07	0.001 - 0.03							
				Selen	-	-							
				Nickel	0.02 - 0.04	0.01							
l	oil, heavy fuel		203	Mercury	1.0[4]								
				Cadmium	1.0[4]								
				Lead	1.3[4]								
				Copper	1.0[4]								
				Zinc	1.0[4]								
				Arsenic	0.5[4]								
				Chromium	2.5[4]								
				Selen									
				Vanadium	4.4[5]								
				Nickel	35[4]								
g	gas, natural		301	Mercury	0.05 - 0.15 g/TJ[3]								

[1] clean gas particle concentration 50 mg/m

[2] FGD = Flue gas desulphurisation, clean gas particle concentration 20 mg/m^3

[3] 2 mg/m^3 gas UBA 1980 /63/; 5 mg/m^3 PARCOM 1992 /101/

[4] general emission factor according to Stobbelaar 1992 /37/

[5] Jockel 1991 /36/

9 SPECIFIC PROFILES

9.1 SO_x emissions

Sulphur dioxide SO_2 and sulphur trioxide SO_3 are formed in the flame. Emissions of SO_2 and SO_3 are often considered together as SO_x. Due to the equilibrium conditions at furnace temperature, sulphur trioxide SO_3 normally decomposes to sulphur dioxide SO_2. Then the amount of SO_2 in the flue gas is approximately 99 %. Therefore, SO_x is given in this chapter as SO_2.

9.2 NO_x emissions

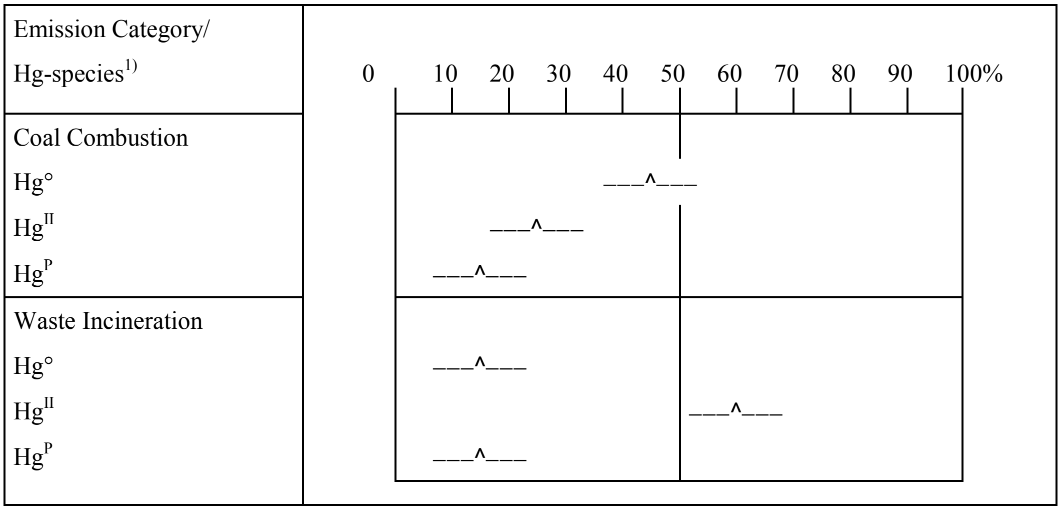
The most important oxides of nitrogen formed with respect to pollution are nitric oxide (NO) and nitrogen dioxide (NO_2), jointly referred to as NO_x. The main compound is NO, which contributes over 90 % to the total NO_x. Other oxides of nitrogen, such as dinitrogen-trioxide (N_2O_3), dinitrogen-tetroxide (N_2O_4), and dinitrogen-pentoxide (N_2O_5), are formed in negligible amounts. Nitrous oxide (N_2O) is considered separrately.

9.3 NMVOC emissions

Due to the minor relevance of NMVOC emissions for power plants no split of species is given.

9.4 Heavy metal emissions

The heavy metals, which are of most environmental concern, are: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn). This selection has been laid down by the UN-ECE Task Force on Heavy Metals, the PARCOM/ATMOS programme (cf. /35/) and the HELCOM programme. In the case of heavy oil combustion, vanadium emissions (V) are also of importance. In fly ash particles most of these elements occur as oxides or chlorides. The contribution of various forms of mercury to the emissions from combustion source categories in Europe is given in the following Figure 2:



[1] Hg° elemental form
Hg^{II} oxidised form
Hg^{P} particle-bound

Figure 2: Contribution of various forms of mercury to the emissions from combustion source categories in Europe in 1987 (in % of total) /29/

10 UNCERTAINTY ESTIMATES

Uncertainties of emission data result from the use of inappropriate or inaccurate emission factors, and from missing or inappropriate statistical information concerning activity data. Uncertainty estimates discussed here are related to the use of emission factors with different background information. At this stage a quantification of the uncertainty related to the use of emission factors is not feasible, due to the limited availability of data. However, the precision of emission estimates can be improved by applying individually determined emission factors.

The aim of the following procedure is to show the Guidebook-user how a lack of information concerning the fuel and technical characteristics of a combustion facility gives rise to a high uncertainty in the allocation of the appropriate emission factor. The whole span of possible emission factors is defined by the specification of the type of fuel used, the type of boiler, and the type of primary and secondary measures. The more information about these topics can be gathered, the smaller the span of possible emission factors becomes.

The following diagram (Figure 3) gives as an example the range of NO_x emission factors [g/GJ] for pulverised coal combustion depending on the level of specification.

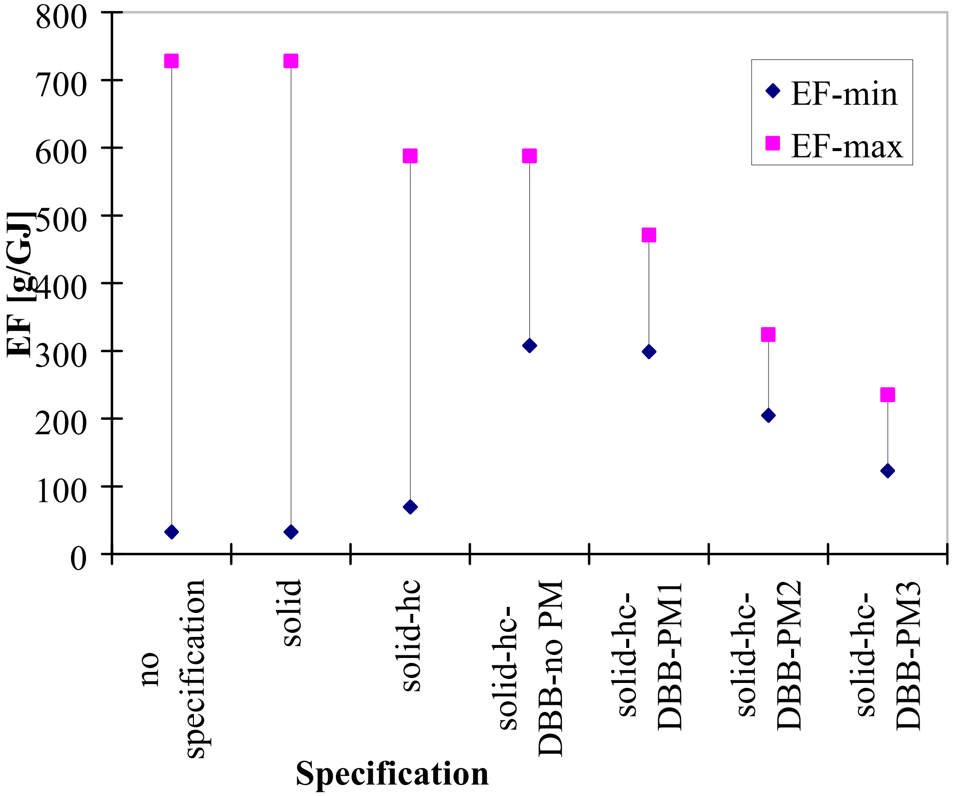


Figure 3: Ranges of NO_x emission factors for the combustion of pulverised coal

The level of specification is defined as follows:

- „no information“	- the whole range of combustion sources is taken into account,
- „solid“	- only solid fuels are taken into account,
- „solid-hc“	- only hard coal is considered,
- „solid-hc-DBB-no PM“	- hard coal and combustion technique are taken into account (here dry bottom boiler (DBB), without primary measures),
- „solid-hc-DBB-PM1“	- hard coal, DBB and primary measures are taken into account with a reduction efficiency of 0.2 ,
- „solid-hc-DBB-PM2“	- hard coal, DBB and primary measures are taken into account with a reduction efficiency of 0.45 ,
- „solid-hc-DBB-PM3“	- hard coal, DBB and primary measures are taken into account with a reduction efficiency of 0.6 .

In Figure 3 a large difference between minimum and maximum emission factors indicates high uncertainties in the allocation of appropriate emission factors. A specification of emission factors only concerning the type of fuel used (e.g. hard coal) is not sufficient. The range of NO_x emission factors for the combustion of pulverised coal is significantly reduced if technique related specifications are considered.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

The weakest aspects discussed here are related to the determination of emission factors. Methodological shortcomings are discussed in this section for the main pollutants SO_2, NO_X and heavy metals.

11.1 SO_2 emissions

The approach for the determination of SO_2 emission factors is based on a simple mass balance calculation as the formation mechanisms of sulphur dioxide within the boiler depend almost entirely on the sulphur input. Therefore, for the formation of sulphur dioxide, fuel characteristics are of main influence. The accuracy of this approach is determined by the following fuel parameters: lower heating value, fuel sulphur content and sulphur retention in ash (see Equation (5)). The sulphur content and the lower heating value can be highly variable between different fuel categories and can furthermore vary to a large extent within one fuel category. Therefore, default values for sulphur content and lower heating value should be avoided. However, if emission factors for SO_2 have to be calculated, representative values for the sulphur content and the lower heating value should be based on measured data from individual fuel analysis.

The sulphur retention in ash α_S depends mainly on the content of alkaline components of the fuel. This is only relevant for coal (e.g. CaO, MgO, Na_2O, K_2O) and for the case of additive injection. For a more precise determination of α_S, the Ca/S ratio (amount of calcium/sulphur content of fuel)[8], the particulate diameter, the surface character of CaO, the temperature (optimum ca. 800 °C), the pressure, the residence time, etc. should be taken into account. Therefore, the assessment of α_S should be based on an extended set of parameters.

Besides the fuel characteristics, the reduction efficiency and availability of secondary measures are of relevance for the determination of the SO_2 emission factors. Default values are proposed in Table 7, but measured data from individual combustion plants should preferably be used.

11.2 NO_X EMISSIONS

The approach for the calculation of NO_X emission factors is based on empirical relations. For fuel-NO only fuel characteristics are taken into account. The formation of thermal-NO increases exponentially with combustion temperatures above 1,300 °C (see /56/). At this

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[8] Alternatively the Ca/S ratio is defined as the amount of additives related to the sulphur content of the flue gas, and is given for a brown coal fired dry bottom boiler as 2.5 - 5 as an example, for a stationary FBC as 2 - 4, for a circulating FBC < 2 etc. /55/.

stage, no satisfactory result has been achieved to determine the thermal-NO formation by using kinetic equations. For inventory purposes, an empirical parameter γ has been introduced (see Annex 5), which represents the fraction of thermal-NO formed. At this stage default values of γ depending on the type of boiler are given. Further work should focus on a more precise determination of this factor.

Load dependence of the pollutant NO_x has been taken into account. For old installations a quantitative relation has been given as an example for German power plants. The validity of this relation should be verified for other countries.

Furthermore, the reduction efficiency of primary or secondary measures are of relevance for the determination of NO_x emission factors. Default values for reduction efficiencies and availabilities are proposed in Tables 10 and 11, but measured data from individual combustion plants should preferably be used.

11.3 Heavy metals

Heavy metals undergo complex transformations during the combustion process and downstream of the boiler, referring to e.g. fly ash formation mechanisms. The approaches for the determination of heavy metal emission factors are based on empirical relations, where fuel and technical characteristics are of main influence. The heavy metal contents can be highly variable between different fuel categories (e.g. coal and heavy fuel oil) and can furthermore vary to a large extent within one fuel category (up to 2 orders of magnitude). Therefore, default values for heavy metal contents in fuel should be avoided and measured values should be used as far as possible.

For inventory purposes, parameters, such as enrichment factors, fractions of fly ash leaving the combustion chamber, fraction of heavy metals emitted in gaseous form, have been introduced. Further work should be invested into a more precise determination of these parameters. In addition, it should be taken into account, that the reduction efficiency of (dust) abatement measures depends on the heavy metal. Heavy metal specific reduction efficiencies should be determined.

11.4 Other aspects

Emission factors for SO_2, NO_2 and CO, whether calculated or given in the tables, are related to full load conditions. In order to assess the relevance of start-up emissions, a detailed investigation has been accomplished by using measured values from different types of boiler (see also Annex 15). The qualitative and quantitative statements obtained in this approach should be verified.

The emission factors have been determined by considering the pollutants separately. Possible mutual interactions between the formation mechanisms of different pollutants (e.g. NO and N_2O) have been neglected and should be assessed in further work.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

This section is not relevant for combustion plants considered as point sources.

13 TEMPORAL DISAGGREGATION CRITERIA

The temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and hourly emission data. Temporal disaggregation of annual emissions released from combustion plants as point sources can be obtained from the temporal change of the production of electrical power or the temporal change of the consumption, taking into account a split into:

- summer and winter time,
- working days and holidays,
- standstill times,
- times of partial load behaviour and
- number of start-ups / type of load design.

This split should be carried out for defined categories of power plants which take into account the main relevant combinations of types of fuel used and types of boiler installed (similar split as used for the emission factor Tables in Section 8).

The disaggregation of annual emissions into monthly, daily or hourly emissions can be based on a step-by-step approach /76/ according to the following equations:

- Monthly emission:

$$E_{M_n} = \frac{E_A}{12} \cdot f_n \tag{25}$$

E_{M_n}	Emission in month n; n = 1, ..., 12 [Mg]
E_A	Annual emission [Mg]
f_n	Factor for month n; n = 1, ..., 12 [ ]

- Daily emission:

$$E_{D_{n,k}} = \frac{E_{M_n}}{D_k} \cdot f_k \cdot \frac{1}{CF_n} \tag{26}$$

$E_{D_{n,k}}$	Emission of day k in month n; k = 1, ..., D_k ; n = 1, ..., 12 [Mg]
E_{M_n}	Emission in month n; n = 1, ..., 12 [Mg]
D_k	Number of days in month n [ ]
f_k	Factor for day k; k = 1, ..., D_k [ ]
CF_n	Correction factor for month n [ ]

- Hourly emission:

$$E_{H_{n,k,l}} = \frac{E_{D_{n,k}}}{24} \cdot f_{n,l} \qquad (27)$$

$E_{H_{n,k,l}}$	Emission in hour l in day k and month n; l = 1, ..., 24; k = 1, ..., D_k ; n = 1, ..., 12 [Mg]
$E_{D_{n,k}}$	Emission of day k in month n; k = 1, ..., D_k ; n = 1, ..., 12 [Mg]
$f_{n,l}$	Factor for hour l in month n; l = 1, ..., 24; n = 1, ..., 12 [ ]
D_k	Number of days in month n [ ]

The factors (relative activities) for month f_n, day f_k and hour $f_{n,l}$ can be related e.g. to the total fuel consumption or the net electricity production in public power plants. Figure 4 gives an example of a split for monthly factors based on the fuel consumption e.g. for Public Power Plants:

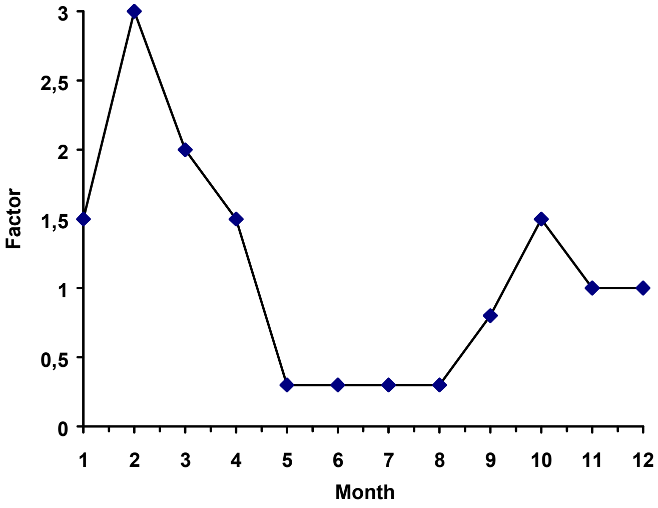
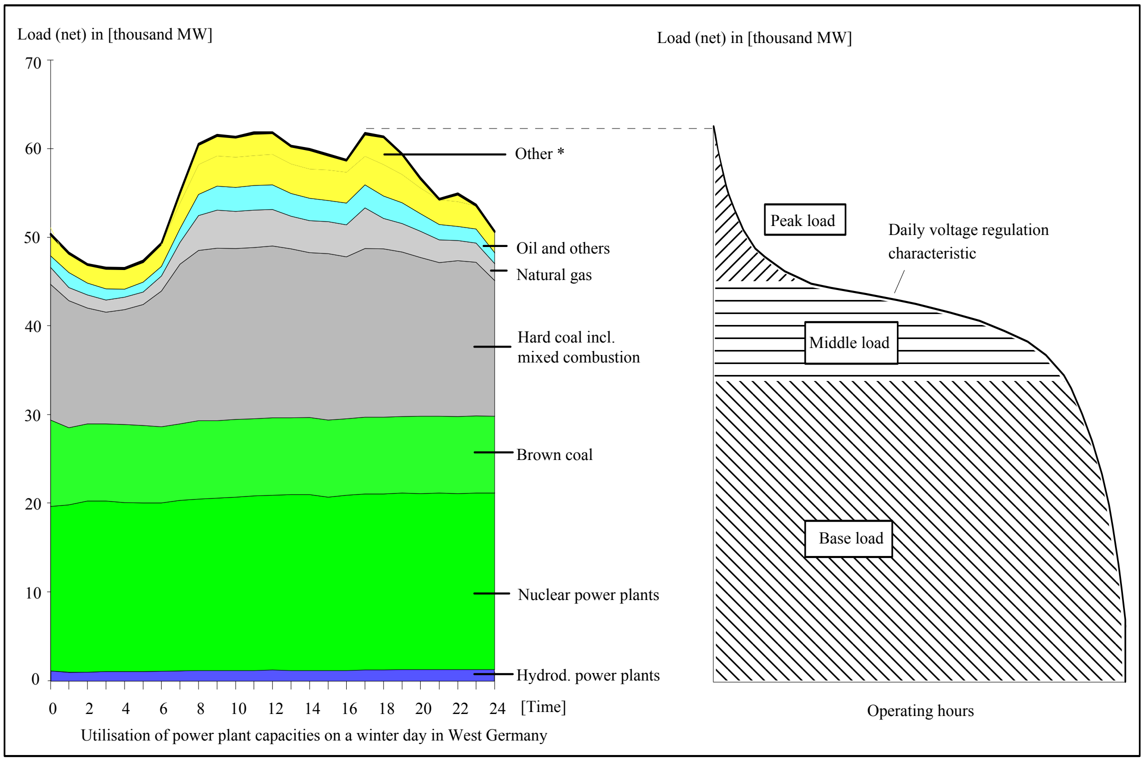


Figure 4: Example of monthly factors for total fuel consumption in Public Power Plants

A split concerning the load design, which determines the annual number of start-ups can be given as follows (see also Table 11):

- Base load: The boiler/plant is normally in continuous operation during the year; start-ups occur relatively seldom (ca. 15 times per year) depending on maintenance periods which occur mostly in summer. The fuel mostly used in base load boilers is brown coal.
- Middle load: The boiler/plant is in operation in order to meet the energy demand on working days (Monday until Friday); start-ups can occur up to 150 times per year. The fuel mostly used in middle load boilers is hard coal.
- Peak load: The boiler/plant is in operation in order to meet the short term energy demand; start-ups can occur up to 200 times per year. The fuels mostly used in peak load boilers are gas or oil.

The allocation of power plants to the different load designs is given as an example in Figure 5.



*Other includes: Storage pump power plants, power supply from industry etc.

Figure 5: Load variation and arrangement of power plants according to the voltage regulation characteristic (cf. /117/, /118/).

It can be assumed that all power plants of a country with the same allocation of fuel, boiler and load have the same temporal behaviour.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

15.1 Computer programme

A computer programme for the calculation of SO_2 and NO_2 emission factors for pulverised coal combustion has been designed, and is available on floppy disc. It has been designed under MICROSOFT EXCEL 4.0 (English version). Default values for the required input data are proposed to the user; a detailed users manual is given in Annex 14. For example, NO_X concentrations in [mg/m³] were calculated with the computer programme and presented together with the emission factors in [g/GJ] as listed in Annexes 10 and 11. An integral part of the computer programme is the calculation of the flue gas volume as given in Annex 6.

15.2 LIST OF ANNEXES

Annex 1: Example of different possible considerations of boilers as a common plant

Annex 2: Determination of SO_2 emission factors (flow sheet)

Annex 3: Determination of SO_2 emission factors (description)

Annex 4: Determination of NO_X emission factors (flow sheet)

Annex 5: Determination of NO_X emission factors (description)

Annex 6: Determination of the specific flue gas volume (flow sheet and description)

Annex 7: Composition and lower heating value (H_u) of hard coal in coal mining countries

Annex 8: Composition and lower heating value (H_u) of brown coal in coal mining countries

Annex 9: Conditions for exemplary calculation of NO_X emission factors

Annex 10: Emission factors and flue gas concentrations for NO_X obtained by model calculations (see Annexes 4 and 5) for hard coal (see Annex 7)

Annex 11: Emission factors and flue gas concentrations for NO_X obtained by model calculations (see Annexes 4 and 5) for brown coal (see Annex 8)

Annex 12: Comparison between measured and calculated SO_2 and NO_X emission data

Annex 13. Sensitivity analysis of the computer programme results

Annex 14: Users' manual for the emission factor calculation programme (for version September, 1995)

Annex 15: Determination of start-up emissions and start-up emission factors.

Annex 16: List of abbreviations

16 VERIFICATION PROCEDURES

As outlined in the chapter "Concepts for Emission Inventory Verification", different general verification procedures can be recommended. The aim of this section is to develop specific verification procedures for emission data from combustion plants as point sources. The verification procedures considered here are principally based on verification on a national and on a plant level. Moreover, it can be distinguished between the verification of activity data, of emission factors and of emission data.

16.1 Verification on a national level

For combustion plants as point sources, emissions and activities have to be verified. The total emissions from point sources are added together to obtain national total emissions (bottom-up approach). These national total emissions should be compared to emission data derived independently (top-down approach). Independent emission estimates can be obtained by using average emission factors and corresponding statistical data like the total fuel input for all sources, total thermal capacity, total heat or power produced, or by using emission estimates from other sources (e.g. organisations like energy agencies).

The total fuel consumption should be reconciled with energy balances, which often have break-downs for large point sources (e.g. electricity, heat generation and industrial boilers). Furthermore, the total number of plants installed as well as their equipment should be checked with national statistics.

Emission density comparisons can be achieved through comparison of e.g. emissions per capita or emissions per GDP with those of countries with a comparable economic structure.

16.2 Verification on a plant level

It should firstly be verified that separate inventories have been compiled for boilers, stationary engines, and gas turbines (according to SNAP code). The verification at plant level relies on comparisons between calculated emission factors and those derived from emission measurements. An example for such a comparison is given in Annex 12.

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19 RELEASE VERSION, DATE AND SOURCE

Version: 3.1

Date: November 1995

Source: Otto Rentz; Dagmar Oertel
University of Karlsruhe (TH)
Germany

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
December 2006

20 POINT OF ENQUIRY

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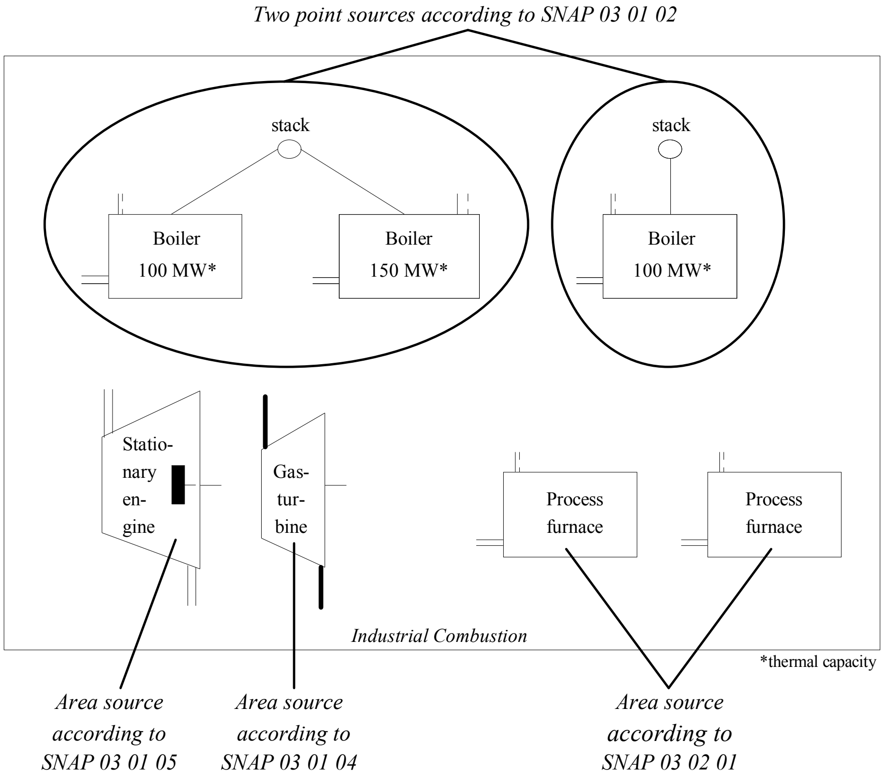
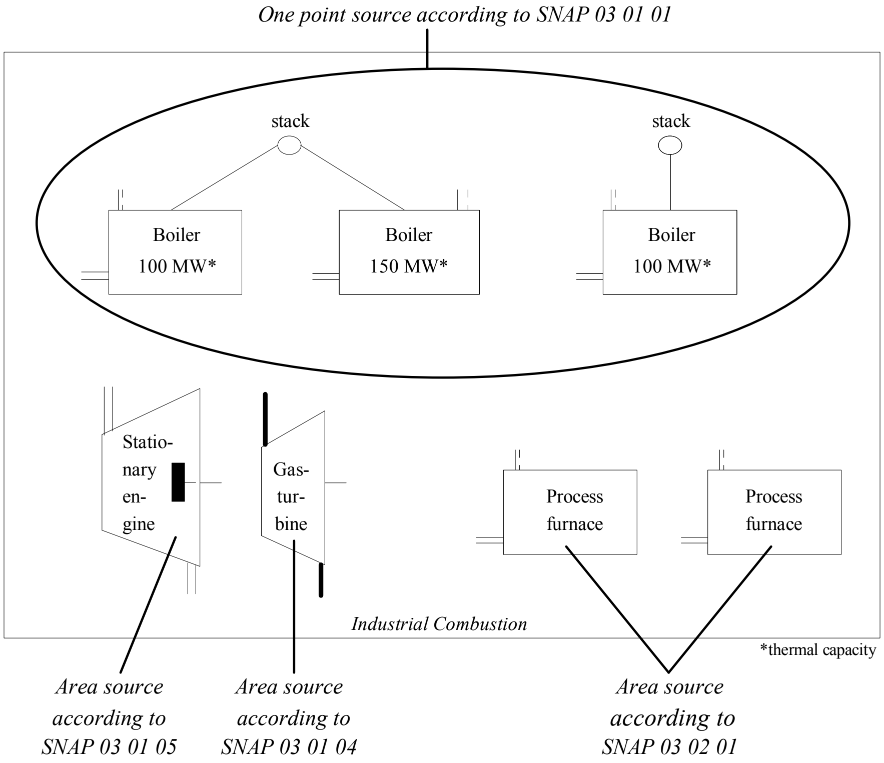
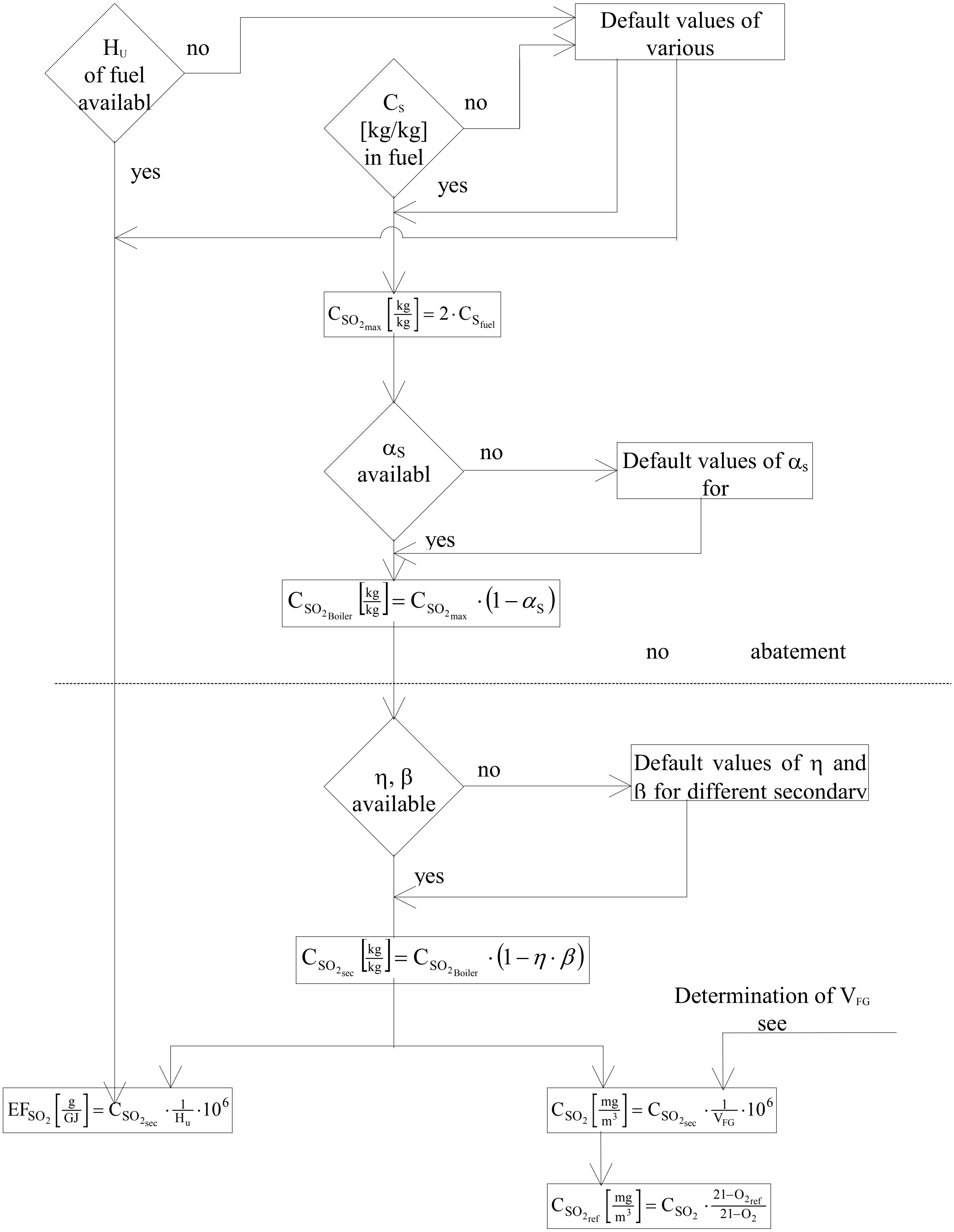
Annex 1: Example of different possible considerations for boilers as a common plant





Annex 2: Determination of SO_2 emission factors (flow sheet, for description see Annex 3)



Annex 3: Determination of SO_2 emission factors (description)

The calculation procedure is performed in three steps:

I The fuel sulphur reacts stoichiometrically with oxygen O_2 to sulphur dioxide SO_2. Default values for the sulphur content $C_{S_{fuel}}$ in hard and brown coal are given in Annexes 7 and 8. The result is the maximum attainable amount of sulphur dioxide $C_{SO_{2.max}}$ given by:

$$C_{SO_{2max}} = 2 \cdot C_{S_{fuel}} \qquad (3\text{-}1)$$

$C_{S_{fuel}}$	sulphur content of fuel (in mass element/mass fuel [kg/kg])
$C_{SO_{2.max}}$	maximum attainable amount of sulphur dioxide (in mass pollutant/mass fuel [kg/kg])

II The maximum attainable amount of sulphur dioxide $C_{SO_{2.max}}$ is corrected by the sulphur retention in ash α_S. As a result, the real boiler emission of sulphur dioxide $C_{SO_{2,boiler}}$ fuel is obtained:

$$C_{SO_{2boiler}} = C_{SO_{2max}} \cdot (1 - \alpha_s) \qquad (3\text{-}2)$$

$C_{SO_{2.boiler}}$	real boiler emission of sulphur dioxide (in mass pollutant/mass fuel [kg/kg])
$C_{SO_{2.max}}$	maximum attainable amount of sulphur dioxide (in mass pollutant/mass fuel [kg/kg])
α_S	sulphur retention in ash [ ]

The sulphur retention in ash depends e.g. on fuel characteristics and temperature inside the boiler. If there is no data for α_S available, default values for various fuels are given in Table 8.

III The boiler emission of sulphur dioxide is corrected by the reduction efficiency η and availability β (for definition of β see Section 3.2) of the secondary measure installed, according to:

$$C_{SO_{2sec}} = C_{SO_{2boiler}} \cdot (1 - \eta \cdot \beta) \qquad (3\text{-}3)$$

$C_{SO_{2.sec}}$	sulphur dioxide downstream secondary measure (in mass pollutant/mass fuel [kg/kg])
$C_{SO_{2.boiler}}$	real boiler emission of sulphur dioxide (in mass pollutant/mass fuel [kg/kg])
η	reduction efficiency of secondary measure [ ]
β	availability of secondary measure [ ]

The result is called secondary sulphur dioxide $C_{SO_{2.sec}}$. If there is no data for η and β available, default values for various flue gas desulphurisation techniques (FGD) are given in Table 7.

The obtained $C_{SO_{2.sec}}$ value is converted to C_{SO_2} in flue gas and to the emission factor EF_{SO_2} according to the following Equations:

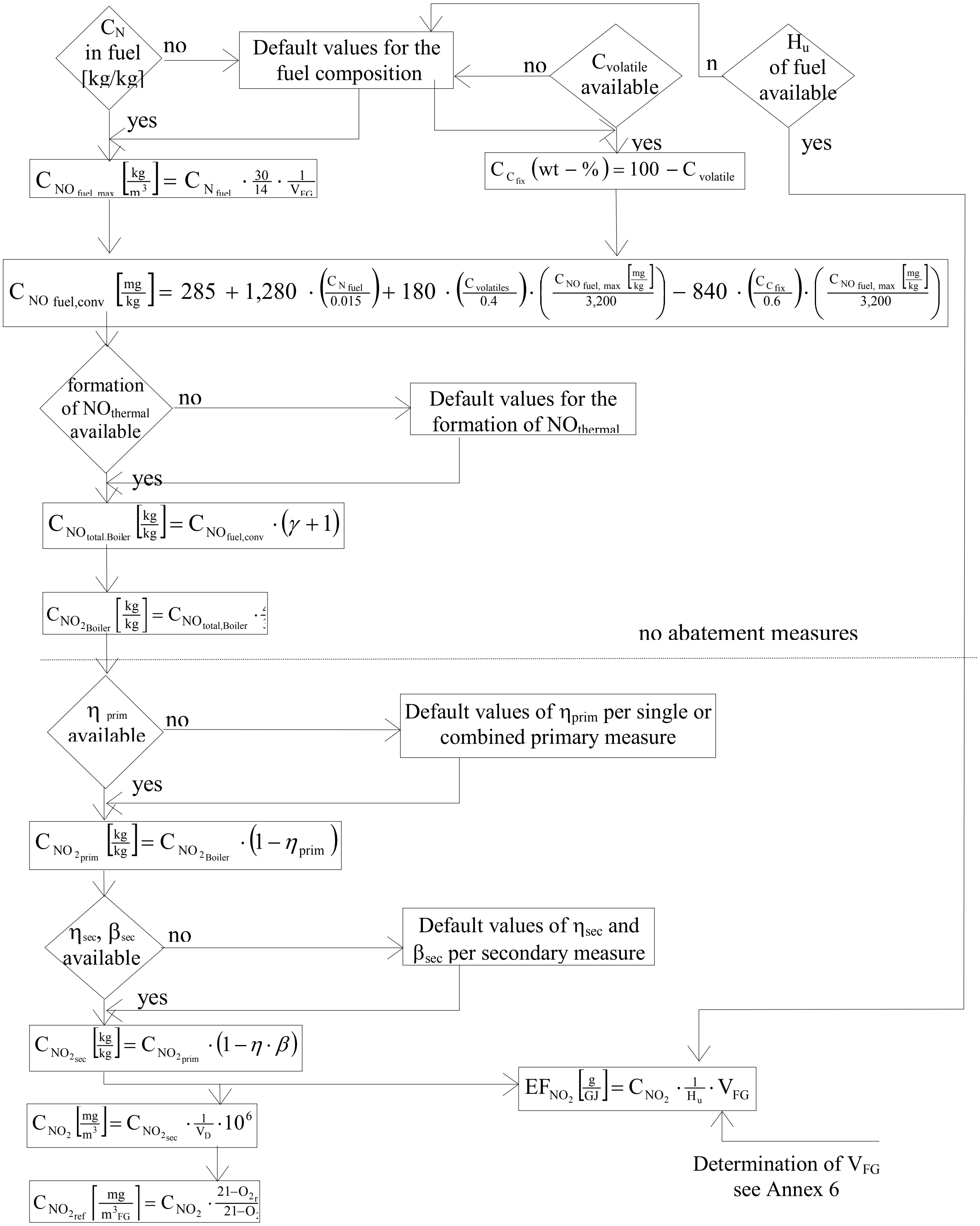
$$C_{SO_2} = C_{SO_{2.sec}} \cdot \frac{1}{V_{FG}} \cdot 10^6 \qquad (3\text{-}4)$$

$$EF_{SO_2} = C_{SO_{2.sec}} \cdot \frac{1}{H_u} \cdot 10^6 \qquad (3\text{-}5)$$

C_{SO_2}	sulphur dioxide in flue gas (in mass pollutant/volume flue gas [mg/m^3])
$C_{SO_{2.sec}}$	sulphur dioxide downstream of secondary measure (in mass pollutant/mass fuel [kg/kg])
V_{FG}	dry flue gas volume volume (in volume flue gas/mass fuel [m^3/kg])
EF_{SO_2}	emission factor for sulphur dioxide [g/GJ]
H_u	lower heating value [MJ/kg]

The dry flue gas volume V_{FG} can be determined according to Annex 6. Emission data in [mg/m^3] are useful to compare measured and calculated values. The same equations are used for the unit conversion of $C_{SO_{2.boiler}}$. Default values for the lower heating values of hard and brown coal are given in Annexes 7 and 8.

Annex 4: Determination of NO_x emission factors (flow sheet, for description see Annex 5)



Annex 5: Determination of NO_X emission factors (description)

The determination of NO_x emission factors takes into account the formation of fuel-NO and thermal-NO. The formation of fuel-NO is based on fuel parameters. But the total amount of fuel-nitrogen cannot be completely converted into fuel-NO (as obtained in Equation (5-1)). Therefore, the realistic formation of fuel-NO is described by an empirical relation (see Equation (5-2)). The formation of thermal-NO is expressed by an an additional fraction which depends on the type of boiler.

The calculation procedure of the NO_X emission factor is performed in three steps: In the first step the maximum NO emission resulting from stoichiometric conversion of fuel nitrogen is calculated. The NO emission obtained is further corrected by taking into account the formation of thermal-NO. NO is converted into NO_2 and primary and secondary measures are taken into account in steps two and three.

I The fuel-nitrogen reacts in a stoichiometric manner with oxygen O_2 to form nitrogen oxide. The default values for the nitrogen content $C_{N_{2fuel}}$ in hard and brown coal are given in Annexes 7 and 8. The maximum attainable amount of fuel nitrogen oxide $C_{NO_{fuel.max}}$ is obtained:

$$C_{NO_{fuel_{max}}} = C_{N_{fuel}} \cdot \frac{30}{14} \cdot \frac{1}{V_{FG}} \tag{5-1}$$

$C_{NO_{fuel.max}}$	maximum attainable amount of fuel nitrogen oxide (in mass pollutant/volume flue gas [kg/m^3])
$C_{N_{fuel}}$	nitrogen content in fuel (in mass nitrogen/mass fuel [kg/kg])
V_{FG}	specific flue gas volume (in volume flue gas/mass fuel [m^3/kg])[9]

The fuel-nitrogen content $C_{N_{fuel}}$ is not completely converted into $C_{NO_{fuel}}$. The converted part of fuel-nitrogen to fuel-NO $C_{NO_{fuel.conv}}$ can be determined by the following empirical formula /50, 51/ related to zero percent of oxygen in dry flue gas:

$$C_{NO_{fuel_{conv}}} = 285 + 1{,}280\left(\frac{C_{N_{fuel}}}{0.015}\right) + 180\left(\frac{C_{volatiles}}{0.4}\right)\left(\frac{C_{NO_{fuel_{max}}}}{3{,}200}\right) - 840\left(\frac{C_{C_{fix}}}{0.6}\right)\left(\frac{C_{NO_{fuel_{max}}}}{3{,}200}\right) \tag{5-2}$$

$C_{NO_{fuel.conv}}$	fuel-NO released (in mass pollutant/mass flue gas [mg/kg])[2]
$C_{N_{fuel}}$	nitrogen content in fuel (in mass nitrogen/mass fuel [kg/kg]), maf
$C_{volatiles}$	fuel content of volatiles (in mass volatiles/mass fuel [kg/kg]), maf
$C_{NO_{fuel.max}}$	maximum attainable amount of fuel nitrogen oxide (in mass pollutant/mass flue gas [mg/kg])[10]
$C_{C_{fix}}$	fixed carbon in fuel (in mass carbon/ mass fuel [kg/kg]), maf

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[9] The programme calculates stoichiometrically the specific flue gas volume based on the complete fuel composition.

[10] Note: $C_{NO.fuel.max}$ and $C_{NO.fuel.conv}$ are given in the unit (mass pollutant/mass flue gas [mg/kg]). For the conversion between (mass pollutant/mass flue gas [mg/kg]) and (mass pollutant/volume flue gas [kg/m3]) the flue gas density (in mass flue gas/volume flue gas [kg/m³]) has to be taken into account, which is calculated stoichiometrically from the fuel composition within the computer programme.

The fixed carbon in the fuel is determined according to the equation $C_{C_{fix}} = 1 - C_{volatiles}$. Equation (5-2) is valid for nitrogen oxide emissions from premixed flames; the coefficient of correlation is $r^2 = 0.9$ for 20 coals and $r^2 = 0.75$ for 46 coals /51/. The data has been obtained by field and pilot-scale measurements. Basically tests are conducted in a 70,000 Btu/hr (20.5 kW) refractory lined furnace with variable heat extraction. Coal was injected through special configurations. A nozzle produces an uniform heterogeneous mixture of coal and air prior to combustion and represents the limit of intensely mixed flames produced with high swirl. Further tests have been established in large scale furnaces. The results from all measurements combined with additional information based on literature data have been used to establish a correlation which predicts the relative dependence of nitrogen oxide emissions on fuel properties. /51/ Further calculations with Equation (5-2) based on measured data have been provided in /50/. The comparison between measured and calculated values has shown that the results from Equation (5-2) are very good for high volatile coals and are satisfactory for medium volatile coals /50/.

Assuming that the formation of fuel-NO is much more important than the formation of thermal-NO (fuel-NO amounts to 70 - 90 %), the content of thermal-NO formed can be expressed as a fraction γ (where γ depends on the type of boiler) of NO_{fuel}. The total content of nitrogen oxide formed in the boiler $C_{NO_{total.boiler}}$ is given by:

$$C_{NO_{total_{boiler}}} = C_{NO_{fuel_{conv}}} + C_{NO_{thermal}} = C_{NO_{fuel_{conv}}} \cdot (1+\gamma) \tag{5-3}$$

$C_{NO_{total.boiler}}$ total content of nitrogen oxide formed in the boiler (in mass pollutant/mass flue gas [kg/kg])

$C_{NO_{fuel.conv}}$ fuel-NO released (in mass pollutant/mass flue gas [kg/kg])

$C_{NO_{thermal}}$ content of thermal-NO formed (in mass pollutant/mass flue gas [kg/kg])

γ fraction for thermal-NO formed [ ]

The following default values for γ can be recommended: DBB $\gamma = 0.05$, WBB $\gamma = 0.3$. Furthermore, the amount of thermal-NO can be influenced by load (see also Section 11.2).

The total boiler emissions of nitrogen dioxide $C_{NO_{2.boiler}}$ can be calculated as follows:

$$C_{NO_{2_{boiler}}} = C_{NO_{total_{boiler}}} \cdot \frac{46}{30} \tag{5-4}$$

$C_{NO_{2_{boiler}}}$ total content of nitrogen dioxide formed in the boiler (in mass pollutant/mass flue gas [kg/kg])

$C_{NO_{total_{boiler}}}$ total content of nitrogen oxide formed in the boiler (in mass pollutant/mass flue gas [kg/kg])

II The total boiler content of nitrogen dioxide given by $C_{NO_{2.boiler}}$ is reduced by taking into account primary measures with the reduction efficiency η_{prim}. The result is the content of primary nitrogen dioxide $C_{NO_{2.prim}}$:

$$C_{NO_{2prim}} = C_{NO_{2boiler}} \cdot \left(1 - \eta_{prim}\right) \tag{5-5}$$

$C_{NO_{2.prim}}$	content of primary nitrogen dioxide (in mass pollutant/mass flue gas [kg/kg])
$C_{NO_{2boiler}}$	total content of nitrogen dioxide formed in the boiler (in mass pollutant/mass flue gas [kg/kg])
η_{prim}	reduction efficiency of primary measure(s) [ ]

As there is only incomplete data available for reduction efficiencies, default values are given for the individual and relevant combinations of primary measures for different types of boilers and fuels (see Table 8). In the case of combined primary measures with known individual reduction efficiencies $\eta_{prim,1}$, $\eta_{prim,2}$, etc., the following equation can be used:

$$C_{NO_{2prim}} = C_{NO_{2boiler}} \cdot \left(1 - \eta_{prim1}\right) \cdot \left(1 - \eta_{prim2}\right) \cdot \left(1 - \eta_{prim3}\right) \tag{5-6}$$

$C_{NO_{2.prim}}$	content of nitrogen dioxide taking into account primary measures (in mass pollutant/mass flue gas [kg/kg])
$C_{NO_{2boiler}}$	total content of nitrogen dioxide formed in the boiler (in mass pollutant/mass flue gas [kg/kg])
η_{prim_k}	individual reduction efficiency of primary measure k [ ]

It should be taken into account, that the reduction efficiencies of primary measures are not independent of each other.

III The emission of primary nitrogen dioxide $C_{NO_{2.prim}}$ is corrected by the reduction efficiency η_{sec} [ ] and the availability β_{sec} [ ] (for definition of β see Section 3.2) of the secondary measure installed, according to:

$$C_{NO_{2sec}} = C_{NO_{2.prim}} \cdot \left(1 - \eta_{sec} \cdot \beta_{sec}\right) \tag{5-7}$$

$C_{NO_{2.sec}}$	nitrogen dioxide downstream of secondary measure (in mass pollutant/mass flue gas [kg/kg])
$C_{NO_{2.prim}}$	content of nitrogen dioxide taking into account primary measures (in mass pollutant/mass flue gas [kg/kg])
η_{sec}	reduction efficiency of secondary measure [ ]
β_{sec}	availability of secondary measure [ ]

If there is no data for η_{sec} and β_{sec} available, default values for various DeNOx techniques are given in Table 9.

The obtained value of $C_{NO_{2.sec}}$ is converted into C_{NO_2} and into the emission factor EF_{NO_2} according to the following equations:

$$C_{NO_2} = C_{NO_{2sec}} \cdot \frac{1}{V_D} \cdot 10^6 \qquad (5\text{-}8)$$

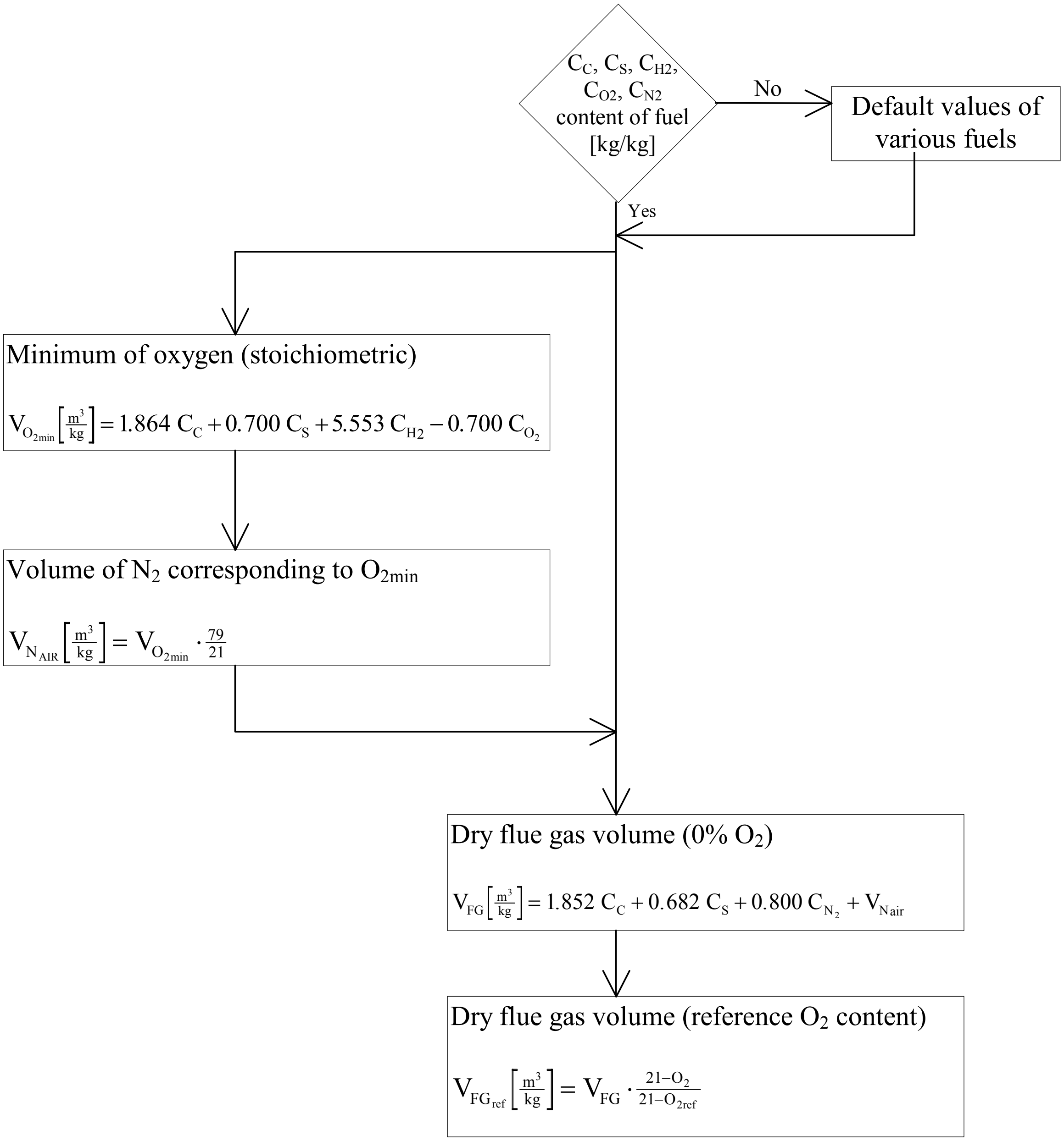
$$EF_{NO_2} = C_{NO_2} \cdot \frac{1}{H_u} \cdot V_{FG} \qquad (5\text{-}9)$$

C_{NO_2}	nitrogen dioxide in flue gas (in mass pollutant/volume flue gas [mg/m^3])
$C_{NO_{2sec}}$	nitrogen dioxide downstream of secondary measure (in mass pollutant/mass flue gas [kg/kg])
V_D	dry flue gas volume (in volume flue gas/mass flue gas [m^3/kg])
V_{FG}	specific dry flue gas volume (in volume flue gas/mass fuel [m^3/kg])
EF_{NO_2}	emission factor for nitrogen dioxide [g/GJ]
H_u	lower heating value [MJ/kg]

The specific dry flue gas volume V_{FG} can be determined according to Annex 6. Emission data expressed in [mg/m^3] are used for comparing measured and calculated values. Default values for lower heating values for hard and brown coal are given in Annexes 7 and 8.

Annex 6: Determination of the specific flue gas volume (flow sheet and description)

The specific flue gas volume has to be determined in order to convert the emission factors, which have been obtained in [g/GJ], into [mg/m^3], which allows a comparison to measured data. The approach is given in the following flow sheet:



For the determination of the flue gas volume, the elemental analysis of the fuel (content of carbon C_C, sulphur C_S, hydrogen C_H, oxygen C_{O_2} and nitrogen C_N (maf)) has to be known. If no data of the elemental analysis is available, default values of hard and brown coals are proposed in Annexes 7 and 8. The volume of oxygen required for a stoichiometric reaction $V_{O_{2min}}$ can be determined as follows:

$$V_{O_{2min}} = 1.864 \cdot C_C + 0.700 \cdot C_S + 5.553 \cdot C_H - 0.700 \cdot C_{O_2} \qquad (6\text{-}1)$$

$V_{O_{2min}}$	volume of oxygen required for stoichiometric reaction (in volume oxygen/mass fuel [m^3/kg])
C_C	content of carbon in fuel (in mass carbon/mass fuel [kg/kg])
C_S	content of sulphur in fuel (in mass sulphur/mass fuel [kg/kg])
C_H	content of hydrogen in fuel (in mass hydrogen/mass fuel [kg/kg])
C_{O_2}	content of oxygen in fuel (in mass oxygen/mass fuel [kg/kg])

The constants in Equation (6-1) represent stoichiometric factors for the volume of oxygen required for the combustion of 1 kg carbon, sulphur or hydrogen in [m^3/kg]. The corresponding volume of nitrogen in the air $V_{N_{air}}$ is given by Equation (6-2):

$$V_{N_{air}} = V_{O_{2min}} \cdot \tfrac{79}{21} \qquad (6\text{-}2)$$

$V_{N_{air}}$	volume of nitrogen in the air (in volume nitrogen/mass fuel [m^3/kg])
$V_{O_{2min}}$	volume of oxygen required for stoichiometric reaction (in volume oxygen/mass fuel [m^3/kg])

The specific dry flue gas volume at 0 % oxygen V_{FG} can be determined by using Equation (6-3):

$$V_{FG} = 1.852 \cdot C_C + 0.682 \cdot C_S + 0.800 \cdot C_N + V_{N_{air}} \qquad (6\text{-}3)$$

V_{FG}	specific dry flue gas volume (in volume flue gas/mass fuel [m^3/kg])
C_C	content of carbon in fuel (in mass carbon/mass fuel [kg/kg])
C_S	content of sulphur in fuel (in mass sulphur/mass fuel [kg/kg])
C_N	content of nitrogen in fuel (in mass nitrogen/mass fuel [kg/kg])
$V_{N_{air}}$	volume of nitrogen in the air (in volume nitrogen/mass fuel [m^3/kg])

The constants in Equation (6-3) represent stoichiometric factors for the volume of oxygen required for the combustion of 1 kg carbon, sulphur or nitrogen in [m^3/kg]. The obtained values of V_{FG} at 0 % oxygen are converted to the reference content of oxygen in flue gas according to Equation (6-4):

$$V_{FG_{ref}} = V_{FG} \cdot \tfrac{21 - O_2}{21 - O_{2_{ref}}} \qquad (6\text{-}4)$$

$V_{FG_{ref}}$	volume of specific flue gas under reference conditions (in volume flue gas/mass fuel [m^3/kg])
V_{FG}	volume of specific flue gas obtained (in volume flue gas/mass fuel [m^3/kg])
O_2	content of oxygen in the flue gas obtained [%]
$O_{2_{ref}}$	content of oxygen in the flue gas under reference conditions [%]

Annex 7: Composition and lower heating value (H_u) of hard coal in coal mining countries

country	elemental analysis (maf) [wt.-%]										volatiles (maf) [wt.-%]		H_u (maf) [MJ/kg]	
	C		N		O		H		S					
	value	standard deviation	value	standard deviation	value	standard deviation	value	standard deviation	value	standard deviation	value	standard deviation	value	standard deviation
Australia1)	84.6	2.26	1.8	0.15	7.8	2.08	5.2	0.29	0.6	0.21	34.0	5.94	33.70	1,03
Canada1)	86.6	1.8	1.4	0.15	6.1	1.5	5.1	0.56	0.9	0.43	33.9	6.34	33.04	2.32
China1)	81.9	1.95	1.1	0.32	11.4	2.4	4.9	0.21	1.05	0.35	36.3	2.32	32.06	0,80
Columbia1)	78.5	6.37	1.5	0.13	12.4	4.3	5.2	0.62	0.9	0.19	42.2	2.70	31.83	1.93
Czech Rep.2)	85.98	2.23	1.5	0.17	6.27	2.30	5.09	0.70	1.16	0.68	30.88	8.92	34.00	2.44
France2)	87.91	1.76	1.29	0.24	5.60	1.58	4.50	0.47	0.70	0.17	22.81	5.82	34.86	1.56
Germany RAG1)6)	90.2	1.77	1.6	0	3	1.41	4.4	0.56	0.9	-	15.8	9.60	35.23	0.29
Ger. others2)	87.00	2.44	1.49	0.27	5.75	1.94	4.76	0.68	1.02	0.32	25.52	6.58	30.10	1.75
CIS1)	77.5	0	0.7	0	16.1	0	5.4	0	0.3	0	39.0	3.20	31.85	1.66
Hungary2)	84.10	1.51	1.42	0.69	5.79	0.54	5.09	0.11	3.62	0.55	24.4	3.98	34.16	1.05
India1)	76.5	3.22	1.3	0.25	16.2	4	5.6	0.4	0.4	0.32	47.9	2.44	29.48	2.25
Poland4)	80.0		1.0		7.0		5.0		1.0		38.5		(21.00)5)	
Portugal3)	87.0		0.95		5.4		4.9		0.94		32.1		(27.58)5)	
South Africa1)	80.3	5.78	2.1	0.73	8.8	1.2	4.9	1.19	0.9	0.24	31.9	2.37	32.36	0.73
UK1)	84.5	0.6	1.8	0	n. a.		5.4	0.06	n. a.		38.2	1.84	33.80	0.58
USA1)	84.3	2	1.6	0.17	7.5	1.65	5.5	0.38	1.1	0.58	38.1	4.31	33.89	0.88
Venezuela1)	84.2	1.7	1.5	0.07	7.6	2.19	6	0.49	0.7	0	43.2	3.98	34.00	1.00

1) Association of German Coal Importers 1992 /72

2) Brandt 1981 /47/

n.a. - no data are available

3) Madeira: Personal communication, EDP-Electricielade Portugal, Lisboa, May 1994

4) Debsky: Personal communication, Energy Information Centre, Warsaw, May 1994

5) lower heating value as received (ar)

6) RAG= Ruhr coal

Annex 8: Composition and lower heating value (H_u) of brown coal in coal mining countries

	elemental analysis (maf) [wt.-%]										volatiles (maf)		H_u (maf)	
country	C		N		O		H		S		[wt.-%]		[MJ/kg]	
	value		value		value		value		value		value		value	
Czech Rep.[2]	70.09	3.32[4]	1.07	0.22[4]	21.74	3.42[4]	5.64	0.64[4]	1.48	0.82[4]	56.67	4.62[4]	28.2	2.39[4]
Germany														
-Rheinisch coal[1]	68	62-72[5]	1.0	0.7-1.3[5]	25.2	22-30[5]	5	4.5-5.5[5]	0.8	0.2-1.1[5]	38[6]	-	27.3	19.4-31.7[5]
-Middle Ger.[1]	72		0.8		18.3		5.5		3.4		57.5		28.8	
-East Ger.[1]	69.5		1.0		23.1		5.8		0.6		58.7		25.7	
Hungary[1] - 1	63.8		(1.1)		26.8		4.8		3.5		61.8		35.7	28.8-42.6[5]
Hungary[2] - 2	69.82	2.62[4]	1.06	0.45[4]	18.91	2.23[4]	5.54	0.12[4]	4.49	2.46[4]	39.30	1.04[4]	28.4	1.20[4]
Poland[7]	69.5	66-73[5]	1.1	0.7-1.5[5]	19	13-25[5]	6	5-7[5]	1		50		25	23 - 26[5]
Portugal[2]	67.44	1.01[4]	0.91	0.18[4]	22.61	2.89[4]	4.4	0.74[4]	4.62	2.43[4]	54.64	8.84[4]	24.8	2.6[4]
Turkey[1] - 1	61.4		0.8		29.6		5.1		5.1		n. a.		21.2	19.8-22.7[5]
Turkey[3] - 2	62.6	7.84[4]	2.0	0.67[4]	24.0	4.48[4]	4.9	0.56[4]	6.2	4.77[4]	56.0	3.93[4]	26.6	

[1] IEA coal research - brown coal

[2] Brandt

[3] Kücükbayrak, S.; Kadioglu, E.: Desulphurisation of some Turkish lignites by pyrolysis, FUEL, Vol. 67, 6/1988

[4] standard deviation

[5] range

[6] value recommended by RAG

[7] Debsky: Personal communication, Energy Information Centre, Warsaw, May 1994

n. a. - no data available

Annex 9: Conditions for exemplary calculation of NO_x emission factors

Annex 9 presents the values which have been chosen for the calculation of NO_x emission factors (according to Section 4.2.1). The results of the calculations are given in the following Annexes 10 (for hard coal) and 11 (for brown coal). Both annexes contain emission factors in [g/GJ] as well as concentrations in [mg/m^3] which have been determined under the conditions given in Table 9-1:

Table 9-1: Selected input parameters for model calculations determining NO_X emission factors as given in Annexes 10 and 11

Type of coal[1]	Type of boiler	Fraction of thermal NO NO_{th} [ ]	Reduction efficiency of primary measures η_{prim}[2] [ ]	Reduction efficiency of secondary measures η_{sec} [ ]	Availability β_{sec} [ ]
hc	DBB	0,05	LNB 0,20 LNB/SAS 0,45 LNB/OFA 0,45 LNB/SAS/OFA 0,60	SCR 0,8	0,99
	WBB	0,30	LNB 0,20 LNB/SAS 0,45 LNB/OFA 0,40 LNB/SAS/OFA 0,60	SCR 0,8	0,99
bc	DBB	0,05	LNB 0,20 LNB/SAS 0,45 LNB/OFA 0,40 LNB/SAS/OFA 0,60	-	-

[1] Elementary analyses of hard and brown coal are given in Annexes 7 and 8.

[2] The reduction efficiency is given as an example for selected primary measures (see Section 4.2).
Abbreviations: hc = hard coal, bc = brown coal

For individual calculations of NO_X emission factors, the computer programme (users' manual see Section 15 and Annex 14) can be used.

Annex 10: Emission factors and flue gas concentrations for NO_X obtained by model calculations (see Annexes 4 and 5) for hard coal (Annex 7)

Hard coal from	Type of boiler	Uncontrolled		Primary control[2)]			Secondary control[3)]	
		EF [g/GJ]	Flue gas concentration [mg/m³]	PM[1)]	EF [g/GJ]	Flue gas concentration [mg/m³]	EF [g/GJ]	Flue gas concentration [mg/m³]
Australia	DBB	568	1620	LNB	454	1300	95	270
				LNB/SAS	312	893	65	186
				LNB/OFA	312	893	65	186
				LNB/SAS/OFA	227	649	47	135
	WBB	703	2140	LNB	562	1720	117	357
				LNB/SAS	387	1180	80	245
				LNB/OFA	422	1290	88	268
				LNB/SAS/OFA	281	858	59	178
Canada	DBB	506	1390	LNB	405	1110	84	230
				LNB/SAS	278	762	58	158
				LNB/OFA	278	762	58	158
				LNB/SAS/OFA	202	554	42	115
	WBB	627	1830	LNB	501	1460	10	304
				LNB/SAS	345	1010	72	209
				LNB/OFA	376	1100	78	228
				LNB/SAS/OFA	251	732	52	152
China	DBB	413	1180	LNB	331	943	69	196
				LNB/SAS	227	648	47	135
				LNB/OFA	227	648	47	135
				LNB/SAS/OFA	165	472	34	98
	WBB	512	1560	LNB	409	1250	85	259
				LNB/SAS	281	856	59	178
				LNB/OFA	307	934	64	194
				LNB/SAS/OFA	205	623	43	130
Columbia	DBB	535	1570	LNB	428	1250	89	261
				LNB/SAS	294	861	61	179
				LNB/OFA	294	861	61	179
				LNB/SAS/OFA	214	626	45	130

for footnotes see bottom of this table

Annex 10 continued, for footnotes see bottom of this table

		Uncontrolled		Primary control[2)]			Secondary control[3)]	
Hard coal from	Type of boiler	EF [g/GJ]	Flue gas concentration [mg/m^3]	PM[1)]	EF [g/GJ]	Flue gas concentration [mg/m^3]	EF [g/GJ]	Flue gas concentration [mg/m^3]
Columbia	WBB	662	2070	LNB	529	1650	110	344
				LNB/SAS	364	1140	76	237
				LNB/OFA	397	1240	83	258
				LNB/SAS/OFA	265	827	51	172
Czech Republic	DBB	483	1370	LNB	387	1100	80	228
				LNB/SAS	266	753	55	157
				LNB/OFA	266	753	55	157
				LNB/SAS/OFA	193	548	40	114
	WBB	598	1810	LNB	479	1450	100	301
				LNB/SAS	329	995	68	207
				LNB/OFA	359	1080	75	226
				LNB/SAS/OFA	239	723	50	150
France	DBB	374	1080	LNB	299	863	62	180
				LNB/SAS	205	594	43	123
				LNB/OFA	205	594	43	123
				LNB/SAS/OFA	149	432	31	90
	WBB	463	1430	LNB	370	1140	77	237
				LNB/SAS	254	784	53	163
				LNB/OFA	278	855	58	178
				LNB/SAS/OFA	185	570	39	119
Germany RAG	DBB	384	1090	LNB	307	872	64	181
				LNB/SAS	211	600	44	125
				LNB/OFA	211	600	44	125
				LNB/SAS/OFA	154	436	32	90
	WBB	476	1440	LNB	381	1150	779	240
				LNB/SAS	262	792	54	165
				LNB/OFA	285	864	59	180
				LNB/SAS/OFA	190	576	40	120

Annex 10 continued, for footnotes see bottom of this table

Hard coal from	Type of boiler	Uncontrolled		Primary control2)			Secondary control3)	
		EF [g/GJ]	Flue gas concentration [mg/m^3]	PM1)	EF [g/GJ]	Flue gas concentration [mg/m^3]	EF [g/GJ]	Flue gas concentration [mg/m^3]
Germany others	DBB	495	1240	LNB	396	990	82	206
				LNB/SAS	272	681	57	142
				LNB/OFA	272	681	57	142
				LNB/SAS/OFA	198	495	41	103
	WBB	613	1630	LNB	490	1310	102	272
				LNB/SAS	337	899	70	187
				LNB/OFA	368	980	76	204
				LNB/SAS/OFA	245	654	51	136
Hungary	DBB	401	1150	LNB	320	920	67	191
				LNB/SAS	220	633	46	132
				LNB/OFA	220	633	46	132
				LNB/SAS/OFA	160	460	33	96
	WBB	496	1520	LNB	397	1220	82	253
				LNB/SAS	273	835	57	174
				LNB/OFA	298	911	62	190
				LNB/SAS/OFA	198	608	41	126
CIS	DBB	308	923	LNB	247	739	51	154
				LNB/SAS	169	508	35	106
				LNB/OFA	169	508	35	106
				LNB/SAS/OFA	123	369	26	77
	WBB	382	1220	LNB	305	975	64	203
				LNB/SAS	210	671	44	139
				LNB/OFA	229	732	48	152
				LNB/SAS/OFA	153	488	32	101
India	DBB	551	1540	LNB	441	1230	92	256
				LNB/SAS	303	845	63	176
				LNB/OFA	303	845	63	176
				LNB/SAS/OFA	220	615	46	128

Annex 10 continued, for footnotes see bottom of this table

Hard coal from	Type of boiler	Uncontrolled		Primary control[2)]			Secondary control[3)]	
		EF [g/GJ]	Flue gas concentration [mg/m^3]	PM[1)]	EF [g/GJ]	Flue gas concentration [mg/m^3]	EF [g/GJ]	Flue gas concentration [mg/m^3]
India	WBB	682	2030	LNB	545	1620	113	338
				LNB/SAS	375	1120	78	232
				LNB/OFA	409	1120	85	253
				LNB/SAS/OFA	273	812	57	169
South Africa	DBB	569	1650	LNB	456	1320	95	275
				LNB/SAS	313	910	65	189
				LNB/OFA	313	910	65	189
				LNB/SAS/OFA	228	662	47	138
	WBB	705	2180	LNB	564	1750	117	364
				LNB/SAS	388	1200	81	250
				LNB/OFA	423	1310	88	273
				LNB/SAS/OFA	282	874	59	182
USA	DBB	563	1610	LNB	450	1290	94	268
				LNB/SAS	310	885	64	184
				LNB/OFA	310	885	64	184
				LNB/SAS/OFA	225	644	47	134
	WBB	697	2120	LNB	558	1700	116	353
				LNB/SAS	383	1170	78	243
				LNB/OFA	418	1270	87	265
				LNB/SAS/OFA	279	850	58	177
Venezuela	DBB	588	1670	LNB	471	1340	98	278
				LNB/SAS	324	919	67	191
				LNB/OFA	324	919	67	191
				LNB/SAS/OFA	235	668	49	139

Annex 10 continued

Hard coal from	Type of boiler	Uncontrolled		Primary control[2]			Secondary control[3]	
		EF [g/GJ]	Flue gas concentration [mg/m^3]	PM[1]	EF [g/GJ]	Flue gas concentration [mg/m^3]	EF [g/GJ]	Flue gas concentration [mg/m^3]
Venezuela	WBB	728	2210	LNB	583	1760	121	367
				LNB/SAS	401	1210	83	252
				LNB/OFA	437	1320	91	275
				LNB/SAS/OFA	291	882	61	184

[1] PM = primary measures

[2] primary measures as mostly used, see Table 8

[3] taking into account secondary measures mostly used: SCR: reduction efficiency = 0.8, availability = 0.99

Annex 11: Emission factors and flue gas concentrations for NO_X obtained by model calculations (see Annexes 4 and 5) for brown coal (see Annex 8)

Brown coal from	Type of boiler	Uncontrolled		Primary control		
		EF $\left[\frac{g}{GJ}\right]$	Conc. $\left[\frac{mg}{m^3}\right]$	PM[1]	EF $\left[\frac{g}{GJ}\right]$	Conc. $\left[\frac{mg}{m^3}\right]$
Czech Republic	DBB	506	1.480	LNB	405	1190
				LNB/SAS	278	816
				LNB/OFA	304	890
				LNB/SAS/OFA	202	593
Germany						
- Rheinisch coal	DBB	325	985	LNB	260	788
				LNB/SAS	179	542
				LNB/OFA	195	591
				LNB/SAS/OFA	130	394
- Middle Germany	DBB	504	1.250	LNB	403	996
				LNB/SAS	277	685
				LNB/OFA	302	747
				LNB/SAS/OFA	202	498
- East Germany	DBB	539	1.460	LNB	431	1.160
				LNB/SAS	296	801
				LNB/OFA	323	873
				LNB/SAS/OFA	215	582
Hungary - 1	DBB	379	1.590	LNB	303	1.270
				LNB/SAS	208	874
				LNB/OFA	227	953
				LNB/SAS/OFA	151	635
Hungary - 2	DBB	379	1.100	LNB	304	879
				LNB/SAS	209	604
				LNB/OFA	228	659
				LNB/SAS/OFA	152	439
Portugal	DBB	461	1.260	LNB	369	1.010
				LNB/SAS	254	696
				LNB/OFA	277	759
				LNB/SAS/OFA	185	506
Turkey - 2	DBB	725	2.240	LNB	580	1.790
				LNB/SAS	399	1.230
				LNB/OFA	435	1.340
				LNB/SAS/OFA	290	895

[1] PM = primary measures as given in Table 8

Annex 12: Comparison between measured and calculated SO_2 and NO_x emission data

The proposed methodology for the determination of SO_2 and NO_x emission factors is described in the Sections 4.1 and 4.2. Calculated flue gas concentrations in [mg/m^3] have been used for the derivation of emission factors in [g/GJ]. A comparison of measured concentrations in combustion plants in [mg/m^3] with calculated concentrations in [mg/m^3] can be used for verification purposes.

A comparison of measured concentrations with calculated flue gas concentrations downstream of the boiler is given as an example for some power plants in Table 12-1.

Table 12-1: Comparison of measured and calculated flue gas concentrations in raw gas of the boiler (taking into account primary reduction measures)[13)]

Type of boiler	Power plant	C_{SO_2} [mg/m^3]		C_{NO_2} [mg/m^3]	
		measured	calculated	measured	calculated
DBB	Altbach (FRG)[1)]	ca. 1,700	1,380 - 1,610	ca. 600	599 - 681
	Münster (FRG)[2)]	1,644 - 1,891	1,380 - 1,440	800 - 900	1,090
	Karlsruhe (FRG)[3)]	1,600 - 2,000	1,310 - 1,650	900 - 1,000	923 - 1,140
	Hanover (FRG)[4)]	1,600 - 1,800	1,610	ca. 800	681
	Mehrum (FRG)[5)]	ca. 2,700	1,610	ca. 800	990
	Nuremberg (FRG)[6)]	ca. 1,800	1,610	n. d.	1,240
	Heilbronn (FRG)[7)]	ca. 1,800	1,900 - 2,200	≤ 800	1,050 - 1,070
	IMATRAN (SF)[8)]	n. d.	1,480 - 1,700	ca. 225	516 - 747
	EPON (NL)[9)]	1,429 - 1,577	1,580 - 2,190	363 - 609	999 - 1,010
WBB	Aschaffenburg (FRG) [10)]	2,400	1,530	1,000	1,010
	Charlottenburg (FRG) [11)]	1,800	1,530	1,300	1,080
	Karlsruhe (FRG) [12)]	1,295 - 1,716	1,610	ca. 960	1,460

[1)] coal: Germany RAG, Germany others; reduction measures: WS; LNB/SAS, SCR; thermal capacity 1,090 MW

[2)] coal: Germany others, $\alpha_S = 0.15$; reduction measure: DESONOX ($\eta_{SO2} = 0.94$, $\eta_{NO2} = 0.82$); thermal capacity 100 MW

[3)] coal: individual data, $\alpha_S = 0.4$; reduction measures: WS ($\eta = 0.85$); LNB/opt. ($\eta = 0.3$); SCR; thermal capacity 1,125 MW

[4)] coal: Germany others; reduction measures: SDA; LNB/OFA, SCR; thermal capacity 359 MW

[5)] coal: Germany others; reduction measures: WS; LNB, SCR; thermal capacity 1,600 MW

[6)] coal: Germany others; reduction measures: SDA; SCR; thermal capacity 110 MW

[7)] coal: individual data; reduction measures: WS ($\eta = 0.95$); OFA, SCR; thermal capacity 1,860 MW

[8] coal: individual data; reduction measures: WS; LNB/OFA; electrical capacity 650 MW

[9] coal: individual data; reduction measures: FGD (η = 0.93); high temperature NO_x reduction (η = 0.4), electrical capacity 630 MW

[10] coal: Germany RAG; reduction measures: WS; SAS, SCR; thermal capacity 395 MW

[11] coal: Germany RAG; reduction measures: WS; OFA; thermal capacity 120 MW

[12] coal: individual data; reduction measures: WS (η = 0.88); SCR (η = 0.9; thermal capacity) 191 MW

[13] values refer to full load conditions

n. d. = no data available

Table 12-2: Comparison of measured and calculated flue gas concentrations downstream of secondary reduction measure (if installed)[13]

Type of boiler	Power plant	C_{SO_2} [mg/m^3]		C_{NO_2} [mg/m^3]	
		measured	calculated	measured	calculated
DBB	Altbach (FRG)[1]	ca. 250	150 - 176	ca. 200	125 - 142
	Münster (FRG)[2]	85 - 181	820 - 859	163 - 176	74
	Karlsruhe (FRG)[3]	240 - 300	208 - 261	190	192 - 238
	Hanover (FRG)[4]	200	176	150	142
	Mehrum (FRG)[5]	400	176	190	206
	Nuremberg (FRG)[6]	50 - 140	176	70 - 100	257
	Heilbronn (FRG)[7]	100 - 200	207 - 240	≤ 200	218 - 223
	IMATRAN (SF)[8]	n. d.	161 - 186	ca. 225	516 - 747
	EPON (NL)[9]	ca. 148	113 - 184	ca. 609	999 - 1,010
WBB	Aschaffenburg (FRG) [10]	70	167	200	209
	Charlottenburg (FRG) [11]	175	167	163	1,080
	Karlsruhe (FRG) [12]	47 - 165	207	ca. 150	159

[1] - [13] for footnotes see Table 12-1 above

n.d. = no data available

The quality and quantity of data obtained by the power plant operators vary greatly. For unknown compositions of coal and other missing parameters default values have been used (e.g. for coal compositions see Annexes 7 and 8).

The values in Table 12-1 are compared in the Figure 12-1 below:

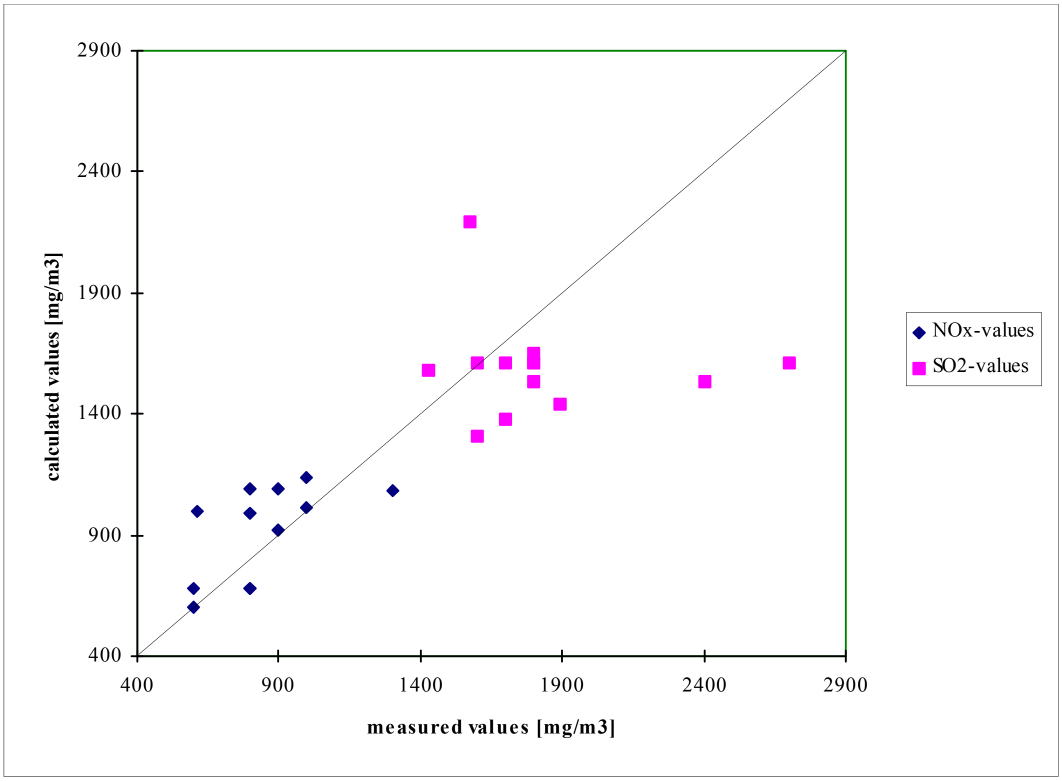


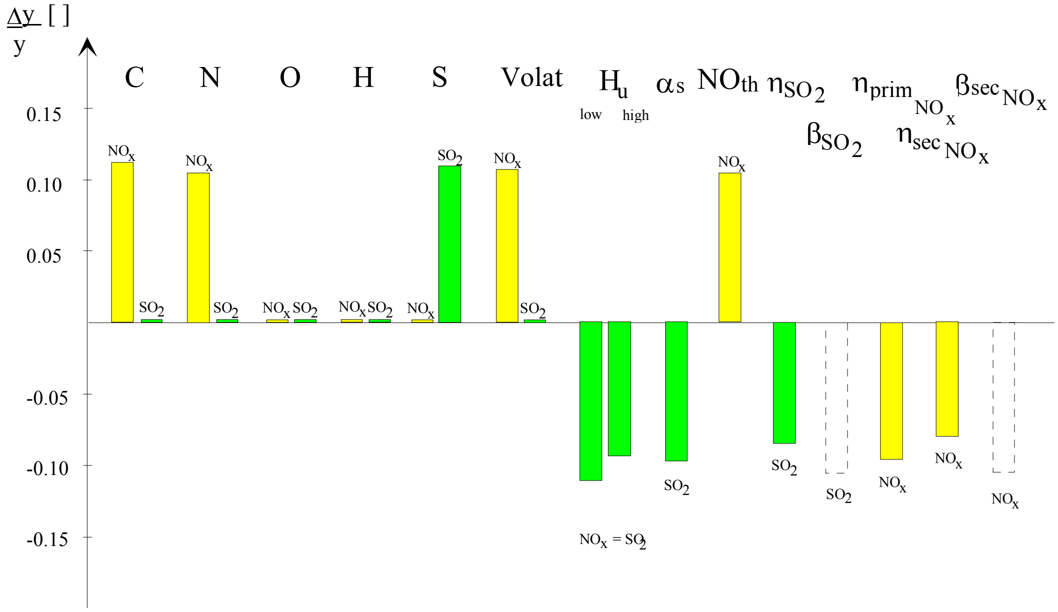
Figure 12-1: Comparison of measured flue gas concentrations [mg/m^3] and calculated flue gas concentrations [mg/m^3] downstream of the boiler

The comparison of measured flue gas concentrations and calculated flue gas concentrations shows that most values are scattered close to the middle axis.

Good correlations between measured and calculated values have been obtained for calculations which are only based on plant specific data provided by power plant operators. But for most calculations a mixture of plant specific data and default values for missing parameters has been used which leads to deviations from the middle axis. In particular strong differences occur for SO_2 emissions which show a tendency to be overestimated. The tendency can be explained by assumptions with regard to default values; e.g. the sulphur retention in ash varies greatly depending on the data availability.

Annex 13: Sensitivity analysis of the computer programme results

A sensitivity analysis was carried out with all model input parameters used. The 14 input parameters (fuel content of carbon C, nitrogen N, oxygen O, hydrogen H, sulphur S, volatiles Volat, lower heating value H_u, sulphur retention in ash α_S, fraction of thermal nitrogen oxide NO_{th}, reduction efficiency η and availability β of abatement measures) was arranged with respect to their influence on SO_2 and NO_x emissions. Each input parameter was varied by ±10 % except β_{SO2} and $\beta_{sec.NOx}$ which were varied only by - 4 % (dashed line); the variation of the calculated emission factors is presented in Figure 13-1.



Δy/y relative change of emission factors (pollutant as indicated)

Figure 13-1: Sensitivity analysis of the emission factor calculation programme results for pulverised coal combustion

For emission factors of SO_2 the sulphur content of fuel and the sulphur retention in ash are highly relevant. For emission factors of NO_x the fuel content of nitrogen, carbon and volatiles as well as the reduction efficiency of primary measures are highly relevant. The fuel contents of oxygen and hydrogen are not relevant. The relative change of emission factors concerning the lower heating value can be described for SO_2 and NO_x as an exponential curve: that means that uncertainties at lower levels of the heating values (e.g. for brown coal) influence the result stronger. The efficiency of secondary measures is of slightly less influence than the efficiency of primary measures. The availability of secondary measures is marked with a dashed line in Figure 13-1; a 4 % variation of this parameter has shown significant influence.

Annex 14: Users’ manual for the emission factor calculation programme (for September 1995 version)

Determination of SO_2 and NO_x emission factors for large combustion plants

1 Computer specifications

This programme requires MICROSOFT WINDOWS 3.1, a 3½" floppy disc drive, and at least 200 Kbyte on the hard disc. The programme has been designed in MICROSOFT EXCEL 4.0 - English Version.

2 Installation

The floppy disc received contains 19 files. All these files have to be installed on the hard disc. The following users’ guide is stored under README.DOC (written with MICROSOFT WORD FOR WINDOWS 2.1).

The software has to be installed on your hard disk "C" by using the following procedure:

- Create a new sub-directory with the name 'POWER_PL' by following the instructions:
  - in DOS go to C:\
  - type: MD POWER_PL
  - hit the <ENTER>-key
  - change into this sub-directory by typing: CD POWER_PL
  - hit the <ENTER>-key.
- To copy all the files from your floppy disc into the sub-directory 'POWER_PL' proceed as follows:
  - insert your disk into slot A (or B) of your PC
  - type COPY A: (or B:)*.*
  - hit the <ENTER>-key.

The installation of the programme is then complete.

3 How to work with the programme

3.1 Start the programme

- Start MICROSOFT WINDOWS 3.1 and MICROSOFT EXCEL 4.0 - English Version (or MICROSOFT EXCEL 5.0 - English Version).
- In 'FILE' - 'OPEN', go to hard disk 'C' and activate the sub-directory 'POWER_PL'. Then you will see all the necessary files in the programme in the left window.
- Choose the file 'POWER_PL.XLW' and hit the <ENTER>-key.
- Then the programme opens all the tables and macros needed.

3.2 Further proceedings with the programme

- When you see the first screen please type 'Ctrl'-'a' (or 'Strg'-'a') to start the programme. By hitting these two keys you start a macro, which takes you through all the levels of the programme. The input data for the programme are divided into background tables for the fuel used, for SO_2-specification and NO_x-specification.

Fuel data input

- First the programme asks for an identification of the model run. You are free to put in the name of the power plant, type of boiler, type of fuel (e. g. Heilbronn - dry bottom boiler - hard coal).
- The next window requests the type of coal (hard coal or lignite).
- The programme asks you to choose one of the fuel compositions listed. Select one of them by typing the corresponding number and hitting the 'OK'-key on the screen$^{1)}$. If the default values of the given fuel compositions do not correspond with your power plant, you have the possibility of putting in corrected values by choosing the last line of the table (line 17 or 10). Then the programme asks you to enter in the individual values. The values given by the 'question-window' can be kept by hitting the 'OK'-key on the screen.
- Then the programme asks for the water content of the fuel and the reference-content of oxygen in the flue gas. The value given by the 'question-window' can be retained by hitting the 'OK'-key on the screen.

SO_2 data specification

- The programme asks you to choose one of the listed numbers as a value for the sulphur retention in ash. Please select one of them by typing the corresponding number and hitting the 'OK'-key on the screen1). If the default values for the sulphur retention in ash do not correspond with your power plant, you have the possibility of putting in corrected values by choosing the last line of the table (line 3). Then the programme asks you to put in the value.
- The programme asks you to choose one of the listed secondary measures SO_2 . Please select one of them by typing the corresponding number and hitting the 'OK'-key on the screen$^{1)}$. If the default values of the efficiencies and availabilities of the secondary measures given do not correspond with those of your power plant, you have the possibility of putting put in corrected values by choosing the last line of the table (line 9). Then the programme asks you to put in the individual values.

  At this point the calculations for SO_2 are finished.

NO_x data specification

- The programme proceeds with the calculations of NO_2 by asking for a value for $NO_{thermal}$[1]. At this stage, the thermal NO (NOthermal) has to be put in as an exogenious value as given in the table. You have the possibility of putting in a new value by following the instructions on the screen.

- The next window requests the type of boiler (wet bottom boiler WBB- dry bottom boiler DBB).
- Then you have to choose a type of combination of primary measure installed. For some primary measures, reduction efficiencies are given as default values[11]. If you have better data available, you can put in new values choosing the last line of the table (line 17) and follow the instructions on the screen.
- Finally, you have to choose a type of combination of secondary measure installed[1]. As mentioned above, you can put in different values of efficiencies and availabilities by choosing one secondary measure from the table (typing the corresponding number). Or else you can put in your own values by selecting the last line of the table (line 6). Please follow the instructions on the screen.

At the end the following message appears on the screen: You can save the data-sheet named 'AINPUSO2.XLS' under a different name.

If you want to do further model runs, just type 'Ctrl'-'a' (or 'Strg'-'a') and the programme starts again.

In order to finish your calculation, just quit EXCEL without saving changes in any of the 19 basic files of this software.

---

[11] If the tables with the default values are overlapped by a 'question-window' you can move this window: point on the headline of this little window with your mouse-pointer, hold your left mouse-button and move it.

Annex 15: Frame conditions of the detailed investigation concerning start-up emissions and start-up emission factors /based on 116/

Approach

Start-ups have to be considered in a boiler-by-boiler approach. In order to determine the relevance of start-up emissions compared to full load emissions, measured emission data for SO_2, NO_2 and CO obtained from power plant operators have been analysed. Start-up emissions and start-up emission factors have been determined in principle by using the detailed methodology described in Section 5.

Technical specifications

The analysis of start-up emissions was accomplished by using measured values from dry bottom boilers, wet bottom boilers and a gas fired boiler. The interpretation of start-up emissions and start-up emission factors should take into account specifications in the design of the boilers and in the configuration of secondary measures installed. In the following, particularities of the boilers considered are given:

- *Dry bottom boiler (thermal capacity 1,050 MW and 1,147 MW, hard coal fuelled)*

  The smaller boiler is equipped with a primary measure for NO_x reduction (SAS). The SCR is arranged in a high dust configuration (SCR-precipitator-FGD). This boiler is often started slowly and directly connected to the FGD.

  The larger boiler is also equipped with a primary measure for NO_x reduction (SAS). The SCR is also arranged in a high dust configuration (SCR-precipitator-FGD). Due to special arrangements (individual construction of two heat exchangers without any slip between raw and clean flue gas) when this boiler is started up the FGD is by-passed. This boiler is also called „quick“ start-up boiler.

- *Wet bottom boiler (thermal capacity 499 MW each, hard coal fuelled)*

  One boiler is equipped with primary measures for NO_x (like OFA and improved coal mills). The other boiler is not equipped with primary measures. Both boilers are equipped with a common FGD. The SCR is arranged in a tail-end-configuration (precipitator-FGD-SCR) and equipped with a natural gas fired additional furnace. The type of FGD is wet scrubbing (WS). Both boilers are started up directly connected to the FGD.

- *Natural gas fired boiler (thermal capacity 1,023 MW)*

  This boiler is rarely used. It is designed for quick start-ups. As a primary measure, special NO_x burners are installed. As a secondary measure an SCR is installed. SO_x abatement is not necessary due to the fact that low sulphur fuels are used.

Boilers without secondary measures show start-up emissions which are below the emissions under full load conditions. During start-ups boilers with secondary measures often show significantly higher SO_2 emissions than during the same time under full load conditions. Start-up emissions are released until the secondary measures are working under optimal conditions (for

SO_2 and NO_2). CO emissions can be significant up to the time when the boiler operates at minimum load.

The relevance of start-up emissions depends on the following parameters which have to be considered when interpreting measured values (emissions or emission factors):

- the type of boiler (e.g. wet bottom boilers always release higher NO_x emissions than dry bottom boilers, due to higher combustion temperatures),
- the type of fuel used (e.g. SO_x emissions are directly related to the sulphur content of the fuel; fuel-nitrogen also contributes to the formation of NO_x),
- the status of the boiler at starting-time (hot, warm or cold start, see Table 11).
    - the specifications of any individual start-up, like
        - the duration and the velocity of the start-up,
        - load level obtained (reduced load or full load),
        - the configuration of secondary measures (e.g. the start-up time of the high-dust-configurations (SCR-precipitator-FGD) depends on the boiler load, due to the fact that the SCR catalyst is directly heated by the flue gas; tail-end-configurations (precipitator-FGD-SCR) can have shorter start-up times, due to the fact that the SCR catalyst can be preheated by an additional burner),
        - start-up of the flue gas desulphurisation directly or in by-pass configuration,
        - emission standards which have to be met (boiler-specific emission standards can be set up below the demands of the LCP Directive).

Annex 16: List of abbreviations

a	Content of ash in coal (wt.-%)
AC	Activated Carbon Process
ar	As received
bc	Brown coal
BFCB	Bubbling Fluidised Bed Combustion
CF_n	Correction factor for month n [ ]
CFBC	Circulating Fluidised Bed Combustion
CC	Combined Cycle
CI	Compression Ignition
$CM_{HM_{FA.raw}}$	Heavy metal concentration in raw gas fly ash $[\frac{g}{Mg}]$
$CM_{HM_{FA.clean}}$	Heavy metal concentration in fly ash in clean flue gas $[\frac{g}{Mg}]$
$\overline{C}$	Expected value (mean value) of the flue gas concentration $[\frac{mg}{m^3}]$
C_i	Concentration $[\frac{kg}{kg}]$, $[\frac{g}{Mg}]$, $[\frac{mg}{m^3}]$, $i = SO_2$, S_{fuel} etc.
CODPOL	Code of pollutants according to CORINAIR
D_k	Number of days per month
DBB	Dry Bottom Boiler
DeNOx	Denitrification unit(s)
DESONOX	Type of simultaneous process for SO_2 and NO_x removal based on catalytic reaction
DSI	Dry Sorbent Injection
E	Emission within the period considered [Mg]
E^A	Emission during start-up period [Mg]
E^V	Emission for full load conditions during start-up period [Mg]
EF^A	Emission factor for start-up time [g/GJ]
$EF^{Reduced\ load}$	Emission factor for reduced load conditions [g/MWh]
EF^V	Emission factor under full load conditions [g/GJ]
EF_i	Emission factor, mostly in the unit $[\frac{g}{GJ}]$, $i = SO_2$, NO_x, CO_2 etc.
EF_f	Fly ash emission factor of raw gas [kg/Mg]
ESP	Electrostatic precipitator
f_a	Fraction of ash leaving combustion chamber as particulate matter (wt.-%)
f_e	Enrichment factor [ ]
f_g	Fraction of heavy metal emitted in gaseous form (wt.-%)
f_k	Factor of day k

f_n	Factor for month
$f_{n,l}$	Factor for hour
F^E	Ratio for start-up and full load emissions [ ]
F^{EF}	Ratio for start-up and full load emission factors [ ]
FBC	Fluidised Bed Combustion
FGD	Flue Gas Desulphurisation
FGR	Flue Gas Recirculation
g	Gaseous state of aggregation
GF	Grate Firing
GHV	Gross Heating Value
GT	Gas Turbine
hc	Hard coal
HM	Heavy metal, trace elements
H_u	Lower heating value [$\frac{MJ}{kg}$]
k^{load}	Ratio of reduced load to full load emission factor [ ]
K_c	Mean efficiency of dust control equipment (%)
K_t	Share of plant capacity connected to dust control equipment (%)
l	Liquid state of aggregation
L	Actual load
LCP	Large Combustion Plant
LIFAC	Special type of DSI, mostly used in Finland
LNB	Low NOx Burner
$\dot{m}^L$	Fuel consumption during periods at reduced load conditions [GJ]
$\dot{m}^V$	Fuel consumption during full load periods [GJ]
$\dot{m}_{fuel}$	Fuel consumption per time unit [$\frac{kg}{a}$], [$\frac{kg}{h}$]
$\dot{m}_{FA}$	Average annually emitted fly ash $\left[\frac{Mg}{a}\right]$
$\dot{m}_q^A$	Fuel consumption during start-up period [GJ]; q= type of start-up (cold start, warm start, hot start)
maf	Moisture and ash free
NMVOC	Non-Methane Volatile Organic Compounds
No_{fuel}	Fuel based emission of nitrogen oxide
$NO_{thermal}$	Thermal nitric oxide
OFA	Overfire Air

P	Daily coal consumption $[\frac{Mg}{d}]$
PM	Primary Measure
RAG	Coal mined in Rhine area in Germany
s	Solid state of aggregation
SAS	Staged Air Supply
SC	Simple Cycle
SCR	Selective Catalytic Reduction
SI	Spark Ignition
SNAP	Selected Nomenclature of Air Pollutants
SNCR	Selective Non-Catalytic Reduction
SNOX	Technical specification of DESONOX-process
SPA	Spray Dryer Absorption
SPF	Split Primary Flow
ST	Stoker
Stat. E.	Stationary Engine
$\dot{V}$	Flue gas volume flow rate $[\frac{m^3}{h}]$
$\bar{\dot{V}}$	Average flow rate $[\frac{m^3}{h}]$
V_D	Dry flue gas volume per mass flue gas $[\frac{m^3}{kg}]$
V_{FG}	Dry flue gas volume per mass fuel $[\frac{m^3}{kg}]$
VOC	Volatile Organic Compounds
WAP	Walter Process
WBB	Wet Bottom Boiler
WL	Wellmann-Lord
WS	Wet Scrubbing
α_s	Sulphur retention in ash [ ]
β_{sec}	Availability of secondary abatement technique [ ]
γ	Fraction of thermal-NO formed [ ]
η_i	Reduction efficiency [ ], i = primary measure, secondary measure

SNAP CODES: (See below)

SOURCE ACTIVITY TITLE: COMBUSTION IN ENERGY & TRANSFORMATION INDUSTRIES *Combustion Plants as Area Sources*

The following activities are taken into account when combustion plants are treated collectively as area sources. Boilers, furnaces (except process furnaces), gas turbines and stationary engines which may also be considered individually as point sources are covered by this chapter as well as by chapter B111 on "Combustion Plants as Point Sources".

SNAP97 Codes	Combustion plants as area sources										
	NOSE CODE	NFR CODE	Boilers/furnaces							Gas turbines	Stationary engines
			Thermal capacity [MW]	Public power and cogeneration plants	District heating	Industrial combustion	Commercial and institutional combustion	Residential combustion	Agriculture forestry and fishing		
01 01 02	101.02	1 A 1 a	≥ 50	X							
01 02 02	101.02	1 A 1 a	and		X						
01.03.02	101.02	1 A 1 b				X					
01.04.02	101.02	1 A 1 c				X					
01.05.02	101.02	1 A 1 c				X					
02 01 02	101.02	1 A 4 a	< 300				X				
02 02 01	101.02	1 A 4 b i						X			
02 03 01	101.02	1 A 4 c i							X		
03 01 02	101.02	1 A 2 a-f				X					
01 01 03	101.03	1 A 1 a	< 50	X							
01 02 03	101.03	1 A 1 a			X						
01 03 02	101.03	1 A 1 b				X					
01 04 02	101.03	1 A 1 c				X					
01 05 02	101.03	1 A 1 c				X					
02 01 03	101.03	1 A 4 a					X				
02 02 02	101.03	1 A 4 b i						X			
02 03 02	101.03	1 A 4 c i							X		
03 01 03	101.03	1 A 2 a-f				X					
01 01 04	101.04	1 A 1 a	Not							X	
01 02 04	101.04	1 A 1 a	Rele							X	
02 01 04	101.04	1 A 4 a	-vant							X	
02 02 03	101.04	1 A 4 b i								X	
02 03 03	101.04	1 A 4 c i								X	
03 01 04	101.04	1 A 2 a-f								X	

SNAP97 Codes	**Combustion plants as area sources**										
	NOSE CODE	NFR CODE	Boilers/furnaces							Gas turbines	Stationary engines
			Thermal capacity [MW]	Public power and cogeneration plants	District heating	Industrial combustion	Commercial and institutional combustion	Residential combustion	Agriculture forestry and fishing		
01 01 05	101.05	1 A 1 a	Not Relevant								X
01 02 05	101.05	1 A 1 a									X
02 01 05	101.05	1 A 4 a									X
02 02 04	101.05	1 A 4 b i									X
02 03 04	101.05	1 A 4 c i									X
03 01 05	101.05	1 A 2 a-									X

X : indicates relevant combination

1 ACTIVITIES INCLUDED

This chapter covers emissions from combustion plants treated collectively as area sources. However, e.g. if only a few units exist and thus only little data is available, the individual approach may be preferable also for small combustion plants.

The subdivision of the SNAP activities according to CORINAIR90 concerning combustion plants takes into account two criteria:

- the economic sector concerning the use of energy:
  - public power and co-generation,
  - district heating,
  - commercial, institutional and residential combustion,
  - industrial combustion,
    (Note: process furnaces are allocated separately.)
- the technical characteristics:
  - the installed thermal capacity,
    - ≥ 50 to < 300 MW,
    - < 50 MW,
  - other combustion technologies,
    - gas turbines,
    - stationary engines.

The emissions considered in this section are released by a controlled combustion process (boiler emissions, furnace emissions, emissions from gas turbines or stationary engines) and are mainly characterised by the types of fuels used. Furthermore, a technical characterisation of the combustion sources may be integrated according to the size and type of plants as well as on primary or secondary reduction measures.[1] Solid, liquid or gaseous fuels are used; whereby solid fuels comprise coal, coke, biomass and waste (as far as waste is used to generate heat or power). In addition a non-combustion process can be a source of ammonia emissions; namely the ammonia slip in connection with some NO_x abatement techniques.[1]

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of area source emissions released by combustion plants to the total emissions in the countries of the CORINAIR90 inventory reported as areas sources is given as follows:

Table 1: Contributions of emissions from combustion plants as area sources to the total emissions of the CORINAIR90 inventory reported as area sources. See chapter ACOR for further information on CORINAIR 90 emissions for these SNAP activities taking point and area sources together

		Contribution to total emissions [%]							
Source category	SNAP code	SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
≥ 300 MW	01 01 01 01 02 01 03 01 01	0	0	0	0	0	0	-	0
50-300 MW	01 01 02 01 02 02 02 01 02 02 02 01 02 03 01 03 01 02	12.1	10.0	1.0	0.1	2.3	9.3	3.3	0.5
< 50 MW	01 01 03 01 02 03 02 01 03 02 02 02 02 03 02 03 01 03	71.3	46.7	41.1	7.2	49.8	66.4	21.8	0.7
Gas turbines	01 01 04 01 02 04 02 01 04 02 02 03 02 03 03 03 01 04	0.1	2.0	0.03	0.03	0.1	1.0	0.2	-
Stationary engines	01 01 05 01 02 05 02 01 05 02 02 04 02 03 04 03 01 05	0.6	2.0	0.2	0.02	0.1	0.4	0.2	0

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[1] Note: Small combustion installations are seldomly equipped with secondary measures.

- : no emissions are reported as area sources

0 : emissions are reported, but the exact amount is under the rounding limit

Plants with a thermal capacity < 50 MW are the major contributors. In particular, the contribution of small units in „Commercial, institutional and residential combustion" with a thermal capacity < 50 MW (SNAP 020002) is significantly high: SO_x 37.0 %, NO_x 24.2 %, NMVOC 39.6 %, CH_4 6.9 %, CO 46.3 %, CO_2 44.4 %, N_2O 14.7 % and NH_3 0.6 % (related to total emissions of CORINAIR90 reported as area sources).
In the literature concerning heavy metal emissions in Europe, area source emissions are not reported separately. In order to show the relevance of the sector residential combustion, the share of the emissions of different heavy metals from this sector in the total emission in Germany is shown as an example in Table 2.

Table 2: Contribution of heavy metal emissions from residential combustion to national total emissions of former West Germany /1/

	Contribution in [wt.-%]	
Pollutant	**1982**	**1990**
As	5.8	15
Cd	3	4.4
Cr	n.d.	n.d.
Cu	4.2	6.4
Hg	1.9	2.8
Ni	4.5	7.7
Pb	0.2	0.4
Se	0.8	3.1
Zn	0.4	0.7

n.d. : no data are available

For Cd and Hg data are also available for Austria. The contribution to total emissions in 1992 was for Cd 38.4% and for Hg 27.8% /2/. The contribution of area sources, such as residential combustion, to total emissions has increased during recent years. This is caused by the fact that large emitters have been equipped with improved dust control facilities in Germany as well as in Austria, and hence the contribution from larger sources has been reduced.

For Particulate Matter:
Combustion Plants < 50 MW (boilers) are now covered in the new supplementary chapter Particulate emissions from smaller Combustion Plants (<50MWth) B111(S1).

Combustion Plants >= 50 and < 300 MW (boilers) are now covered in the new supplementary chapter Particulate emissions from large Combustion Plants (>50MWth) B111(S2).

Gas Turbines are now covered in the new supplementary chapter Particulate emissions from gas turbines and internal combustion engines B111(S3).

3 GENERAL

3.1 Description

The emissions considered in this chapter are generated in boilers or in gas turbines and stationary engines regardless of the allocation of combustion plants to SNAP activities. In addition, residential combustion is relevant for this chapter. Emissions from process furnaces and from waste incineration are excluded.

3.2 Definitions

Integrated Coal Gasification Combined Cycle Gas Turbine (IGCC)	gas turbine fuelled by gas which is a product of a coal gasification process.
Boiler	any technical apparatus in which fuels are oxidised in order to generate heat for locally separate use.
Co-generation plant	steam production in (a) boiler(s) for both power generation (in a steam turbine) and heat supply.
Combined Cycle Gas Turbine (CCGT)	gas turbine combined with a steam turbine. The boiler can also be fuelled separately.
Furnace	fireplace in which fuels are oxidised to heat the direct surroundings.
Plant	element of the collective of emission sources (e.g. residential combustion) treated as an area source.
Stationary engines	spark-ignition engines or compression-ignition engines.

3.3 Techniques

3.3.1 Medium-sized combustion plants - boilers, gas turbines, stationary engines - (thermal capacity ≥ 50 and < 300 MW)

For the combustion of solid, liquid and gaseous fuels in medium-sized combustion plants techniques are used which have already been described in Section 3.3 of chapter B111 on “Combustion Plants as Point Sources”.

3.3.2 Small-sized combustion plants - boilers and furnaces - (thermal capacity < 50 MW)

Small sized combustion plants are divided here into industrial combustion and non-industrial combustion:

- Industrial combustion:
  The techniques used for the combustion of solid, liquid and gaseous fuels in industrial combustion plants have already been described in Section 3.3 of chapter B111 on

"Combustion Plants as Point Sources". The share of combustion techniques used is different: for the combustion of solid fuels mainly grate firing and stationary fluidised bed combustion are applied.

- Non-industrial combustion:
  Non-industrial combustion which includes other small consumers and residential combustion, is characterised by a great variety of combustion techniques.

  For the combustion of solid fuels e.g. mainly grate firing units are installed which can be distinguished by the type of stoking and the air supply. For example, in manually fed combustion units (such as single stoves) emissions mainly result from frequent start-ups/shut-downs; automatically fed combustion units are mainly emission relevant when the fuel is kept glowing. Normally, older combustion installations release more emissions than modern combustion installations. Furthermore, combustion installations which often operate with reduced load conditions are highly emission relevant: this operation mode occurs frequently in the case of over-dimensioned combustion units. /4, 5/

  For the combustion of liquid and gaseous fuels, in principle similar technologies are applied, such as those described in chapter B111 on "Combustion Plants as Point Sources" (Section 3.3).

3.4 Emissions

Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxide (CO), non-methane volatile organic compounds (NMVOC), methane (CH_4) and heavy metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), zinc (Zn) and in the case of heavy oil also vanadium (V)). Emissions of nitrous oxide (N_2O) and ammonia (NH_3) are normally of less importance.

The main influencing parameters which determine the emissions and species profiles of some pollutants are given in Sections 3.4 and 9 of chapter B111 on "Combustion Plants as Point Sources". In particular for small combustion installations (e.g. residential combustion) emissions of NMVOC and CO can occur in considerable amounts; these emissions are mostly released from inefficiently working stoves (e.g. wood-burning stoves). VOC emissions released from domestic wood-fired boilers (0.5 - 10 MW) can be significant. Emissions can be up to ten times higher at 20 % load than those at maximum load /29/.

The emissions are released through the stack. The relevance of fugitive emissions (from seals etc.) can be neglected for combustion installations. Due to the fact that most references do not clearly distinguish between SO_x and SO_2, for the following sections it can be assumed that SO_2 includes SO_3, if not stated otherwise.

3.5 Controls

3.5.1 Medium-sized combustion plants - boilers, gas turbines, stationary engines - (thermal capacity ≥ 50 and < 300 MW)

It can be assumed, that the smaller the combustion installation considered are, the lower is the probability to be equipped with secondary measures. For cases where abatement technologies for SO_2, NO_x or heavy metals (controlled as particulates) are installed, the corresponding technical details are given in Section 3.5 of chapter B111 on “Combustion Plants as Point Sources”. For SO_2 abatement in Germany, larger boilers are mainly controlled by the limestone wet scrubbing process. In the case of smaller facilities dry sorption processes are preferred.

3.5.2 Small-sized combustion plants - boilers and furnaces - (thermal capacity < 50 MW)

Small-sized combustion plants have been split into industrial combustion and non-industrial combustion:

- Industrial combustion:

  For cases where abatement technologies for SO_2, NO_x or heavy metals are installed the corresponding technical details are given in Section 3.5 of chapter B111 on “Combustion Plants as Point Sources”. If NO_x reduction measures are installed mostly primary reduction measures (e.g. low NO_x burner) are applied.

- Non-industrial combustion:

  For small consumers / residential combustion only primary emission control measures are relevant. Emission reduction is mainly achieved by optimised operation conditions (older installations) and improved combustion efficiencies (modern installations).

4 SIMPLER METHODOLOGY

For combustion plants treated as area sources only a simpler methodology is given; a detailed methodology is not applicable (see Section 5). Here “simpler methodology“ refers to the calculation of emissions based on emission factors and activities and covers all relevant pollutants (SO_2, NO_x, NMVOC, CH_4, CO, CO_2, N_2O, heavy metals). Emissions of NH_3 are of less relevance (they are only released as ammonia slip in connection with secondary measures for NO_x abatement).

The annual emission E is determined by an activity A and an emission factor:

$$E_i = EF_i \cdot A \tag{1}$$

E_i	annual emission of pollutant i
EF_i	emission factor of pollutant i
A	annual activity rate

The activity rate A and the emission factor EF_i have to be determined on the same level of aggregation depending on the availability of data. The activity A should be determined within the considered territorial unit by using adequate statistics (see also Section 6). The activity should refer to the energy input of the emission sources considered (fuel consumption in [GJ]). Alternatively, secondary statistics (surrogate data) can be used for the determination of the fuel consumption [GJ]. The quality of surrogate data can be characterised by two criteria:

- level of correlation

  The surrogate data should be directly related to the required data (e.g. fuel consumption of households derived from heat demand of households).

- level of aggregation
  The surrogate data should be provided on the same level of aggregation (e.g. spatial, sectoral and seasonal resolution).

Examples for activity rate and surrogate data and origins of possible inaccuracies are listed in the following:

- annual fuel consumption (recommended activity rate):
  - Statistics concerning the annual fuel consumption are often not further specified for different economic branches, and emission source categories, respectively. Furthermore, no technical split can be provided.
- annual fuel production [Gg], e.g. production of hard coal, lignite, natural gas:
  - The specifications of the fuel used (e.g. different types of coal) are not given. For the conversion of the unit [Gg] into unit [GJ] only an average heating value can be used.
- density of population, number of households:
  - Population statistics correspond to a very high level of aggregation. Further information has to be used (e.g. percentages of fuel consumed) in order to determine the activity rate for small consumers (e.g. residential combustion). In particular for fuels which are distributed by pipelines (e.g. natural gas) this assessment leads to an uncertainty in the activity rate determined.
- number of enterprises, number of employees, turnover of enterprises [Mio ECU]:
  - The statistical data on enterprise level are often allocated to the economic sector (e.g. “Production and Distribution of Electric Power, Production and Distribution of Steam, Hot Water, Compressed Air, District Heating Plants” /EUROSTAT, see Section 6/). On the other hand, emission factors are specified with regard to the type of fuel and often also to the type of boiler used.
- heat consumption:
  - The specific heat consumption per capita (e.g. [J/employee], [J/inhabitant]) or related to the area heated (e.g. [J/building], [J/m²]) can be determined by using area and branch specific data (e.g. differentiation between branches, number of employees, number of inhabitants).

The emission factor EF_i should be calculated as a mean value of all combustion installations within the territorial unit considered. In practice, a limited number of installations are selected to determine a representative emission factor which is applied to the total population of the installations considered. Usually, such emission factors are only specified as a function of fuel characteristics. However, further parameters should be taken into account, in particular the technology distribution as well as the size and age distribution of the boilers. Furthermore, evidence has been given that emissions are significantly affected by the operating conditions (e.g. inefficiently working stoves).

The emission factor EF_i (see Equation (1)) takes into account abatement measures (primary and secondary). If not stated otherwise the emission factors presented refer to full load conditions.

In the following a calculation procedure for SO_2 emission factors is proposed according to Equation (2):

$$EF_{SO_2} = 2 \cdot \overline{C}_{S_{fuel}} \cdot (1 - \overline{\alpha}_s) \cdot \frac{1}{\overline{H}_u} \cdot 10^6 \qquad (2)$$

EF_{SO_2}	emission factor for SO_2 [g/GJ]
$\overline{C}_{S_{fuel}}$	average sulphur content of fuel (in mass S/mass fuel [kg/kg])
$\overline{H}_u$	average lower heating value [Mg/kg]
$\overline{\alpha}_s$	average sulphur retention in ash [ ]

In cases where secondary reduction measures are installed, the reduction efficiency has to be integrated by applying one of the following assumptions:

- if the total population of combustion installations is equipped with secondary measures, a mean reduction efficiency of these measures should be used;
- if only few combustion installations are equipped with secondary measures, either these installations should be treated separately or the mean reduction efficiency should be calculated with regard to the total population.

Reduction efficiencies for different individual secondary measures are given in Tables 10 and 11 in chapter B111 on “Combustion Plants as Point Sources”.

Equation (2) can be used for all fuels, but for liquid and gaseous fuels the sulphur retention in ash α_s is not relevant. If certain input data of Equation (2) are not available, provided default values based on literature data can be used:

$\overline{C}_{S_{fuel}}$	sulphur contents of different fuels see Table 4[2] (in Section 8),
$\overline{\alpha}_S$	sulphur retention in ash of different types of boiler see Table 8[2] in chapter B111 on “Combustion Plants as Point Sources“,
$\overline{H}_u$	lower heating values of different types of fuels see Table 21[2] in chapter B111 on “Combustion Plants as Point Sources“.

For other pollutants, according to Equation (1) fuel and technology specific emission factors EF_i are given in Tables 5 - 12 based on literature data; for activity data see Section 6.

5 DETAILED METHODOLOGY

For combustion plants a detailed methodology means the determination of emissions based on measured data. This is not applicable to area sources as only few emission sources are monitored directly.

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[2] A mean value has to be calcutated with regard to the area concerned.

6 RELEVANT ACTIVITY STATISTICS

The following gives a list of available statistics on a national level for the determination of fuel consumption, installed capacities, socio-economic data, etc.:

- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992
- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1993
- OECD (ed.): Environmental Data, Données OCDE sur l'environnement; Compendium; 1993
- Commission of the European Communities (ed.): Energy in Europe; 1993 - Annual Energy Review; Special Issue; Brussels; 1994
- EUROSTAT (ed.): Panorama of EU Industry'94; Office for official publications of the European Communities; Luxembourg; 1994

A brief discussion of potential surrogate data for the determination of the activity rate is given in Section 4.

7 POINT SOURCE CRITERIA

This section is not relevant since this chapter only covers area sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Medium-sized combustion plants (thermal capacity ≥ 50 and < 300 MW)

For medium combustion installations, emission factors for the pollutants NO_x, NMVOC, CH_4, CO, CO_2, N_2O and heavy metals are given in Tables 24 - 31 in chapter B111 on "Combustion Plants as Point Sources".

8.2 Small-sized combustion plants (thermal capacity < 50 MW)

Tables 4 - 12 contain emission factors for all pollutants except for SO_2 where sulphur contents of different fuels are given. All emission factor tables have been designed in a homogeneous structure: Table 3 provides a split of combustion techniques (types of boilers, etc.); this standard table has been used for all pollutants. The selection of fuels is based on the CORINAIR90 inventory.

For small-sized combustion installations, emission factors are given related to the type of fuel consumed and, if useful, related to technical specifications based on literature data. These emission factors normally refer to stationary operating conditions. Modifications are indicated as footnotes (instationary conditions e.g. due to manually fed boilers, etc.).

The sequence of the following emission factor tables is:

Table 3: Standard table for emission factors for different pollutants

Table 4: Sulphur contents of selected fuels

Table 5: NO_x emission factors [g/GJ]

Table 6: NMVOC emission factors [g/GJ]

Table 7: CH_4 emission factors [g/GJ]

Table 8: CO emission factors [g/GJ]

Table 9: CO_2 emission factors [kg/GJ]

Table 10: N_2O emission factors [g/GJ]

Table 11: NH_3 emission factors [g/GJ]

Table 12: Heavy metal emission factors (mass pollutant/mass fuel [g/Mg])

Table 3: Standard table of emission factors for the relevant pollutants

						no technical specification	Technical specification									
							Industrial combustion							Non-industrial combustion		
Fuel category[1]				NAPFUE code[1]	P1[2]		no specification[10]	DBB[3]	WBB[4]	FBC[5]	GF[6]	GT[7]	Stat. E.[8]	no specification	Small consumers	Residential combustion[9]
s	coal		no specification	-												
s	coal	hc[11]		101 - 103												
s	coal	bc[11]		106												
...	...	...	...	...												
s	biomass		wood	111												
...	...		...	...												
s	waste		municipal	114												
...	...		...	...												
l	oil		no specification	-												
l	oil		residual	201												
...	...		...	...												
g	gas		no specification	-												
g	gas		natural	301												
...	...		...	...												

[1] the fuel category is based on the NAPFUE-code

[2] P1 = sulphur content of fuel

[3] DBB = Dry bottom boiler

[4] WBB = Wet bottom boiler

[5] FBC = Fluidised bed combustion

[6] GF = Grate firing; ST1, ST2 = Type of stoker

[7] GT = Gas turbine

[8] Stat. E. = Stationary engine

[9] A differentiation between old and modern techniques can be made for the ranges of emission factors given so that e.g. the smaller values relate to modern units.

[10] Here only related to combustion in boilers; gas turbines and stationary engines are excluded.

[11] hc = hard coal, bc = brown coal

Table 4: Sulphur contents of selected fuels

Fuel category				NAPFUE code	Sulphur content of fuel	
					range	unit
s	coal	hc	coking, steam, sub-bituminous	101 - 103	0.4 - 6.2	wt.-% (maf)
s	coal	bc	brown coal/lignite	105	0.4 - 6.2	wt.-% (maf)
s	coal	bc	briquettes	106		
s	coke	hc, bc	coke oven, petroleum	107, 108, 110	0.5 - 1 [1] [2]	wt.-% (maf)
s	biomass		wood	111	< 0.03[1]	wt.-% (maf)
s	biomass		peat	113		
s	waste		municipal	114		
s	waste		industrial	115		
l	oil		residual	203	0.3[3] - 3.5[4]	wt.-%
l	oil		gas	204	0.08 - 1.0	wt.-%
l	oil		diesel	205		
l	kerosene			206		
l	gasoline		motor	208	< 0.05[5]	wt.-%
g	gas		natural	301		
g	gas		liquified petroleum gas	303		
g	gas		coke oven	304		
g	gas		blast furnace	305		
g	gas		refinery	308	<= 8[6]	$g \cdot m^{-3}$
g	gas		gas works	311		

[1] Marutzky 1989 /25/

[2] Boelitz 1993 /24/

[3] Personal communication Mr. Hietamäki (Finland)

[4] Referring to NL-handbook 1988 /26/ the range is 2.0 - 3.5

[5] $\alpha_S = 0$

[6] NL-handbook 1988 /26/

Table 5: NO$_x$ emission factors [g/GJ]

Fuel category				NAPFUE code	no technical specification	Technical specification									
						Industrial combustion							Non-industrial combustion		
						no specification	DBB	WBB	FBC	GF	GT	Stat. E.	no specification	Small consumers	Residential combustion
s	coal		no specification	-											60-232***
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	50 - 668[11]	155[13]							50[1][2]	150[9]	50[9]
s	coal	bc	brown coal/lignite	105	7.5 - 604[11]								12[2] - 100[1]		
s	coal	bc	briquettes	106	17 - 300[11]										100[9]
s	coke	hc,bc	coke oven, petroleum	107, 108, 110	13 - 323[11]								45	50[9][10]	50[9][10]
s	biomass		wood	111	130 - 968[11]	206[13]				100-300*, 30-120**			12 - 80[1]	75[9]	50[9], 147-200[4]
s	biomass		peat	113	130 - 240[11]								100[1]		
s	waste		municipal	114	140 - 280[11]										
s	waste		industrial	115	100 - 193[11]										
s	waste		wood	116	80 - 258[11]										
s	waste		agricultural	117	80 - 100[11]										
l	oil		no specification	-									50[2]		
l	oil		residual	203	98 - 520[11]	165[13]					350[12]	75 - 1,889[12]			
l	oil		gas	204	55 - 1,624[11]	70[13]					100 - 531[12]	80 - 1,493[12]	50[1], 51[4]	48[9]	47[9]
l	oil		diesel	205	300 - 373[11]						380[12]	840[12],[13]			
l	kerosene			206	45 - 100[11]						120[12]	45 - 1,038[12]	50[1]		
l	gasoline		motor	208	80[11]							375[12]			
l	naphtha			210	24 - 1,085[11]										
g	gas		no specification	-									30[2]-50[3]		
g	gas		natural	301	32 - 307[11]	62[13]					81 - 360[12], 165[13][14]	75 - 1,200[12], 165[13]	50[1]	38[9]	30[8], 46[9]
g	gas		liquified petroleum gas	303	18 - 105[11]						120[12]		50[1],	57[9]	47[4], 69[9]
g	gas		coke oven	304	2 - 399[11]						250[12]		50[1]	38[9]	46[9]
g	gas		blast furnace	305	25 - 1,520[11]						250[12]				
g	gas		waste	307	52 - 238[11]										
g	gas		refinery	308	65 - 155[11]						55 - 357[12]				
g	gas		biogas	309	4 - 132[11]										
g	gas		from gas works	311	50 - 411[11]								50[1]		

[1] CORINAIR 1992 /8/

[2] LIS 1977 /15/

[3] UBA 1981 /21/, Kolar 1990 /14/

[4] Radian 1990 /18/, IPCC 1994 /12/

[5] spruce wood

[6] chip board, phenol bonded

[7] chip board, urea bonded

[8] LIS 1987 /16/

[9] UBA 1995 /23/

[10] coke from hard coal

[11] CORINAIR90 data of combustion plants as area sources

[12] CORINAIR90 data, area sources

[13] UBA 1995 /30/

[14] at 50 % load: 130 g/GJ

* 100[3][5], 120[3][6], 300[3][7] for underfeed stoker

** 30[3][5], 80[3][6], 120[3][7] for overfeed stoker

*** 60[8], 149[4], 232[4]

Table 6: NMVOC emission factors [g/GJ]

						Technical specification									
						Industrial combustion							Non-industrial combustion		
Fuel category				NAPFUE code	no technical specification	no specification	DBB	WBB	FBC	GF	GT	Stat. E.	no specification	Small consumers	Residential combustion
s	coal		no specification	-							╳	╳			
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	1-511[5]								400[1] - 600[2]		50[3]
s	coal	bc	brown coal/lignite	105	1-800[5]			╳							
s	coal	bc	briquettes	106	1.5-700[5]								150[1][2]		225[3]
s		hc,bc	coke oven, petroleum	107,108, 110	0.5-700[5]								12[2]		225[3][4]
s	biomass		wood	111	7-1,000[5]								150[2] - 800[1]		480[3]
s	biomass		peat	113	3-600[5]								150[1]		
s	waste		municipal	114	9-70[5]		╳								
s	waste		industrial	115	0.5-134[5]										
s	waste		wood	116	48-600[5]										
s	waste		agricultural	117	50-600[5]										
l	oil		no specification	-			╳	╳	╳	╳			15[2]		
l	oil		residual	203	2.1-34[5]						3 - 4[6]	1.4 - 103.7[6]			
l	oil		gas	204	1.5-116[5]						0.7 - 5[6]	1.5 - 250[6]	15[1]		1.5[3]
l	oil		diesel	205	1.5-2.5[5]						5[6]	3.5[6]			
l	kerosene			206	1-14[5]						1[6]	1.5 - 244[6]	15[1]		
l	gasoline		motor	208	2[5]							437[6]			
l	naphtha			210	1-5[5]										
g	gas		no specification	-			╳	╳	╳	╳			1.5[2]		
g	gas		natural	301	0.3-205[5]						0.1 - 5.7[6]	0.3 - 47[6]	10[1]		2.5[3]
g	gas		liquified petroleum gas	303	0.3-14[5]						1[6]				3.5[3]
g	gas		coke oven	304	0.3-12[5]						2[6]		25[1]		2.5[3]
g	gas		blast furnace	305	0.2-1.5[5]										
g	gas		waste	307	2-16[5]										
g	gas		refinery	308	0.3-2.5[5]						2[6]				
g	gas		biogas	309	2.4-10[5]										
g	gas		from gas works	311	0.6-10[5]								25[1]		

[1] CORINAIR 1992 /8/

[2] LIS 1977 /15/

[3] UBA 1995 /23/

[4] coke from hard coal

[5] CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

[6] CORINAIR90 data, area sources

Table 7: CH_4 emission factors [g/GJ]

					no technical specification	Technical specification									
						Industrial combustion							Non-industrial Combustion		
Fuel category				NAPFUE code		no specification	DBB	WBB	FBC	GF	GT	Stat. E.	no specification	Small consumers	Residential combustion
s	coal		no specification	-											
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	2 - 511$^{4)}$										450$^{2)}$
s	coal	bc	brown coal/lignite	105	0.2 - 532$^{4)}$										
s	coal	bc	briquettes	106	1 - 350$^{4)}$										225$^{2)}$
s	coke	hc,bc	coke oven, petroleum	107, 108, 110	1.5 - 200$^{4)}$										225$^{2)\ 3)}$
s	biomass		wood	111	21 - 601$^{4)}$										74-200$^{1)}$, 320$^{2)}$
s	biomass		peat	113	5 - 400$^{4)}$										
s	waste		municipal	114	6 - 32$^{4)}$										
s	waste		industrial	115	0.3 - 38$^{4)}$										
s	waste		wood	116	30 - 400$^{4)}$										
s	waste		agricultural	117	10 - 400$^{4)}$										
l	oil		no specification	-											
l	oil		residual	203	0.1 - 10$^{4)}$						1 - 3$^{5)}$	0,02 - 7,5$^{5)}$			
l	oil		gas	204	0.1 - 19$^{4)}$						1 - 20,9$^{5)}$	0,04 - 14$^{5)}$			3.5$^{2)}$, 5$^{1)}$
l	oil		diesel	205	1.5 - 2.5$^{4)}$							3,5$^{5)}$			
l	kerosene			206	0.02 - 7$^{4)}$						1$^{5)}$	0,02 - 7,4$^{5)}$			
l	gasoline		motor	208	1							49$^{5)}$			
l	naphtha			210	0.02 - 5$^{4)}$										
g	gas		no specification	-									1$^{1)}$		
g	gas		natural	301	0.3 - 205$^{4)}$						0,3 - 22,5$^{5)}$	0,02 - 153$^{5)}$			2.5$^{2)}$
g	gas		liquified petroleum gas	303	0.02 - 6$^{4)}$						1$^{5)}$				1.1$^{1)}$, 1.5$^{2)}$
g	gas		coke oven	304	0.02 - 12$^{4)}$						2$^{5)}$				2.5$^{2)}$
g	gas		blast furnace	305	0.02 - 4$^{4)}$										
g	gas		waste	307	0.4 - 2.5$^{4)}$										
g	gas		refinery	308	0.02 - 2.5$^{4)}$						2$^{5)}$				
g	gas		biogas	309	0.4 - 10$^{4)}$										
g	gas		from gas works	311	0.6 - 10$^{4)}$										

1) Radian 1990 /18/, IPCC 1994 /12/

2) UBA 1995 /23/

3) coke from hard coal

4) CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

5) CORINAIR90 data, area sources

Table 8: CO emission factors [g/GJ]

			Fuel category	NAPFUE code	no technical specification	Technical specification									
						Industrial combustion						Non-industrial Combustion			
						no specification	DBB	WBB	FBC	GF	GT	Stat. E.	no specification	Small consumers	Residential combustion
s	coal		no specification	-						178-196*, 100 2)-107 6)			185 5)		160-3,580**
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	9 - 5,000 11)	73 13)								500 9)	4,800 9)
s	coal	bc	brown coal/lignite	105	4 - 6,000 11)										
s	coal	bc	briquettes	106	11 - 5,200 11)								7,000 7)		4,300 9)
s	coke	hc,bc	coke oven, petroleum		2 - 5,500 11)									1,000 9) 10)	4,800 9) 10)
s	biomass		wood	111	82 - 10,000 11)	627 13)							7,000 7)	3,600 9)	5,790 9)
s	biomass		peat	113	65 - 10,000 11)										18-18,533***
s	waste		municipal	114	33 - 2,188 11)										
s	waste		industrial	115	15 - 510 11)										
s	waste		wood	116	61 - 8,500 11)										
s	waste		agricultural	117	200 - 8,500 11)										
l	oil		no specification	-									70 8)		
l	oil		residual	203	29 - 1,754 11)	10 13)					10 - 30.4 12)	11.7 - 438 12)	20 2)		13 4)
l	oil		gas	204	5.3 - 547 11)	10 13)					10 - 123 12)	12 - 691 12)		41 9)	43 9)
l	oil		diesel	205	12 - 547 11)						12 12)	190 12),13)			
l	kerosene			206	3 - 151 11)						12 12)	3.4 - 669 12)			
l	gasoline		motor	208	12 11)										
l	naphtha			210	0.2 - 89 11)										
g	gas		no specification	-									70 8)		10 4)
g	gas		natural	301	2.4 - 500 11)	10 13)					8-123 12), 10 13)14)	2.4-335 12), 136 13)	252)	41 9)	25-250***
g	gas		liquified petroleum gas	303	3.3 - 250 11)									41 9)	10 4), 53 9)
g	gas		coke oven	304	3.3 - 279 11)						13 12)			41 9)	53 9)
g	gas		blast furnace	305	3 - 279 11)						13 12)				
g	gas		waste	307	8.8 - 27 11)										
g	gas		refinery	308	3.3 - 279 11)						2 12)				
g	gas		biogas	309	7.8 - 41 11)										
g	gas		from gas works	311	6.4 - 225 11)										

1) EPA 1987 /10/, CORINAIR 1992 /8/

2) CORINAIR 1992 /8/ for overfed stoker

3) OECD 1989 /31/, CORINAIR 1992 /8/

4) Radian 1990 /18/, IPCC 1994 /12/

5) EPA 1987 /10/, CORINAIR 1992 /8/

6) EPA 1985 /9/, CORINAIR 1992 /8/ for overfeed stoker

7) LIS 1987 /16/

8) LIS 1977 /15/

9) UBA 1995 /23/

10) coke from hard coal

11) CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

12) CORINAIR90 data, area sources

13) UBA 1995 /30/

14) at 50 % load: 76 g/GJ

* 178 1), 190 2), 196 3) for underfeed stoker

**160 3), 484 4), 1,500 5), 1,607 6), 2,000 2), 3,400 3), 3,580 4)

*** 18 4), 53 9),4,949 4), 6,002 4), 18,533 4)

**** 25 2), 200 2), 250 2) (cooker)

Table 9: CO_2 emission factors [kg/GJ]

Fuel category				NAPFUE code	Emission factors		
					value	range	remarks
s	coal		no specification	-			
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	94[6]	93 - 99[5], 55.9 - 106.8[2]	
s	coal	bc	brown coal/lignite	105		74 - 105.5[5], 67.5 - 116[2]	
s	coal	bc	briquettes	106	97[6]	97 - 113[3], 85.6 - 110.9[2]	
s	coke	hc,bc	coke oven, petroleum	107, 108, 110	105[6]	96 - 122[1][4], 85.6 - 151[2]	
s	biomass		wood	111		100 - 125[1][4], 83 - 322.6[2]	
s	biomass		peat	113		98 - 115[2]	
s	waste		municipal	114		109 - 141[1], 15 - 117[2]	
s	waste		industrial	115		20 - 153.3[2]	
s	waste		wood	116		83 - 92[2]	
s	waste		agricultural	117		69 - 100[2]	
l	oil		no specification	-			
l	oil		residual	203		76 - 78[3][4], 64 - 99[2]	
l	oil		gas	204	74[6]	73 - 74[5], 69 - 97[2]	
l	oil		diesel	205		73 - 74[2][4]	
l	kerosene			206	73[5]	67.7 - 78.6[2]	
l	gasoline		motor	208	71[2], 73[5]	71 - 74[1][3][4]	
l	naphtha			210	73[3]	72.1 - 74[2]	
g	gas		no specification	-			
g	gas		natural	301	56[6]	55 - 61[3][4][5], 52 - 72[2]	
g	gas		liquified petroleum gas	303	65[6]	55 - 75.5[2]	
g	gas		coke oven	304	44[6], 49[5]	44 - 192[2]	
g	gas		blast furnace	305		105 - 290[2]	
g	gas		waste	307		62.5 - 87.1[2]	
g	gas		refinery	308		55 - 66[2]	
g	gas		biogas	309		60 - 103.4[2]	
g	gas		from gas works	311		52 - 56[2]	

[1] Schenkel 1990 /20/

[2] CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

[3] IPCC 1993 /11/

[4] Kamm 1993 /13/

[5] BMU 1994 /7/

[6] UBA 1995 /30/

Table 10: N_2O emission factors [g/GJ]

Fuel category				NAPFUE code	no technical specification	Technical specification									
						Industrial combustion							Non-industrial combustion		
						no specification	DBB	WBB	FBC	GF	GT	Stat. E.	no specification	Small consumers	Residential combustion
s	coal		no specification	-											
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	5 - 30[1]										
s	coal	bc	brown coal/lignite	105	1.4 - 18.2[1]										
s	coal	bc	briquettes	106	1.4 - 14[1]										
s	coke	hc,bc	coke oven, petroleum	107, 108, 110	1.4 - 14[1]										
s	biomass		wood	111	1.6 - 20[1]										
s	biomass		peat	113	2 - 14[1]										
s	waste		municipal	114	4[1]										
s	waste		industrial	115	2 - 5.9[1]										
s	waste		wood	116	4[1]										
s	waste		agricultural	117	1.4 - 4[1]										
l	oil		no specification	-											
l	oil		residual	203	0.8 - 46.5[1]						2.5 - 25[2]	1.1 - 2.1[2]			
l	oil		gas	204	0.6 - 17.8[1]						0.5 - 25[2]	0.6 - 14[2]			
l	oil		diesel	205	2 - 15.7[1]						15.7[2]	2 - 4[2]			
l	kerosene			206	2 - 14[1]						14[2]	2[2]			
l	gasoline		motor	208	14[1]							2[2]			
l	naphtha			210	12[1]										
g	gas		no specification	-											
g	gas		natural	301	0.1 - 14[1]						0.1-3[2]	0.1-3[2]			
g	gas		liquified petroleum gas	303	1 - 14[1]						14[2]				
g	gas		coke oven	304	1 - 12[1]						3[2]				
g	gas		blast furnace	305	0.8 - 34.6[1]						3[2]				
g	gas		waste	307	3.7 - 5[1]										
g	gas		refinery	308	1.5[1]						3[2]				
g	gas		biogas	309	1.5 - 3.7[1]										
g	gas		from gas works	311	2 - 3[1]										

[1] CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

[2] CORINAIR90 data, area sources

Table 11: NH_3 emission factors [g/GJ]

Fuel category				NAPFUE code	no technical specification	Technical specification	
						Gas turbines	Stationary engines
s	coal		no specification	-			
s	coal	hc	coking, steam, sub-bituminous	101, 102, 103	0.14 - 0.48[1]		
s	coal	bc	brown coal/lignite	105	0.01 - 0.86[1]		
s	coal	bc	briquettes	106	0.01 - 0.86[1]		
s	coke	hc,bc	coke oven, petroleum	107, 108, 110	0.01 - 0.86[1]		
s	biomass		wood	111	5 - 9[1]		
s	biomass		peat	113			
s	waste		municipal	114			
s	waste		industrial	115			
s	waste		wood	116			
s	waste		agricultural	117			
l	oil		no specification	-			
l	oil		residual	203	0.01[1]		
l	oil		gas	204	0.01 - 2.68[1]		0.1 - 0.2[1]
l	oil		diesel	205			
l	kerosene			206			0.2[1]
l	gasoline		motor	208			
l	naphtha			210			
g	gas		no specification	-			
g	gas		natural	301	0.15 - 1[1]		
g	gas		liquified petroleum gas	303	0.01[1]		
g	gas		coke oven	304	0.87[1]		
g	gas		blast furnace	305			
g	gas		waste	307			
g	gas		refinery	308			
g	gas		biogas	309	15[1]		
g	gas		from gas works	311			

[1] CORINAIR90 data, combustion plants as area sources with a thermal capacity of > 300, 50 - 300, < 50 MW

Table 12: Heavy metal emission factors (mass pollutant/mass fuel [g/Mg])

Fuel category			NAPFUE code	Heavy metal element	no technical specification	Technical specification							
						Industrial combustion					Non-industrial combustion		
						no specification	DBB	WBB	FBC	GF	no specification	Small consumer	Residential combustion
s	coal	hc	101/102	Mercury		1.7 g/TJ$^{2)}$							0.3$^{1)}$
				Cadmium		0.1 g/TJ$^{2)}$							0.15$^{1)}$
				Lead		6.0 g/TJ$^{2)}$							2.5$^{1)}$
				Copper		3.1 g/TJ$^{2)}$							1.2$^{1)}$
				Zinc		10.5 g/TJ$^{2)}$							1$^{1)}$
				Arsenic		3.2 g/TJ$^{2)}$							1.2$^{1)}$
				Chromium		2.3 g/TJ$^{2)}$							0.9$^{1)}$
				Selen		0.5 g/TJ$^{2)}$							0.15$^{1)}$
				Nickel		4.4 g/TJ$^{2)}$							1.8$^{1)}$
s	coal	bc	105	Mercury		4.4 g/TJ$^{2)}$							0.1$^{2)}$
				Cadmium		0.4 g/TJ$^{2)}$							0. 04$^{2)}$
				Lead		3.9 g/TJ$^{2)}$							0.24$^{2)}$
				Copper		2.0 g/TJ$^{2)}$							
				Zinc		10.6 g/TJ$^{2)}$							0.14$^{2)}$
				Arsenic		4.2 g/TJ$^{2)}$							
				Chromium		3.1 g/TJ$^{2)}$							
				Selen									
				Nickel		3.9 g/TJ$^{2)}$							
l	oil, heavy fuel		203	Mercury		0.15-0.2$^{1)}$							
				Cadmium		0.1-1$^{1)}$							
				Lead		0.6-1.3$^{1)}$							
				Copper		0.05-1$^{1)}$							
				Zinc		0.02-0.2$^{1)}$							
				Arsenic		0.14-1$^{1)}$							
				Chromium		0.2-2.5$^{1)}$							
				Selen		0.003-1$^{1)}$							
				Nickel		17-35$^{1)}$							
g	gas		301	Mercury									

1) Winiwarter 1995 /6/ 2) Jockel 1995 /1/

9 SPECIES PROFILES

For species profiles of selected pollutants see Section 9 in chapter B111 on "Combustion Plants as Point Sources".

10 UNCERTAINTY ESTIMATES

Uncertainties of emission data result from inappropriate emission factors and from missing statistical information on the emission generating activity. Those discussed here are related to emission factors. Usually uncertainties associated with emission factors can be assessed by comparing them with emission factors obtained by using measured data or other literature data. However, at this stage, the available emission factors based on literature data are often poorly documented without a specification concerning the area of application. A range of emission factors, depending on the parameters available (as given in chapter B111 on "Combustion Plants as Point Sources", Section 10), can therefore not be given here.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors.

The average emission factor of a territorial unit should integrate the diversity of the combustion techniques installed within the territorial unit. Therefore, the number and diversity of the selected combustion installations for the calculation of the average emission factor should correspond with the number and diversity of the installations within the territorial unit (target population). Further work should be carried out to characterise territorial units with regard to the technologies in place (technology distribution, age distribution of combustion technique, etc.).

For all pollutants considered, neither qualitative nor quantitative load dependencies have yet been integrated into the emission factors. In particular for oil, coal and wood fired small stoves, increased emissions occur due to a high number of start-ups per year (e.g. up to 1,000 times a year) or due to load variations (e.g. manual furnace charging). Emissions from residential firing can be highly relevant (e.g. combustion of wood in the Nordic countries, in particular for VOC and CO emissions). Further work should be invested to clarify this influence with respect to the emission factors published.

For the weakest aspects related to the determination of activities based on surrogate data see Section 4. Uncertainty estimates of activity data should take into account the quality of available statistics. In particular, emissions from the combustion of wood in single stoves may increase as some national statistics have underestimated wood consumption to date /3/.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Spatial disaggregation of annual emission data (top-down approach) can be related

- for industrial combustion e.g. to the number of industrial employees in industrial areas and
- for residential combustion e.g. to the number of inhabitants in high density and low density areas and to the type of fuel.

In general the following disaggregation steps for emissions released from residential combustion can be used /cf. 27/:

- differentiation in spatial areas, e.g. administrative units (country, province, district, etc.), inhabited areas, settlement areas (divided in high and low density settlements),
- determination of regional emission factor per capita depending on the population density and the type of fuel used.

For emissions released from industrial combustion, spatial disaggregation takes into account the following steps:

- differentiation in spatial areas with regard to industrial areas,
- determination of emission factors related to the number of industrial employees.

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and/or hourly emission data. For annual emissions released from combustion plants as area sources this data can be obtained for:

- industrial combustion by using in principle the disaggregation criteria and the procedure as described in Section 13 of chapter B111 on “Combustion Plants as Point Sources” by taking into account the number of plants in the area considered.
- non-industrial combustion (small consumer/residential combustion) by using a relation between the consumption of fuel and the heating degree-days.

The disaggregation of annual emissions released from non-industrial combustion (small consumers/residential combustion) has to take into account a split into:

- summer and winter time (heating periods),
- working days and holidays and
- daily fluctuations of load

for the main relevant fuels and, if possible, for the main relevant combustion techniques (manually fed stoves, etc.)

The procedure of disaggregation consists of the following step-by-step approach /cf. 28/:

- determination of the temporal variation of the heat consumption (based e.g. on user behaviour),

- determination of the fuel consumption e.g. by using statistics for district heat or consumption of gas, by using fuel balances for the estimation of coal and wood consumption (e.g. as given in /3/),
- correlation of the heating degree-days with the consumption of fuel (e.g. for gas, district heat). Typical heating degree-days are available in statistics. The correlation can be linear as given e.g. in /28/.
- determination of the relative activity (e.g. fuel consumption per hour per day) by using adequate statistics.

This approach makes it possible to determine annual, weekly and/or daily correction factors. For the determination of hourly emissions the following Equation (3) /cf. 28/ can be given as an example:

$$E_H(t) = \frac{E_A}{8{,}760[h]} \cdot f_a(t) \cdot f_w(t) \cdot f_d(t) \tag{3}$$

E_H	emission per hour(s) [Mg/h]
E_A	annual emission [Mg]
f_a	annual correction factor [ ]
f_w	weekly correction factor [ ]
f_d	daily correction factor [ ]
t	time

The constant (8,760 h) in Equation (3) represents the number of hours per year.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in chapter B111 on ”Concepts for Emission Inventory Verification“ different verification procedures can be used. The aim of this section is to select those which are most adequate for emission data from combustion plants as area sources. Verification procedures considered here are principally based on the verification of emission data on a territorial unit level (national level).

The annual emissions related to a territorial unit can be compared to independently derived emission estimates. These independent emission estimates can be obtained by using econometric relations between annual emissions and exogenous variables, such as population equivalents, number of households, fossil fuel prices, etc.

Another possibility is to make emission density comparisons of e.g. emissions per capita or emissions per GDP between countries with comparable economic structures.

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19 RELEASE VERSION, DATE AND SOURCE

Version : 3.1

Date : December 1995

Source : Otto Rentz; Dagmar Oertel
University of Karlsruhe (TH)
Germany

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
December 2006

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Annex 1: List of abbreviations

A_i	Activity rate of the emission source i
bc	Brown coal
CCGT	Combined Cycle Gas Turbine
CFBC	Circulating Fluidised Bed Combustion
DBB	Dry Bottom Boiler
E	Emission
EF_i	Emission factor of the emission source i, e.g. in [g/GJ]
f_a	Annual correction factor [ ]
f_d	Daily correction factor [ ]
f_w	Weekly correction factor [ ]
FBC	Fluidised Bed Combustion
g	Gaseous state of aggregation
GF	Grate Firing
GT	Gas Turbine
H	Lower heating value of fuel
hc	Hard coal
IGCC	Integrated Coal Gasification Combined Cycle Gas Turbine
l	Liquid state of aggregation
PFBC	Pressurised Fluidised Bed Combustion
s	Solid state of aggregation
S	Sulphur content of fuel
Stat. E.	Stationary Engine
t	Time
WBB	Wet Bottom Boiler

SNAP CODE:	**010104** **010204** **010304** **010404** **010504** **020104** **020203** **020303** **030104**
SOURCE ACTIVITY TITLE:	**COMBUSTION IN ENERGY &TRANSFORMATION INDUSTRIES** ***Gas Turbines***
NOSE CODE:	**101.04**
NFR CODE:	**1 A 1 a** **1 A 1 b** **1 A 1 c** **1 A 2 a-f** **1 A 4 a** **1 A 4 b i** **1 A 4 c i**

The emission factors for these activities are actually contained in Chapters B111 and B112.

For particulate matter emissions please see chapter B111 (S3) Particulate emissions from gas turbines and internal combustion engines[1].

1 RELEASE VERSION, DATE AND SOURCE

Version: 3
Date: September 2006

Source: Carlo Trozzi
Techne Consulting
Italy

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SNAP CODE:	**010302** **010303** **010305**
SOURCE ACTIVITY TITLE:	**PETROLEUM AND/OR GAS REFINING PLANTS** ***Combustion Plants >= 50 and < 300 MW (boilers)*** ***Combustion Plants < 50 MW (boilers)*** ***Stationary Engines***
NOSE CODE:	**101.02** **101.03** **101.05**
NFR CODE:	**1 A 1 b**

The emission factors for these activities are actually contained in Chapters B111 and B112.

(These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006)).[1]

1. RELEASE VERSION, DATE AND SOURCE

Version: 2
Date: September 2006

Source: Carlo Trozzi
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Email: carlo.trozzi@techne-consulting.com

SNAP CODE: **010306**

SOURCE ACTIVITY TITLE: **PETROLEUM AND/OR GAS REFINING PLANTS**
Process Furnaces

NOSE CODE: **104.08.03**

NFR CODE: **1 A 1 b**

1 ACTIVITIES INCLUDED

This chapter covers emissions released from combustion processes within a refinery for the heating of crude and petroleum products without contact between flame and products. Primary reduction measures are taken into account (if installed). The emission generating process is the combustion of heavy fuel oil, refinery gas and/or petroleum coke. Thermal cracking units are also taken into account.

The following activities are excluded: power plants installed within a refinery (producing steam and/or electricity) as well as internal combustion engines and gas turbines are considered in chapters B111 on “Combustion Plants as Point Sources” and B112 on “Combustion Plants as Area Sources”; fluid catalytic cracking/CO boilers are treated under SNAP 040102; sulphur recovery plants are covered by SNAP 040103; flaring in the oil industry is treated under SNAP 090204 (waste treatment and disposal). Process specific emissions from refineries are covered by SNAP 040104 “Storage and Handling of Petroleum Products in a Refinery”.

2 CONTRIBUTION TO TOTAL EMISSIONS

The contribution of emissions released from refinery process furnaces to the total emissions in countries of the CORINAIR90 inventory is given as follows:

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code †**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Process Furnaces without Contact	010306	1.4	0.5	0.2	0	0.1	1.0	0.2	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported
† = SNAP90 code 030201
* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

In a modern refinery up to 80 %, in some cases even 90 %, of all SO_2 emissions and also a major part of the NO_x emissions and particulate emissions (combined with heavy metals) of the refinery are dependent or directly related to the types of fuel used and their respective shares of the total fuel consumption of the refinery /14/. A split of total refinery emissions can be given as an example for SO_2 and NO_x emissions (Western Europe) /cf. 1, 9/:

SO_2:	- Process heaters and boilers:	69 %	of total SO_2 emissions from refineries
	- FCC units (CO boilers):	7 %	”
	- sulphur recovery unit:	10 %	”
	- flares:	9 %	”
	- other sources (e.g. gas turbines, stationary engines):	6 %	”
NO_x:	- process heaters:	46 %	of total NO_x emissions from refineries
	- boilers:	17 %	”
	- FCC units (CO boilers):	16 %	”
	- engines (for pumps etc.):	11 %	”
	- gas turbines and combined cycle systems:	10 %	“

Process heaters contribute about 40 % to the total refinery emissions of SO_2 and NO_x, whereas the contribution of refineries to the total anthropogenic emissions is about 1 % (average for SO_2 and NO_x).

3 GENERAL

3.1 Description

The most relevant emission sources within this sector are process heaters. In most refining processes it is necessary to apply heat to raise the temperature of the feedstock to a required temperature. Process heaters are therefore used, and where processes are self-contained each process usually has its own separate process heater.

3.2 Definitions

Cracking	one of the process steps within a refinery for splitting long-chain hydrocarbons into short-chain hydrocarbons. Two types of cracking can be distinguished: catalytic and thermal. Catalytic cracking (e.g. FCC) is the most common type of cracking implemented in refineries. Thermal cracking is of less importance with the exception of visbreaking (thermal cracking of high-boiling residues).

3.3 Techniques

Process heaters are installed as for example pipe still or pre-heaters; they are mostly located at the atmospheric distillation, before the vacuum distillation, before the visbreaker, before the

FCC units, before thermal cracking units[1], and before the sulphur recovery units. The burners are mostly situated at the bottom of the installations. Refineries can have about 4 up to more than 40 process heaters depending on the complexity of operations. The refinery gas, produced by petroleum processing, provides a significant part of the fuel for process heaters. Different processes contribute varying amounts and varying compositions to the refinery gas. However, major components of the gas are hydrogen and light hydrocarbons. In principle, refineries use gaseous fuels (refinery gas, sometimes also natural gas /14/), which are supplemented by liquid fuels (heavy fuel oil or other residues) and solid fuels (petroleum coke). In many applications, dual-fuel burners are used with gas and liquid fuel being consumed by the same burners. The columns can also be heated by using the process steam generated in boilers. The fuel used for steam generation may be different from commercial fuel as its nature is determined by the optimal use of resources within each refinery at a given time. /cf. 1, 3/.

3.4 Emissions

Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x) and carbon dioxide (CO_2). SO_3 emissions are negligible for all fuels used. For normal operating conditions emissions of carbon monoxide (CO), nitrous oxide (N_2O), and heavy metals are of less relevance. Emissions of volatile organic compounds (non-methane VOC and methane (CH_4)) can occur, but they are often negligible. Normally, emissions of ammonia (NH_3) are not relevant.

Emissions considered here are associated with continuous operation of the refinery. Emissions are released through stacks. Nevertheless, frequent start-ups and shut-downs of process heaters may occur, due to unexpected changes in operating conditions or from regular non-operating times (e.g. for maintenance).

The emissions of sulphur dioxide (SO_2) are directly related to the sulphur content of the fuel(s) used. The sulphur content of refinery gas varies from 0.01 to 5 %, averaging 0.8 % /2/. Refinery gases are produced in almost all hydrocarbon processing installations. They can be classified as sulphur-free gases and gases containing sulphur: /14/

- sources of sulphur-free gases: [2]
    - isomerisation plants, catalytic reforming plants, hydrogen manufacturing plants, gasification of coke in some coke operations,
- sources of sulphur-containing gases: [3]

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[1] Thermal cracking units are of less importance within refineries, but they are commonly used in the petrol chemistry (e.g. olefin cracking units).

[2] As a consequence of the use of sulphur sensitive catalysts in isomerisation and catalytic reforming, these processes require virtually sulphur free feedstocks. As a result, the gas streams from these units are nearly sulphur free. The gases produced in hydrogen manufacturing plants and from gasification units can also be desulphurised. /cf. 14/

[3] Most other gases produced in the refinery contain hydrogen sulphide (H_2S) and often small quantities of mercaptans.

-- crude distillation, hydro-treating/hydro-desulphurisation, catalytic cracking, thermal cracking/coking/visbreaking, residue conversion, flare gas recovery[4], gasification of coke from some coke operations /14/ [5]

Liquid fuels used in a refinery originate from various processes (e.g. crude oil distillation, high vacuum distillation, thermal or catalytical cracking). In general, the liquid fuels comprise the following components: atmospheric and vacuum residues, thermally cracked residues, heavy catalytically cracked cycle oil and hydrocracked residues. Sulphur contents of liquid refinery fuels and/or components are given in Table 2. /14/

Table 2: Sulphur contents of liquid refinery fuels (cf. /14/)

Residue	**Sulphur content of residues [wt.-%] from**	
	Crude oil from North Sea	**Crude oil from Middle East**
Atmospheric residue	0.6 - 1.1	2.3 - 4.4
Vacuum residue	1.1 - 1.8	3.6 - 6.1
Cracked residue	n. d.	3.5 - 6.5

n. d. : no data are available

However, lower amounts of sulphur in liquid refinery fuels may occur (e.g. Swedish refineries use fuel oil with a sulphur content of 0.4 - 0.5 wt.-% /cf. 15/.). An average sulphur content of fuel oil used in refineries is given as 2.8 wt.-% in /cf. 2/. A weighted average sulphur content of the mix of refinery gas and heavy fuel oil can be given as 1.7 wt.-% /2/.

The sulphur content of the petroleum coke produced and consumed by refineries depends on the type of crude oil/fractions used. In practice, the sulphur content of coke varies between ca. 0.93 wt.-% sulphur (petroleum coke produced mostly from delayed coking process) and ca. 1.4 wt.-% sulphur (petroleum coke produced mostly from fluid coking process) /cf. 6/.

The formation of nitrogen oxides (NO_x) can be split into “fuel-NO”, “thermal-NO” and “prompt-NO” as discussed in chapter B111 on “Combustion Plants as Point Sources” (Section 3). Within the temperature range under consideration, the formation of “prompt-NO” can be neglected. “Fuel-NO” results from the oxidation of the fuel nitrogen content. For liquid fuels, the content of nitrogen in heavy fuel oil varies between 0.1 and 0.8 wt.-% /7/. The content of nitrogen in gaseous fuels (refinery gas) as well as in solid fuels (petroleum coke contain ca. 0.2 wt.-% /6/) is negligible. Relatively high NO_x emissions may be released by thermal cracking units in petrochemical industry (e.g. at olefin cracking units

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[4] The flare gas recovery system is in fact a refinery safety device which under normal conditions has no flow /14/.

[5] For a description of selected units see chapter B411 on "Petroleum Products Processing".

concentrations of about 130 up to 1,600 mg/m^3 may occur /18/). The design of burner and furnace as well as the operating conditions determine the NO_x formation. NO_x emissions vary considerably for existing and new (optimised) furnaces in refineries (see Table 3).

Table 3: Ranges of NO_x concentrations for existing and new (optimised) furnaces in refineries (according to /14/)[1]

Type of process furnace	**NO_x concentration [mg/Nm³]**	
	Gas[2]	**Refinery fuel[3]**
Existing furnace	160 - 1,300	280 - 1,000
Furnace with optimal burner and furnace design	100 - 200	about 250[4]

[1] Apart from firing either gas or liquid fuel separately, mixed gas/liquid firing in the same furnace is also practised in refineries, and emission values may differ considerably from the values observed in the case of gas fired units /14/.

[2] The lower range relates to natural gas firing /14/.

[3] Thermally cracked residue /14/; liquid fuel

[4] However, low-NO_x-burners are reported not to be available for low grade liquid fuels. /cf. 14/

Emissions of carbon monoxide (CO), methane (CH_4) and non-methane volatile organic compounds (NMVOC) are mainly associated with poorly regulated combustion processes; they are small when processes are managed correctly.

Heavy metal emissions are mainly determined by the type of fuel used; only liquid and solid fuels are of relevance. Most of the heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, V) are normally released as compounds (e.g. chlorides) in association with particulates (see also chapter B111 on “Combustion Plants as Point Sources”, Section 9). In the case of heavy fuel oil mainly Ni and V are of relevance. Particulate emissions originate from two different sources within a refinery; firstly from process heaters and boilers and secondly from FCC units (CO-boilers), which are not considered here. Their contribution to the total emissions is roughly equal. /cf. 8/.

3.5 Controls

SO_2 emissions from process furnaces are only controlled by the use of low sulphur fuels (e.g. by switching from liquid fuels to gaseous fuels, which contain less sulphur).

For the control of NO_x emissions from process furnaces only primary measures are installed (e.g. low-NO_x-burner, flue gas recirculation). The reduction efficiencies for low-NO_x-burners vary between 10 and 30 %, and for flue gas recirculation between 5 and 15 %. At thermal cracking units in petrochemical industry (e.g. olefine cracking units) also secondary abatement measures may be installed (e.g. SCR, SNCR) /18/.

4/5 SIMPLER AND DETAILED METHODOLOGY

Here both approaches refer to the calculation of emissions based on emission factors and activities, which are jointly discussed in the following. The “simpler methodology” is considered as an overall approach, where activity data refer to production figures. The “detailed methodology” is considered as the recommended approach, where activity data concerning the fuel consumption in refinery process furnaces is available for individual plants. The simpler and the detailed methodologies cover all relevant pollutants.

The annual emission is determined according to Equation (1) by an activity and an emission factor:

$$E_i = EF_i \cdot A \tag{1}$$

E_i annual emission of pollutant i
EF_i emission factor of pollutant i
A activity

The activity A and the emission factor EF_i have to be determined on the same level of aggregation by using available data. The CORINAIR90 methodology requires for refinery process furnaces activity data, which is related to the type of fuel consumed in [GJ/a].

4.1 Simpler methodology

The simpler methodology corresponds to an approach, which takes into account activity rates derived from data of comparable installations or from literature data. Here, it is assumed, that the required activity data (according to CORINAIR90) are not available (see Equation (1)). In practice, statistical material (see also Section 6), which often provides only the throughput of crude oil in [Mg/a], has to be used. Some national statistics publications also provide throughputs per individual refinery.

In order to approximate activity data referring to the energy input into process heaters in [GJ/a] the specific energy consumption has to be taken into account as given e.g. in Equation (2):

$$A_{COR} = F \cdot A_{Stat} \tag{2}$$

A_{COR} activity in CORINAIR-compatible unit (energy input [GJ])
F specific energy consumption (energy input/mass crude oil [GJ/Mg])
A_{stat} activity directly obtained from statistics (mass crude oil [Mg])

For the determination of the specific energy consumption F, related to the throughput of crude oil, only the own consumption of the refinery has to be taken into account. The own consumption of a refinery amounts to about 5 % (average in 1990) of the input (crude oil and intermediate products) /3, 5/. For hydroskimming refineries[6] the fuel demand may vary between 2 and 3 wt.-% and for complex, high conversion refineries between 6 and 8 wt.-% /14/. About 40 % of the refinery fuel consumption is used for process heaters. The fuel split of refinery fuel for its own consumption can be given as: heavy fuel oil (ca. 35 %), petroleum coke (ca. 10 %) and refinery gas (ca. 55 %); the relevance of gas oil is < 1% and can be neglected /3/.

However, the simpler approach leads to significant uncertainties. Therefore, no emission factors are provided for this edition.

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[6] The simplest type of refineries, the so-called „hydro-skimming“ refineries, carry out very little conversion into various products. The product distribution is largely determined by the composition of the crude oil processed and cannot be influenced to a great extent by modifying the operating mode of the refineries. /14/

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.

4.2 Detailed methodology

The detailed methodology corresponds to a plant specific approach, which takes into account as far as possible plant specific information. Here, CORINAIR90 compatible activity data for refinery process furnaces (related to the type of fuel consumed in [GJ/a]) are directly available (Equation (1)).

The following two sections provide individual approaches for the determination of SO_2 and CO_2 emission factors.

4.2.1 SO_2 emission factors

Emission factors for SO_2 in [g/GJ] are given in Table 6 (see Section 8) based on literature data. SO_2 emissions can be directly correlated to the sulphur content of the fuel and the fuel consumption. Emission factors for SO_2 in [g/GJ] can be obtained by using Equation (2):

$$EF_{SO_2} = 2 \cdot C_{S_{fuel}} \cdot \frac{1}{H_u} \cdot 10^6 \tag{2}$$

EF_{SO_2} emission factor of SO_2 [g/GJ]

$C_{S_{fuel}}$ sulphur content of fuel [wt.-%]

H_u lower heating value [MJ/kg]

If no data is available, default values are recommended:

- sulphur content of fuel: see Section 3.4,
- lower heating value: see Table 4.

Table 4: Lower heating values of refinery fuels

Fuel used	NAPFUE code	Lower heating value [MJ/kg] /10/
Petroleum coke	110	29.31
Gas oil	204	42.70
Heavy fuel oil	203	41.03
Refinery gas	308	48.36

4.2.2 CO_2 emission factors

Emission factors for CO_2 are given in Table 6 (Section 8) based on literature data. Own estimations can be made according to Equation (3) and by using an approximation for the composition of oil, gas and coke as given in Table 5:

$$EF_{CO_2} = \frac{M_{CO_2}}{M_i} \cdot \frac{1}{H_u} \cdot 10^6 \tag{3}$$

EF_{CO_2} emission factor for CO_2 [g/GJ]
M_{CO_2} molecular weight of CO_2 [g/mol]
M_i molecular weight of fuel i (see Table 5) [g/mol]
H_u lower heating value [MJ/kg]

Table 5: Approximations for the molecular weight /3/

Fuel	**Approximation**	**Molecular weight [g/mol]**
Fuel oil	HC	13
Petroleum coke	C	12
Refinery gas	CH_4/C_2H_6	23¹⁾

1) An assumption concerning the average molecular weight has been made as both fractions are included with a mass portion of 50:50.

4.2.3 Emission factors for other pollutants

Emission factors for the pollutants NO_x, CH_4, NMVOC, CO, and N_2O are given in Table 6 (see Section 8) based on literature data depending on the type of fuel used. Emission factors for heavy metals are given in Table 7 (see Section 8).

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a measurement protocol such as that illustrated in Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

The following statistics can be used for the determination of the throughput of crude oil. The consumption of intermediate products has to be taken into account separately. In some national statistics also the total own consumption of fuels within the refineries is reported.

- Statistical Office of the European Communities (EUROSTAT) (ed.): CRONOS Databank; 1993 (Crude oil production XX 93 0603 3, Crude oil treated in refineries XX 93 0604 3)
- Office for Official Publication of the European Communities (ed.): Annual Statistics 1990; Luxembourg; 1992

Information concerning European refineries is also provided by Concawe (Den Haag).

7 POINT SOURCE CRITERIA

Refineries have to be treated as point sources according to the CORINAIR90 methodology. Process furnaces within a refinery have to be reported collectively as a part of a refinery.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The following Table 6 contains emission factors for selected pollutants based on literature data.

Table 6: Emission factors of gaseous pollutants for process heaters in refineries[10]

Type of fuel			NAPFUE code	Emission factors						
				SO_2 [g/GJ]	NO_x [g/GJ]	NMVOC [g/GJ]	CH_4 [g/GJ]	CO [g/GJ]	CO_2 [kg/GJ]	N_2O [g/GJ]
s[1]	coke	petroleum	110		300[7]				101[5]	22[7] g/Mg
l[2]	oil	residual	203	245 - 1,962[9]	100 - 210[8] 75 - 328[9]	1 - 41[9]	0.1 - 3.5[9]	7 - 350[9]	78[5] 53 - 79[9]	22[7] g/Mg 2 - 22[9]
G	gas	natural	301	0.7 - 432[9]	1.4 - 140[9]	0.3 - 7[9]	0.3 - 4[9]	1.3 - 280[9]	53 - 55[9]	1.5 - 22[9],
G[3]	gas	liquified petroleum	303	1.7[9]		14[9]	6[9]	45[9]	64[9]	1.5[9]
G	gas	refinery	308	12.5 - 1,423[9]	90[8], 140[7], 155[6] 30 - 150[8] 35 - 756[9]	0.3 - 10[9]	0.3[6] 0.3 - 4[9]	280[6] 10 - 280[9]	60[4), 6)] 10 - 57[9]	1.5[6], 0.3 - 22[9], 22[7] g/Mg
l/g	mixtur	of oil/gas	-	220[4] g/Mg	350[4] g/Mg					

[1] In CORINAIR90 also NAPFUE codes 103 and 105 have been reported

[2] In CORINAIR90 also NAPFUE code 204 has been reported

[3] In CORINAIR90 also NAPFUE code 303 has been reported

[4] CONCAWE /9/, range for SO_2 emission factors: 70 - 430 g/Mg

[5] BMU, Germany 1993 /12/

[6] BMU, Germany 1994 /16/

[7] CORINAIR /4/

[8] CONCAWE /1/

[9] CORINAIR90 data

[10] At this stage emission factors for thermal cracking units are not available.

Table 7: Heavy metal emission factors for gaseous fuels fired in refinery process heaters /13/

Source	Emission factor [g/TJ]			
	Cr (total)	Cr^{6+} (Hex)[1]	As	Cd
Process heater:				
- Single stage	0.10	0.19	0.03	0.01
- With LNB	0.05	0.01	0	0
- With air preheater	0.05	0	0	0.14
- Reformer	0.09	0.19	0	0

[1] Cr^{6+} is reported separately due to the high toxicity of this species.

For refinery process heaters, which are fed with fuel oil, emission factors for heavy metals are approximately the same as given in Table 31 in chapter B111 on “Combustion Plants as Point Sources”. Residues fuelled in refineries need not be comparable to heavy fuel oils as a product. Therefore, composition data of residues are needed in order to estimate heavy metal emissions /17/.
Table 8 contains the AP 42 emission factors for particulate matter (US EPA, 1996).

Table 8: AP 42 Particulate matter emission factors* for Process Furnaces /19/

Process (g/10^3 L fresh feed)	**PM**
Fluid catalytic cracking units: uncontrolled	695
Fluid catalytic cracking units: ESP and CO boiler	128
Moving-bed catalytic cracking units	4.9
Fluid cooking units: uncontrolled	1500
Fluid cooking units: ESP and CO boiler	19.6

* = In the absence of more appropriate data use the AP 42 emission factors

9 SPECIES PROFILES

Species profiles (oxides of sulphur and nitrogen) are comparable to those released from combustion installations. Details can be found in chapter B111 “Combustion Plants as Point Sources” (Section 9).

10 UNCERTAINTY ESTIMATES

At this stage no information is available.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Weakest aspects discussed here are related to emission factors and activities.

Data provided by CORINAIR90 project can only be used in order to give a range of emission factors. Further work should be invested to develop emission factors, which take into account technical specifications and fuel characteristics.

Most refineries process crude oil as well as intermediate products coming from other refineries. The energy demand for the processing of intermediate products differs from the energy demand for the processing of crude oil. The share of intermediate products processing varies strongly. Therefore, further work should be invested in providing characteristic profiles for the energy consumption (own consumption) of a refinery, which are suitable for inventorying purposes.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Temporal disaggregation of annual emission data (top-down approach) provides a split into monthly, weekly, daily and/or hourly emission data. Temporal disaggregation of annual emissions released from process furnaces in refineries can be obtained by taking into account the:

- time of operation and
- variation of load.

Data for the annual time of operation in refineries is available from statistics. In principle, refineries produce continuously during the whole year except during standstill time due to maintenance.

The load of the refinery is determined by the variation of production due to the varying demand for petroleum products. Information concerning the variation in the production or the demand for refinery products can only be obtained directly from refinery operators. (Note: the short time demand for refinery products is met by refinery products being stored in tanks.).

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As outlined in the chapter on “Concepts for Emission Inventory Verification” different verification procedures can be recommended. Verification procedures considered here are principally based on the verification of emission data on a national level and on a plant level.
The verification on a plant level relies on comparisons between calculated emissions/emission factors and those derived from emission measurements.

17 REFERENCES

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19 RELEASE VERSION, DATE AND SOURCE

Version : 2.1

Date : December 1995

Source : Otto Rentz; Dagmar Oertel
University of Karlsruhe (TH)
Germany

Updated with particulate matter details by:
Mike Woodfield
AEA Technology
UK
December 2006

20 POINT OF ENQUIRY

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Abbreviations

FCC	Fluid Catalytic Cracking
g	gaseous state of aggregation
l	liquid state of aggregation
LNB	Low-NO_x-Burner
s	solid state of aggregation
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction

SNAP CODES: **040101**
040102

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Petroleum Products Processing
Fluid Catalytic Cracking

NOSE CODE: **105.08.01**
105.08.02

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

A basic refinery converts crude petroleum into a variety of sub-products. Principal products of a petroleum refinery include:

Table 1.1: Refinery Principal Products

Product Type	**Principal Products**
Liquid Fuels	Motor Gasoline
	Aviation Gasoline
	Aviation Turbine Fuel
	Illuminating Kerosene
	High-Speed Diesel
	Distillate Heating Fuel
	Medium-Speed Diesel
	Residual Oil
By-Product Fuels and Feedstocks	Naphtha
	Lubricants
	Asphalt
	Liquefied Petroleum Gases
	Coke
	Sulphur (Product of Auxiliary Facility)
	White Oils
Primary Petrochemicals	Ethylene
	Propylene
	Butadiene
	Benzene
	Toluene
	Xylene

The production of the latter group, primary petrochemicals, is, however, not included in this chapter, even if these chemicals are produced at a petroleum refinery. Please refer to the relevant chapters for sub-sector 040500 (chapters B451-B4522).

The petroleum refining industry employs a wide variety of processes. The types of processes operating at any one facility depend on a variety of economic and logistic considerations such as the quality of the crude oil feedstock, the accessibility and cost of crude (and alternative feedstocks), the availability and cost of equipment and utilities, and refined product demand. The four categories of general refinery processes are listed in Table 1.2.

Table 1.2: General Refinery Processes and Products

General Process	**Products**
Separation Processes	Atmospheric Distillation
	Vacuum Distillation
	Light Ends Recovery (Gas Processing)
Petroleum Conversion Processes	Cracking (Thermal and Catalytic)
	Coking
	Viscosity Breaking
	Catalytic Reforming
	Isomerization
	Alkylation
	Polymerization
Petroleum Treating Processes	Hydrodesulfurization
	Hydrotreating
	Chemical Sweetening
	Acid Gas Removal
	Deasphalting
Blending	Motor Gasoline
	Light Fuel Oil
	Heavy Fuel Oil

The major direct process emission sources of NMVOCs are vacuum distillation, catalytic cracking, coking, chemical sweetening and asphalt blowing (U.S.EPA 1985a). Process-unit turnaround (periodical shut-down of units) has also been reported as contributing to VOC emissions (CEC 1991).

Fugitive emissions from equipment leaks are also a significant source of NMVOC emissions from process operations at a refinery. Emissions from storage and handling are also classified as fugitive emissions. To avoid confusion, fugitive emissions from equipment leaks will be referred to as fugitive process emissions in this chapter.

Table 1.3 summarises significant sources of common pollutants from process and fugitive process emissions sources at refineries.

Table 1.3: Significant Process Emissions Sources at Petroleum Refineries (U.S. EPA 1985)

Process	**Particulate**	**NO_x**	**SO_x**	**CO**	**NMVOC**
Vacuum Distillation	x	x	x	x	X
Catalytic Cracking	**X**	x	x	**X**	X
Thermal Cracking	x	x		x	X
Sweetening					**X**
Blowdown Systems	x	x	x	x	**X**

X - Possibly significant sources (depending upon the degree of contract)
x - Minor sources

This section is a summary of the main products possibly produced at a refinery and the major processes that could be present, with an indication of the processes that are potentially significant sources of emissions to the air. All of these processes are currently under SNAP code 040101, with the exception of FCCs with CO boiler. However it is difficult to use this code separately from other processes, particularly for simpler emission estimation methods, which tend to encompass a wide variety of sources. It is therefore proposed that FCCs with CO boiler also be inventoried under 040101.

It is important to note that fugitive process emissions are somewhat difficult to characterise by their area (process vs. storage/handling vs. waste treatment), as they are estimated based on equipment counts and are not usually classified as to type of use or area of the refinery. Therefore fugitive process emissions for the entire refinery are inventoried under SNAP code 040101.

2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2.1 summarises emissions from petroleum refining processes in the CORINAIR90 inventory. In a Canadian study (CPPI and Environment Canada 1991), the process/fugitive process sources contributed 51.5% (process 4.7% (Only FCCU estimated) and fugitive process 46.8%) of total VOC emissions for 29 refineries surveyed. Blending losses were not estimated separately. The process/fugitive process sources would represent approximately 2.6% of total anthropogenic emissions.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**								
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3	PM*
Petroleum Products Process.	040101	0.5	0.1	0.7	0	0	0.2	0.1	-	-
Fluid Catalytic Cracking	040102	0.4	0.1	0	-	0	0.1	-	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

* = PM (inclusive of TSP, PM_{10} and $PM_{2.5}$) is <0.1% of total PM emissions

-

3 GENERAL

3.1 Description

3.1.1 Direct Process Sources

There are four main categories of processes in a petroleum refinery:

Separation Processes

Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulphur, nitrogen, oxygen and metals. The first phase in petroleum refining operations is the separation of crude oil into common boiling point fractions using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing).

Conversion Processes

Where there is a high demand for high-octane gasoline, jet fuel and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions. Cracking, coking and visbreaking processes break large petroleum molecules into smaller petroleum molecules. Polymerization and alkylation processes rearrange the structure of petroleum molecules into larger ones. Isomerization and reforming processes rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecule size.

Treating Processes

Petroleum treating processes stabilise and upgrade petroleum products. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks prior to refining. Undesirable elements such as sulphur, nitrogen and oxygen are removed from product intermediates by hydrodesulphurization, hydrotreating, chemical sweetening and acid gas removal. Deasphalting is used to separate asphalt from other products. Asphalt may then be polymerised and stabilised by blowing (see SNAP code 060310).

Blending

Streams from various units are combined to produce gasoline, kerosene, gas oil and residual oil, and in some cases a few speciality items.

3.1.2 Fugitive Process Sources

Fugitive process emission sources are defined as NMVOC sources not associated with a specific process but scattered throughout the refinery. Fugitive process emissions sources include valves of all types, flanges, pump and compressor seals, pressure relief valves, sampling connections and process drains. These sources may be used in the transport of crude oil, intermediates, wastes or products.

Note that this category will actually include fugitive emissions from all such refinery sources, rather than those sources only associated with process emissions.

3.2 Definitions

3.3 Techniques

See section 3.1 (above).

3.4 Emissions/Controls

3.4.1 Direct Process Emissions

Vacuum distillation, catalytic cracking, thermal cracking, sweetening, blowdown systems, sulphur recovery, asphalt blowing and flaring processes have been identified as being potentially significant sources of SO_2 and NMVOC from those sources included under SNAP code 040101, with a relatively smaller contribution of particulate, NOx and CO. (U.S.EPA 1985a).

Vacuum Distillation
Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high-boiling-point hydrocarbons. The topped crude is separated into common-boiling-point fractions by vaporisation and condensation in a vacuum column at a very low pressure and in a steam atmosphere. A major portion of the vapours withdrawn from the column by steam ejectors or vacuum pumps are recovered in condensers. Historically, the non-condensable portion has been vented to the atmosphere.

The major NMVOC emission sources related to the vacuum column include steam ejectors and vacuum pumps that withdraw vapours through a condenser.

Methods of controlling these emissions include venting into blowdown systems or fuel gas systems, and incineration in furnaces (SNAP code 090201) or waste heat boilers (SNAP code 030100). These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions.

Note that the emissions from blowdown and vapour recovery systems have been included under this SNAP code rather than under SNAP code 090100 (see below).

Catalytic Cracking
Catalytic crackers use heat, pressure and catalysts to convert heavy oils into lighter products with product distributions favouring the gasoline and distillate blending components.

Fluidised-bed catalytic cracking (FCC) processes use finely divided catalysts that are suspended in a riser with hot vapours of the fresh feed. The hydrocarbon vapour reaction products are separated from the catalyst particles in cyclones and sent to a fractionator. The spent catalyst is conveyed to a regenerator unit, in which deposits are burned off before recycling.

Moving-bed catalytic cracking (TCC) involves concurrent mixing of the hot feed vapours with catalyst beads that flow to the separation and fractionating section of the unit.

Aside from combustion products from heaters, emissions from catalytic cracking processes are from the catalyst regenerator. These emissions include NMVOC, NOx, SOx, CO, particulates, ammonia, aldehydes, and cyanides.

In FCC units, particulate emissions are controlled by cyclones and/or electrostatic precipitators. CO waste heat boilers may be used to reduce the CO and hydrocarbon emissions to negligible levels.

TCC catalyst regeneration produces much smaller quantities of emissions than is the case for FCC units. Particulate emissions may be controlled by high-efficiency cyclones. CO and NMVOC emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner.

SOx from catalyst regeneration may be removed by passing the flue gases through a water or caustic scrubber.

Thermal Cracking

Thermal cracking units break heavy oil molecules by exposing them to higher temperatures. In viscosity breaking (visbreaking), topped crude or vacuum residuals are heated and thermally topped in a furnace and then put into a fractionator. In coking, vacuum residuals and thermal tars are cracked at high temperature and low pressure. Historically, delayed coking is the most common process used, although fluid coking is becoming the more preferred process.

Emissions from these units are not well characterised. In delayed coking, particulate and hydrocarbon emissions are associated with removing coke from the coke drum and subsequent handling and storage operations. Generally there is no control of hydrocarbon emissions from delayed coking, although in some cases coke drum emissions are collected in an enclosed system and routed to a refinery flare.

Sweetening

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may then be followed by an extraction step in which the disulfides are removed.

Hydrocarbon emissions are mainly from the contact between the distillate product and air in the air-blowing step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.

Asphalt Blowing

Please refer to SNAP code 060310 for inventory methods for asphalt blowing.

Sulphur Recovery

Please refer to SNAP code 040103 for inventory methods for sulphur recovery plants.

Flaring

Please refer to SNAP code 090203 for inventory methods for flaring in a refinery.

Blowdown Systems

Many of the refining process units subject to hydrocarbon discharges are manifolded into a collection unit (i.e., blowdown system), comprising a series of drums and condensers, whereby liquids are separated for recycling and vapours are recycled or flared with steam injection. Uncontrolled blowdown emissions consist primarily of hydrocarbons, while vapour recovery and flaring systems (see SNAP code 090203) release lesser NMVOC and greater combustion products including SO_2, NOx and CO.

3.4.2 Fugitive Process Emissions

Fugitive process emissions sources include valves of all types, flanges, pumps in hydrocarbon service (packed or sealed), compressor seals, pressure relief devices, open-ended lines or valves, sampling connections, and process drains or oily water drains.

For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. For compressors, gases passing through are classified as either hydrogen or hydrocarbon service. For all other sources, streams are classified into one of three stream groups: gas/vapour streams, light liquid/two phase streams, and kerosene and heavier liquid streams. It has been found that sources in gas/vapour service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals.

Of these sources of NMVOC, valves are the major source type. This is due to their number and relatively high leak rate.

Normally, control of fugitive emissions involves minimising leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping and maintenance practices.

Applicable control technologies are summarised in Table 3.1.

Table 3.1: Control Technologies for Fugitive Sources (U.S. EPA 1985a)

Fugitive Source	**Control Technology**
Pipeline Valves	monitoring and maintenance programs
Open-Ended Valves	Instillation of cap or plug on open end of valve /line
Flanges	monitoring and maintenance
Pump Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Compressor Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Process Drains	Traps and covers
Pressure/Relief Valves	Rupture disks upstream of relief and/or venting to a flare

4 SIMPLER METHODOLOGY

The simplest inventory methodology is to combine the crude oil throughput of each refinery with either a single emission factor, or two emission factors (one for process and one for fugitive process emissions) for each refinery. The first approach would be the easiest to use if very limited information is available. However, the second approach would allow the user to in some way reflect the type of processes and related controls at the refinery as well as accounting for the sophistication of the fugitive emissions inspection and maintenance programs typical of the region and/or that particular refinery.

It is strongly recommended that the detailed methodology be used for petroleum refineries.

N.B There are no emission factors available for $PM_{2.5}$. The source is <0.1% of the total PM emissions for most countries.[1]

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to estimate its process emissions for each process, using detailed throughput information and emission factors. Site specific emission factors or data would be preferable, wherever possible. Remote sensing, using Fourier transform techniques, is making it possible to measure total refinery emissions, although it may be difficult to identify the individual source strengths.

The state-of-the-art technology for estimating fugitive process emissions is to use an emission testing program to classify equipment into groupings and then estimate emissions using emission factors or algorithms (see section 16, Verification Procedures). However, this is a very expensive and time-consuming proposition and is considered beyond the resources of most inventory personnel. The methodology proposed below is a compromise between a testing program vs. estimates of the number of each type of equipment that might be in a refinery based on either its throughput or production data.

Fugitive process emissions, which are considered to be the major source of NMVOCs at a petroleum refinery, are inventoried using emission factors for each type of equipment and stream, based on a count of the number of sources, a characterisation of the NMVOC content of the stream in question and whether the refinery conducts an inspection and maintenance program.

The U.S. EPA has published a detailed protocol for equipment leak emissions estimates (U.S.EPA 1993). In the average emission factor method, the following unit-specific data is required:

1. the number of each type of component in a unit (valve, connector etc.);
2. the service each component is in (gas, light liquid, or heavy liquid);
3. the NMVOC concentration in the stream (weight fraction) and;
4. the number of hours per year the component was in service.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

The equipment is then grouped into streams, where all of the equipment within the stream has approximately the same NMVOC weight percent. Annual emissions are then calculated for each stream using equation 1 as follows:

$$\mathbf{NMVOCs = AEF * WFnmvoc * N} \qquad (1)$$

where:

NMVOCs	= NMVOC emission rate from all equipment in the stream of a given equipment type (kg/hr)
AEF	= applicable average emission factor for the equipment type (kg/hr/source)
WFnmvoc	= average weight fraction of NMVOC in the stream and
N	= the number of pieces of equipment of the applicable equipment type in the stream.

If there are several streams at the refinery, as is usually the case, the total NMVOC emission rate for an equipment type is the sum of emissions from each of the streams. The total emission rates for all of the equipment types are summed to generate the process unit total NMVOC emission rate from fugitive process sources.

Should a key source analysis indicate this to be a major source of particulate matter (TSP, PM_{10} or $PM_{2.5}$) then installation level data should be collected using a protocol such as that illustrated in the Measurement Protocol Annex.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the crude oil throughput of each refinery is required.
For the detailed methodology, specific data will be required on the throughput for each process area. For fugitive process emissions estimates, each emission source must be counted by type and process stream, and the NMVOC content for each stream must then be characterised. The number of annual hours of operation for each stream is also required. Finally it must be determined if an inspection and maintenance program is conducted at the refinery.

7 POINT SOURCE CRITERIA

All refineries are to be inventoried as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

The CONCAWE Air Quality Management Group identify a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.
The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

CONCAWE suggests a conservative overall fugitive emission factor of 0.30 kg NMVOC/metric tonnes refinery feed .

Total hydrocarbon emission factors based on an inventory of Canadian refineries in 1988 (CPPI and Environment Canada 1991) were 0.05 kg/m3 feedstock for process emissions and 0.53 kg/m3 for fugitive process emissions. Of the latter, valves accounted for 0.35 kg/m3 feedstock. Data was not available for NMVOC only. This inventory was based on a survey of individual refineries, in which some reported their own emission estimates and some reported base quantity data for which emissions were estimated using a variety of techniques.

The use of CONCAWE derived VOC emission factors, based upon a hypothetical 5 Mt/yr refinery, as follows was recommended as a default method for the Corinair 1990 project (CEC 1991). The emission factor for fugitive process emissions is 0.25 kg/t crude (0.21 kg/m^3 crude assuming specific gravity of 0.85 (BP 86)).

Sixty percent of these emissions are reported to be from valves. CONCAWE also indicates that average fugitive emissions in the same refinery with a maintenance and monitoring programme is 0.01% by weight (.085 kg/m3) of refinery throughput (CONCAWE Report 87/52 1987). The CORINAIR90 default emission handbook also reports a U.S.EPA factor of 0.18 kg/Mg crude (U.S.EPA 1985b) for process unit turnaround, and estimates that Western European refineries would emit half of this for turnaround, or 0.09 kg/Mg.

It is apparent that detailed emission inventory data is required for several refineries in differing regions in order to develop meaningful emission factors. Major factors affecting regional differences include crude characteristics, product demand (and hence refinery processes) and regulatory requirements.

Emission factors for non-combustion process sources of other contaminants were not identified, other than as provided in Table 4 of SNAP sector 040100.

8.2 Detailed Methodology

The more detailed methodology involves the use of process-specific emission factors based on the throughput of the unit and fugitive process emission factors based on equipment counts. Emission factors from CONCAWE in the following sub-section are the best available estimate. It is important to note that the factors presented below must be used with caution, as they do not account for regional differences in crude, product demand and regulatory requirements. Wherever possible, site-specific emission estimates based on monitoring should be considered.

8.2.1 Process Emission Factors

A 2006 schematic representation of process emission factors from CONCAWE are reported in Table 8.1 for main pollutants, Table 8.2 for heavy metals and 8.3 for Polycyclic Aromatic Hydrocarbons (PAHs).

The gaseous emissions from refinery blowdown systems are normally recovered and/or flared. The emission factors of Table 8.1 are referred at the case where these controls are not operational and the emissions are emitted to atmosphere.

The gaseous emissions from bitumen blowing are normally passed through a scrubber and then fed to an incinerator. The emission factors of Table 8.1 are referred at the case where these controls are not operational and the emissions are emitted to atmosphere.

Table 8.1: Uncontrolled (^) emission factors for petroleum refineries processes (Concawe, 2006)

Process	PM_{10}	SOx (as SO_2)	CO	NMVOC	NOx (as NO_2)	NH_3	C_6H_6
Catalytic cracking unit regenerators							
Full Burn Regeneration (°)	0.549	1.41	Neg	Neg	0.204	Neg	Neg
Partial Burn with CO Boiler (°)	0.549	1.41	Neg	Neg	0.204	Neg	Neg
Partial Burn without CO Boiler (°)	0.549	1.41	39,2	0.63	0.204	0.155	0.00105
Catalytic reforming unit units (°°)		0.00363	0,0416				
Fluid coking units (°°)							
Controlled with CO or Fired Waste heat boiler (°°)				Neg			Neg
Uncontrolled	0.765			0.046			0.000175
Uncontrolled blowdown systems (°°°)				1.65			0.00632
Uncontrolled bitume blowing (°°°°)				27,2			

(^) For PM10 emissions from *catalytic cracking unit regenerators* is assumed that there is a primary cyclone installed
(°) expressed as kg of mass emitted × volume of fresh feed to unit (in m^3)
(°°) expressed as kg of mass emitted × feed to unit (in m^3)
(°°°) expressed as kg of mass emitted × refinery feed (in m^3)
(°°°°) expressed as kg of mass emitted × mass of blown bitumen (in tonne)

Table 8.2: Heavy metals uncontrolled (^) emission factors for petroleum refineries processes (Concawe, 2006)

Process	As	Cd	Cu	Hg	Ni	Pb	Zn
Catalytic cracking unit regenerators (°)	0.0139	0.0625	0.139	0,0695	0.612	0.32	0.118
Fluid coking units (°)	2.16		0.015	0,03	0.57	0.045	0.045

(^) For emissions from *catalytic cracking unit regenerators* is assumed that there is a primary cyclone installed
(°) expressed as g of mass emitted × volume of fresh feed to unit (in m^3); for a unit with a primary cyclone installed

Table 8.3: PAHs uncontrolled emission factors for catalytic cracking unit regenerators (Concawe, 2006)

PAH	Emission Factor mg/tonnes of coke burned
Benzo(a)pyrene	2.966
Benzo(b)fluoranthene	2.915
Benzo(k)fluoranthene	2.892
Indeno(1,2,3-cd)pyrene	2.883
Benzo(g,h,i)perylene	2.886
Fluoranthene	5.471

For comparison, Table 8.4 lists emission factors for refinery processes based on tests conducted in the 1970's, noting that overall, less than 1 % of the total hydrocarbons emissions are methane (U.S.EPA 1985a). The VOC emission factors listed in Table 8.5 were used to estimate emissions from processes in the United Kingdom (Passant n.d.).

Table 8.4: Emission Factors for Petroleum Refineries (U.S. EPA 1985a and 1995)

Process	Particulate	Sox (as SO_2)	CO	THC[a]	NOx (as NO_2)	Aldehydes	NH_3	Quality
Fluid catalytic cracking units								
Uncontrolled kg/10^3 liters fresh feed	0.695 (0.267-0.976)[b]	1.143 (0.286-1.505)	39.2	0.630	0.204 (0.107-0.416)	0.054	0.155	B
ESP and CO boiler kg/10^3 liters fresh feed	0.128 (0.020-0.428)	1.413 (0.286-1.505)	Neg[c]	Neg	0.204[d] (0.107-0.416)	Neg	Neg	B
Moving-bed catalytic cracking units								
kg/10^3 liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid coking units								
Uncontrolled kg/10^3 liters fresh feed	1.5	NA[e]	NA	NA	NA	NA	NA	C
ESP and CO boiler kg/10^3 liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Blowdown systems								
Uncontrolled kg/10^3 liters refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
Vacuum distillation column condensers								
Uncontrolled	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C

Process	Particulate	Sox (as SO_2)	CO	THC[a]	NOx (as NO_2)	Aldehydes	NH_3	Quality
kg/10^3 liters refinery feed								
Uncontrolled kg/10^3 liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

[a] Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane

[b] Numbers in parenthesis indicate range of values observed

[c] Negligible emission

[d] May be higher due to the combustion of ammonia

[e] NA, Not Available.

Table 8.5: United Kingdom VOC Emission Factors (Passant n.d.)

Process		Emission Factor	Quality
Catalytic Cracker	Uncontrolled	628 g/m^3 feed	D
	Controlled	negligible	D
Fluid Coking	Uncontrolled	384 g/m^3 feed	D
	Controlled	Negligible	D
Vacuum Distillation	Uncontrolled	51.6 g/m^3 feed	D
	Controlled	negligible	D
Asphalt Blowing	Uncontrolled	27.2 kg/Mg asphalt	D
	Controlled	0.54 kg/Mg asphalt	D

8.2.2 Fugitive Process Emission Factors

Emissions factors for fugitive process emissions of NMVOC are expressed as losses per equipment unit per day. As previously discussed, the methods for estimating mass emissions from process equipment leaks range from the use of emission factors with equipment counts to comprehensive field measurement techniques. These methods have evolved from a number of studies of the organic chemical and petroleum refining industries for the U.S. EPA.

Concawe study (Concawe, 2006) provides separately emission factors for pressurized components (Table 8.4) and from low pressure equipment such as drains, oil-water separators and product storage tanks.

Table 8.4: Uncontrolled fugitive average emission factors for petroleum refineries for pressurized components (Concawe, 2006)

Equipment Type	Service	Emission Factor kg/hr/source
Valves	Gas	0.0268
	Light Liquid	0.109
Pump seals	Light Liquid	0.114
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.160

Flanges and non-flanged connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.015

The following algorithm provides an estimate for emissions from the entire refinery process drain system. Process drain openings (sumps, etc.) are normally fitted with an emission control device such as a water seal or sealed cover. An assessment needs to be made to establish how many of the drain covers are unsealed and vent directly to atmosphere.

$$E\ (\text{kg}) = 0{,}032 \times N \times h$$

where:

- N = number of unsealed covers in the refinery process drain system.
- h = period of emission estimate in hours e.g. for annual reports = 365 × 24.

If the total number of drains is unknown a drain count of 2.6 drains per pump in process areas can be used .

For oil-water separators, emissions are dependent on the type of separator installed.

$$E\ (\text{kg}) = F_{SEP} \times V_{WATER}$$

where:

- F_{SEP} = Emission factor for the type of separator given in Table 8.5.
- V_{WATER} = Volume of waste water treated by the separator (in m^3).

Emissions from basins and ponds that handle clean water or storm water are considered negligible. For ponds temporarily storing oily-water use the emission factor for an uncovered, gravity type separator in Table 8.5.

Table 8.5: Emission Factors for Oil-Water Separators (Concawe, 2006)

Separator type	**Emission factor (F_{SEP})**
Gravity type - uncovered	0.111
Gravity type - covered	0.0033
Gravity type – covered and connected to flare	0
DAF or IAF (°) - uncovered	0.004
DAF or IAF (°) - covered	0.00012
DAF or IAF (°) - covered and connected to flare	0

(°) DAF = Dissolved air floatation type, IAF = Induced air floatation type

Emissions from cooling water towers are considered negligible as sound refinery engineering practice ensures that oil is prevented from entering these systems.

For comparison, Table 8.6 provides U.S. EPA (1993) NMVOC emission factors for pressurized components.

Table 8.6: Process Fugitive Average NMVOC Emission Factors for Petroleum Refineries (U.S.EPA 1993)

Source		**Emission Factor (kg/hr-source)**	**Quality**
Valves	Gas	0.0268	
	Light Liquid	0.0109	

	Heavy Liquid	0.00023	
Open-ended Lines	All Streams	0.0023	
Connectors	All Streams	0.00025	
Pump Seals*	Light Liquid	0.114	
	Heavy Liquid	0.021	
Compressor Seals	Gas	0.636	
Sampling Connections	All Streams	0.0150	
Pressure Vessel Relief Valves	Gas	0.16	

* The light liquid pump seal factor can be used to estimate the leak rate from agitator seals

These emission factors, however, are in most cases considered to overestimate NMVOC emissions from sources in more modern facilities. The U.S. EPA allows a 75% reduction in emissions estimated by using these emission factors if an approved I and M program is conducted at the petroleum refining facility.

Passant (1993) used the VOC emission factors presented in Table 8.7, which were referenced to U.S.EPA 1988.

Table 8.7: Process Fugitive Emission Factors for Petroleum Refineries (Passant 1993)

Source		**Emission Factor (kg/hr)**	Quality
Valve	Gas	0.0056	D
	Light	0.0071	D
	Heavy	0.0023	D
Pump Seals	Light	0.0494	D
	Heavy	0.0214	D
Compressor Seals	all streams	0.2280	D
Pressure Relief Seals	all streams	0.104	D
Flanges	all streams	0.00083	D
Open-ended Lines	all streams	0.0017	D
Sample Connections	all streams	0.015	D

Although the derivation of the emission factors in table 8.4 is not given, it would appear that these are actually average synthetic organic chemical manufacturing industry (SOCMI) (1988) uncontrolled emission factors. These sets of factors are thought to be biased on the high side for petroleum refineries due to the inclusion of ethylene plants, which operate at 15,000 to 40,000 psig.

9 SPECIES PROFILES

9.1 Applicability of Generalised VOC Species Profiles

In both North America and Europe, VOC species profiles have been published based on measurements or engineering judgement. There is a need to produce generalised profiles for use by models, the alternative being to obtain refinery specific data. Generalised profiles can be generated at the most detailed process level, however, there are several important influences which should be considered in attempting to specify such generally applicable data. Some of these influences are:

<u>Meteorological and Climatological effects</u>: Ambient temperature and temperature ranges may have important influences on the emitted species profiles. Due to the logarithmic behaviour of vapour pressure, higher temperatures tend to favour the loss of the lower molecular weight compounds from storage vessels and some process streams.

<u>Variability of Raw Materials:</u> The type of crude oil being processed can influence the fraction of more volatile and more easily emitted compounds.

<u>Process Variability:</u> Different refineries will have process differences. Where the species profiles are based on individual operations, process differences can be allowed for. However, overall average refinery profiles will differ between refineries.

<u>Maintenance and Regulation:</u> Equipment maintenance and the enforcement of regulations will have significant effects on the overall emitted species distribution depending on which processes or operations are impacted by maintenance practices or by regulation.

The broad application of generalised profiles should be done with some caution. Where such profiles are necessary, consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material etc.

9.2 Simplified VOC Speciation

For some applications, where there is no process detail, or where refineries are grouped as a single emission source, there is a need for a single overall species profile to characterise the emissions for modelling or other purposes. Process specific species profiles can be combined into a single overall refinery profile by appropriately weighting the individual profiles according to their relative contribution to the total refinery emissions.

Consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material (crude) etc.
CONCAWE reports (Report 2/86) that refinery emissions are essentially saturated, with the saturated hydrocarbon content lying between 80 and 90% by weight. The balance of 10 to 20% is unsaturated and/or aromatic hydrocarbons, the actual values depending on the nature of the refinery processes installed. Several overall refinery species profiles are available, such as those reviewed by Veldt (1991) for application to the EMEP and CORINAIR 1990

emissions inventories. On the basis of this review, this chapter proposes an overall species profile for petroleum refining by mass fraction.

Table 9.1: CONCAWE Petroleum Refinery Speciation Profile

Species	**CONCAWE (%)**	**Quality**
Methane	0	(Unknown)
Ethane	5	
Propane	20	
n-Butane	15	
i-Butane	5	
Pentanes	20	
Hexanes	10	
Heptanes	5	
>Heptanes	5	
Ethene	1	
Propene	1	
Butene	0.5	
Benzene	2	
Toluene	3	
o-Xylene	0.7	
M,p-Xylene	1.3	
Ethylbenzene	0.5	
TOTAL	100	

The Air Emission Species Manual (AESM) for VOC (U.S. EPA 1994) provides an overall refinery species profile (Profile 9012: Petroleum Industry - Average, Data Quality E - based on engineering judgement) as summarised in Table 9.2.

Table 9.2: US EPA Petroleum Refinery Speciation Profile

Species	**CAS Number**	**Wt (%)**	**Quality**
Methane	74-82-8	13	E
Ethane	74-84-0	6.05	E
Propane	74-98-6	19.7	E
n-Butane	106-97-8	7.99	E
i-Butane	75-28-5	2.89	E
Pentanes	(109-66-0)	21.4	E
Hexanes	(110-54-3)	8.02	E
Heptanes	(142-82-5)	1.87	E
Octanes	(111-65-9)	2.13	E
Nonanes	(111-84-2)	1.01	E
Decanes	(124-18-5)	1.01	E
Cyclo-hexane	110-82-7	0.08	E
Cyclo-heptanes		2.27	E
Cyclo-octanes		0.66	E
Cyclo-nonanes		0.11	E
Propene	115-07-01	1.75	E
Butene	106-98-9	0.15	E
Benzene	71-43-2	0.38	E
Toluene	108-88-3	0.44	E
Xylenes	1330-20-7	0.19	E
Formaldehyde	50-00-0	8.88	E
Total		100.02	

The suggested applications are:

Blowdown system - vapour recovery./Flare
Blowdown system - without controls
Wastewater treatment - excl. Separator
Vacuum distillation - column condenser
Sludge converter - general
Fluid coking - general
Petroleum coke - calciner
Bauxite burning
Lube oil manufacturing

9.3 Detailed Process VOC Speciation

The most detailed speciation of VOC is achievable at the process level using the U.S. EPA AESM (U.S.EPA 1994). Such a detailed method is generally only applicable on an individual refinery basis where estimates of the emission contributions from the various process streams and operations are available. The generalised profiles, which are available for individual processes and operations, as well as fugitive process emissions, are summarised below. These profiles are based on United States data, and in many instances on data from California.

U.S. EPA petroleum refinery species profiles applicable to petroleum refinery process and fugitive process emissions are presented in Tables 9.3 through 9.8.

Table 9.3: Profile 0029: Refinery Fluid Catalytic Cracker.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	13.00	C
74-82-8	Methane	36.00	C
50-00-0	Formaldehyde	51.00	C
TOTAL		100.00	

Table 9.4: Profile: 0031 Refinery Fugitive Emissions - Covered Drainage / Separation Pits.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	12.20	C
	C-7 cycloparaffins	16.90	C
	C-8 cycloparaffins	5.20	C
	Isomers of pentane	10.10	C
74-82-8	Methane	2.90	C
74-84-0	Ethane	1.70	C
74-98-6	Propane	5.90	C
106-97-8	N-Butane	14.30	C
75-28-5	Iso-Butane	4.50	C
109-66-0	N-Pentane	12.00	C
110-54-3	Hexane	11.90	C
71-43-2	Benzene	2.40	C
TOTAL		100.00	

Used for: Fugitive hydrocarbon emissions - drains - all streams

Table 9.5: Profile: 0039 Description: Refinery Fugitive Emissions - Compressor Seals - Refinery Gas.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	1.00	D
	Isomers of heptane	0.10	D
	Isomers of pentane	8.60	D
74-82-8	Methane	13.30	D
74-84-0	Ethane	5.60	D
74-98-6	Propane	16.00	D
115-07-01	Propene	8.80	D
106-97-8	N-Butane	23.20	D
106-98-9	Butene	1.20	D
75-28-5	Iso-Butane	10.00	D
109-66-0	N-Pentane	7.60	D
110-54-3	Hexane	4.60	D
TOTAL		100.00	

Used for: Compressor seal - gas streams
Compressor seal - heavy liquid streams

Table 9.6: Profile: 0047 Description: Refinery Fugitive Emissions - Relief Valves - Liquefied Petroleum Gas

CAS Number	Name	Wt %	Quality
74-84-0	Ethane	4.10	D
74-98-6	Propane	90.40	D
115-07-01	Propene	5.10	D
75-28-5	Iso-Butane	0.40	D
TOTAL		100.00	

Used for: Vessel relief valves
Pipeline valves - gas streams
Pipeline valves - lt liq/gas streams
Pipeline valves - heavy liqd streams
Pipeline valves - hydrogen streams
Open-ended valves - all streams
Flanges - all streams
Vessel relief valves - all streams

Table 9.7: Profile: 0316 Description: Pipe / Valve Flanges

CAS Number	Name	Wt %	Quality
	C-7 cycloparaffins	0.20	C
	C-9 cycloparaffins	0.10	C
	Isomers of pentane	7.80	C
74-82-8	Methane	28.60	C
74-84-0	Ethane	5.80	C
74-98-6	Propane	11.50	C
115-07-01	Propene	0.10	C
106-97-8	N-Butane	18.30	C
75-28-5	Iso-Butane	7.40	C
109-66-0	N-Pentane	7.70	C
(10-54-3)	Hexanes	5.00	C
(42-82-5)	Heptanes	2.20	C
(11-65-9)	Octanes	2.20	C
(11-84-2)	Nonanes	1.10	C
(24-18-5)	Decanes	1.10	C
110-82-7	Cyclohexane	0.10	C
1330-20-7	Isomers of Xylene	0.20	C
71-43-2	Benzene	0.10	C
108-88-3	Toluene	0.50	C
TOTAL		100.00	

Used for: Pipeline - valves / flanges

Table 9.8: Profile: 0321 Description: Pump Seals – Composite.

CAS Number	Name	Wt %	Quality
	C-7 cycloparaffins	1.10	C
	C-8 cycloparaffins	0.10	C
	C-9 cycloparaffins	0.80	C
74-82-8	Methane	3.30	C
74-84-0	Ethane	1.20	C
74-98-6	Propane	3.70	C
106-97-8	N-Butane	8.10	C
75-28-5	Iso-Butane	0.80	C
109-66-0	Pentanes	17.70	C
(110-54-3)	Hexanes	16.50	C
(142-82-5)	Heptanes	12.60	C
(111-65-9)	Octanes	14.80	C
(111-84-2)	Nonanes	7.00	C
(124-18-5)	Decanes	7.00	C
(110-82-7	Cyclohexane	0.50	C
1330-20-7	Isomers of Xylene	1.30	C
71-43-2	Benzene	0.50	C
108-88-3	Toluene	3.00	C
TOTAL		100.00	

Used for: Pump seals - with/without controls
Pump seals - light liq/gas streams
Pump seals - heavy liqd streams
Sampling/purging/blind changing

10 UNCERTAINTY ESTIMATES

See next section on: Weakest Aspects/Priority Areas for Improvement in Current Methodology

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

More measurements of emissions from petroleum refineries should be done: based on testing programs in the United Kingdom, currently available emission factors have underestimated emissions typically by 30%.

Emission factors must be developed that can account for regional differences in the major sources of NMVOCs in refineries (see above and this part of section 040104). There are also difficulties in determining what the data really represents, as there is a wide variation in the definition of total hydrocarbons, hydrocarbons, non-methane hydrocarbons, VOCs and NMVOCs. There is a need to identify a standard method or definition of speciation of NMVOCS towards which all expert panels could work.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

No spatial disaggregation (of national emissions estimates) should be required since refineries are to be inventoried as point sources. However if data is not available on individual refineries, total regional or national crude processing data could be disaggregated based on refining capacity.

13 TEMPORAL DISAGGREGATION CRITERIA

No temporal disaggregation is possible if the simpler methodology is used.
If the detailed methodology is used, then individual refineries can indicate the temporal aspects of shutdowns.

None of the computational methods used to estimate fugitive leaks are based on parameters that show seasonal or diurnal changes. Therefore it is not possible to disaggregate fugitive process emissions at this time.

14 ADDITIONAL COMMENTS

In the European community, CONCAWE (1992) reports that the complexity of refineries has increased with the installation of additional conversion units (e.g. thermal crackers, catalytic crackers and hydrocrackers) as the demand for fuel oil production decreases and the demand for a higher yield of gasoline and other light products. This is shown on the table in which CONCAWE uses a system of refinery classifications that are based on increasing complexity.

Table 14.1: Concawe Petroleum Refinery Classification System

Year	No. of Refineries Reporting	Type I		Type II		Type III		Type IV	
		No.	**%**	**No.**	**%**	**No.**	**%**	**No.**	**%**
1969	81	34	42	31	38	16	20	-	-
1974	110	49	45	40	36	21	19	-	-
1978	111	50	45	36	32	25	23	-	-
1981	105	38	36	44	42	23	22	-	-
1984	85	18	22	47	54	20	24	-	-
1987	89	12	13	53	60	19	22	5	5
1990	95	9	9	53	56	22	23	11	12

Notes:

Type I:	Simple (non-conversion refinery: composed of crude oil distillation, reforming, treatment of distillate products, including desulphurization and/or other quality improvement processes (i.e. isomerization or specialty manufacturing).
Type II:	Type I plus catalytic cracking and/or thermal cracking and/or hydrocracking.
Type III:	Type II plus steam cracking and/or lubricant production within the refinery fence.
Type IV:	Refineries not in above categories, e.g. those producing only bitumen, lubes, etc. which import their feedstocks from other sources.

This classification system could be adopted for use in developing generic emission factors for application in the simpler inventory method. It could also be useful in developing generic speciation profiles.

15 SUPPLEMENTARY DOCUMENTS

There are no supplementary documents.

16 VERIFICATION PROCEDURES

There are more sophisticated and accurate methods to estimate fugitive process emissions, as developed by the U.S.EPA (1993). All of these methods involve the use of screening data, which are collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration, in ppmv, of leaking compounds in the ambient air near the equipment in question. The EPA has detailed what is involved in an acceptable screening program in the protocol for equipment leak emissions estimation manual (U.S.EPA 1993).

The approaches to estimating equipment leak emissions based on screening data are:

1. Screening Ranges Approach
2. EPA Correlation Approach and
3. Unit -Specific Correlation Approach.

In the screening value approach, it is assumed that components having screening values greater than 10,000 ppmv have a different average emission rate than components with screening values less than 10,000 ppmv.

The EPA Correlation approach offers an additional refinement by providing an equation to predict mass emission rate as a function of screening value.

In the last approach, mass emissions rates are determined by bagging a specific type of equipment. The associated screening value can then be used to develop a leak rate/screening value correlation for that equipment in that process unit.

All of these methods are described in detail in the protocol document (U.S.EPA 1993).
As previously discussed, remote sensing monitoring programs can also provide verification of emissions estimates based on emission factors. However it is often difficult to differentiate between different refinery sources, and so this method would more often be used to verify total refinery emissions (i.e., more than just process and fugitive process emissions).

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19 RELEASE VERSION, DATE AND SOURCE

Version : 2.3

Date : August 2006

Source : Marc Deslauriers
Environment Canada
Canada

Integrated with CONCAWE (CONCAWE, 2006) data, and updated the default emission factors for simpler methodology by:
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SNAP CODE: **040104**

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Storage and Handling of Products in Refinery

NOSE CODE: **105.08.04**

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

Only the emissions of NMVOC from the storage and handling of volatile intermediates and products are considered in this chapter. These intermediates and products are categorised as follows:

Table 1.1: Categories of Products

Category	Product
Liquid fuels	motor gasoline
	aviation gasoline
	aviation turbine fuel
	illuminating gasoline
	high-speed diesel
	distillate heating fuel
By product Fuels	Naphtha
	liquefied petroleum gases
	white oils
Primary petrochemicals	Ethylene
	Propylene
	Butadiene
	Benzene
	Toluene
	Xylene

The storage and handling of crude oil, the raw material of refineries, is dealt with in SNAP sub-sector 0502.

The storage and handling of refinery products outside a refinery is dealt with in SNAP codes 0504 and 0505.

2 CONTRIBUTION TO TOTAL EMISSIONS

Emissions from the storage and handling of intermediates and products typically contribute to between 1% and 6% of a country's total NMVOC emissions from anthropogenic sources. Table 2.1 and 2.2 summarise emissions of NMVOC from these sources.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Storage and Handling of Products in Refinery	040104	-	-	0.4	-	-	-	0.1	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Table 2.2: Emissions of NMVOC from Petroleum Product Storage at Petroleum Refineries in Canada

Country	NMVOC	
	Emissions (Mg)	% Total Anthropogenic
Canada (1988)	25280	5.16
Canada (1995)		

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

3 GENERAL

3.1 Description

Storage and handling of intermediates and products in a refinery is one part of the refining process.

Emissions arise as a result of evaporation from storage tanks, the displacement of vapour during volume changes, loading and unloading and spillage.

Intermediates and products may be stored in a variety of tanks. This chapter considers the following categories of tanks:

fixed roof tanks
external floating roof
internal floating roof
other tank types such as variable vapour space

Pressure tanks are considered to be minor sources and are not included in this chapter.

3.2 Definitions

3.3 Techniques

<u>Fixed Roof Tanks</u> - A typical vertical fixed roof tank consists of a cylindrical steel shell with a permanently affixed roof, which may vary in design from cone- or dome-shaped to flat. These tanks are either freely vented or equipped with a pressure/vacuum vent, which prevent the release of vapours during very small changes in temperature, pressure, or liquid level. This tank is considered the minimum acceptable equipment for storing organic liquids.

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[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

Horizontal fixed roof tanks are constructed for both above-ground and underground service. These are generally small storage tanks with capacities with capacities of less than 40,000 gallons. Horizontal tanks are usually equipped with pressure-vacuum vents, gauge hatches and sample wells, and manholes. For underground storage tanks, emissions are associated mainly with changes in the liquid level in the tank.

External Floating Roof Tanks - An external floating roof tank typically consists of an open-topped cylindrical steel shell equipped with a roof that floats on the surface of the storage liquid. These tanks are equipped with a seal system, which is attached to the roof perimeter and contacts the tank wall. The floating roof system and seal act to reduce evaporative losses of the contents. Evaporative losses from the external floating roof design are limited to losses from the seal system and roof fittings (standing storage loss) and any exposed liquid on the tank walls (withdrawal loss).

Internal Floating Roof Tanks - An internal floating roof tank has a permanent fixed roof as well as an internal floating deck. Fixed roof tanks that have been retrofitted with an internal deck typically have the roof supported by vertical columns within the tank. Converted external floating roof tanks typically have a self-supporting roof. A newly constructed internal floating roof tank may have either. The deck may be a contact deck (floats directly on the liquid) or non-contact (floats on pontoons which float on the liquid surface). Both types incorporate rim seals and deck fittings. Evaporation losses from decks may come from deck fittings, non-welded deck seams, and the annular space between the deck and the wall. Circulation vents on the fixed roof allows these emissions to freely vent.

Variable Vapour Space Tanks - These tanks are equipped with expandable vapour reservoirs to accommodate vapour volume fluctuations due to temperature and barometric pressure changes. These are normally connected to the vapour space of one, or more, fixed roof tanks. Lifter roof tanks (a telescoping roof) and flexible diaphragm tanks are the two most common types of variable vapour space tanks. Losses occur from these tanks during tank filling when vapour is displaced by liquid.

3.4 Emissions

For all tanks, the total emission of NMVOC is the result of two types of losses. The first is the breathing or standing loss, which is the release of overhead vapours in the tank, due to changes in meteorological conditions such as temperature and pressure, without any appreciable change in the liquid level of the tank. The second is working or withdrawal loss resulting from the displacement of tank vapours occurring during filling or emptying. (CPPI and Environment Canada 1991)

3.5 Controls

All intermediates and final products should be stored in the appropriate container: pressure vessels for gases, floating roof tanks for volatile liquids, fixed roof tanks for heavy fuel oils and non-volatile liquids.

Improved operational procedures are an important part of a NMVOC emission control program. This may include such items as ensuring roof hatches etc are not opened unnecessarily; keeping storage temperatures as low as possible, frequent inspections and painting all tanks a light shade.

Vapour balancing, in which the vapours displaced during handling are collected and recovered or control, can have control efficiencies of 90 to 98 percent. Vapour recovery methods include vapour/liquid absorption, vapour compression, vapour cooling and/or vapour/solid adsorption. Efficiencies as high as 90 to 98 percent may be achieved, depending on the methods used, the design of the unit, the composition of vapours recovered, and the mechanical condition of the system. Control will involve thermal oxidation. Typically the air/vapour mixture is injected into an incinerator, with control efficiencies ranging from 96 to 98 percent. (U.S. EPA 1992)
Other control programs involve design changes and are more specific to the tank in question, as summarised, by tank type, below.

Fixed Roof Tanks - Fixed roof tank emissions vary as a function of vessel capacity, vapour pressure of the contents, utilisation rate of the tank and atmospheric conditions. Emissions can be controlled by the installation of an internal roof and seals, with a control efficiency of 60 to 99 percent. The control efficiency depends on the type of roof and seals installed as well as on the type of organic liquid being stored.

External Floating Roof Tanks - Efficiencies of primary seals may be improved through the used of weather shields. Additional control may be added through a secondary seal. External floating roof tanks may also be retrofitted with a fixed roof. Losses from roof fittings can be minimised through proper design, installation, maintenance and use.

Internal Floating Roof Tanks - Additional control of standing losses can be achieved through the installation of secondary seals. As for external floating roof tanks, losses from roof fittings can be minimised through proper design, installation, maintenance and use.

4 SIMPLER METHODOLOGY

The simplest methodology is to combine the crude oil throughput of each refinery with an emission factor. Emission estimates should be calculated for each refinery in the country and the emission factor used will depend on the type of tanks used to store volatile materials.

The storage and handling emission from each refinery may then be reported and assigned to a grid reference.

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to calculate the emission from each tank according to techniques developed by the American Petroleum Institute (API, 2002; 2003) (http://www.api.org/) or better. This methodology requires considerable input data and should be carried out by qualified engineers. The methodology allows typical diurnal and monthly variations to be reported.

The U.S. EPA has issued a new section for AP-42 which outlines all of the methods for estimating emissions from storage of organic liquids (Section 7, http://www.epa.gov/ttn/chief/). This may be more accessible for some people than API reports. API and the U.S. EPA have worked together to develop these modules.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the crude oil throughput of each refinery is required, together with the proportion of different types of storage tanks used for volatile products.

For the detailed methodology, specific data on the throughput of the intermediates and products via each tank is required together with the physical properties of the intermediate or product. Other data required include such average meteorological data as the temperature, wind speed, barometric pressure and data specific to the tank such as type, dimensions, colour, seal type and condition of the tank.

7 POINT SOURCE CRITERIA

Each refinery should be considered as a point source.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

The Corinair1990 Default Emission Factor Handbook (CEC, 1992) proposed default emission factors of 0.25 g/kg crude oil throughput for a modern refinery (Data quality C) and 1.00 g/kg for an old refinery (Data Quality E).

The following emission factors are for the storage and handling of materials and are obtained by combining the Corinair Data with information obtained from Canada and the UK on proportion of losses from Storage and Handling.

Table 8.1: Canadian and UK Storage and Handling Losses

Refinery Type	Emission Factor (% of feedstock)	Quality
“Modern” Corinair	0.03	(Unknown)
Typical	0.05	(Unknown)
“Old” Corinair	0.12	(Unknown)

The following emission factors, together with conditions under which they should be used, have been developed by the U.S. EPA. However, they are considered dated and have a high uncertainty:

Table 8.2: EPA Emission Factors for Storage and Handling Losses

Emission Factor	Condition	Quality
0.17 g/kg	where the majority of volatile products are stored in floating roof tanks with secondary seals	(E)
0.67 g/kg	where the majority of volatile products are stored in floating roof tanks with only primary seals	(E)
4.9 g/kg	where the majority of volatile products are stored in fixed roof tanks	(E)

These emissions are intended to account for evaporative losses during storage and the displacement losses resulting from the loading and unloading of storage tanks.

8.2 Detailed Methodology

The CONCAWE Air Quality Management Group (Concawe, 2006) has identified a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR),

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.
The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

Concawe report suggests the use of the latest edition of API documents for Floating Roof Tanks (API,2003), and Vertical Fixed Roof Tanks (API, 2002). For Aboveground Horizontal Tanks, Concawe report suggests to use the latest edition of U.S. EPA methodology (U.S.EPA, 1995). Note that this reference normally contains the latest version of previously quoted API methodologies. An emission calculation software is available from the US EPA via their website, http://www.epa.gov, or on a CD-ROM (U.S.EPA, 2005). This CD also contains the EPA publication (U.S.EPA, 1995) and API documents (API 2002; 2003).

9 SPECIES PROFILES

Refinery products and intermediates vary considerably in the make up of emissions and only a very general speciated profile may be given. Where possible, speciated profiles should be obtained for each refinery. The U.S. EPA methodology provides a method for calculating tank-specific speciation factors.

10 UNCERTAINTY ESTIMATES

Uncertainties in throughput statistics are considered to be less than 5%.

Field measurements by the UK suggest that emission estimates based on API calculations underestimates emissions by factors of 2-4. Mass balance calculations carried out by the UK Institute of Petroleum suggest a similar scale of underestimate.

The emission factors relating crude oil throughput (feedstock) to emission vary by more than a factor of ten in some cases.

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

Simpler Methodology

This approach uses single emission factors to estimate emissions from an entire refinery. Little account is taken of the variation between refineries and changes in the quantity and type of volatile products manufactured. For example, NMVOC emissions from a refinery, which reduces production of kerosene and increases production of motor spirit, could be expected to change, even if the crude oil throughput remains the same.

As an illustration of how product output may vary, the table below shows the increase in the production of volatile products between 1980 and 1990, in the U.K.:

Table 11.1: UK Volatile Products Production

Year	Total Crude Processed (10^3 Mg)	Total Volatile Products (10^3 Mg)
1980	86393	28979
1990	88692	40455

In this example, using crude oil throughput as the activity statistic would result in a similar NMVOC emissions between 1980 and 1990. If emission factors could be derived for each of the volatile product outputs, then a significant change in emission estimates is likely.

Detailed Methodology

The U.S. EPA and API methodologies require detailed information from each oil refinery. However, emission estimates based on this method have been shown to differ significantly from measurements taken at refineries in the U.K. A detailed review of this discrepancy and the calculation of these emissions should be considered. If the U.S. EPA model appears promising for emission estimation, the addition of default climate parameters, for other regions of the world, to the TANKS model should be considered. This would ensure that different regions using the detailed method are calculating emissions in a consistent fashion. If a country did not have the resources to do a detailed emissions estimate, then the TANK model could be used to derive representative emission factors for a typical refinery for use in the simple methodology.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

Each refinery should be considered a point source.

13 TEMPORAL DISAGGREGATION CRITERIA

No temporal disaggregation is possible if the simpler methodology is used.

If the detailed methodology is used, the refineries should report a typical diurnal variation (average hourly over 24 hours) and seasonal (average monthly over one year).

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Compare estimates with mass balance calculations, i.e. the difference between crude throughput and products produced.

17 REFERENCES

API, 2002. Manual of petroleum measurement standards. Chapter 19: Evaporative loss measurement, Section 1: Evaporative loss from fixed-roof tanks. Formerly, API Publication 2518. Washington DC: American Petroleum Institute report no. 9/05R

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19 RELEASE VERSION, DATE AND SOURCE

Version	1.5
Date	August 2006
Source:	Stephen Richardson AEA Technology Environment UK
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Integrated with CONCAWE (CONCAWE, 2006) suggestion by:
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SNAP CODE: **091001**
091002

SOURCE ACTIVITY: **OTHER WASTE TREATMENT**
Waste Water Treatment in Industry
Waste Water Treatment in Residential/Commercial Sectors

NOSE CODE: **109.02.41**
109.02.42

NFR CODE: **6 B 1**
6 B 2

1 ACTIVITIES INCLUDED

The installations described are biological treatment plants. During the treatment process carbon dioxide, methane, and nitrous oxide can be produced. The emission factors given apply to a typical installation in the Netherlands in 1993.

This chapter was originally written for SNAP90 code 090100 Waste Water Treatment which covered the Industry and Residential/Commercial Sectors without differentiation.

2 CONTRIBUTION TO TOTAL EMISSION

The contribution of the emissions into air is minor, and only of local importance.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Waste Water Treatment	090100 *	0	0	0.1	0.5	-	-	0.4	0.2

* = SNAP90 code
0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

These activities are not believed to be a significant source of $PM_{2.5}$ (as of December 2006).

3 GENERAL

3.1 Description of activities

3.2 Definitions

The main type of wastewater treatment plants in the Netherlands are low-load biological treatment plants with aeration by point aerators. For dephosphatizing the simultaneous process is mostly used. Denitrification generally occurs by creating anaerobic zones in the wastewater treatment basin.

4 SIMPLER METHODOLOGY

A calculation of the emissions from wastewater treatment plants should be based on a summation of emissions from individual plants. The emission factors given below should only be used as default values.

5 DETAILED METHODOLOGY

Emission calculations should be based on plant specific conditions.

6 RELEVANT ACTIVITY STATISTICS

In the Netherlands statistical material about individual wastewater treatment plants is gathered yearly by the Central Bureau of Statistics. The enquiry includes information about the load, the effluent and sludge quality, as well as economical aspects.

7 POINT SOURCE CRITERIA

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Table 2: Emission factors for emissions to air from wastewater treatment plants

Substance	Emission factor	
Emission to air	kg.ie^{-1}	g m^{-3}
carbondioxide	27.4	339.1
methane	0.3	3.7
dinitrogenoxide	0.02	0.25

i.e.: capita equivalent

The emission factors are based on mean values for the situation in the Netherlands in 1991. They can therefore not be applied to an individual plant, and give only a first approximation of the emissions. The accuracy classification is estimated to be D.

9 SPECIES PROFILES

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENTS IN CURRENT METHODOLOGY

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION CRITERIA

Wastewater treatment is generally a continuous process.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

Emissions calculated should be compared with measurements at an individual plant.

17 REFERENCES

1 WESP document "RIOOLWATERZUIVERINGSINRICHTINGEN (RWZI's) RIVM report 7730030003, RIZA report 93.046/M1 (in dutch)

2 C.Kroeze (1994). Nitrous oxide emission inventory and options for control in the Netherlands. RIVM report 773001004

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19 RELEASE VERSION, DATE AND SOURCE

Version: 1

Date: November 1995

Source: J.J.M. Berdowski, P.F.J van der Most
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SNAP CODE: **090203**

SOURCE ACTIVITY TITLE: **WASTE INCINERATION**
Flaring in Oil Refinery

NOSE CODE: **109.03.11**

NFR CODE: **1 B 2 c**

1 ACTIVITIES INCLUDED

Flares are commonly used during petroleum refining for the safe disposal of waste gases during process upsets (e.g., start-up, shut-down, system blow-down) and emergencies to combust the organic content of waste emission streams without recovering/using the associated energy.

2 CONTRIBUTION TO TOTAL EMISSIONS

Although flaring emission estimates are approximate, total hydrocarbon emissions from flaring at Canadian petroleum refineries during 1988 represented about 0.1% of the refinery sector process and fugitive emissions that also included petroleum marketing emissions (CPPE, 1990). Thus the flaring operation at refineries is estimated to contribute a very small fraction of the total HC emissions in Canada. Emissions from flaring activities may also include: particulate, SOx, NOx, CO and other NMVOC. The CO_2 contribution of both miscellaneous vent and flare emission sources represented approximately 9% of the total petroleum refinery SO_2 emission in Canada during 1988.

Emissions estimates from flaring in petroleum refineries as reported in the CORINAIR90 inventory are summarised in Table 1.

Table 1: Contribution to total emissions of the CORINAIR90 inventory (*28 countries*)

Source-activity	**SNAP-code**	**Contribution to total emissions [%]**							
		SO_2	NO_x	NMVOC	CH_4	CO	CO_2	N_2O	NH_3
Flaring in Petroleum Refineries	090203	0.1	0.1	0	-	0	0	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

This activity is not believed to be a significant source of $PM_{2.5}$ (as of December 2006).[1]

---

[1] Updated with particulate matter details by: Mike Woodfield, AEA Technology, UK, December 2006

3 GENERAL

3.1 Description

Blowdown systems are used at petroleum refineries (see SNAP Code 0401) to collect and separate both liquid and vapour discharges from various refinery process units and equipment (U.S. EPA 1985, 1992). The gaseous fraction, that may represent a planned or unplanned hydrocarbon discharge, may be either recycled or flared. Flaring provides a widely-used safety mechanism and emission control option for blowdown systems when the heating value of the emission stream cannot be recovered due to uncertain or intermittent releases during process upsets/emergencies. Non-condensed vapours from the blowdown system may be combusted in a flare which is designed to handle large fluctuations of both the flow rate and hydrocarbon content of the discharge. Alternatively, thermal incineration is preferable to flaring for destroying gas releases that contain more corrosive halogenated or sulphur-bearing components.

Although different types of flares exist, the steam-assisted elevated flare systems are most commonly used at petroleum refineries whereby steam is injected in the combustion zone of the flare to provide turbulence and inspirated air to the flame. For waste gases of insufficient heating value, auxiliary fuels may also be used to sustain combustion.

3.2 Definitions

3.3 Techniques

Steam-assisted elevated flares are installed at a sufficient height above the plant and located at appropriate distances from other refinery facilities. The flare generally comprises a refractory flame platform with a windshield, steam nozzles, auxiliary gas/air injectors and a pilot burner mounted upon a stack containing a gas barrier. As reported (U.S. EPA 1980, 1992, MacDonald 1990), the flare combustion efficiency typically exceeds 98% with dependence on the following factors (i.e., for efficient performance):

excess steam assist (i.e., steam/fuel gas ratio less than 2),

sufficient gas heating value (i.e., greater than 10 MJ/m3),

low wind speed conditions (i.e., above 10 m/sec.),

sufficient gas exit velocity (i.e., above 10 m/sec.)

Similarly, different types of flare burners, designed primarily for safety requirements, may result in different efficiencies.

3.4 Emissions/Controls

Depending on the waste gas composition and other factors, the emissions of pollutants from flaring may consist of unburned fuel components (e.g., methane, NMVOC), by-products of the combustion process (e.g., soot, partially combusted products, CO, CO_2, NOx) and sulphur oxides (e.g., SO_2) where sulphur components are present in the waste gas. Steam injection is used to enhance combustion for smokeless burning and to reduce NOx by lowering the flame temperature. Increased combustion efficiency may reduce CH_4 and NMVOC, but will not reduce CO_2 emissions. Flaring emissions might best be reduced by minimising amounts of gases to be flared, provided that the associated wastes gases are not vented directly.

4 SIMPLER METHODOLOGY

Where limited information is available, the simplest inventory methodology is to combine the amounts of gases flared by petroleum refineries with a single hydrocarbon emission factor (i.e., derived in units of mass emission per volume of gas flared), with the assumption of a constant flare combustion efficiency. In the event that flare gas volumes are unavailable, an alternative but older emission estimation methodology would be to apply individual emission factors of various pollutants for petroleum refinery blowdown systems (i.e., including vapour recovery systems and flaring) in combination with total petroleum refinery feed (i.e., crude oil throughput).

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to estimate its flaring emissions using available information on the composition of flare gas, the types of smoke control used and the flare combustion efficiency in combination with flare gas volumes, using either measurement data, available emission factors or mass balance approaches. It is recognised that flare emissions are challenging to estimate and/or quantify with certainty, since: conventional or direct extractive source testing is not feasible for elevated flares; both flare gas volume determinations and/or gas composition may be very uncertain especially during process upsets or emergency releases; and very limited data are available with respect to flare combustion efficiencies which depend on both process and external wind condition factors. For normal operations, the general types of refinery and other information required to estimate flare emissions, as currently done at Canadian refineries (CPPI 1991), are:

- the actual quantities of gases flared at each flare (e.g. m^3/year) based upon measured flare gas flowmeter or other records,
- the average composition of flare gas including: H/C molar ratio on the basis of flare design or test data, the molecular weight and sulphur content,
- the types of smoke controls used, such as: steam/air, manual/automatic and/or TV monitor,
- an emission HC factor based upon typical steam/fuel gas ratios, gas heating values and/or flare combustion efficiencies,
- a sulphur mass balance of fuels consumed by flaring and other refinery process heaters/boilers.

In some instances, flare emissions may only be estimated currently by difference or rough approximations. However, remote sensing of flare emissions by LIDAR/DIAL measurements of plume cross section seams are assisting in determining or verifying flare emission rates and the composition of refinery flare emissions (Bodon, Moncrieff and Wootton, 1992).

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, either the quantities of flare gases consumed or the refinery crude oil feed is required. For more detailed methodology, the quantities, composition and heating values of flare gases burned are required for each petroleum refinery.

7 POINT SOURCE CRITERIA

All significant refinery flares are to be inventoried as part of refinery point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

The CONCAWE Air Quality Management Group (Concawe, 2006) has identified a lot of issues with regard to the data submissions for both European Pollutant Emission Register (EPER) mandated by European Directive 96/61/EC on integrated pollution prevention and control (IPPC) and UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR).

In particular CONCAWE initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the EPER threshold values from sources found at the majority of European refineries. CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants (Concawe, 2006). The compendium can not be considered fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.

The CONCAWE report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. [I assume that for flaring abatement is not relevant] Where emission factors are available, algorithms are provided for sources found in the majority of European refineries.

CONCAWE suggests emission factors for the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, they recommend using the combustion emission factors.

The emission factors (Table 2) are available as a function of GJ of flare gas combusted, when mass and composition of the flare stream are known or based on refinery feed (otherwise).

Table 2: Emission Factors for Refinery Flares

Pollutant	Emission Factor g/GJ of gas flareed (°)	Emission Factor kg/m^3 of refinery feed
SO_2 (°°)	2000000 S	0,077
NOx	3.22	0.054
NMVOC	5	0.002
CO	177	0.012
PM_{10}	Neg	Neg
C_6H_6(°°°)	5 B	0.00166

(°) for SO_2, NMVOC and C_6H_6 expressed as g/ton of gas flared

(°°) S = mass fraction of sulphur in flare gas
(°°°) B = mass fraction of benzene in flare gas

In U.S. EPA CHIEF database, the VOC emission factor for petroleum refinery flares is: 5.6 lb VOC/million cubic feet of flare gas burned with a quality rating of D. The above mentioned VOC emission factor comprises: methane (20%), ethane (30%), propane (30%) and formaldehyde (20%).

A VOC emission factor, reported in a Norwegian survey (OLF Report Phase 1, Part A), of 0.0095 kg/m3 of flare gas was cited in documentation of the UNECE Task Force - VOC Emissions from Stationary Sources. The flare emissions were reported to consist of 65% methane and 35% NMVOC and suggested a typical flare efficiency of 99.2%.

Remote sensing (DIAL) measurements of full-sized flare emissions at a Norwegian petroleum refinery under normal operating conditions also has indicated that the flare combustion efficiency exceeded 98%, comprising various amounts of methane and C2 to C6+ alkane components (Boden, Moncrieff and Wootton, 1992).

Flare combustion efficiencies, under atypical operating or other conditions and presumably during upset conditions, may have lower destruction efficiencies, based upon other test data (MacDonald 1990).

9 SPECIES PROFILES

(See section 8).

10 UNCERTAINTY ESTIMATES

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

As flare emissions can vary significantly with dependence on several factors, more measurements to determine flare combustion efficiencies and chemical composition should be done (e.g., perhaps using remote sensing techniques) under a variety of conditions, in order to verify available emission estimates and assure that flare combustion efficiencies generally represent the stated efficiencies.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

13 TEMPORAL DISAGGREGATION DATA

No temporal apportionment of these emissions is possible if the simpler methodology is used. Temporal disaggregation of detailed emission estimates can be done from records of petroleum refinery shutdowns and other operating data.

14 ADDITIONAL COMMENTS

15 SUPPLEMENTARY DOCUMENTS

16 VERIFICATION PROCEDURES

As noted above, remote sensing monitoring programs may be useful to verify flaring emission estimates.

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19 RELEASE VERSION, DATE AND SOURCE

Version: 1.4

Date: August 2006

Source: Marc Deslauriers
Environment Canada
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1.3 Fuel Oil Combustion

1.3.1 General[1-3]

Two major categories of fuel oil are burned by combustion sources: distillate oils and residual oils. These oils are further distinguished by grade numbers, with Nos. 1 and 2 being distillate oils; Nos. 5 and 6 being residual oils; and No. 4 being either distillate oil or a mixture of distillate and residual oils. No. 6 fuel oil is sometimes referred to as Bunker C. Distillate oils are more volatile and less viscous than residual oils. They have negligible nitrogen and ash contents and usually contain less than 0.3 percent sulfur (by weight). Distillate oils are used mainly in domestic and small commercial applications, and include kerosene and diesel fuels. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5 and 6) may need to be heated for ease of handling and to facilitate proper atomization. Because residual oils are produced from the residue remaining after the lighter fractions (gasoline, kerosene, and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur. Residual oils are used mainly in utility, industrial, and large commercial applications.

1.3.2 Firing Practices[4]

The major boiler configurations for fuel oil-fired combustors are watertube, firetube, cast iron, and tubeless design. Boilers are classified according to design and orientation of heat transfer surfaces, burner configuration, and size. These factors can all strongly influence emissions as well as the potential for controlling emissions.

Watertube boilers are used in a variety of applications ranging from supplying large amounts of process steam to providing space heat for industrial facilities. In a watertube boiler, combustion heat is transferred to water flowing through tubes which line the furnace walls and boiler passes. The tube surfaces in the furnace (which houses the burner flame) absorb heat primarily by radiation from the flames. The tube surfaces in the boiler passes (adjacent to the primary furnace) absorb heat primarily by convective heat transfer.

Firetube boilers are used primarily for heating systems, industrial process steam generators, and portable power boilers. In firetube boilers, the hot combustion gases flow through the tubes while the water being heated circulates outside of the tubes. At high pressures and when subjected to large variations in steam demand, firetube units are more susceptible to structural failure than watertube boilers. This is because the high-pressure steam in firetube units is contained by the boiler walls rather than by multiple small-diameter watertubes, which are inherently stronger. As a consequence, firetube boilers are typically small and are used primarily where boiler loads are relatively constant. Nearly all firetube boilers are sold as packaged units because of their relatively small size.

A cast iron boiler is one in which combustion gases rise through a vertical heat exchanger and out through an exhaust duct. Water in the heat exchanger tubes is heated as it moves upward through the tubes. Cast iron boilers produce low pressure steam or hot water, and generally burn oil or natural gas. They are used primarily in the residential and commercial sectors.

Another type of heat transfer configuration used on smaller boilers is the tubeless design. This design incorporates nested pressure vessels with water in between the shells. Combustion gases are fired into the inner pressure vessel and are then sometimes recirculated outside the second vessel.

1.3.3 Emissions[5]

Emissions from fuel oil combustion depend on the grade and composition of the fuel, the type and size of the boiler, the firing and loading practices used, and the level of equipment maintenance. Because the combustion characteristics of distillate and residual oils are different, their combustion can produce significantly different emissions. In general, the baseline emissions of criteria and noncriteria pollutants are those from uncontrolled combustion sources. Uncontrolled sources are those without add-on air pollution control (APC) equipment or other combustion modifications designed for emission control. Baseline emissions for sulfur dioxide (SO_2) and particulate matter (PM) can also be obtained from measurements taken upstream of APC equipment.

1.3.3.1 Particulate Matter Emissions[6-15] -

Particulate emissions may be categorized as either filterable or condensable. Filterable emissions are generally considered to be the particules that are trapped by the glass fiber filter in the front half of a Reference Method 5 or Method 17 sampling van. Vapors and particles less than 0.3 microns pass through the filter. Condensable particulate matter is material that is emitted in the vapor state which later condenses to form homogeneous and/or heterogeneous aerosol particles. The condensable particulate emitted from boilers fueled on coal or oil is primarily inorganic in nature.

Filterable particulate matter emissions depend predominantly on the grade of fuel fired. Combustion of lighter distillate oils results in significantly lower PM formation than does combustion of heavier residual oils. Among residual oils, firing of No. 4 or No. 5 oil usually produces less PM than does the firing of heavier No. 6 oil.

In general, filterable PM emissions depend on the completeness of combustion as well as on the oil ash content. The PM emitted by distillate oil-fired boilers primarily comprises carbonaceous particles resulting from incomplete combustion of oil and is not correlated to the ash or sulfur content of the oil. However, PM emissions from residual oil burning are related to the oil sulfur content. This is because low-sulfur No. 6 oil, either from naturally low-sulfur crude oil or desulfurized by one of several processes, exhibits substantially lower viscosity and reduced asphaltene, ash, and sulfur contents, which results in better atomization and more complete combustion.

Boiler load can also affect filterable particulate emissions in units firing No. 6 oil. At low load (50 percent of maximum rating) conditions, particulate emissions from utility boilers may be lowered by 30 to 40 percent and by as much as 60 percent from small industrial and commercial units. However, no significant particulate emission reductions have been noted at low loads from boilers firing any of the lighter grades. At very low load conditions (approximately 30 percent of maximum rating), proper combustion conditions may be difficult to maintain and particulate emissions may increase significantly.

1.3.3.2 Sulfur Oxides Emissions[1-2,6-9,16] -

Sulfur oxides (SO_x) emissions are generated during oil combustion from the oxidation of sulfur contained in the fuel. The emissions of SO_x from conventional combustion systems are predominantly in the form of SO_2. Uncontrolled SO_x emissions are almost entirely dependent on the sulfur content of the fuel and are not affected by boiler size, burner design, or grade of fuel being fired. On average, more than 95 percent of the fuel sulfur is converted to SO_2, about 1 to 5 percent is further oxidized to sulfur trioxide (SO_3), and 1 to 3 percent is emitted as sulfate particulate. SO_3 readily reacts with water vapor (both in the atmosphere and in flue gases) to form a sulfuric acid mist.

1.3.3.3 Nitrogen Oxides Emissions[1-2,6-10,15,17-27] -

Oxides of nitrogen (NO_x) formed in combustion processes are due either to thermal fixation of atmospheric nitrogen in the combustion air ("thermal NO_x"), or to the conversion of chemically bound nitrogen in the fuel ("fuel NO_x"). The term NO_x refers to the composite of nitric oxide (NO) and nitrogen dioxide (NO_2). Test data have shown that for most external fossil fuel combustion systems, over 95 percent of the emitted NO_x is in the form of nitric oxide (NO). Nitrous oxide (N_2O) is not included in NO_x but has recently received increased interest because of atmospheric effects.

Experimental measurements of thermal NO_x formation have shown that NO_x concentration is exponentially dependent on temperature, and proportional to N_2 concentration in the flame, the square root of O_2 concentration in the flame, and the residence time. Thus, the formation of thermal NO_x is affected by four factors: (1) peak temperature, (2) fuel nitrogen concentration, (3) oxygen concentration, and (4) time of exposure at peak temperature. The emission trends due to changes in these factors are generally consistent for all types of boilers: an increase in flame temperature, oxygen availability, and/or residence time at high temperatures leads to an increase in NO_x production.

Fuel nitrogen conversion is the more important NO_x-forming mechanism in residual oil boilers. It can account for 50 percent of the total NO_x emissions from residual oil firing. The percent conversion of fuel nitrogen to NO_x varies greatly, however; typically from 20 to 90 percent of nitrogen in oil is converted to NO_x. Except in certain large units having unusually high peak flame temperatures, or in units firing a low nitrogen content residual oil, fuel NO_x generally accounts for over 50 percent of the total NO_x generated. Thermal fixation, on the other hand, is the dominant NO_x-forming mechanism in units firing distillate oils, primarily because of the negligible nitrogen content in these lighter oils. Because distillate oil-fired boilers are usually smaller and have lower heat release rates, the quantity of thermal NO_x formed in them is less than that of larger units which typically burn residual oil.[28]

A number of variables influence how much NO_x is formed by these two mechanisms. One important variable is firing configuration. NO_x emissions from tangentially (corner) fired boilers are, on the average, less than those of horizontally opposed units. Also important are the firing practices employed during boiler operation. Low excess air (LEA) firing, flue gas recirculation (FGR), staged combustion (SC), reduced air preheat (RAP), low NO_x burners (LNBs), burning oil/water emulsions (OWE), or some combination thereof may result in NO_x reductions of 5 to 60 percent. Load reduction (LR) can likewise decrease NO_x production. Nitrogen oxide emissions may be reduced from 0.5 to 1 percent for each percentage reduction in load from full load operation. It should be noted that most of these variables, with the exception of excess air, only influence the NO_x emissions of large oil-fired boilers. Low excess air-firing is possible in many small boilers, but the resulting NO_x reductions are less significant.

1.3.3.4 Carbon Monoxide Emissions[29-32] -

The rate of carbon monoxide (CO) emissions from combustion sources depends on the oxidation efficiency of the fuel. By controlling the combustion process carefully, CO emissions can be minimized. Thus if a unit is operated improperly or not well maintained, the resulting concentrations of CO (as well as organic compounds) may increase by several orders of magnitude. Smaller boilers, heaters, and furnaces tend to emit more of these pollutants than larger combustors. This is because smaller units usually have a higher ratio of heat transfer surface area to flame volume than larger combustors have; this leads to reduced flame temperature and combustion intensity and, therefore, lower combustion efficiency.

The presence of CO in the exhaust gases of combustion systems results principally from incomplete fuel combustion. Several conditions can lead to incomplete combustion, including insufficient oxygen (O_2) availability; poor fuel/air mixing; cold-wall flame quenching; reduced combustion temperature; decreased combustion gas residence time; and load reduction (i. e., reduced combustion intensity). Since various combustion modifications for NO_x reduction can produce one or more of the above conditions, the possibility of increased CO emissions is a concern for environmental, energy efficiency, and operational reasons.

1.3.3.5 Organic Compound Emissions[29-39] -

Small amounts of organic compounds are emitted from combustion. As with CO emissions, the rate at which organic compounds are emitted depends, to some extent, on the combustion efficiency of the boiler. Therefore, any combustion modification which reduces the combustion efficiency will most likely increase the concentrations of organic compounds in the flue gases.

Total organic compounds (TOCs) include VOCs, semi-volatile organic compounds, and condensable organic compounds. Emissions of VOCs are primarily characterized by the criteria pollutant class of unburned vapor phase hydrocarbons. Unburned hydrocarbon emissions can include essentially all vapor phase organic compounds emitted from a combustion source. These are primarily emissions of aliphatic, oxygenated, and low molecular weight aromatic compounds which exist in the vapor phase at flue gas temperatures. These emissions include all alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes (e. g., benzene, toluene, xylene, and ethyl benzene).

The remaining organic emissions are composed largely of compounds emitted from combustion sources in a condensed phase. These compounds can almost exclusively be classed into a group known as polycyclic organic matter (POM), and a subset of compounds called polynuclear aromatic hydrocarbons (PAH or PNA). There are also PAH-nitrogen analogs. Information available in the literature on POM compounds generally pertains to these PAH groups.

Formaldehyde is formed and emitted during combustion of hydrocarbon-based fuels including coal and oil. Formaldehyde is present in the vapor phase of the flue gas. Formaldehyde is subject to oxidation and decomposition at the high temperatures encountered during combustion. Thus, larger units with efficient combustion (resulting from closely regulated air-fuel ratios, uniformly high combustion chamber temperatures, and relatively long gas retention times) have lower formaldehyde emission rates than do smaller, less efficient combustion units.

1.3.3.6 Trace Element Emissions[29-32,40-44] -

Trace elements are also emitted from the combustion of oil. For this update of AP-42, trace metals included in the list of 189 hazardous air pollutants under Title III of the 1990 Clean Air Act Amendments are considered. The quantity of trace elements entering the combustion device depends solely on the fuel composition. The quantity of trace metals emitted from the source depends on combustion temperature, fuel feed mechanism, and the composition of the fuel. The temperature determines the degree of volatilization of specific compounds contained in the fuel. The fuel feed mechanism affects the separation of emissions into bottom ash and fly ash. In general, the quantity of any given metal emitted depends on the physical and chemical properties of the element itself; concentration of the metal in the fuel; the combustion conditions; and the type of particulate control device used, and its collection efficiency as a function of particle size.

Some trace metals concentrate in certain waste particle streams from a combustor (bottom ash, collector ash, flue gas particulate), while others do not. Various classification schemes to describe this partitioning have been developed. The classification scheme used by Baig, et al.[44] is as follows:

- Class 1: Elements which are approximately equally distributed between fly ash and bottom ash, or show little or no small particle enrichment.

- Class 2: Elements which are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size.

- Class 3: Elements which are emitted in the gas phase.

By understanding trace metal partitioning and concentration in fine particulate, it is possible to postulate the effects of combustion controls on incremental trace metal emissions. For example, several NO_x controls for boilers reduce peak flame temperatures (e. g., SC, FGR, RAP, OWE, and LR). If combustion temperatures are reduced, fewer Class 2 metals will initially volatilize, and fewer will be available for subsequent condensation and enrichment on fine PM. Therefore, for combustors with particulate controls, lower volatile metal emissions should result due to improved particulate removal. Flue gas emissions of Class 1 metals (the non-segregating trace metals) should remain relatively unchanged.

Lower local O_2 concentrations is also expected to affect segregating metal emissions from boilers with particle controls. Lower O_2 availability decreases the possibility of volatile metal oxidation to less volatile oxides. Under these conditions, Class 2 metals should remain in the vapor phase as they enter the cooler sections of the boiler. More redistribution to small particles should occur and emissions should increase. Again, Class 1 metal emissions should remain unchanged.

1.3.3.7 Greenhouse Gases[45-50] -

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions are all produced during fuel oil combustion. Nearly all of the fuel carbon (99 percent) in fuel oil is converted to CO_2 during the combustion process. This conversion is relatively independent of firing configuration. Although the formation of CO acts to reduce CO_2 emissions, the amount of CO produced is insignificant compared to the amount of CO_2 produced. The majority of the fuel carbon not converted to CO_2 is due to incomplete combustion in the fuel stream.

Formation of N_2O during the combustion process is governed by a complex series of reactions and its formation is dependent upon many factors. Formation of N_2O is minimized when combustion temperatures are kept high (above 1475°F) and excess air is kept to a minimum (less than 1 percent). Additional sampling and research is needed to fully characterize N_2O emissions and to understand the N_2O formation mechanism. Emissions can vary widely from unit to unit, or even from the same unit at different operating conditions. Average emission factors based on reported test data have been developed for conventional oil combustion systems.

Methane emissions vary with the type of fuel and firing configuration, but are highest during periods of incomplete combustion or low-temperature combustion, such as the start-up or shut-down cycle for oil-fired boilers. Typically, conditions that favor formation of N_2O also favor emissions of CH_4.

1.3.4 Controls

Control techniques for criteria pollutants from fuel oil combustion may be classified into three broad categories: fuel substitution/alteration, combustion modification, and postcombustion control. Emissions of noncriteria pollutants such as particulate phase metals have been controlled through the use of post combustion controls designed for criteria pollutants. Fuel substitution reduces SO_2 or NO_x and involves burning a fuel with a lower sulfur or nitrogen content, respectively. Particulate matter will generally be reduced when a lighter grade of fuel oil is burned.[6,8,11] Fuel alteration of heavy oils includes mixing water and heavy oil using emulsifying agents for better atomization and lower combustion temperatures. Under some conditions, emissions of NO_x, CO, and PM may be reduced significantly. Combustion modification includes any physical or operational change in the furnace or boiler and is applied primarily for NO_x control purposes, although for small units, some reduction in PM emissions may be available through improved combustion practice. Postcombustion control is a device after the combustion of the fuel and is applied to control emissions of PM, SO_2, and NO_x.

1.3.4.1 Particulate Matter Controls[51] -

Control of PM emissions from residential and commercial units is accomplished by improving burner servicing and improving oil atomization and combustion aerodynamics. Optimization of combustion aerodynamics using a flame retention device, swirl, and/or recirculation is considered effective toward achieving the triple goals of low PM emissions, low NO_x emissions, and high thermal efficiency.

Large industrial and utility boilers are generally well-designed and well-maintained so that soot and condensable organic compound emissions are minimized. Particulate matter emissions are more a result of emitted fly ash with a carbon component in such units. Therefore, postcombustion controls (mechanical collectors, ESP, fabric filters, etc.) or fuel substitution/alteration may be used to reduce PM emissions from these sources.

Mechanical collectors, a prevalent type of control device, are primarily useful in controlling particulates generated during soot blowing, during upset conditions, or when a very dirty heavy oil is fired. For these situations, high-efficiency cyclonic collectors can achieve up to 85 percent control of particulate. Under normal firing conditions, or when a clean oil is combusted, cyclonic collectors are not nearly so effective because of the high percentage of small particles (less than 3 micrometers in diameter) emitted.

Electrostatic precipitators (ESPs) are commonly used in oil-fired power plants. Older precipitators, usually small, typically remove 40 to 60 percent of the emitted PM. Because of the low ash content of the oil, greater collection efficiency may not be required. Currently, new or rebuilt ESPs can achieve collection efficiencies of up to 90 percent.

In fabric filtration, a number of filtering elements (bags) along with a bag cleaning system are contained in a main shell structure incorporating dust hoppers. The particulate removal efficiency of the fabric filter system is dependent on a variety of particle and operational characteristics including particle size distribution, particle cohesion characteristics, and particle electrical resistivity. Operational parameters that affect collection efficiency include air-to-cloth ratio, operating pressure loss, cleaning sequence, interval between cleaning, and cleaning intensity. The structure of the fabric filter, filter composition, and bag properties also affect collection efficiency. Collection efficiencies of baghouses may be more than 99 percent.

Scrubbing systems have also been installed on oil-fired boilers to control both sulfur oxides and particulate. These systems can achieve SO_2 removal efficiencies of 90 to 95 percent and particulate control efficiencies of 50 to 60 percent.

Fuel alteration of heavy oil by mixing with water and an emulsifying agent has reduced PM emissions significantly in controlled tests.

1.3.4.2 SO_2 Controls[52-53] -

Commercialized postcombustion flue gas desulfurization (FGD) processes use an alkaline reagent to absorb SO_2 in the flue gas and produce a sodium or a calcium sulfate compound. These solid sulfate compounds are then removed in downstream equipment. Flue gas desulfurization technologies are categorized as wet, semi-dry, or dry depending on the state of the reagent as it leaves the absorber vessel. These processes are either regenerable (such that the reagent material can be treated and reused) or nonregenerable (in which case all waste streams are de-watered and discarded).

Wet regenerable FGD processes are attractive because they have the potential for better than 95 percent sulfur removal efficiency, have minimal waste water discharges, and produce a saleable sulfur product. Some of the current nonregenerable calcium-based processes can, however, produce a saleable gypsum product.

To date, wet systems are the most commonly applied. Wet systems generally use alkali slurries as the SO_x absorbent medium and can be designed to remove greater than 90 percent of the incoming SO_x. Lime/limestone scrubbers, sodium scrubbers, and dual alkali scrubbing are among the commercially proven wet FGD systems. Effectiveness of these devices depends not only on control device design but also on operating variables.

1.3.4.3 NO_x Controls[41,54-55] -

In boilers fired on crude oil or residual oil, the control of fuel NO_x is very important in achieving the desired degree of NO_x reduction since fuel NO_x typically accounts for 60 to 80 percent of the total NO_x formed. Fuel nitrogen conversion to NO_x is highly dependent on the fuel-to-air ratio in the combustion zone and, in contrast to thermal NO_x formation, is relatively insensitive to small changes in combustion zone temperature. In general, increased mixing of fuel and air increases nitrogen conversion which, in turn, increases fuel NO_x. Thus, to reduce fuel NO_x formation, the most common combustion modification technique is to suppress combustion air levels below the theoretical amount required for complete combustion. The lack of oxygen creates reducing conditions that, given sufficient time at high temperatures, cause volatile fuel nitrogen to convert to N_2 rather than NO.

Several techniques are used to reduce NO_x emissions from fuel oil combustion. Fuel substitution consists of burning lower nitrogen fuels. Fuel alteration includes burning emulsified heavy oil and water mixtures. In addition to these, the primary techniques can be classified into one of two fundamentally different methods — combustion controls and postcombustion controls. Combustion controls reduce NO_x by suppressing NO_x formation during the combustion process while postcombustion controls reduce NO_x emissions after their formation. Combustion controls are the most widely used method of controlling NO_x formation in all types of boilers and include low excess air, burners out of service, biased-burner firing, flue gas recirculation, overfire air, and low-NO_x burners. Postcombustion control methods include selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). These controls can be used separately, or combined to achieve greater NO_x reduction.

Operating at low excess air involves reducing the amount of combustion air to the lowest possible level while maintaining efficient and environmentally compliant boiler operation. NO_x formation is inhibited because less oxygen is available in the combustion zone. Burners out of service involves withholding fuel flow to all or part of the top row of burners so that only air is allowed to pass through. This method simulates air staging, or overfire air conditions, and limits NO_x formation by lowering the oxygen level in the burner area. Biased-burner firing involves firing the lower rows of burners more fuel-rich than the upper row of burners. This method provides a form of air staging and limits NO_x formation by limiting the amount of oxygen in the firing zone. These methods may change the normal operation of the boiler and the effectiveness is boiler-specific. Implementation of these techniques may also reduce operational flexibility; however, they may reduce NO_x by 10 to 20 percent from uncontrolled levels.

Flue gas recirculation involves extracting a portion of the flue gas from the economizer section or air heater outlet and readmitting it to the furnace through the furnace hopper, the burner windbox, or both. This method reduces the concentration of oxygen in the combustion zone and may reduce NO_x by as much as 40 to 50 percent in some boilers.

Overfire air is a technique in which a percentage of the total combustion air is diverted from the burners and injected through ports above the top burner level. Overfire air limits NO_x by (1) suppressing thermal NO_x by partially delaying and extending the combustion process resulting in less intense combustion and cooler flame temperatures; (2) a reduced flame temperature that limits thermal NO_x formation, and/or (3) a reduced residence time at peak temperature which also limits thermal NO_x formation.

Low NO_x burners are applicable to tangential and wall-fired boilers of various sizes. They have been used as a retrofit NO_x control for existing boilers and can achieve approximately 35 to 55 percent reduction from uncontrolled levels. They are also used in new boilers to meet NSPS limits. Low NO_x burners can be combined with overfire air to achieve even greater NO_x reduction (40 to 60 percent reduction from uncontrolled levels).

SNCR is a postcombustion technique that involves injecting ammonia or urea into specific temperature zones in the upper furnace or convective pass. The ammonia or urea reacts with NO_x in the flue gas to produce nitrogen and water. The effectiveness of SNCR depends on the temperature where reagents are injected; mixing of the reagent in the flue gas; residence time of the reagent within the required temperature window; ratio of reagent to NO_x; and the sulfur content of the fuel that may create sulfur compound that deposit in downstream equipment. There is not as much commercial experience to base effectiveness on a wide range of boiler types; however, in limited applications, NO_x reductions of 25 to 40 percent have been achieved.

SCR is another postcombustion technique that involves injecting ammonia into the flue gas in the presence of a catalyst to reduce NO_x to nitrogen and water. The SCR reactor can be located at various positions in the process including before an air heater and particulate control device, or downstream of the air heater, particulate control device, and flue gas desulfurization systems. The performance of SCR is influenced by flue gas temperature, fuel sulfur content, ammonia to NO_x ratio, inlet NO_x concentration, space velocity, and catalyst condition. NO_x emission reductions of 75 to 85 percent have been achieved through the use of SCR on oil-fired boilers operating in the U.S.

Fuel alteration for NO_x reduction includes use of oil/water emulsion fuels. In controlled tests, a mixture of 9 percent water in No. 6 oil with a petroleum based emulsifying agent reduced NO_x emissions by 36 percent on a Btu basis or 41 percent on a volume basis, compared with the same fuel in unaltered form. The reduction appears to be due primarily to improved atomization with a corresponding reduction of excess combustion air, with lower flame temperature contributing slightly to the reduction.[84]

Tables 1.3-1 and 1.3-3 present emission factors for uncontrolled criteria pollutants from fuel oil combustion. Tables in this section present emission factors on a volume basis ($lb/10^3gal$). To convert to an energy basis (lb/MMBtu), divide by a heating value of 150 $MMBtu/10^3gal$ for Nos. 4, 5, 6, and residual fuel oil, and 140 $MMBtu/10^3gal$ for No. 2 and distillate fuel oil. Table 1.3-2 presents emission factors for condensible particulate matter. Tables 1.3-4, 1.3-5, 1.3-6, and 1.3-7 present cumulative size distribution data and size-specific emission factors for particulate emissions from uncontrolled and controlled fuel oil combustion. Figures 1.3-1, 1.3-2, 1.3-3, and 1.3-4 present size-specific emission factors for particulate emissions from uncontrolled and controlled fuel oil combustion. Emission factors for N_2O, POM, and formaldehyde are presented in Table 1.3-8. Emission factors for speciated organic compounds are presented in Table 1.3-9. Emission factors for trace elements in distillate oil are given in Table 1.3-10. Emission factors for trace metals residual oil are given in Table 1.3-11. Default emission factors for CO_2 are presented in Table 1.3-12. A summary of various SO_2 and NO_x controls for fuel-oil-fired boilers is presented in Table 1.3-13 and 1.3-14, respectively. Emission factors for CO, NO_x, and PM from burning No. 6 oil/water emulsion fuel are presented in Table 1.3-15.

1.3.5 Updates Since the Fifth Edition

The Fifth Edition was released in January 1995. Revisions to this section since that date are summarized below. For further detail, consult the memoranda describing each supplement or the background report for this section. These and other documents can be found on the CHIEF web site (http://www.epa.gov/ttn/chief/).

Supplement A, February 1996

- The formulas presented in the footnotes for filterable PM were moved into the table.
- For SO_2 and SO_3 emission factors, text was added to the table footnotes to clarify that "S" is a weight percent and not a fraction. A similar clarification was made to the CO and NO_x footnotes. SCC A2104004/A2104011 was provided for residential furnaces.
- For industrial boilers firing No. 6 and No. 5 oil, the methane emission factor was changed from 1 to 1.0 to show two significant figures.
- For SO_2 and SO_3 factors, text was added to the table footnotes to clarify that "S" is a weight percent and not a fraction.
- The N_2O, POM, and formaldehyde factors were corrected.
- Table 1.3-10 was incorrectly labeled 1.1-10. This was corrected.

Supplement B, October 1996

- Text was added concerning firing practices.
- Factors for N_2O, POM, and formaldehyde were added.
- New data for filterable PM were used to create a new PM factor for residential oil-fired furnaces.
- Many new factors were added for toxic organics, toxic metals from distillate oil, and toxic metals from residual oil.
- A table was added for new CO_2 emission factors.

Supplement E, September 1998

- Table 1.3-1, the sub-heading for "Industrial Boilers" was added to the first column.
- Table 1.3-3, the emission factor for uncontrolled PM less than 0.625 micron was corrected to 1.7A, the emission factor for scrubber controlled PM less than 10 micron was corrected to 0.50A, and the relationships for each content in various fuel oils was corrected in footnote C.
- Table 1.3-4 and 1.3-6, the relationship for ash content in various fuel oils was corrected in the footnote C of each table.

- Table 1.3-9, the emission factors for trace metals in distillate oil were updated with newer data where available.

- 1.3-10, the title of the table was changed to clarify these factors apply to uncontrolled fuel oil boilers.

- Text and emission factors were added pertaining to No. 6 oil/water emulsion fuel.

- Table 1.3-1 was revised to include new NO_x emission factors.

- Emission factors for condensable particulate matter were added (Table 1.3-2).

Table 1.3-1. CRITERIA POLLUTANT EMISSION FACTORS FOR FUEL OIL COMBUSTION[a]

Firing Configuration (SCC)[a]	SO_2[b]		SO_3[c]		NO_x[d]		CO[e]		Filterable PM[f]	
	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING
Boilers > 100 Million Btu/hr										
No. 6 oil fired, normal firing (1-01-004-01), (1-02-004-01), (1-03-004-01)	157S	A	5.7S	C	47	A	5	A	9.19(S)+3.22	A
No. 6 oil fired, normal firing, low NO_x burner (1-01-004-01), (1-02-004-01)	157S	A	5.7S	C	40	B	5	A	9.19(S)+3.22	A
No. 6 oil fired, tangential firing, (1-01-004-04)	157S	A	5.7S	C	32	A	5	A	9.19(S)+3.22	A
No. 6 oil fired, tangential firing, low NO_x burner (1-01-004-04)	157S	A	5.7S	C	26	E	5	A	9.19(S)+3.22	A
No. 5 oil fired, normal firing (1-01-004-05), (1-02-004-04)	157S	A	5.7S	C	47	B	5	A	10	B
No. 5 oil fired, tangential firing (1-01-004-06)	157S	A	5.7S	C	32	B	5	A	10	B
No. 4 oil fired, normal firing (1-01-005-04), (1-02-005-04)	150S	A	5.7S	C	47	B	5	A	7	B
No. 4 oil fired, tangential firing (1-01-005-05)	150S	A	5.7S	C	32	B	5	A	7	B
No. 2 oil fired (1-01-005-01), (1-02-005-01), (1-03-005-01)	157S	A	5.7S	C	24	D	5	A	2	A
No.2 oil fired, LNB/FGR, (1-01-005-01), (1-02-005-01), (1-03-005-01)	157S	A	5.7S	A	10	D	5	A	2	A

Table 1.3-1. (cont.)

Firing Configuration (SCC)[a]	SO_2[b]		SO_3[c]		NO_x[d]		CO[e]		Filterable PM[f]	
	Emission Factor ($lb/10^3$ gal)	EMISSION FACTOR RATING	Emission Factor ($lb/10^3$ gal)	EMISSION FACTOR RATING	Emission Factor ($lb/10^3$ gal)	EMISSION FACTOR RATING	Emission Factor ($lb/10^3$ gal)	EMISSION FACTOR RATING	Emission Factor ($lb/10^3$ gal)	EMISSION FACTOR RATING
Boilers < 100 Million Btu/hr										
No. 6 oil fired (1-02-004-02/03) (1-03-004-02/03)	157S	A	2S	A	55	A	5	A	10	B
No. 5 oil fired (1-03-004-04)	157S	A	2S	A	55	A	5	A	9.19(S)+3.22	A
No. 4 oil fired (1-03-005-04)	150S	A	2S	A	20	A	5	A	7	B
Distillate oil fired (1-02-005-02/03) (1-03-005-02/03)	142S	A	2S	A	20	A	5	A	2	A
Residential furnace (A2104004/A2104011)	142S	A	2S	A	18	A	5	A	0.4[g]	B

[a] To convert from $lb/10^3$ gal to $kg/10^3$ L, multiply by 0.120. SCC = Source Classification Code.

[b] References 1-2,6-9,14,56-60. S indicates that the weight % of sulfur in the oil should be multiplied by the value given. For example, if the fuel is 1% sulfur, then S = 1.

[c] References 1-2,6-8,16,57-60. S indicates that the weight % of sulfur in the oil should be multiplied by the value given. For example, if the fuel is 1% sulfur, then S = 1.

[d] References 6-7,15,19,22,56-62. Expressed as NO_2. Test results indicate that at least 95% by weight of NO_x is NO for all boiler types except residential furnaces, where about 75% is NO. For utility vertical fired boilers use 105 $lb/10^3$ gal at full load and normal (>15%) excess air. Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are related to fuel nitrogen content, estimated by the following empirical relationship: lb $NO_2/10^3$ gal = 20.54 + 104.39(N), where N is the weight % of nitrogen in the oil. For example, if the fuel is 1% nitrogen, then N = 1.

[e] References 6-8,14,17-19,56-61. CO emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.

[f] References 6-8,10,13-15,56-60,62-63. Filterable PM is that particulate collected on or prior to the filter of an EPA Method 5 (or equivalent) sampling train. Particulate emission factors for residual oil combustion are, on average, a function of fuel oil sulfur content where S is the weight % of sulfur in oil. For example, if fuel oil is 1% sulfur, then S = 1.

[g] Based on data from new burner designs. Pre-1970's burner designs may emit filterable PM as high as 3.0 $1b/10^3$ gal.

Table 1.3-2. CONDENSABLE PARTICULATE MATTER EMISSION FACTORS FOR OIL COMBUSTION[a]

Firing Configuration[b] (SCC)	Controls	CPM - TOT[c, d]		CPM - IOR[c, d]		CPM - ORG[c, d]	
		Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING	Emission Factor (lb/10^3 gal)	EMISSION FACTOR RATING
No. 2 oil fired (1-01-005-01, 1-02-005-01, 1-03-005-01)	All controls, or uncontrolled	1.3[d, e]	D	65% of CPM-TOT emission factor[c]	D	35% of CPM-TOT emission factor[c]	D
No. 6 oil fired (1-01-004-01/04, 1-02-004-01, 1-03-004-01)	All controls, or uncontrolled	1.5[f]	D	85% of CPM-TOT emission factor[d]	E	15% of CPM-TOT emission factor[d]	E

[a] All condensable PM is assumed to be less than 1.0 micron in diameter.

[b] No data are available for numbers 3, 4, and 5 oil. For number 3 oil, use the factors provided for number 2 oil. For numbers 4 and 5 oil, use the factors provided for number 6 oil.

[c] CPM-TOT = total condensable particulate matter.
CPM-IOR = inorganic condensable particulate matter.
CPM-ORG = organic condensable particulate matter.

[d] To convert to lb/MMBtu of No. 2 oil, divide by 140 MMBtu/10^3 gal. To convert to lb/MMBtu of No. 6 oil, divide by 150 MMBtu/10^3 gal.

[e] References: 76-78.

[f] References: 79-82.

Table 1.3-3. EMISSION FACTORS FOR TOTAL ORGANIC COMPOUNDS (TOC), METHANE, AND NONMETHANE TOC (NMTOC) FROM UNCONTROLLED FUEL OIL COMBUSTION[a]

EMISSION FACTOR RATING: A

Firing Configuration (SCC)	TOC[b] Emission Factor (lb/10^3 gal)	Methane[b] Emission Factor (lb/10^3 gal)	NMTOC[b] Emission Factor (lb/10^3 gal)
Utility boilers			
No. 6 oil fired, normal firing (1-01-004-01)	1.04	0.28	0.76
No. 6 oil fired, tangential firing (1-01-004-04)	1.04	0.28	0.76
No. 5 oil fired, normal firing (1-01-004-05)	1.04	0.28	0.76
No. 5 oil fired, tangential firing (1-01-004-06)	1.04	0.28	0.76
No. 4 oil fired, normal firing (1-01-005-04)	1.04	0.28	0.76
No. 4 oil fired, tangential firing (1-01-005-05)	1.04	0.28	0.76
Industrial boilers			
No. 6 oil fired (1-02-004-01/02/03)	1.28	1.00	0.28
No. 5 oil fired (1-02-004-04)	1.28	1.00	0.28
Distillate oil fired (1-02-005-01/02/03)	0.252	0.052	0.2
No. 4 oil fired (1-02-005-04)	0.252	0.052	0.2
Commercial/institutional/residential combustors			
No. 6 oil fired (1-03-004-01/02/03)	1.605	0.475	1.13
No. 5 oil fired (1-03-004-04)	1.605	0.475	1.13
Distillate oil fired (1-03-005-01/02/03)	0.556	0.216	0.34
No. 4 oil fired (1-03-005-04)	0.556	0.216	0.34
Residential furnace (A2104004/A2104011)	2.493	1.78	0.713

[a] To convert from lb/10^3 gal to kg/10^3 L, multiply by 0.12. SCC = Source Classification Code.

[b] References 29-32. Volatile organic compound emissions can increase by several orders of magnitude if the boiler is improperly operated or is not well maintained.

Table 1.3-4. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR UTILITY BOILERS FIRING RESIDUAL OIL[a]

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size			Cumulative Emission Factor lb/10^3 gal)					
		Controlled		Uncontrolled[c]		ESP Controlled[d]		Scrubber Controlled[e]	
	Uncon-trolled	ESP	Scrubber	Emission Factor	EMISSION FACTOR RATING	Emission Factor	EMISSION FACTOR RATING	Emission Factor	EMISSION FACTOR RATING
15	80	75	100	6.7A	C	0.05A	E	0.50A	D
10	71	63	100	5.9A	C	0.042A	E	0.50A	D
6	58	52	100	4.8A	C	0.035A	E	0.50A	D
2.5	52	41	97	4.3A	C	0.028A	E	0.48A	D
1.25	43	31	91	3.6A	C	0.021A	E	0.46A	D
1.00	39	28	84	3.3A	C	0.018A	E	0.42A	D
0.625	20	20	64	1.7A	C	0.007A	E	0.32A	D
TOTAL	100	100	100	8.3A	C	0.067A	E	0.50A	D

[a] Reference 26. Source Classification Codes 1-01-004-01/04/05/06 and 1-01-005-04/05. To convert from lb/10^3 gal to kg/m^3, multiply by 0.120. ESP = electrostatic precipitator.

[b] Expressed as aerodynamic equivalent diameter.

[c] Particulate emission factors for residual oil combustion without emission controls are, on average, a function of fuel oil grade and sulfur content where S is the weight % of sulfur in the oil. For example, if the fuel is 1.00% sulfur, then S = 1.
No. 6 oil: $A = 1.12(S) + 0.37$
No. 5 oil: $A = 1.2$
No. 4 oil: $A = 0.84$

[d] Estimated control efficiency for ESP is 99.2%.

[e] Estimated control efficiency for scrubber is 94%

Table 1.3-5. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR INDUSTRIAL BOILERS FIRING RESIDUAL OIL[a]

Particle Size[b] (μm)	Cumulative Mass % $\leq$ Stated Size		Cumulative Emission Factor[c] (lb/10^3 gal)			
			Uncontrolled		Multiple Cyclone Controlled[d]	
	Uncontrolled	Multiple Cyclone Controlled	Emission Factor	EMISSION FACTOR RATING	Emission Factor	EMISSION FACTOR RATING
15	91	100	7.59A	D	1.67A	E
10	86	95	7.17A	D	1.58A	E
6	77	72	6.42A	D	1.17A	E
2.5	56	22	4.67A	D	0.33A	E
1.25	39	21	3.25A	D	0.33A	E
1.00	36	21	3.00A	D	0.33A	E
0.625	30	—[e]	2.50A	D	—[e]	NA
TOTAL	100	100	8.34A	D	1.67A	E

[a] Reference 26. Source Classification Codes 1-02-004-01/02/03/04 and 1-02-005-04. To convert lb/10^3 gal to kg/10^3 L, multiply by 0.120. NA = not applicable.

[b] Expressed as aerodynamic equivalent diameter.

[c] Particulate emission factors for residual oil combustion without emission controls are, on average, a function of fuel oil grade and sulfur content where S is the weight % of sulfur in the oil. For example, if the fuel is 1.0% sulfur, then S = 1.

No. 6 oil: $A = 1.12(S) + 0.37$
No. 5 oil: $A = 1.2$
No. 4 oil: $A = 0.84$

[d] Estimated control efficiency for multiple cyclone is 80%.

[e] Insufficient data.

Table 1.3-6. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR UNCONTROLLED INDUSTRIAL BOILERS FIRING DISTILLATE OIL[a]

EMISSION FACTOR RATING: E

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size	Cumulative Emission Factor ($lb/10^3$ gal)
15	68	1.33
10	50	1.00
6	30	0.58
2.5	12	0.25
1.25	9	0.17
1.00	8	0.17
0.625	2	0.04
TOTAL	100	2.00

[a] Reference 26. Source Classification Codes 1-02-005-01/02/03. To convert from $lb/10^3$ gal to $kg/10^3$ L, multiply by 0.12.
[b] Expressed as aerodynamic equivalent diameter.

Table 1.3-7. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS UNCONTROLLED COMMERCIAL BOILERS BURNING RESIDUAL OR DISTILLATE OIL[a]

EMISSION FACTOR RATING: D

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size		Cumulative Emission Factor[c] ($lb/10^3$ gal)	
	Residual Oil	Distillate Oil	Residual Oil	Distillate Oil
15	78	60	6.50A	1.17
10	62	55	5.17A	1.08
6	44	49	3.67A	1.00
2.5	23	42	1.92A	0.83
1.25	16	38	1.33A	0.75
1.00	14	37	1.17A	0.75
0.625	13	35	1.08A	0.67
TOTAL	100	100	8.34A	2.00

[a] Reference 26. Source Classification Codes: 1-03-004-01/02/03/04 and 1-03-005-01/02/03/04. To convert from $lb/10^3$ gal to $kg/10^3$ L, multiply by 0.12.
[b] Expressed as aerodynamic equivalent diameter.
[c] Particulate emission factors for residual oil combustion without emission controls are, on average, a function of fuel oil grade and sulfur content where S is the weight % of sulfur in the fuel. For example, if the fuel is 1.0% sulfur, then S = 1.
No. 6 oil: $A = 1.12(S) + 0.37$
No. 5 oil: $A = 1.2$
No. 4 oil: $A = 0.84$
No. 2 oil: $A = 0.24$

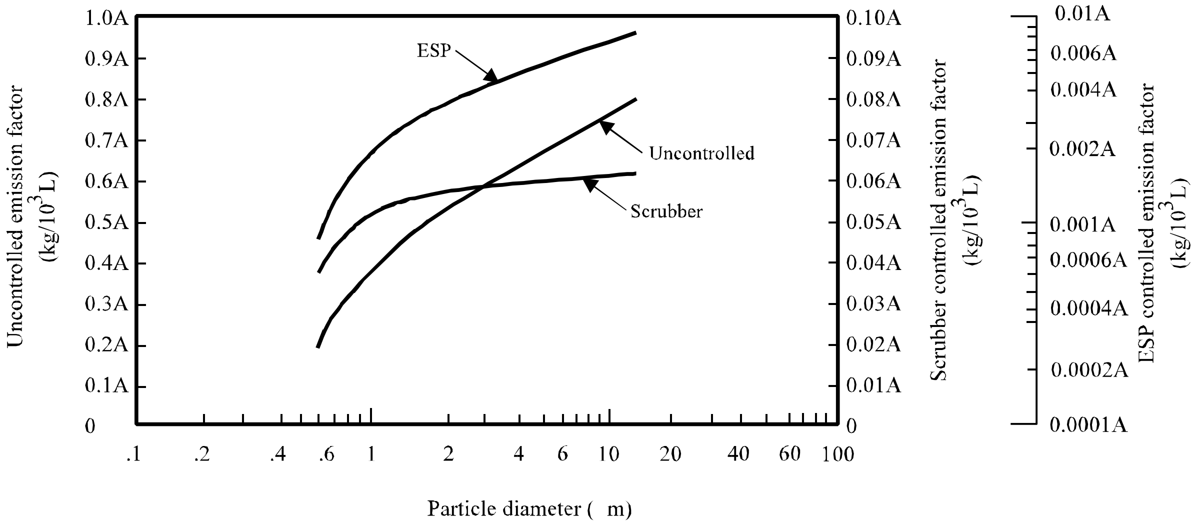

Figure 1.3-1. Cumulative size-specific emission factors for utility boilers firing residual oil.

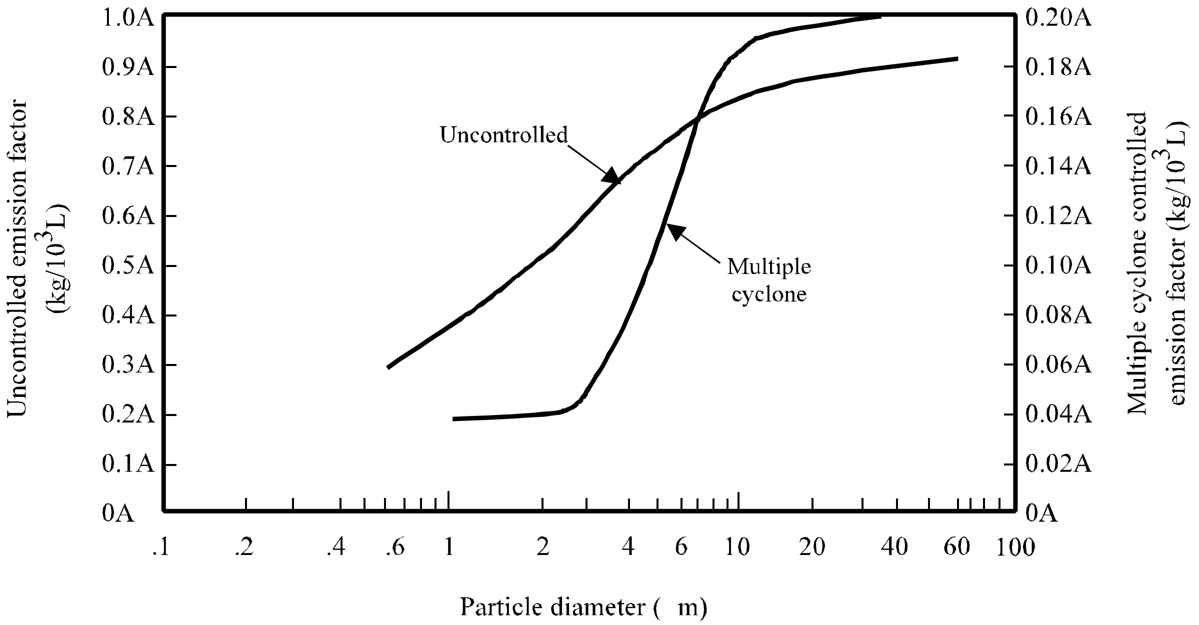

Figure 1.3-2. Cumulative size-specific emission factors for industrial boilers firing residual oil.

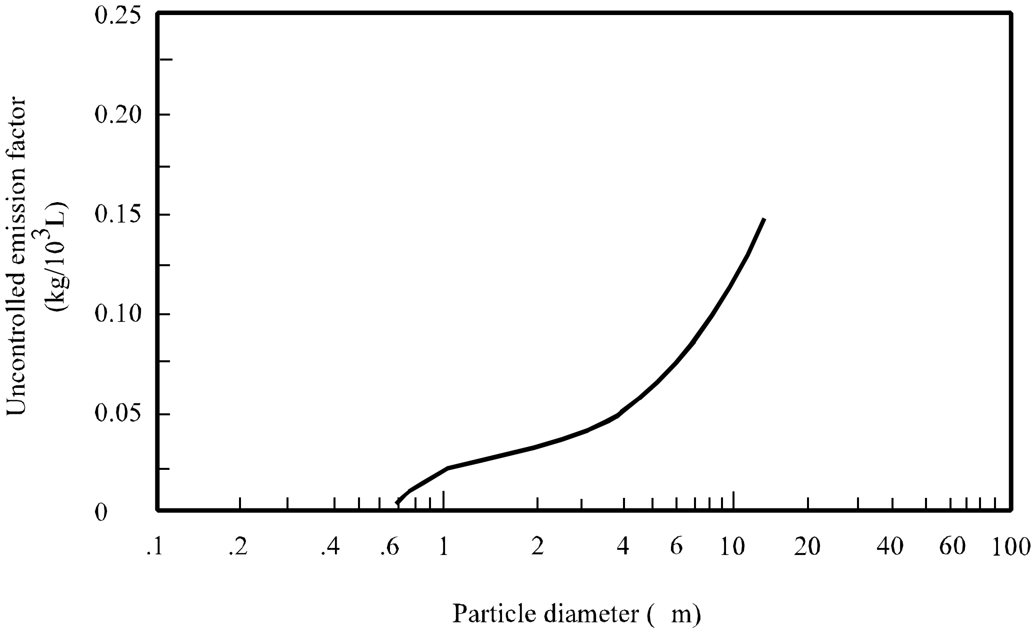

Figure 1.3-3. Cumulative size-specific emission factors for uncontrolled industrial boilers firing distillate oil.

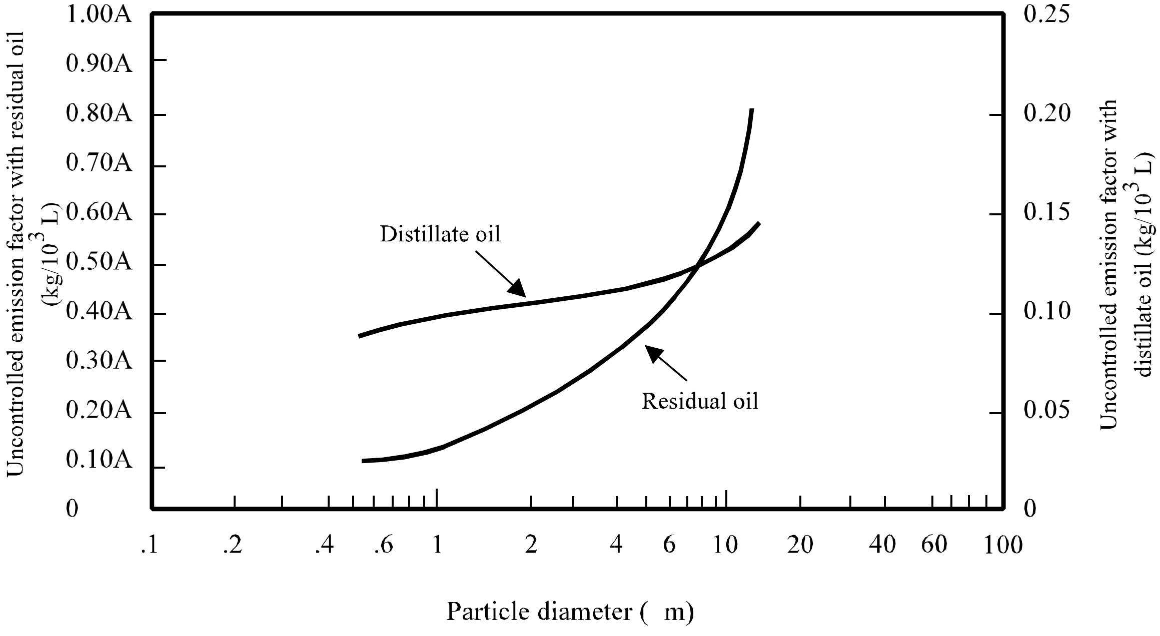

Figure 1.3-4. Cumulative size-specific emission factors for uncontrolled commercial boilers burning residual and distillate oil.

Table 1.3-8. EMISSION FACTORS FOR NITROUS OXIDE (N_2O), POLYCYCLIC ORGANIC MATTER (POM), AND FORMALDEHYDE (HCOH) FROM FUEL OIL COMBUSTION[a]

EMISSION FACTOR RATING: E

Firing Configuration (SCC)	Emission Factor (lb/10^3 gal)		
	N_2O[b]	POM[c]	HCOH[c]
Utility/industrial/commercial boilers			
No. 6 oil fired (1-01-004-01, 1-02-004-01, 1-03-004-01)	0.11	0.0011 - 0.0013[d]	0.024 - 0.061
Distillate oil fired (1-01-005-01, 1-02-005-01, 1-03-005-01)	0.11	0.0033[e]	0.035 - 0.061
Residential furnaces (A2104004/A2104011)	0.05	ND	ND

[a] To convert from lb/10^3 gal to kg/10^3 L, multiply by 0.12. SCC = Source Classification Code. ND = no data.

[b] References 45-46. EMISSION FACTOR RATING = B.

[c] References 29-32.

[d] Particulate and gaseous POM.

[e] Particulate POM only.

Table 1.3-9. EMISSION FACTORS FOR SPECIATED ORGANIC COMPOUNDS FROM FUEL OIL COMBUSTION[a]

Organic Compound	Average Emission Factor[b] (lb/10^3 Gal)	EMISSION FACTOR RATING
Benzene	2.14E-04	C
Ethylbenzene	6.36E-05[c]	E
Formaldehyde[d]	3.30E-02	C
Naphthalene	1.13E-03	C
1,1,1-Trichloroethane	2.36E-04[c]	E
Toluene	6.20E-03	D
o-Xylene	1.09E-04[c]	E
Acenaphthene	2.11E-05	C
Acenaphthylene	2.53E-07	D
Anthracene	1.22E-06	C
Benz(a)anthracene	4.01E-06	C
Benzo(b,k)fluoranthene	1.48E-06	C
Benzo(g,h,i)perylene	2.26E-06	C
Chrysene	2.38E-06	C
Dibenzo(a,h) anthracene	1.67E-06	D
Fluoranthene	4.84E-06	C
Fluorene	4.47E-06	C
Indo(1,2,3-cd)pyrene	2.14E-06	C
Phenanthrene	1.05E-05	C
Pyrene	4.25E-06	C
OCDD	3.10E-09[c]	E

[a] Data are for residual oil fired boilers, Source Classification Codes (SCCs) 1-01-004-01/04.

[b] References 64-72. To convert from lb/10^3 gal to kg/10^3 L, multiply by 0.12.

[c] Based on data from one source test (Reference 67).

[d] The formaldehyde number presented here is based only on data from utilities using No. 6 oil. The number presented in Table 1.3-7 is based on utility, commercial, and industrial boilers.

Table 1.3-10. EMISSION FACTORS FOR TRACE ELEMENTS FROM DISTILLATE FUEL OIL COMBUSTION SOURCES[a]

EMISSION FACTOR RATING: E

Firing Configuration (SCC)	Emission Factor (lb/10^{12} Btu)										
	As	Be	Cd	Cr	Cu	Pb	Hg	Mn	Ni	Se	Zn
Distillate oil fired (1-01-005-01, 1-02-005-01, 1-03-005-01)	4	3	3	3	6	9	3	6	3	15	4

[a] Data are for distillate oil fired boilers, SCC codes 1-01-005-01, 1-02-005-01, and 1-03-005-01. References 29-32, 40-44 and 83. To convert from lb/10^{12} Btu to pg/J, multiply by 0.43.

Table 1.3-11. EMISSION FACTORS FOR METALS FROM UNCONTROLLED NO. 6 FUEL OIL COMBUSTION[a]

Metal	Average Emission Factor[b, d] ($lb/10^3$ Gal)	EMISSION FACTOR RATING
Antimony	5.25E-03[c]	E
Arsenic	1.32E-03	C
Barium	2.57E-03	D
Beryllium	2.78E-05	C
Cadmium	3.98E-04	C
Chloride	3.47E-01	D
Chromium	8.45E-04	C
Chromium VI	2.48E-04	C
Cobalt	6.02E-03	D
Copper	1.76E-03	C
Fluoride	3.73E-02	D
Lead	1.51E-03	C
Manganese	3.00E-03	C
Mercury	1.13E-04	C
Molybdenum	7.87E-04	D
Nickel	8.45E-02	C
Phosphorous	9.46E-03	D
Selenium	6.83E-04	C
Vanadium	3.18E-02	D
Zinc	2.91E-02	D

[a] Data are for residual oil fired boilers, Source Classification Codes (SCCs) 1-01-004-01/04.

[b] References 64-72. 18 of 19 sources were uncontrolled and 1 source was controlled with low efficiency ESP. To convert from $lb/10^3$ gal to $kg/10^3$ L, multiply by 0.12.

[c] References 29-32,40-44.

[d] For oil/water mixture, reduce factors in proportion to water content of the fuel (due to dilution). To adjust the listed values for water content, multiply the listed value by 1-decimal fraction of water (ex: For fuel with 9 percent water by volume, multiply by 1-0.9=.91).

Table 1.3-12. DEFAULT CO_2 EMISSION FACTORS FOR LIQUID FUELS[a]

EMISSION FACTOR RATING: B

Fuel Type	%C[b]	Density[c] (lb/gal)	Emission Factor (lb/10^3 gal)
No. 1 (kerosene)	86.25	6.88	21,500
No. 2	87.25	7.05	22,300
Low Sulfur No. 6	87.26	7.88	25,000
High Sulfur No. 6	85.14	7.88	24,400

[a] Based on 99% conversion of fuel carbon content to CO_2. To convert from lb/gal to gram/cm^3, multiply by 0.12. To convert from lb/10^3 gal to kg/m^3, multiply by 0.12.

[b] Based on an average of fuel carbon contents given in references 73-74.

[c] References 73, 75.

Table 1.3-13. POSTCOMBUSTION SO_2 CONTROLS FOR FUEL OIL COMBUSTION SOURCES

Control Technology	Process	Typical Control Efficiencies	Remarks
Wet scrubber	Lime/limestone	80-95+%	Applicable to high-sulfur fuels, Wet sludge product
	Sodium carbonate	80-98%	5-430 MMBtu/hr typical application range, High reagent costs
	Magnesium oxide/hydroxide	80-95+%	Can be regenerated
	Dual alkali	90-96%	Uses lime to regenerate sodium-based scrubbing liquor
Spray drying	Calcium hydroxide slurry, vaporizes in spray vessel	70-90%	Applicable to low-and medium-sulfur fuels, Produces dry product
Furnace injection	Dry calcium carbonate/hydrate injection in upper furnace cavity	25-50%	Commercialized in Europe, Several U.S. demonstration projects underway
Duct injection	Dry sorbent injection into duct, sometimes combined with water spray	25-50+%	Several R&D and demonstration projects underway, Not yet Commercially available in the U.S.

Table 1.3-14. NO_x CONTROL OPTIONS FOR OIL-FIRED BOILERS[a]

Control Technique	Description Of Technique	NO_x Reduction Potential (%)		Range Of Application	Commercial Availability/ R&D Status	Comments
		Residual Oil	Distillate Oil			
Low Excess Air (LEA)	Reduction of combustion air	0 to 28	0 to 24	Generally excess O_2 can be reduced to 2.5% representing a 3% drop from baseline	Available for boilers with sufficient operational flexibility.	Added benefits included increase in boiler efficiency. Limited by increase in CO, HC, and smoke emissions.
Staged Combustion (SC)	Fuel-rich firing burners with secondary combustion air ports	20 to 50	17 to 44	70-90% burner stoichiometries can be used with proper installation of secondary air ports	Technique is applicable on packaged and field-erected units. However, not commercially available for all design types.	Best implemented on new units. Retrofit is probably not feasible for most units, especially packaged ones.
Burners Out of Service (BOOS)	One or more burners on air only. Remainder of burners firing fuel-rich	10 to 30	ND	Most effective on boilers with 4 or more burners in a square pattern.	Available.	Requires careful selection of BOOS pattern and control of air flow. May result in boiler de-rating unless fuel delivery system is modified.
Flue Gas Recirculation (FGR)	Recirculation of portion of flue gas to burners	15 to 30	58 to 73	Up to 25-30% of flue gas recycled. Can be implemented on most design types.	Available. Best suited for new units.	Requires extensive modifications to the burner and windbox. Possible flame instability at high FGR rates.
Flue Gas Recirculation Plus Staged Combustion	Combined techniques of FGR and staged combustion	25 to 53	73 to 77	Maximum FGR rates set at 25% for distillate oil and 20% for residual oil.	Available for boilers with sufficient operational flexibility.	May not be feasible on all existing boiler types. Best implemented on new units.

Table 1.3-14 (cont.).

Control Technique	Description Of Technique	NO_x Reduction Potential (%)		Range Of Application	Commercial Availability/ R&D Status	Comments
		Residual Oil	Distillate Oil			
Load Reduction (LR)	Reduction of air and fuel flow to all burners in service	33% decrease to 25% increase in No$_x$	31% decrease to 17% increase in NO_x	Applicable to all boiler types and sizes. Load can be reduced to 25% of maximum.	Available in retrofit applications.	Technique not effective when it necessitates an increase in excess O_2 levels. LR possibly implemented in new designs as reduced combustion intensity (i. e., enlarged furnace plan area).
Low NO_x Burners (LNB)	New burner designs with controlled air/fuel mixing and increased heat dissipation	20 to 50	20 to 50	New burners described generally applicable to all boilers.	Commercially available.	Specific emissions data from industrial boilers equipped with LNB are lacking.
Reduced Air Preheat (RAP)	Bypass of combustion air preheater	5 to 16	ND	Combustion air temperature can be reduced to ambient conditions.	Available.	Application of this technique on new boilers requires installation of alternate heat recovery system (e. g., an economizer).
Selective Noncatalytic Reduction (SNCR)	Injection of NH_3 or urea as a reducing agent in the flue gas	40 to 70	40 to 70	Applicable for large packaged and field-erected watertube boilers. May not be feasible for fire-tube boilers.	Commercially offered but not widely demonstrated on large boilers.	Elaborate reagent injection, monitoring, and control system required. Possible load restrictions on boilers and air preheater fouling when burning high sulfur oil. Must have sufficient residence time at correct temperature.
Conventional Selective Catalytic Reduction (SCR)	Injections of NH_3 in the presence of a catalyst (usually upstream of air heater).	Up to 90% (estimated)	Up to 90% (estimated)	Typically large boiler designs	Commercially offered but not widely demonstrated.	Applicable to most boiler designs as a retrofit technology or for new boilers.

Table 1.3-14 (cont.).

Control Technique	Description Of Technique	NO_x Reduction Potential (%)		Range Of Application	Commercial Availability/ R&D Status	Comments
		Residual Oil	Distillate Oil			
Air Heater (SCR)	Catalyst-coated baskets in the air heater.	40-65 (estimated)	40-65 (estimated)	Boilers with rotating-basket air heaters	Available but not widely demonstrated	Design must address pressure drop and maintain heat transfer.
Duct SCR	A smaller version of conventional SCR is placed in existing ductwork	30 (estimated)	30 (estimated)	Typically large boiler designs	Available but not widely demonstrated.	Location of SCR in duct is temperature dependent.
Activated Carbon SCR	Activated carbon catalyst, installed downstream of air heater.	ND	ND	Typically large boiler designs	Available but not widely demonstrated.	High pressure drop.
Oil/Water Emulsified Fuel[a,b]	Oil/water fuel with emulsifying agent	41	ND	Firetube boilers	Available but not widely demonstrated	Thermal efficiency reduced due to water content

[a] ND = no data.

[b] Test conducted by EPA using commercially premixed fuel and water (9 percent water) containing a petroleum based emulsifying agent. Test boiler was a 2400 lb/hr, 15 psig Scotch Marine firetube type, fired at 2 x 10^6 Btu/hr.

Table 1.3-15. EMISSION FACTORS FOR NO. 6 OIL/WATER EMULSION IN INDUSTRIAL/COMMERCIAL/INSTITUTIONAL BOILERS[a]

Pollutant	Emission Factor ($lb/10^3$ gal)	Factor Rating	Comments
CO	1.90	C	33% Reduction from plain oil
NO_x	38.0	C	41% Reduction
PM	14.9	C	45% Reduction

[a] Test conducted by EPA using commercially premixed fuel and water (9 percent water) containing a petroleum based emulsifying agent. Test boiler was a 2400 lb/hr, 15 psig Scotch Marine firetube type, fired at 2 x 10^6 Btu/hr.

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1.4 Natural Gas Combustion

1.4.1 General[1-2]

Natural gas is one of the major combustion fuels used throughout the country. It is mainly used to generate industrial and utility electric power, produce industrial process steam and heat, and heat residential and commercial space. Natural gas consists of a high percentage of methane (generally above 85 percent) and varying amounts of ethane, propane, butane, and inerts (typically nitrogen, carbon dioxide, and helium). The average gross heating value of natural gas is approximately 1,020 British thermal units per standard cubic foot (Btu/scf), usually varying from 950 to 1,050 Btu/scf.

1.4.2 Firing Practices[3-5]

There are three major types of boilers used for natural gas combustion in commercial, industrial, and utility applications: watertube, firetube, and cast iron. Watertube boilers are designed to pass water through the inside of heat transfer tubes while the outside of the tubes is heated by direct contact with the hot combustion gases and through radiant heat transfer. The watertube design is the most common in utility and large industrial boilers. Watertube boilers are used for a variety of applications, ranging from providing large amounts of process steam, to providing hot water or steam for space heating, to generating high-temperature, high-pressure steam for producing electricity. Furthermore, watertube boilers can be distinguished either as field erected units or packaged units.

Field erected boilers are boilers that are constructed on site and comprise the larger sized watertube boilers. Generally, boilers with heat input levels greater than 100 MMBtu/hr, are field erected. Field erected units usually have multiple burners and, given the customized nature of their construction, also have greater operational flexibility and NO_x control options. Field erected units can also be further categorized as wall-fired or tangential-fired. Wall-fired units are characterized by multiple individual burners located on a single wall or on opposing walls of the furnace while tangential units have several rows of air and fuel nozzles located in each of the four corners of the boiler.

Package units are constructed off-site and shipped to the location where they are needed. While the heat input levels of packaged units may range up to 250 MMBtu/hr, the physical size of these units are constrained by shipping considerations and generally have heat input levels less than 100 MMBtu/hr. Packaged units are always wall-fired units with one or more individual burners. Given the size limitations imposed on packaged boilers, they have limited operational flexibility and cannot feasibly incorporate some NO_x control options.

Firetube boilers are designed such that the hot combustion gases flow through tubes, which heat the water circulating outside of the tubes. These boilers are used primarily for space heating systems, industrial process steam, and portable power boilers. Firetube boilers are almost exclusively packaged units. The two major types of firetube units are Scotch Marine boilers and the older firebox boilers. In cast iron boilers, as in firetube boilers, the hot gases are contained inside the tubes and the water being heated circulates outside the tubes. However, the units are constructed of cast iron rather than steel. Virtually all cast iron boilers are constructed as package boilers. These boilers are used to produce either low-pressure steam or hot water, and are most commonly used in small commercial applications.

Natural gas is also combusted in residential boilers and furnaces. Residential boilers and furnaces generally resemble firetube boilers with flue gas traveling through several channels or tubes with water or air circulated outside the channels or tubes.

1.4.3 Emissions[3-4]

The emissions from natural gas-fired boilers and furnaces include nitrogen oxides (NO_x), carbon monoxide (CO), and carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), volatile organic compounds (VOCs), trace amounts of sulfur dioxide (SO_2), and particulate matter (PM).

Nitrogen Oxides -

Nitrogen oxides formation occurs by three fundamentally different mechanisms. The principal mechanism of NO_x formation in natural gas combustion is thermal NO_x. The thermal NO_x mechanism occurs through the thermal dissociation and subsequent reaction of nitrogen (N_2) and oxygen (O_2) molecules in the combustion air. Most NO_x formed through the thermal NO_x mechanism occurs in the high temperature flame zone near the burners. The formation of thermal NO_x is affected by three furnace-zone factors: (1) oxygen concentration, (2) peak temperature, and (3) time of exposure at peak temperature. As these three factors increase, NO_x emission levels increase. The emission trends due to changes in these factors are fairly consistent for all types of natural gas-fired boilers and furnaces. Emission levels vary considerably with the type and size of combustor and with operating conditions (e.g., combustion air temperature, volumetric heat release rate, load, and excess oxygen level).

The second mechanism of NO_x formation, called prompt NO_x, occurs through early reactions of nitrogen molecules in the combustion air and hydrocarbon radicals from the fuel. Prompt NO_x reactions occur within the flame and are usually negligible when compared to the amount of NO_x formed through the thermal NO_x mechanism. However, prompt NO_x levels may become significant with ultra-low-NO_x burners.

The third mechanism of NO_x formation, called fuel NO_x, stems from the evolution and reaction of fuel-bound nitrogen compounds with oxygen. Due to the characteristically low fuel nitrogen content of natural gas, NO_x formation through the fuel NO_x mechanism is insignificant.

Carbon Monoxide -

The rate of CO emissions from boilers depends on the efficiency of natural gas combustion. Improperly tuned boilers and boilers operating at off-design levels decrease combustion efficiency resulting in increased CO emissions. In some cases, the addition of NO_x control systems such as low NO_x burners and flue gas recirculation (FGR) may also reduce combustion efficiency, resulting in higher CO emissions relative to uncontrolled boilers.

Volatile Organic Compounds -

The rate of VOC emissions from boilers and furnaces also depends on combustion efficiency. VOC emissions are minimized by combustion practices that promote high combustion temperatures, long residence times at those temperatures, and turbulent mixing of fuel and combustion air. Trace amounts of VOC species in the natural gas fuel (e.g., formaldehyde and benzene) may also contribute to VOC emissions if they are not completely combusted in the boiler.

Sulfur Oxides -

Emissions of SO_2 from natural gas-fired boilers are low because pipeline quality natural gas typically has sulfur levels of 2,000 grains per million cubic feet. However, sulfur-containing odorants are added to natural gas for detecting leaks, leading to small amounts of SO_2 emissions. Boilers combusting unprocessed natural gas may have higher SO_2 emissions due to higher levels of sulfur in the natural gas. For these units, a sulfur mass balance should be used to determine SO_2 emissions.

Particulate Matter -

Because natural gas is a gaseous fuel, filterable PM emissions are typically low. Particulate matter from natural gas combustion has been estimated to be less than 1 micrometer in size and has filterable and condensable fractions. Particulate matter in natural gas combustion are usually larger molecular weight hydrocarbons that are not fully combusted. Increased PM emissions may result from poor air/fuel mixing or maintenance problems.

Greenhouse Gases -[6-9]

CO_2, CH_4, and N_2O emissions are all produced during natural gas combustion. In properly tuned boilers, nearly all of the fuel carbon (99.9 percent) in natural gas is converted to CO_2 during the combustion process. This conversion is relatively independent of boiler or combustor type. Fuel carbon not converted to CO_2 results in CH_4, CO, and/or VOC emissions and is due to incomplete combustion. Even in boilers operating with poor combustion efficiency, the amount of CH_4, CO, and VOC produced is insignificant compared to CO_2 levels.

Formation of N_2O during the combustion process is affected by two furnace-zone factors. N_2O emissions are minimized when combustion temperatures are kept high (above 1475°F) and excess oxygen is kept to a minimum (less than 1 percent).

Methane emissions are highest during low-temperature combustion or incomplete combustion, such as the start-up or shut-down cycle for boilers. Typically, conditions that favor formation of N_2O also favor emissions of methane.

1.4.4 Controls[4,10]

NO_x Controls -

Currently, the two most prevalent combustion control techniques used to reduce NO_x emissions from natural gas-fired boilers are flue gas recirculation (FGR) and low NO_x burners. In an FGR system, a portion of the flue gas is recycled from the stack to the burner windbox. Upon entering the windbox, the recirculated gas is mixed with combustion air prior to being fed to the burner. The recycled flue gas consists of combustion products which act as inerts during combustion of the fuel/air mixture. The FGR system reduces NO_x emissions by two mechanisms. Primarily, the recirculated gas acts as a dilutent to reduce combustion temperatures, thus suppressing the thermal NO_x mechanism. To a lesser extent, FGR also reduces NO_x formation by lowering the oxygen concentration in the primary flame zone. The amount of recirculated flue gas is a key operating parameter influencing NO_x emission rates for these systems. An FGR system is normally used in combination with specially designed low NO_x burners capable of sustaining a stable flame with the increased inert gas flow resulting from the use of FGR. When low NO_x burners and FGR are used in combination, these techniques are capable of reducing NO_x emissions by 60 to 90 percent.

Low NO_x burners reduce NO_x by accomplishing the combustion process in stages. Staging partially delays the combustion process, resulting in a cooler flame which suppresses thermal NO_x formation. The two most common types of low NO_x burners being applied to natural gas-fired boilers are staged air burners and staged fuel burners. NO_x emission reductions of 40 to 85 percent (relative to uncontrolled emission levels) have been observed with low NO_x burners.

Other combustion control techniques used to reduce NO_x emissions include staged combustion and gas reburning. In staged combustion (e.g., burners-out-of-service and overfire air), the degree of staging is a key operating parameter influencing NO_x emission rates. Gas reburning is similar to the use of overfire in the use of combustion staging. However, gas reburning injects additional amounts of natural gas in the upper furnace, just before the overfire air ports, to provide increased reduction of NO_x to NO_2.

Two postcombustion technologies that may be applied to natural gas-fired boilers to reduce NO_x emissions are selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). The SNCR system injects ammonia (NH_3) or urea into combustion flue gases (in a specific temperature zone) to reduce NO_x emission. The Alternative Control Techniques (ACT) document for NO_x emissions from utility boilers, maximum SNCR performance was estimated to range from 25 to 40 percent for natural gas-fired boilers.[12] Performance data available from several natural gas fired utility boilers with SNCR show a 24 percent reduction in NO_x for applications on wall-fired boilers and a 13 percent reduction in NO_x for applications on tangential-fired boilers.[11] In many situations, a boiler may have an SNCR system installed to trim NO_x emissions to meet permitted levels. In these cases, the SNCR system may not be operated to achieve maximum NO_x reduction. The SCR system involves injecting NH_3 into the flue gas in the presence of a catalyst to reduce NO_x emissions. No data were available on SCR performance on natural gas fired boilers at the time of this publication. However, the ACT Document for utility boilers estimates NO_x reduction efficiencies for SCR control ranging from 80 to 90 percent.[12]

Emission factors for natural gas combustion in boilers and furnaces are presented in Tables 1.4-1, 1.4-2, 1.4-3, and 1.4-4.[11] Tables in this section present emission factors on a volume basis (lb/10^6 scf). To convert to an energy basis (lb/MMBtu), divide by a heating value of 1,020 MMBtu/10^6 scf. For the purposes of developing emission factors, natural gas combustors have been organized into three general categories: large wall-fired boilers with greater than 100 MMBtu/hr of heat input, boilers and residential furnaces with less than 100 MMBtu/hr of heat input, and tangential-fired boilers. Boilers within these categories share the same general design and operating characteristics and hence have similar emission characteristics when combusting natural gas.

Emission factors are rated from A to E to provide the user with an indication of how “good” the factor is, with “A” being excellent and “E” being poor. The criteria that are used to determine a rating for an emission factor can be found in the Emission Factor Documentation for AP-42 Section 1.4 and in the introduction to the AP-42 document.

1.4.5 Updates Since the Fifth Edition

The Fifth Edition was released in January 1995. Revisions to this section are summarized below. For further detail, consult the Emission Factor Documentation for this section. These and other documents can be found on the Emission Factor and Inventory Group (EFIG) home page (http://www.epa.gov/ttn/chief).

Supplement D, March 1998

- Text was revised concerning Firing Practices, Emissions, and Controls.

- All emission factors were updated based on 482 data points taken from 151 source tests. Many new emission factors have been added for speciated organic compounds, including hazardous air pollutants.

July 1998 - minor changes

- Footnote D was added to table 1.4-3 to explain why the sum of individual HAP may exceed VOC or TOC, the web address was updated, and the references were reordered.

Table 1.4-1. EMISSION FACTORS FOR NITROGEN OXIDES (NO_x) AND CARBON MONOXIDE (CO) FROM NATURAL GAS COMBUSTION[a]

Combustor Type (MMBtu/hr Heat Input) [SCC]	NO_x[b]		CO	
	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
Large Wall-Fired Boilers (>100) [1-01-006-01, 1-02-006-01, 1-03-006-01]				
Uncontrolled (Pre-NSPS)[c]	280	A	84	B
Uncontrolled (Post-NSPS)[c]	190	A	84	B
Controlled - Low NO_x burners	140	A	84	B
Controlled - Flue gas recirculation	100	D	84	B
Small Boilers (<100) [1-01-006-02, 1-02-006-02, 1-03-006-02, 1-03-006-03]				
Uncontrolled	100	B	84	B
Controlled - Low NO_x burners	50	D	84	B
Controlled - Low NO_x burners/Flue gas recirculation	32	C	84	B
Tangential-Fired Boilers (All Sizes) [1-01-006-04]				
Uncontrolled	170	A	24	C
Controlled - Flue gas recirculation	76	D	98	D
Residential Furnaces (<0.3) [No SCC]				
Uncontrolled	94	B	40	B

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. To convert from lb/10^6 scf to kg/10^6 m^3, multiply by 16. Emission factors are based on an average natural gas higher heating value of 1,020 Btu/scf. To convert from 1b/10^6 scf to lb/MMBtu, divide by 1,020. The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. SCC = Source Classification Code. ND = no data. NA = not applicable.

[b] Expressed as NO_2. For large and small wall fired boilers with SNCR control, apply a 24 percent reduction to the appropriate NO_X emission factor. For tangential-fired boilers with SNCR control, apply a 13 percent reduction to the appropriate NO_X emission factor.

[c] NSPS=New Source Performance Standard as defined in 40 CFR 60 Subparts D and Db. Post-NSPS units are boilers with greater than 250 MMBtu/hr of heat input that commenced construction modification, or reconstruction after August 17, 1971, and units with heat input capacities between 100 and 250 MMBtu/hr that commenced construction modification, or reconstruction after June 19, 1984.

TABLE 1.4-2. EMISSION FACTORS FOR CRITERIA POLLUTANTS AND GREENHOUSE GASES FROM NATURAL GAS COMBUSTION[a]

Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
CO_2[b]	120,000	A
Lead	0.0005	D
N_2O (Uncontrolled)	2.2	E
N_2O (Controlled-low-NO_X burner)	0.64	E
PM (Total)[c]	7.6	D
PM (Condensable)[c]	5.7	D
PM (Filterable)[c]	1.9	B
SO_2[d]	0.6	A
TOC	11	B
Methane	2.3	B
VOC	5.5	C

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by 16. To convert from $lb/10^6$ scf to 1b/MMBtu, divide by 1,020. The emission factors in this table may be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. TOC = Total Organic Compounds.
VOC = Volatile Organic Compounds.

[b] Based on approximately 100% conversion of fuel carbon to CO_2. $CO_2[lb/10^6$ scf] = (3.67) (CON) (C)(D), where CON = fractional conversion of fuel carbon to CO_2, C = carbon content of fuel by weight (0.76), and D = density of fuel, 4.2×10^4 $lb/10^6$ scf.

[c] All PM (total, condensible, and filterable) is assumed to be less than 1.0 micrometer in diameter. Therefore, the PM emission factors presented here may be used to estimate PM_{10}, $PM_{2.5}$ or PM_1 emissions. Total PM is the sum of the filterable PM and condensible PM. Condensible PM is the particulate matter collected using EPA Method 202 (or equivalent). Filterable PM is the particulate matter collected on, or prior to, the filter of an EPA Method 5 (or equivalent) sampling train.

[d] Based on 100% conversion of fuel sulfur to SO_2.
Assumes sulfur content is natural gas of 2,000 grains/10^6 scf. The SO_2 emission factor in this table can be converted to other natural gas sulfur contents by multiplying the SO_2 emission factor by the ratio of the site-specific sulfur content (grains/10^6 scf) to 2,000 grains/10^6 scf.

TABLE 1.4-3. EMISSION FACTORS FOR SPECIATED ORGANIC COMPOUNDS FROM NATURAL GAS COMBUSTION[a]

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
91-57-6	2-Methylnaphthalene[b, c]	2.4E-05	D
56-49-5	3-Methylchloranthrene[b, c]	<1.8E-06	E
	7,12-Dimethylbenz(a)anthracene[b,c]	<1.6E-05	E
83-32-9	Acenaphthene[b,c]	<1.8E-06	E
203-96-8	Acenaphthylene[b,c]	<1.8E-06	E
120-12-7	Anthracene[b,c]	<2.4E-06	E
56-55-3	Benz(a)anthracene[b,c]	<1.8E-06	E
71-43-2	Benzene[b]	2.1E-03	B
50-32-8	Benzo(a)pyrene[b,c]	<1.2E-06	E
205-99-2	Benzo(b)fluoranthene[b,c]	<1.8E-06	E
191-24-2	Benzo(g,h,i)perylene[b,c]	<1.2E-06	E
205-82-3	Benzo(k)fluoranthene[b,c]	<1.8E-06	E
106-97-8	Butane	2.1E+00	E
218-01-9	Chrysene[b,c]	<1.8E-06	E
53-70-3	Dibenzo(a,h)anthracene[b,c]	<1.2E-06	E
25321-22-6	Dichlorobenzene[b]	1.2E-03	E
74-84-0	Ethane	3.1E+00	E
206-44-0	Fluoranthene[b,c]	3.0E-06	E
86-73-7	Fluorene[b,c]	2.8E-06	E
50-00-0	Formaldehyde[b]	7.5E-02	B
110-54-3	Hexane[b]	1.8E+00	E
193-39-5	Indeno(1,2,3-cd)pyrene[b,c]	<1.8E-06	E
91-20-3	Naphthalene[b]	6.1E-04	E
109-66-0	Pentane	2.6E+00	E
85-01-8	Phenanathrene[b,c]	1.7E-05	D

TABLE 1.4-3. EMISSION FACTORS FOR SPECIATED ORGANIC COMPOUNDS FROM NATURAL GAS COMBUSTION (Continued)

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
74-98-6	Propane	1.6E+00	E
129-00-0	Pyrene[b, c]	5.0E-06	E
108-88-3	Toluene[b]	3.4E-03	C

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by 16. To convert from $1b/10^6$ scf to lb/MMBtu, divide by 1,020. Emission Factors preceeded with a less-than symbol are based on method detection limits.

[b] Hazardous Air Pollutant (HAP) as defined by Section 112(b) of the Clean Air Act.

[c] HAP because it is Polycyclic Organic Matter (POM). POM is a HAP as defined by Section 112(b) of the Clean Air Act.

[d] The sum of individual organic compounds may exceed the VOC and TOC emission factors due to differences in test methods and the availability of test data for each pollutant.

TABLE 1.4-4. EMISSION FACTORS FOR METALS FROM NATURAL GAS COMBUSTION[a]

CAS No.	Pollutant	Emission Factor ($lb/10^6$ scf)	Emission Factor Rating
7440-38-2	Arsenic[b]	2.0E-04	E
7440-39-3	Barium	4.4E-03	D
7440-41-7	Beryllium[b]	<1.2E-05	E
7440-43-9	Cadmium[b]	1.1E-03	D
7440-47-3	Chromium[b]	1.4E-03	D
7440-48-4	Cobalt[b]	8.4E-05	D
7440-50-8	Copper	8.5E-04	C
7439-96-5	Manganese[b]	3.8E-04	D
7439-97-6	Mercury[b]	2.6E-04	D
7439-98-7	Molybdenum	1.1E-03	D
7440-02-0	Nickel[b]	2.1E-03	C
7782-49-2	Selenium[b]	<2.4E-05	E
7440-62-2	Vanadium	2.3E-03	D
7440-66-6	Zinc	2.9E-02	E

[a] Reference 11. Units are in pounds of pollutant per million standard cubic feet of natural gas fired. Data are for all natural gas combustion sources. Emission factors preceeded by a less-than symbol are based on method detection limits. To convert from $lb/10^6$ scf to $kg/10^6$ m^3, multiply by l6. To convert from $lb/10^6$ scf to 1b/MMBtu, divide by 1,020.

[b] Hazardous Air Pollutant as defined by Section 112(b) of the Clean Air Act.

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1.5 Liquefied Petroleum Gas Combustion

1.5.1 General[1]

Liquefied petroleum gas (LPG or LP-gas) consists of propane, propylene, butane, and butylenes; the product used for domestic heating is composed primarily of propane. This gas, obtained mostly from gas wells (but also, to a lesser extent, as a refinery by-product) is stored as a liquid under moderate pressures. There are three grades of LPG available as heating fuels: commercial-grade propane, engine fuel-grade propane (also known as HD-5 propane), and commercial-grade butane. In addition, there are high-purity grades of LPG available for laboratory work and for use as aerosol propellants. Specifications for the various LPG grades are available from the American Society for Testing and Materials and the Gas Processors Association. A typical heating value for commercial-grade propane and HD-5 propane is 90,500 British thermal units per gallon (Btu/gal), after vaporization; for commercial-grade butane, the value is 97,400 Btu/gal.

The largest market for LPG is the domestic/commercial market, followed by the chemical industry (where it is used as a petrochemical feedstock) and the agriculture industry. Propane is also used as an engine fuel as an alternative to gasoline and as a standby fuel for facilities that have interruptible natural gas service contracts.

1.5.2 Firing Practices[2]

The combustion processes that use LPG are very similar to those that use natural gas. Use of LPG in commercial and industrial applications may require a vaporizer to provide the burner with the proper mix of air and fuel. The burner itself will usually have different fuel injector tips as well as different fuel-to-air ratio controller settings than a natural gas burner since the LPG stoichiometric requirements are different than natural gas requirements. LPG is fired as a primary and backup fuel in small commercial and industrial boilers and space heating equipment and can be used to generate heat and process steam for industrial facilities and in most domestic appliances that typically use natural gas.

1.5.3 Emissions[1,3-5]

1.5.3.1 Criteria Pollutants -

LPG is considered a "clean" fuel because it does not produce visible emissions. However, gaseous pollutants such as nitrogen oxides (NO_x), carbon monoxide (CO), and organic compounds are produced as are small amounts of sulfur dioxide (SO_2) and particulate matter (PM). The most significant factors affecting NO_x, CO, and organic emissions are burner design, burner adjustment, boiler operating parameters, and flue gas venting. Improper design, blocking and clogging of the flue vent, and insufficient combustion air result in improper combustion and the emission of aldehydes, CO, hydrocarbons, and other organics. NO_x emissions are a function of a number of variables, including temperature, excess air, fuel and air mixing, and residence time in the combustion zone. The amount of SO_2 emitted is directly proportional to the amount of sulfur in the fuel. PM emissions are very low and result from soot, aerosols formed by condensable emitted species, or boiler scale dislodged during combustion. Emission factors for LPG combustion are presented in Table 1.5-1.

Table 1.5-1 presents emission factors on a volume basis (lb/10^3gal). To convert to an energy basis (lb/MMBtu), divide by a heating value of 91.5 MMBtu/10^3gal for propane and 102 MMBtu/10^3gal for butane.

1.5.3.2 Greenhouse Gases[6-11] -

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions are all produced during LPG combustion. Nearly all of the fuel carbon (99.5 percent) in LPG is converted to CO_2 during the combustion process. This conversion is relatively independent of firing configuration. Although the formation of CO acts to reduce CO_2 emissions, the amount of CO produced is insignificant compared to the amount of CO_2 produced. The majority of the 0.5 percent of fuel carbon not converted to CO_2 is due to incomplete combustion in the fuel stream.

Formation of N_2O during the combustion process is governed by a complex series of reactions and its formation is dependent upon many factors. Formation of N_2O is minimized when combustion temperatures are kept high (above 1475^oF) and excess air is kept to a minimum (less than 1 percent).

Methane emissions are highest during periods of low-temperature combustion or incomplete combustion, such as the start-up or shut-down cycle for boilers. Typically, conditions that favor formation of N_2O also favor emissions of CH_4.

1.5.4 Controls

The only controls developed for LPG combustion are to reduce NO_x emissions. NO_x controls have been developed for firetube and watertube boilers firing propane or butane. Vendors are now guaranteeing retrofit systems to levels as low as 30 to 40 ppm (based on 3 percent oxygen). These systems use a combination of low-NO_x burners and flue gas recirculation (FGR). Some burner vendors use water or steam injection into the flame zone for NO_x reduction. This is a trimming technique which may be necessary during backup fuel periods because LPG typically has a higher NO_x-forming potential than natural gas; conventional natural gas emission control systems may not be sufficient to reduce LPG emissions to mandated levels. Also, LPG burners are more prone to sooting under the modified combustion conditions required for low NO_x emissions. The extent of allowable combustion modifications for LPG may be more limited than for natural gas.

One NO_x control system that has been demonstrated on small commercial boilers is FGR. NO_x emissions from propane combustion can be reduced by as much as 50 percent by recirculating about 16 percent of the flue gas. NO_x emission reductions of over 60 percent have been achieved with FGR and low-NO_x burners used in combination.

1.5.5 Updates Since the Fifth Edition

The Fifth Edition was released in January 1995. Revisions to this section since that date are summarized below. For further detail, consult the memoranda describing each supplement or the background report for this section.

Supplement A, February 1996

No changes.

Supplement B, October 1996

- Text was added concerning firing practices.
- The CO_2 emission factor was updated.
- Emission factors were added for N_2O and CH_4.

Table 1.5-1. EMISSION FACTORS FOR LPG COMBUSTION[a]

EMISSION FACTOR RATING: E

Pollutant	Butane Emission Factor ($lb/10^3$ gal) Industrial Boilers[b] (SCC 1-02-010-01)	Butane Emission Factor ($lb/10^3$ gal) Commercial Boilers[c] (SCC 1-03-010-01)	Propane Emission Factor ($lb/10^3$ gal) Industrial Boilers[b] (SCC 1-02-010-02)	Propane Emission Factor ($lb/10^3$ gal) Commercial Boilers[c] (SCC 1-03-010-02)
PM[d]	0.6	0.5	0.6	0.4
SO_2[e]	0.09S	0.09S	0.10S	0.10S
NO_x[f]	21	15	19	14
N_2O[g]	0.9	0.9	0.9	0.9
CO_2[h,j]	14,300	14,300	12,500	12,500
CO	3.6	2.1	3.2	1.9
TOC	0.6	0.6	0.5	0.5
CH_4[k]	0.2	0.2	0.2	0.2

[a] Assumes emissions (except SO_x and NO_x) are the same, on a heat input basis, as for natural gas combustion. The NO_x emission factors have been multiplied by a correction factor of 1.5, which is the approximate ratio of propane/butane NO_x emissions to natural gas NO_x emissions. To convert from $lb/10^3$ gal to $kg/10^3$ L, multiply by 0.12. SCC = Source Classification Code.

[b] Heat input capacities generally between 10 and 100 million Btu/hour.

[c] Heat input capacities generally between 0.3 and 10 million Btu/hour.

[d] Filterable particulate matter (PM) is that PM collected on or prior to the filter of an EPA Method 5 (or equivalent) sampling train. For natural gas, a fuel with similar combustion characteristics, all PM is less than 10 µm in aerodynamic equivalent diameter (PM-10).

[e] S equals the sulfur content expressed in gr/100 ft^3 gas vapor. For example, if the butane sulfur content is 0.18 gr/100 ft^3, the emission factor would be (0.09 x 0.18) = 0.016 lb of $SO_2/10^3$ gal butane burned.

[f] Expressed as NO_2.

[g] Reference 12.

[h] Assuming 99.5% conversion of fuel carbon to CO_2.

[j] EMISSION FACTOR RATING = C.

[k] Reference 13.

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5.1 Petroleum Refining[1]

5.1.1 General Description

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage preparatory to shipping the refined products from the refinery.

The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 5.1-1 shows the general processing arrangement used by refineries in the United States for major refinery processes. The arrangement of these processes will vary among refineries, and few, if any, employ all of these processes. Petroleum refining processes having direct emission sources are presented on the figure in bold-line boxes.

Listed below are 5 categories of general refinery processes and associated operations:

1. Separation processes
    a. Atmospheric distillation
    b. Vacuum distillation
    c. Light ends recovery (gas processing)
2. Petroleum conversion processes
    a. Cracking (thermal and catalytic)
    b. Reforming
    c. Alkylation
    d. Polymerization
    e. Isomerization
    f. Coking
    g. Visbreaking
3. Petroleum treating processes
    a. Hydrodesulfurization
    b. Hydrotreating
    c. Chemical sweetening
    d. Acid gas removal
    e. Deasphalting
4. Feedstock and product handling
    a. Storage
    b. Blending
    c. Loading
    d. Unloading
5. Auxiliary facilities
    a. Boilers
    b. Waste water treatment
    c. Hydrogen production
    d. Sulfur recovery plant

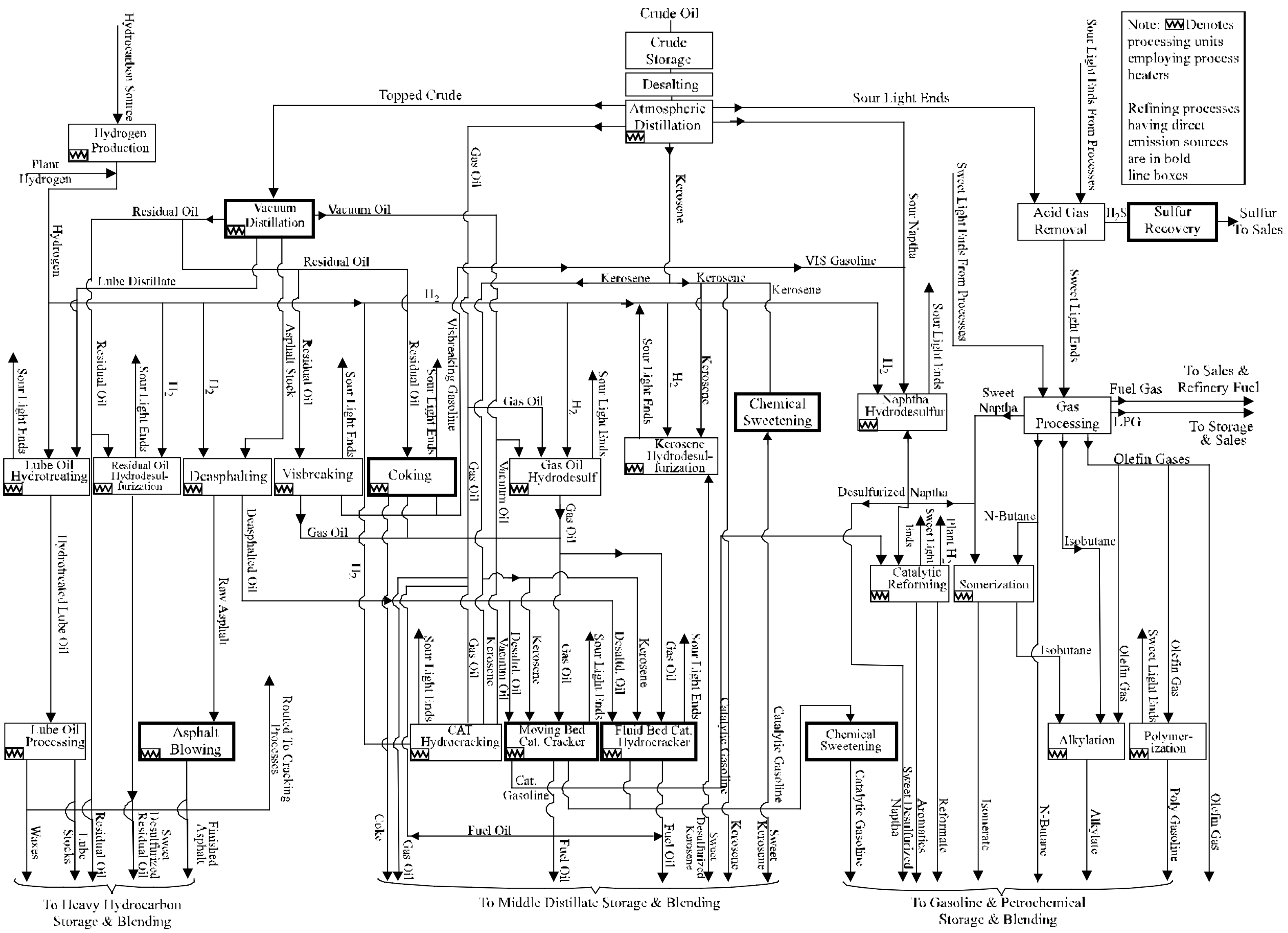

Figure 5.1-1. Schematic of an example integrated petroleum refinery.

e. Cooling towers
f. Blowdown system
g. Compressor engines

These refinery processes are defined below, and their emission characteristics and applicable emission control technology are discussed.

5.1.1.1 Separation Processes -

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using 3 petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing). Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons with small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes separate these crude oil constituents into common boiling-point fractions.

5.1.1.2 Conversion Processes -

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions. Cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller ones. Polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes are applied to rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecular size.

5.1.1.3 Treating Processes -

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products and by removing objectionable elements. Undesirable elements such as sulfur, nitrogen, and oxygen are removed by hydrodesulfurization, hydrotreating, chemical sweetening, and acid gas removal. Treating processes, employed primarily for the separation of petroleum products, include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks before refining. Asphalt blowing is used for polymerizing and stabilizing asphalt to improve its weathering characteristics.

5.1.1.4 Feedstock And Product Handling -

The refinery feedstock and product handling operations consist of unloading, storage, blending, and loading activities.

5.1.1.5 Auxiliary Facilities -

A wide assortment of processes and equipment not directly involved in the refining of crude oil is used in functions vital to the operation of the refinery. Examples are boilers, waste water treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Products from auxiliary facilities (clean water, steam, and process heat) are required by most process units throughout the refinery.

5.1.2 Process Emission Sources And Control Technology

This section presents descriptions of those refining processes that are significant air pollutant contributors. Process flow schemes, emission characteristics, and emission control technology are discussed for each process. Table 5.1-1 lists the emission factors for direct-process emissions in

Table 5.1-1 (Metric And English Units). EMISSION FACTORS FOR PETROLEUM REFINERIES[a]

Process	Particulate	Sulfur Oxides (as SO_2)	Carbon Monoxide	Total Hydro-carbons[b]	Nitrogen Oxides (as NO_2)	Aldehydes	Ammonia	EMISSION FACTOR RATING
Boilers and process heaters								
Fuel oil	See Section 1.3 - "Fuel Oil Combustion"							
Natural gas	See Section 1.4 - "Natural Gas Combustion"							
Fluid catalytic cracking units (FCC)[c]								
Uncontrolled								
kg/10^3 L fresh feed	0.695	1.413	39.2	0.630	0.204	0.054	0.155	B
	(0.267 to 0.976)	(0.286 to 1.505)			(0.107 to 0.416)			
lb/10^3 bbl fresh feed	242	493	13,700	220	71.0	19	54	B
	(93 to 340)	(100 to 525)			(37.1 to 145.0)			
Electrostatic precipitator and CO boiler								
kg/10^3 L fresh feed	0.128[d]	1.413	Neg	Neg	0.204[e]	Neg	Neg	B
	(0.020 to 0.428)	(0.286 to 1.505)			(0.107 to 0.416)			
lb/10^3 bbl fresh feed	45[d]	493	Neg	Neg	71.0[e]	Neg	Neg	B
	(7 to 150)	(100 to 525)			(37.1 to 145.0)			
Moving-bed catalytic cracking units[f]								
kg/10^3 L fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
lb/10^3 bbl fresh feed	17	60	3,800	87	5	12	6	B
Fluid coking units[g]								
Uncontrolled								
kg/10^3 L fresh feed	1.50	ND	ND	ND	ND	ND	ND	C
lb/10^3 bbl fresh feed	523	ND	ND	ND	ND	ND	ND	C
Electrostatic precipitator and CO boiler								
kg/10^3 L fresh feed	0.0196	ND	Neg	Neg	ND	Neg	Neg	C
lb/10^3 bbl fresh feed	6.85	ND	Neg	Neg	ND	Neg	Neg	C

Table 5.1-1 (cont.).

Process	Particulate	Sulfur Oxides (as SO_2)	Carbon Monoxide	Total Hydro-carbons[b]	Nitrogen Oxides (as NO_2)	Aldehydes	Ammonia	EMISSION FACTOR RATING
Delayed coking units	ND	ND	ND	ND	ND	ND	ND	NA
Compressor engines[h]								
Reciprocating engines								
$kg/10^3\ m^3$ gas burned	Neg	2s[j]	7.02	21.8	55.4	1.61	3.2	B
$lb/10^3\ ft^3$ gas burned	Neg	2s	0.43	1.4	3.4	0.1	0.2	B
Gas turbines								
$kg/10^3\ m^3$ gas burned	Neg	2s	1.94	0.28	4.7	ND	ND	B
$lb/10^3\ ft^3$ gas burned	Neg	2s	0.12	0.02	0.3	ND	ND	B
Blowdown systems[k]								
Uncontrolled								
$kg/10^3$ L refinery feed	Neg	Neg	Neg	1,662	Neg	Neg	Neg	C
$lb/10^3$ bbl refinery feed	Neg	Neg	Neg	580	Neg	Neg	Neg	C
Vapor recovery system and flaring								
$kg/10^3$ L refinery feed	Neg	0.077	0.012	0.002	0.054	Neg	Neg	C
$lb/10^3$ bbl refinery feed	Neg	26.9	4.3	0.8	18.9	Neg	Neg	C
Vacuum distillation column condensers[m]								
Uncontrolled								
$kg/10^3$ L vacuum feed	Neg	Neg	Neg	0.14 (0 to 0.37)	Neg	Neg	Neg	C
$lb/10^3$ bbl vacuum feed	Neg	Neg	Neg	50 (0 to 130)	Neg	Neg	Neg	C
Controlled (vented to heater or incinerator)	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

Table 5.1-1 (cont.).

Process	Particulate	Sulfur Oxides (as SO_2)	Carbon Monoxide	Total Hydrocarbons[b]	Nitrogen Oxides (as NO_2)	Aldehydes	Ammonia	EMISSION FACTOR RATING
Claus plant and tail gas treatment	See Section 8.13 - "Sulfur Recovery"							

[a] Numbers in parentheses indicate range of values observed. Neg = negligible. ND = no data.

[b] Overall, less than 1 weight % of total hydrocarbon emissions is methane.

[c] References 2-8.

[d] Under the New Source Performance Standards, controlled FCC regenerators must have particulate emissions lower than 0.054 kg/10^3 L (19 lb/10^3 bbl) fresh feed.

[e] May be higher, from the combustion of ammonia.

[g] Reference 2.

[g] Reference 5.

[h] References 9-10.

[j] Based on 100% combustion of sulfur to SO_2. s = refinery gas sulfur content (in kg/1000 m^3 or lb/1000 ft^3, depending on desired units for emission factor).

[k] References 2,11.

[m] References 2,12-13. If refinery feed rate is known, rather than vacuum feed rate, assume vacuum feed is 36% of refinery feed. Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column.

petroleum refineries. Factors are expressed in units of kilograms per 1000 liters (kg/10^3 L) or kilograms per 1000 cubic meters (kg/10^3 m^3) and pounds per 1000 barrels (lb/10^3 bbl) or pounds per 1000 cubic feet (lb/10^3 ft^3). The following process emission sources are discussed here:

1. Vacuum distillation
2. Catalytic cracking
3. Thermal cracking processes
4. Utility boilers
5. Heaters
6. Compressor engines
7. Blowdown systems
8. Sulfur recovery

5.1.2.1 Vacuum Distillation -

Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high boiling-point hydrocarbons. When distilled at atmospheric pressures, the crude oil decomposes and polymerizes and will foul equipment. To separate topped crude into components, it must be distilled in a vacuum column at a very low pressure and in a steam atmosphere.

In the vacuum distillation unit, topped crude is heated with a process heater to temperatures ranging from 370 to 425°C (700 to 800°F). The heated topped crude is flashed into a multitray vacuum distillation column operating at absolute pressures ranging from 350 to 1400 kilograms per square meter (kg/m^2) (0.5 to 2 pounds per square inch absolute [psia]). In the vacuum column, the topped crude is separated into common boiling-point fractions by vaporization and condensation. Stripping steam is normally injected into the bottom of the vacuum distillation column to assist the separation by lowering the effective partial pressures of the components. Standard petroleum fractions withdrawn from the vacuum distillation column include lube distillates, vacuum oil, asphalt stocks, and residual oils. The vacuum in the vacuum distillation column is usually maintained by the use of steam ejectors but may be maintained by the use of vacuum pumps.

The major sources of atmospheric emissions from the vacuum distillation column are associated with the steam ejectors or vacuum pumps. A major portion of the vapors withdrawn from the column by the ejectors or pumps is recovered in condensers. Historically, the noncondensable portion of the vapors has been vented to the atmosphere from the condensers. There are approximately 0.14 kg of noncondensable hydrocarbons per m^3 (50 lb/10^3 bbl) of topped crude processed in the vacuum distillation column.[2,12-13] A second source of atmospheric emissions from vacuum distillation columns is combustion products from the process heater. Process heater requirements for the vacuum distillation column are approximately 245 megajoules per cubic meter (MJ/m^3) (37,000 British thermal units per barrel [Btu/bbl]) of topped crude processed in the vacuum column. Process heater emissions and their control are discussed below. Fugitive hydrocarbon emissions from leaking seals and fittings are also associated with the vacuum distillation unit, but these are minimized by the low operating pressures and low vapor pressures in the unit. Fugitive emission sources are also discussed later.

Control technology applicable to the noncondensable emissions vented from the vacuum ejectors or pumps includes venting into blowdown systems or fuel gas systems, and incineration in furnaces or waste heat boilers.[2,12-13] These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions, but they also contribute to the emission of combustion products.

5.1.2.2 Catalytic Cracking -

Catalytic cracking, using heat, pressure, and catalysts, converts heavy oils into lighter products with product distributions favoring the more valuable gasoline and distillate blending components. Feedstocks are usually gas oils from atmospheric distillation, vacuum distillation, coking, and deasphalting processes. These feedstocks typically have a boiling range of 340 to 540°C (650 to 1000°F). All of the catalytic cracking processes in use today can be classified as either fluidized-bed or moving-bed units.

5.1.2.2.1 Fluidized-bed Catalytic Cracking (FCC) -

The FCC process uses a catalyst in the form of very fine particles that act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introduced into the bottom of a vertical transfer line or riser with hot regenerated catalyst. The hot catalyst vaporizes the feed, bringing both to the desired reaction temperature, 470 to 525°C (880 to 980°F) The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and oil mixture flows upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionator for separation.

The spent catalyst falls to the bottom of the reactor and is steam stripped as it exits the reactor bottom to remove absorbed hydrocarbons. The spent catalyst is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. Regenerator temperature is usually 590 to 675°C (1100 to 1250°F). The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

5.1.2.2.2 Moving-bed Catalytic Cracking-

In the moving-bed system, typified by the Thermafor Catalytic Cracking (TCC) units, catalyst beads (~0.5 centimeters [cm] [0.2 inches (in.)]) flow into the top of the reactor, where they contact a mixed-phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator, where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed. The operating temperatures of the reactor and regenerator in the TCC process are comparable to those in the FCC process.

Air emissions from catalytic cracking processes are (1) combustion products from process heaters and (2) flue gas from catalyst regeneration. Emissions from process heaters are discussed below. Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide (CO), and particulates (Table 5.1-1). The particulate emissions from FCC units are much greater than those from TCC units because of the higher catalyst circulation rates used.[2-3,5]

FCC particulate emissions are controlled by cyclones and/or electrostatic precipitators. Particulate control efficiencies are as high as 80 to 85 percent.[3,5] Carbon monoxide waste heat boilers reduce the CO and hydrocarbon emissions from FCC units to negligible levels.[3] TCC catalyst regeneration produces similar pollutants to FCC units, but in much smaller quantities (Table 5.1-1). The particulate emissions from a TCC unit are normally controlled by high-efficiency cyclones. Carbon monoxide and hydrocarbon emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner. In some installations, sulfur oxides are removed by passing the regenerator flue gases through a water or caustic scrubber.[2-3,5]

5.1.2.3 Thermal Cracking -

Thermal cracking processes include visbreaking and coking, which break heavy oil molecules by exposing them to high temperatures.

5.1.2.3.1 Visbreaking -

Topped crude or vacuum residuals are heated and thermally cracked (455 to 480°C, 3.5 to 17.6 kg/cm^2 [850 to 900°F, 50 to 250 pounds per square inch gauge (psig)]) in the visbreaker furnace to reduce the viscosity, or pour point, of the charge. The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products. A heavy distillate recovered from the fractionator liquid can be used as either a fuel oil blending component or catalytic cracking feed.

5.1.2.3.2 Coking -

Coking is a thermal cracking process used to convert low value residual fuel oil to higher-value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils, and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future.

In the delayed coking process, heated charge stock is fed into the bottom of a fractionator, where light ends are stripped from the feed. The stripped feed is then combined with recycle products from the coke drum and rapidly heated in the coking heater to a temperature of 480 to 590°C (900 to 1100°F). Steam injection is used to control the residence time in the heater. The vapor-liquid feed leaves the heater, passing to a coke drum where, with controlled residence time, pressure (1.8 to 2.1 kg/cm^2 [25 to 30 psig]), and temperature (400°C [750°F]), it is cracked to form coke and vapors. Vapors from the drum return to the fractionator, where the thermal cracking products are recovered.

In the fluid coking process, typified by Flexicoking, residual oil feeds are injected into the reactor, where they are thermally cracked, yielding coke and a wide range of vapor products. Vapors leave the reactor and are quenched in a scrubber, where entrained coke fines are removed. The vapors are then fractionated. Coke from the reactor enters a heater and is devolatilized. The volatiles from the heater are treated for fines and sulfur removal to yield a particulate-free, low-sulfur fuel gas. The devolatilized coke is circulated from the heater to a gasifier where 95 percent of the reactor coke is gasified at high temperature with steam and air or oxygen. The gaseous products and coke from the gasifier are returned to the heater to supply heat for the devolatilization. These gases exit the heater with the heater volatiles through the same fines and sulfur removal processes.

From available literature, it is unclear what emissions are released and where they are released. Air emissions from thermal cracking processes include coke dust from decoking operations, combustion gases from the visbreaking and coking process heaters, and fugitive emissions. Emissions from the process heaters are discussed below. Fugitive emissions from miscellaneous leaks are significant because of the high temperatures involved, and are dependent upon equipment type and configuration, operating conditions, and general maintenance practices. Fugitive emissions are also discussed below. Particulate emissions from delayed coking operations are potentially very significant. These emissions are associated with removing the coke from the coke drum and subsequent handling and storage operations. Hydrocarbon emissions are also associated with cooling and venting the coke drum before coke removal. However, comprehensive data for delayed coking emissions have not been included in available literature.[4-5]

Particulate emission control is accomplished in the decoking operation by wetting down the coke.[5] Generally, there is no control of hydrocarbon emissions from delayed coking. However, some facilities are now collecting coke drum emissions in an enclosed system and routing them to a refinery flare.[4-5]

5.1.2.4 Utilities Plant -

The utilities plant supplies the steam necessary for the refinery. Although the steam can be used to produce electricity by throttling through a turbine, it is primarily used for heating and separating hydrocarbon streams. When used for heating, the steam usually heats the petroleum indirectly in heat exchangers and returns to the boiler. In direct contact operations, the steam can serve as a stripping medium or a process fluid. Steam may also be used in vacuum ejectors to produce a vacuum. Boiler emissions and applicable emission control technology are discussed in much greater detail in Chapter 1.

5.1.2.5 Sulfur Recovery Plant -

Sulfur recovery plants are used in petroleum refineries to convert the hydrogen sulfide (H_2S) separated from refinery gas streams into the more disposable byproduct, elemental sulfur. Emissions from sulfur recovery plants and their control are discussed in Section 8.13, "Sulfur Recovery".

5.1.2.6 Blowdown System -

The blowdown system provides for the safe disposal of hydrocarbons (vapor and liquid) discharged from pressure relief devices.

Most refining processing units and equipment subject to planned or unplanned hydrocarbon discharges are manifolded into a collection unit, called blowdown system. By using a series of flash drums and condensers arranged in decreasing pressure, blowdown material is separated into vapor and liquid cuts. The separated liquid is recycled into the refinery. The gaseous cuts can either be smokelessly flared or recycled.

Uncontrolled blowdown emissions primarily consist of hydrocarbons but can also include any of the other criteria pollutants. The emission rate in a blowdown system is a function of the amount of equipment manifolded into the system, the frequency of equipment discharges, and the blowdown system controls.

Emissions from the blowdown system can be effectively controlled by combustion of the noncondensables in a flare. To obtain complete combustion or smokeless burning (as required by most states), steam is injected in the combustion zone of the flare to provide turbulence and air. Steam injection also reduces emissions of nitrogen oxides by lowering the flame temperature. Controlled emissions are listed in Table 5.1-1.[2,11]

5.1.2.7 Process Heaters -

Process heaters (furnaces) are used extensively in refineries to supply the heat necessary to raise the temperature of feed materials to reaction or distillation level. They are designed to raise petroleum fluid temperatures to a maximum of about 510°C (950°F). The fuel burned may be refinery gas, natural gas, residual fuel oils, or combinations, depending on economics, operating conditions, and emission requirements. Process heaters may also use CO-rich regenerator flue gas as fuel.

All the criteria pollutants are emitted from process heaters. The quantity of these emissions is a function of the type of fuel burned, the nature of the contaminants in the fuel, and the heat duty of the furnace. Sulfur oxides can be controlled by fuel desulfurization or flue gas treatment. Carbon monoxide and hydrocarbons can be controlled by more combustion efficiency. Currently, 4 general techniques or modifications for the control of nitrogen oxides are being investigated: combustion modification, fuel modification, furnace design, and flue gas treatment. Several of these techniques are being applied to large utility boilers, but their applicability to process heaters has not been established.[2,14]

5.1.2.8 Compressor Engines -

Many older refineries run high-pressure compressors with reciprocating and gas turbine engines fired with natural gas. Natural gas has usually been a cheap, abundant source of energy. Examples of refining units operating at high pressure include hydrodesulfurization, isomerization, reforming, and hydrocracking. Internal combustion engines are less reliable and harder to maintain than are steam engines or electric motors. For this reason, and because of increasing natural gas costs, very few such units have been installed in the last few years.

The major source of emissions from compressor engines is combustion products in the exhaust gas. These emissions include CO, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present, depending on the sulfur content of the natural gas. All these emissions are significantly higher in exhaust from reciprocating engines than from turbine engines.

The major emission control technique applied to compressor engines is carburetion adjustment similar to that applied on automobiles. Catalyst systems similar to those of automobiles may also be effective in reducing emissions, but their use has not been reported.

5.1.2.9 Sweetening -

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may be followed by an extraction step for removal of the alkyl disulfides. In the conversion process, sulfur is added to the sour distillate with a small amount of caustic and air. The mixture is then passed upward through a fixed-bed catalyst, counter to a flow of caustic entering at the top of the vessel. In the conversion and extraction process, the sour distillate is washed with caustic and then is contacted in the extractor with a solution of catalyst and caustic. The extracted distillate is then contacted with air to convert mercaptans to disulfides. After oxidation, the distillate is settled, inhibitors are added, and the distillate is sent to storage. Regeneration is accomplished by mixing caustic from the bottom of the extractor with air and then separating the disulfides and excess air.

The major emission problem is hydrocarbons from contact of the distillate product and air in the "air blowing" step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.[4]

5.1.2.10 Asphalt Blowing -

The asphalt blowing process polymerizes asphaltic residual oils by oxidation, increasing their melting temperature and hardness to achieve an increased resistance to weathering. The oils, containing a large quantity of polycyclic aromatic compounds (asphaltic oils), are oxidized by blowing heated air through a heated batch mixture or, in a continuous process, by passing hot air countercurrent to the oil flow. The reaction is exothermic, and quench steam is sometimes needed for temperature control. In some cases, ferric chloride or phosphorus pentoxide is used as a catalyst to increase the reaction rate and to impart special characteristics to the asphalt.

Air emissions from asphalt blowing are primarily hydrocarbon vapors vented with the blowing air. The quantities of emissions are small because of the prior removal of volatile hydrocarbons in the distillation units, but the emissions may contain hazardous polynuclear organics. Emissions are 30 kg/megagram (Mg) (60 lb/ton) of asphalt.[13] Emissions from asphalt blowing can be controlled to negligible levels by vapor scrubbing, incineration, or both.[4,13]

5.1.3 Fugitive Emissions And Controls

Fugitive emission sources include leaks of hydrocarbon vapors from process equipment and evaporation of hydrocarbons from open areas, rather than through a stack or vent. Fugitive emission sources include valves of all types, flanges, pump and compressor seals, process drains, cooling towers, and oil/water separators. Fugitive emissions are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally, control of fugitive emissions involves minimizing leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping, and maintenance practices. Controlled and uncontrolled fugitive emission factors for the following sources are listed in Table 5.1-2:

- Oil/water separators (waste water treatment)
- Storage
- Transfer operations
- Cooling towers

Emission factors for fugitive leaks from the following types of process equipment can be found in *Protocol For Equipment Leak Emission Estimates*, EPA-453/R-93-026, June 1993, or subsequent updates:

- Valves (pipeline, open ended, vessel relief)
- Flanges
- Seals (pump, compressor)
- Process drains

5.1.3.1 Valves, Flanges, Seals, And Drains -

For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. The four stream service types are (1) hydrocarbon gas/vapor streams (including gas streams with up to 50 percent hydrogen by volume), (2) light liquid and gas/liquid streams, (3) kerosene and heavier liquid streams (includes all crude oils), and (4) gas streams containing more than 50 percent hydrogen by volume. It is found that sources in gas/vapor stream service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals. The size of valves, flanges, pump seals, compressor seals, relief valves, and process drains does not affect their leak rates.[17] The emission factors are independent of process unit or refinery throughput.

Valves, because of their number and relatively high emission factor, are the major emission source. This conclusion is based on an analysis of a hypothetical refinery coupled with the emission rates. The total quantity of fugitive VOC emissions in a typical oil refinery with a capacity of 52,500 m^3 (330,000 bbl) per day is estimated as 20,500 kg (45,000 lb) per day (see Table 5.1-3). This estimate is based on a typical late 1970s refinery without a leak inspection and maintenance (I/M) program. See the *Protocol* document for details on how to estimate emissions for a specific refinery.

Table 5.1-2 (Metric And English Units). FUGITIVE EMISSION FACTORS FOR PETROLEUM REFINERIES[a]

EMISSION FACTOR RATING: D

Emission Source	Emission Factor Units	Emission Factors		Applicable Control Technology
		Uncontrolled Emissions	Controlled Emissions	
Cooling towers[b]	kg/10^6 L cooling water	0.7	0.08	Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons
	lb/10^6 gal cooling water	6	0.7	Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons
Oil/water separators[c]	kg/10^3 L waste water	0.6	0.024	Covered separators and/or vapor recovery systems
	lb/10^3 gal waste water	5	0.2	Covered separators and/or vapor recovery systems
Storage	See Chapter 7 - Liquid Storage Tanks			
Loading	See Section 5.2 - Transportation And Marketing Of Petroleum Liquids			

[a] References 2,4,12-13.

[b] If cooling water rate is unknown (in liters or gallons) assume it is 40 times the refinery feed rate (in liters or gallons). Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column. 1 bbl (oil) = 42 gallons (gal), 1 m^3 = 1000 L.

[c] If waste water flow rate to oil/water separators is unknown (in liters or gallons) assume it is 0.95 times the refinery feed rate (in liters or gallons). Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column. 1 bbl (oil) = 42 gal, 1 m^3 = 1000 L.

5.1.3.2 Storage -

All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to ensure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 160 m^3 to more than 79,500 m^3 (1,000 to 500,000 bbl). Storage tank designs, emissions, and emission control technology are discussed in detail in AP-42 Chapter 7, and the *TANKS* software program is available to perform the emissions calculations, if desired.

Table 5.1-3 (Metric And English Units). FUGITIVE VOC EMISSIONS FROM AN UNCONTROLLED OIL REFINERY OF 52,500 m^3/day (330,000 bbl/day) CAPACITY[a]

Source	Number	VOC Emissions	
		kg/day	lb/day
Valves	11,500	3,100	6,800
Flanges	46,500	300	600
Pump seals	350	590	1,300
Compressor seals	70	500	1,100
Relief valves	100	200	500
Drains	650	450	1,000
Cooling towers[b]	1	730	1,600
Oil/water separators (uncovered)[b]	1	14,600	32,100
TOTAL	—	20,500	45,000

[a] Reference 17.
[b] Based on limited data.

5.1.3.3 Transfer Operations -

Although most refinery feedstocks and products are transported by pipeline, some are transported by trucks, rail cars, and marine vessels. They are transferred to and from these transport vehicles in the refinery tank farm area by specialized pumps and piping systems. The emissions from transfer operations and applicable emission control technology are discussed in much greater detail in Section 5.2, "Transportation And Marketing Of Petroleum Liquids".

5.1.3.4 Waste Water Treatment Plant -

All refineries employ some form of waste water treatment so water effluents can safely be returned to the environment or reused in the refinery. The design of waste water treatment plants is complicated by the diversity of refinery pollutants, including oil, phenols, sulfides, dissolved solids, and toxic chemicals. Although the treatment processes employed by refineries vary greatly, they generally include neutralizers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems, coagulators, aerated lagoons, and activated sludge ponds. Refinery water effluents are collected from various processing units and are conveyed through sewers and ditches to the treatment plant. Most of the treatment occurs in open ponds and tanks.

The main components of atmospheric emissions from waste water treatment plants are fugitive VOCs and dissolved gases that evaporate from the surfaces of waste water residing in open process drains, separators, and ponds (Table 5.1-2). Treatment processes that involve extensive contact of waste water and air, such as aeration ponds and dissolved air flotation, have an even greater potential for atmospheric emissions. Section 4.3, "Waste Water Collection, Treatment And Storage", discusses estimation techniques for such water treatment operations. *WATER8* and *SIMS* software models are available to perform the calculations.

The control of waste water treatment plant emissions involves covering systems where emission generation is greatest (such as oil/water separators and settling basins) and removing dissolved gases from water streams with sour water strippers and phenol recovery units before their contact with the atmosphere. These control techniques potentially can achieve greater than 90 percent reduction of waste water system emissions.[13]

5.1.3.5 Cooling Towers -

Cooling towers are used extensively in refinery cooling water systems to transfer waste heat from the cooling water to the atmosphere. The only refineries not employing cooling towers are those with once-through cooling. The increasing scarcity of a large water supply required for once-through cooling is contributing to the disappearance of that form of refinery cooling. In the cooling tower, warm cooling water returning from refinery processes is contacted with air by cascading through packing. Cooling water circulation rates for refineries commonly range from 7 to 70 L/minute per m^3/day (0.3 to 3.0 gal/minute per bbl/day) of refinery capacity.[2,16]

Atmospheric emissions from the cooling tower consist of fugitive VOCs and gases stripped from the cooling water as the air and water come into contact. These contaminants enter the cooling water system from leaking heat exchangers and condensers. Although the predominant contaminants in cooling water are VOCs, dissolved gases such as H_2S and ammonia may also be found (see Table 5.1-2).[2,4,17]

Control of cooling tower emissions is accomplished by reducing contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.[4]

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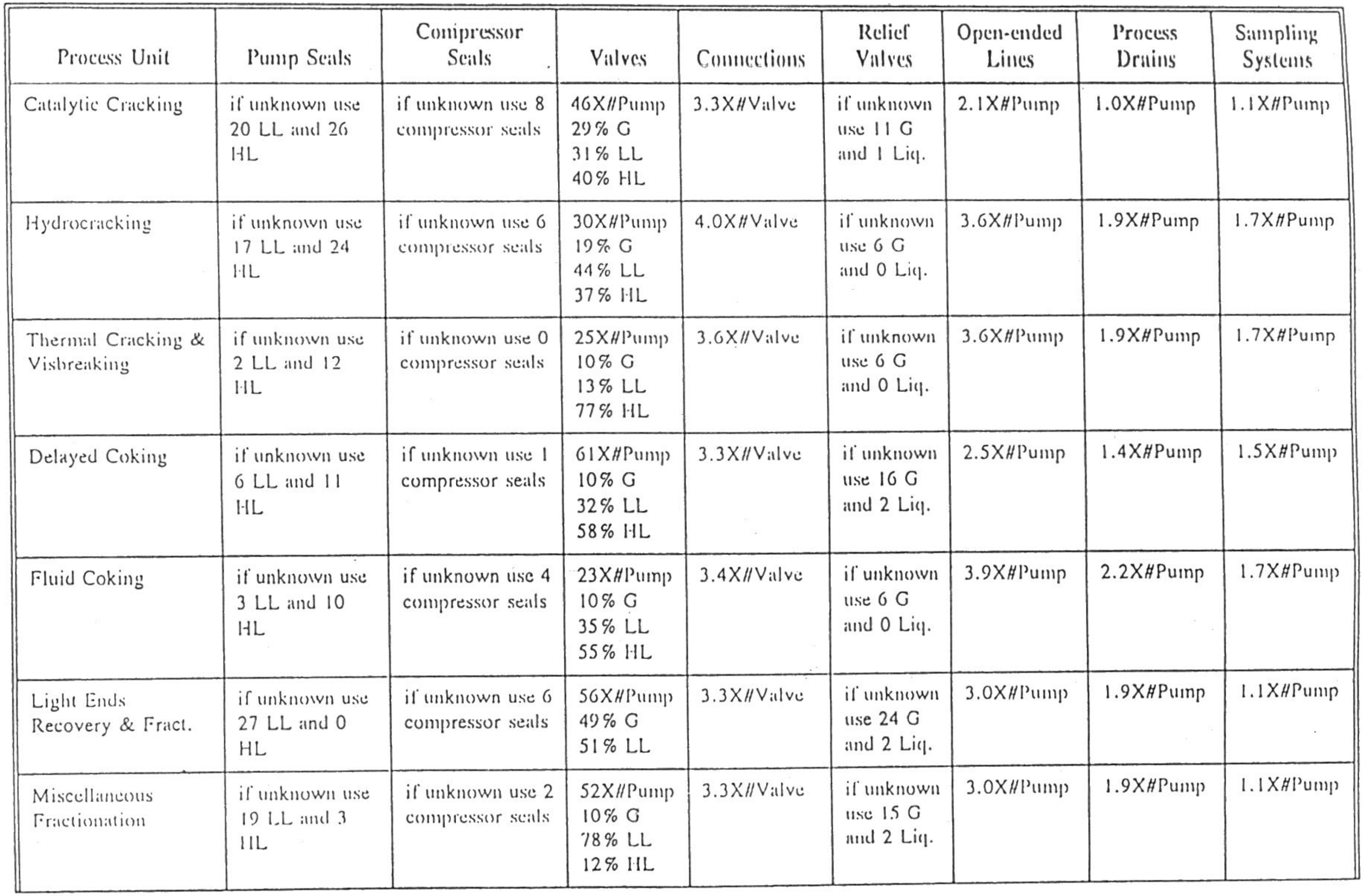
Component Count Estimation Methods for Refinery Units

(U.S. EPA, 1984)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Atmospheric Crude Distillation	if unknown use 12 LL and 19 HL	if unknown assume no compressor seals	41X#Pump 10% G 35% LL 55% HL	3.5X#Valve	if unknown use 16 G and 2 Liq.	3.1X#Pump	1.8X#Pump	1.3X#Pump
Vacuum Crude Distillation	if unknown use 1 LL and 21 HL	if unknown assume no compressors	39X#Pump 10% G 4% LL 86% HL	3.4XValve	if unknown use 8 G and 4 Liq.	3.0X#Pump	2.0X#Pump	1.0X#Pump
Naphtha Hydrotreating	if unknown use 14 LL and 0 HL	if unknown use 4 compressor seals	66X#Pump 30% G 70% LL	3.5X#Valve	if unknown use 13 G and 1 Liq.	3.5X#Pump	1.8X#Pump	1.7X#Pump
Middle Distillate Hydrotreating	if unknown use 4 LL and 13 HL	if unknown use 6 compressor seals	62X#Pump 52% G 11% LL 37% HL	3.5X#Valve	if unknown use 14 G and 2 Liq.	3.1X#Pump	1.4X#Pump	1.7X#Pump
Vacuum Resid Hydro-desulfurization	if unknown use 0 LL and 11 HL	if unknown use 4 compressor seals	71X#Pump 35% G 0% LL 65% HL	3.3X#Valve	if unknown use 12 G and 1 Liq.	3.8X#Pump	2.2X#Pump	1.6X#Pump
Catalytic Reforming	if unknown use 15 LL and 1 HL	if unknown use 6 compressor seals	59X#Pump 23% G 72% LL 5% HL	3.5X#Valve	if unknown use 11 G and 1 Liq.	3.5X#Pump	2.0X#Pump	1.5X#Pump
Aromatics Extraction	if unknown use 22 LL and 5 HL	if unknown use 0 compressor seals	49X#Pump 10% G 73% LL 17% HL	3.4X#Valve	if unknown use 18 G and 2 Liq.	3.2X#Pump	1.9X#Pump	1.3X#Pump

Component Count Estimation Methods for Refinery Units
(U.S. EPA, 1984)
(Continued)



Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Catalytic Cracking	if unknown use 20 LL and 26 HL	if unknown use 8 compressor seals	46X#Pump 29% G 31% LL 40% HL	3.3X#Valve	if unknown use 11 G and 1 Liq.	2.1X#Pump	1.0X#Pump	1.1X#Pump
Hydrocracking	if unknown use 17 LL and 24 HL	if unknown use 6 compressor seals	30X#Pump 19% G 44% LL 37% HL	4.0X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Thermal Cracking & Visbreaking	if unknown use 2 LL and 12 HL	if unknown use 0 compressor seals	25X#Pump 10% G 13% LL 77% HL	3.6X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Delayed Coking	if unknown use 6 LL and 11 HL	if unknown use 1 compressor seals	61X#Pump 10% G 32% LL 58% HL	3.3X#Valve	if unknown use 16 G and 2 Liq.	2.5X#Pump	1.4X#Pump	1.5X#Pump
Fluid Coking	if unknown use 3 LL and 10 HL	if unknown use 4 compressor seals	23X#Pump 10% G 35% LL 55% HL	3.4X#Valve	if unknown use 6 G and 0 Liq.	3.9X#Pump	2.2X#Pump	1.7X#Pump
Light Ends Recovery & Fract.	if unknown use 27 LL and 0 HL	if unknown use 6 compressor seals	56X#Pump 49% G 51% LL	3.3X#Valve	if unknown use 24 G and 2 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump
Miscellaneous Fractionation	if unknown use 19 LL and 3 HL	if unknown use 2 compressor seals	52X#Pump 10% G 78% LL 12% HL	3.3X#Valve	if unknown use 15 G and 2 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump

Component Count Estimation Methods for Refinery Units
(U.S. EPA, 1984)
(Continued)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Alkylation	if unknown use 24 LL and 0 HL	if unknown use 2 compressor seals	49X#Pump 13% G 87% LL	3.4X#Valve	if unknown use 12 G and 1 Liq.	3.1X#Pump	1.9X#Pump	1.2X#Pump
Polymerization	if unknown use 17 LL and 0 HL	if unknown use 0 compressor seals	50X#Pump 35% G 65% LL	3.3X#Valve	if unknown use 11 G and 1 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump
Isomerization	if unknown use 14 LL and 0 HL	if unknown use 4 compressor seals	46X#Pump 53% G 47% LL	3.6X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Lubes Processing - Volatile Organic Solvents	if unknown use 8 LL and 12 HL	if unknown use 2 compressor seals	36X#Pump 10% G 36% LL 54% HL	3.6X#Valve	if unknown use 9 G and 1 Liq.	1.7X#Pump	1.9X#Pump	1.7X#Pump
Lubes Processing - Other	if unknown use 0 LL and 12 HL	if unknown use 0 compressor seals	59X#Pump 0% G 0% LL 100% HL	3.1X#Valve	if unknown use 6 G and 6 Liq.	3.2X#Pump	1.9X#Pump	1.3X#Pump
Asphalt Production	if unknown use 0 LL and 6 HL	if unknown use 0 compressor seals	50X#Pump 0% G 0% LL 100% HL	3.6X#Valve	if unknown use 3 G and 3 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Hydrogen Production	if unknown use 2 LL and 2 HL	if unknown use 6 compressor seals	251XPump 15% G 43% LL 42% HL	3.3X#Valve	if unknown use 15 G and 2 Liq.	10.4XPump	4.3X#Pump	6.1X#Pump

Component Count Estimation Methods for Refinery Units
(U.S. EPA, 1984)
(Continued)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Gasoline Treating	if unknown use 6 LL and 5 HL	if unknown use 0 compressor seals	71X#Pump 5% G 52% LL 43% HL	3.3X#Valve	if unknown use 4 G and 4 Liq.	3.1X#Pump	1.9X#Pump	1.2X#Pump
Other Product Treating	if unknown use 0 LL and 8 HL	if unknown use 0 compressor seals	55X#Pump 2% G 0% LL 98% HL	3.4X#Valve	if unknown use 1 G and 1 Liq.	3.4X#Pump	1.9X#Pump	1.5X#Pump
Olefins Production	if unknown use 17 LL and 5 HL	if unknown use 4 compressor seals	103XPump 54% G 36% LL 10% HL	3.6X#Valve	if unknown use 30 G and 5 Liq.	5.2X#Pump	3.3X#Pump	1.9X#Pump
Other Volatile Petrochemicals	if unknown use 25 LL and 6 HL	if unknown use 2 compressor seals	21X#Pump 28% G 58% LL 14% HL	3.4X#Valve	if unknown use 9 G and 2 Liq.	4.7X#Pump	2.2X#Pump	2.4X#Pump
Low Volatility Petrochemicals	if unknown use 4 LL and 8 HL	if unknown use 2 compressor seals	43X#Pump 13% G 29% LL 58% HL	3.5X#Valve	if unknown use 8 G and 6 Liq.	3.4X#Pump	1.9X#Pump	1.5X#Pump

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EPA-454/R-98-011
June 1998

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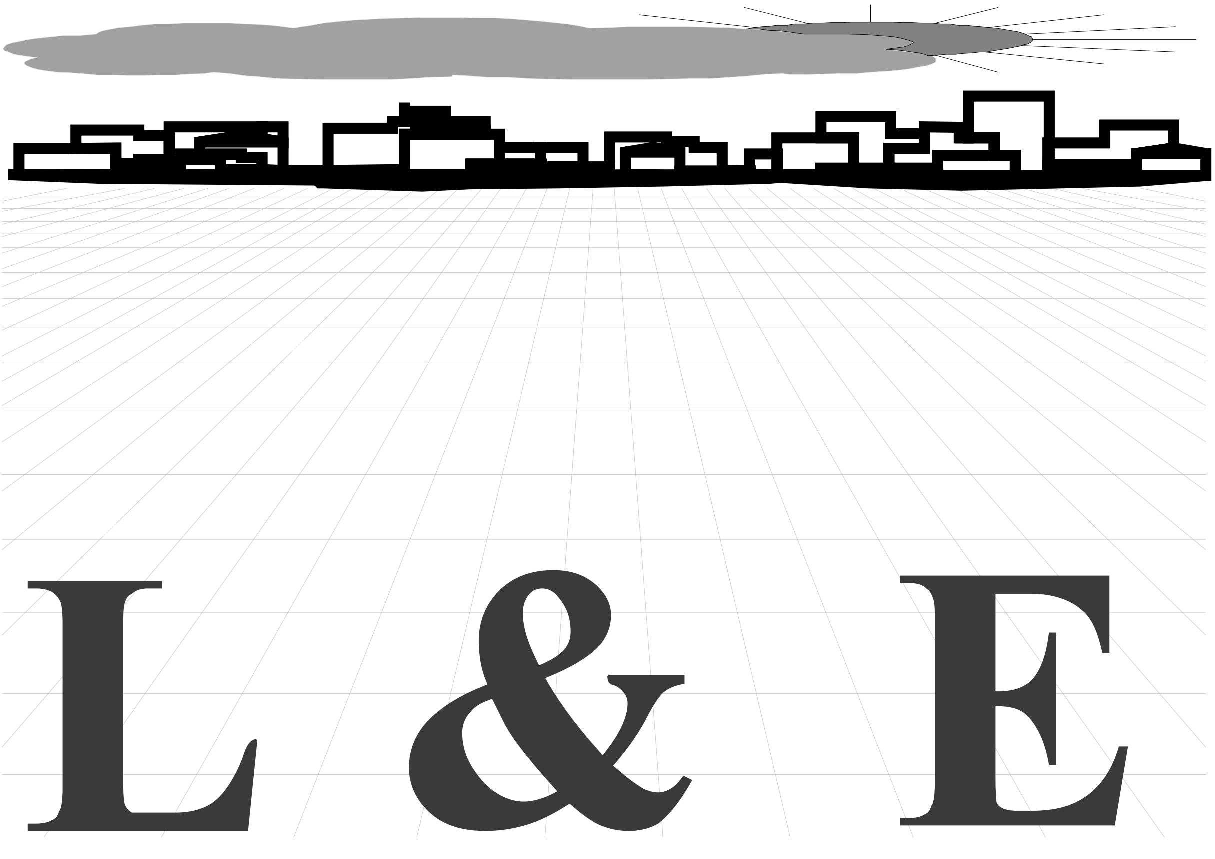
LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF BENZENE



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EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments contain a list of 188 hazardous air pollutants (HAPs) which the U.S. Environmental Protection Agency must study, identify sources of, and determine if regulations are warranted. One of these HAPs, benzene, is the subject of this document. This document describes the properties of benzene as an air pollutant, defines its production and use patterns, identifies source categories of air emissions, and provides benzene emission factors. The document is a part of an ongoing EPA series designed to assist the general public at large, but primarily State/local air agencies, in identifying sources of HAPs and developing emissions estimates.

Benzene is primarily used in the manufacture of other organic chemicals, including ethylbenzene/styrene, cumene/phenol, cyclohexane, and nitrobenzene/aniline. Benzene is emitted into the atmosphere from its production, its use as a chemical feedstock in the production of other chemicals, the use of those other chemicals, and from fossil fuel and biomass combustion. Benzene is also emitted from a wide variety of miscellaneous sources including oil and gas wellheads, glycol dehydrators, petroleum refining, gasoline marketing, wastewater treatment, landfills, pulp and paper mills, and from mobile sources.

In addition to identifying sources of benzene emissions, information is provided that specifies how individual sources of benzene may be tested to quantify air emissions.

SECTION 1.0
PURPOSE OF DOCUMENT

The U.S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or about the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of locating and estimating (L&E) documents such as this one that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

Substance	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Arsenic	(Document under revision)
Butadiene	EPA-454/R-96-008
Cadmium	EPA-454/R-93-040
Carbon Tetrachloride	EPA-450/4-84-007b
Chlorobenzene (update)	EPA-454/R-93-044
Chloroform	EPA-450/4-84-007c
Chromium (supplement)	EPA-450/2-89-002
Chromium	EPA-450/4-84-007g

Substance	EPA Publication Number
Coal and Oil Combustion Sources	EPA-450/2-89-001
Cyanide Compounds	EPA-454/R-93-041
Dioxins and Furans	EPA-454/R-97-003
Epichlorohydrin	EPA-450/4-84-007j
Ethylene Dichloride	EPA-450/4-84-007d
Ethylene Oxide	EPA-450/4-84-007l
Formaldehyde	EPA-450/4-91-012
Lead	EPA-454/R-98-006
Manganese	EPA-450/4-84-007h
Medical Waste Incinerators	EPA-454/R-93-053
Mercury and Mercury Compounds (under revision)	EPA-453/R-93-023
Methyl Chloroform	EPA-454/R-93-045
Methyl Ethyl Ketone	EPA-454/R-93-046
Methylene Chloride	EPA-454/R-93-006
Municipal Waste Combustors	EPA-450/2-89-006
Nickel	EPA-450/4-84-007f
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013
Phosgene	EPA-450/4-84-007i
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p
Sewage Sludge Incinerators	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Toluene	EPA-454/R-93-047
Vinylidene Chloride	EPA-450/4-84-007k
Xylenes	EPA-454/R-93-048

This document deals specifically with benzene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of benzene and estimating their air emissions.

Because of the limited availability of data on potential sources of benzene emissions and the variability in process configurations, control equipment, and operating procedure among facilities, this document is best used as a primer on (1) types of sources that may emit benzene, (2) process variations and release points that may be expected, and (3) available emissions information on the potential for benzene releases into the air. The reader is cautioned against using the emissions information in this document to develop an exact assessment of emissions from any particular facility.

Emission estimates may need to be adjusted to take into consideration participation in EPA's voluntary emission reduction program or compliance with State or local regulations.

It is possible, in some cases, that orders-of-magnitude differences may result between actual and estimated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in all situations where an accurate assessment of benzene emissions is necessary, the source-specific information should be obtained to confirm the existence of particular emitting operations and the types and effectiveness of control measures, and to determine the impact of operating practices. A source test and/or material balance calculation should be considered as better methods of determining air emissions from a specific operation.

In addition to the information presented in this document, another potential source of emissions data for benzene from facilities is the Toxic Chemical Release Inventory (TRI) form required by Title III, Section 313 of the 1986 Superfund Amendments and Reauthorization Act (SARA).[1] Section 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes that manufacture, import, process, or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data.

The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. SARA Section 313 requires sources to use available stack monitoring data for reporting but does not require facilities to perform stack monitoring or other types of emissions measurement. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment. In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). The EPA recommends use of TRI data in conjunction with the information provided in this document to locate potential emitters of benzene and to make preliminary estimates of air emissions from these facilities.

For mobile sources, more data are becoming available for on-road vehicles. Additionally, the EPA model that generates emission factors undergoes regular update. The on-road mobile sources section in this document should therefore be viewed as an example of how emissions can be determined and the reader should look for more detailed data for the most accurate estimates.

Data on off-road vehicles and other stationary sources remain unavailable. However, with EPA's increased emphasis on air toxics, more benzene data are likely to be generated in the future.

As standard procedure, L&E documents are sent to government, industry, and environmental groups wherever EPA is aware of expertise. These groups are given the opportunity to review a document, comment, and provide additional data where applicable. Where necessary, the document is then revised to incorporate these comments. Although this document has undergone extensive review, there may still be shortcomings. Comments subsequent to publication are welcome and will be addressed based on available time and resources. In addition, any information on process descriptions, operating parameters, control measures, and emissions information that would enable EPA to improve on the contents of this document is welcome. All comments should be sent to:

Group Leader
Emission Factor and Inventory Group (MD-14)
Office of Air Quality Planning and Standards
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 2.0
OVERVIEW OF DOCUMENT CONTENTS

This section briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 provides a brief summary of the physical and chemical characteristics of benzene and an overview of its production, uses, and emissions sources. This background section may be useful to someone who needs to develop a general perspective on the nature of benzene, how it is manufactured and consumed, and sources of emissions.

Section 4.0 focuses on the production of benzene and the associated air emissions. For each major production source category described in Section 4.0, an example process description and a flow diagram(s) with potential emission points are given. Available emissions estimates are used to calculate emission factors that show the potential for benzene emissions before and after controls employed by industry. Also provided are estimates of emissions from process vents, equipment leaks, storage tanks, and wastewater. Individual companies that are reported in trade publications to produce benzene are named.

Section 5.0 describes major source categories that use benzene as a feedstock to produce industrial organic chemicals. For each major production process, a description(s) of the process is given along with a process flow diagram(s). Potential emission points are identified on the diagrams and emission ranges are presented, where available. Individual companies that use benzene as a feedstock are reported.

Section 6.0 describes emission sources where benzene is emitted as the by-product of a process (such as petroleum refineries) and post-manufacturing activities where releases from benzene-containing products may occur (such as from gasoline distribution). Example process descriptions and flow diagrams are provided in addition to available emission factors for each major industrial category described in this section.

Section 7.0 presents information on stationary combustion sources (such as municipal waste combustors) and area combustion sources (such as open burning). Example incinerator, furnace, or boiler diagrams are given, when appropriate. Emission factors are also given, when available.

Section 8.0 provides a brief summary on benzene emissions from mobile sources. This section addresses both on-road and off-road sources. Section 9.0 summarizes available procedures for source sampling and analysis of benzene. This section provides an overview of applicable sampling procedures and cites references for those interested in conducting source tests. Section 10.0 presents a list of all the references cited in this document.

Appendix A presents a summary table of the emission factors contained in this document. This table also presents the factor quality rating and the Source Classification Code (SCC) or Area/Mobile Source (AMS) code associated with each emission factor. Appendix B presents a list of all the petroleum refineries in the United States.

Each emission factor listed in Sections 4.0 through 8.0 was assigned an emission factor rating (A, B, C, D, E, or U), based on the criteria for assigning data quality ratings and emission factor ratings as discussed in the document *Procedures for Preparing Emission Factor Documents*.[2] The criteria for assigning the data quality ratings are as follows:

A - Tests are performed by using an EPA reference test method, or when not applicable, a sound methodology. Tests are reported in enough detail for adequate validation, and, raw data are provided that can be used to duplicate the emission results presented in the report.

B - Tests are performed by a generally sound methodology, but lacking enough detail for adequate validation. Data are insufficient to completely duplicate the emission result presented in the report.

C - Tests are based on an unproven or new methodology, or are lacking a significant amount of background information.

D - Tests are based on generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

Once the data quality ratings for the source tests had been assigned, these ratings along with the number of source tests available for a given emission point were evaluated. Because of the almost impossible task of assigning a meaningful confidence limit to industry-specific variables (e.g., sample size vs. sample population, industry and facility variability, method of measurement), the use of a statistical confidence interval for establishing a representative emission factor for each source category was not practical. Therefore, some subjective quality rating was necessary. The following emission factor quality ratings were used in the emission factor tables in this document:

A - Excellent. Emission factor is developed primarily from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability.

B - Above average. Emission factor is developed primarily from A- or B-rated test data from a moderate number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.

C - Average. Emission factor is developed primarily from A-, B-, and C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.

D - Below average. Emission factor is developed primarily form A-, B-, and C-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.

E - Poor. Factor is developed from C- rated and D-rated test data from a very few number of facilities, and there may be reasons to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

U - Unrated (Only used in the L&E documents). Emission factor is developed from source tests which have not been thoroughly evaluated, research papers, modeling data, or other sources that may lack supporting documentation. The data are not necessarily “poor,” but there is not enough information to rate the factors according to the rating protocol.

This document does not contain any discussion of health or other environmental effects of benzene, nor does it include any discussion of ambient air levels.

SECTION 3.0
BACKGROUND INFORMATION

3.1 NATURE OF POLLUTANT

Benzene is a clear, colorless, aromatic hydrocarbon that has a characteristic sickly sweet odor. It is both volatile and flammable. Chemical identification information for benzene is found in Table-3-1. Selected physical and chemical properties of benzene are presented in Table 3-2 .[4-7]

Benzene contains 92.3 percent carbon and 7.7 percent hydrogen (by mass). The benzene molecule is represented by a hexagon formed by six sets of carbon and hydrogen atoms bonded together with alternating single and double bonds.

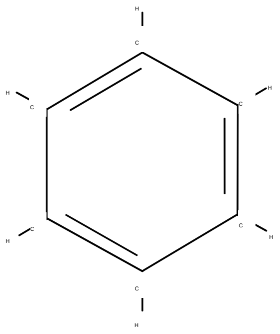


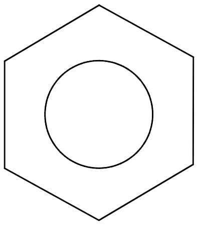
TABLE 3-1. CHEMICAL IDENTIFICATION OF BENZENE

Chemical Name	Benzene
Synonyms	Benzol, phenyl hydride, coal naphtha, phene, benxole, cyclohexatriene
Molecular formula	C_6H_6
Identification numbers[a]	
CAS Registry	71-43-2
NIOSH RTECS	CY 1400000
DOT/UN/NA	UN 1114; Benzene (Benzol)
DOT Designation	Flammable liquid

Source: References 4 and 5.

[a] Chemical Abstract Services (CAS); National Institute of Occupational Safety and Health (NIOSH); Registry of Toxic Effects of Chemical Substances (RTECS); Department of Transportation/United Nations/North American (DOT/UN/NA).

The chemical behavior of benzene indicates that the benzene molecule is more realistically represented as a resonance-stabilized structure:



in which the carbon-to-carbon bonds are identical. The benzene molecule is the cornerstone for aromatic compounds, all of which contain one or more benzene rings.[8]

Because of its resonance properties, benzene is highly stable for an unsaturated hydrocarbon. However, it does react with other compounds, primarily by substitution and, to a lesser degree, by addition. Some reactions can rupture the molecule or result in other groups cleaving to the molecule. Through all these types of reactions, many commercial chemicals are produced from benzene.[8] The most common commercial grade of benzene contains 50 to

TABLE 3-2. PHYSICAL AND CHEMICAL PROPERTIES OF BENZENE

Property	Value
Molecular weight	0.17 lbs (78.12 g)
Melting point	41.9°F (5.5°C)
Boiling point at 1 atmosphere (760 mm Hg)	176.18°F (80.1°C)
Density, at 68°F (20°C)	0.0141 lb/ft^3 (0.8794 g/cm^3)
Physical state (ambient conditions)	Liquid
Color	Clear
Odor	Characteristic
Viscosity (absolute) at 68°F (20°C)	0.6468 cP
Surface tension at 77°F (25°C)	0.033 g/cm^3 (28.18 dynes/cm^3)
Heat of vaporization at 176.18°F (80.100°C)	33.871 KJ/Kg·mol (8095 Kcal/Kg·mol)
Heat of combustion at constant pressure and 77°F (25°C) (liquid C_6H_6 to liquid H_2O and gaseous CO_2)	41.836 KJ/g (9.999 Kcal/g)
Odor threshold	0.875 ppm
Solubility:	
Water at 77°F (25°C)	Very slightly soluble (0.180 g/100 mL, 1800 ppm)
Organic Solvents	Soluble in alcohol, ether, acetone, carbon tetrachloride, carbon disulfide, and acetic acid
Vapor pressure at 77°F (25°C)	95.2 mm Hg (12.7 kPa)
Auto ignition temperature	1044°F (562°C)
Flashpoint	12°F (-11.1°C) (closed cup)
Conversion factors (Vapor weight to volume)	1 ppm = 319 mg/m^3 at 77°F (25°C); 1 mg/L = 313 ppm

Source: References 4, 5, 6, and 7.

100 percent benzene, the remainder consisting of toluene, xylene, and other constituents that distill below 248°F (120°C).[4]

Laboratory evaluations indicate that benzene is minimally photochemically reactive in the atmosphere compared to the reactivity of other hydrocarbons. Reactivity can be determined by comparing the influence that different hydrocarbons have on the oxidation rate of nitric oxide (NO) to nitrogen dioxide (NO_2), or the relative degradation rate of various hydrocarbons when reacted with hydroxyl radicals (OH), atomic oxygen or ozone. For example, based on the NO oxidation test, the photochemical reactivity rate of benzene was determined to be one-tenth that of propylene and one-third that of n-hexane.[9]

Benzene shows long-term stability in the atmosphere.[8] Oxidation of benzene will occur only under extreme conditions involving a catalyst or elevated temperature or pressure. Photolysis is possible only in the presence of sensitizers and is dependent on wavelength absorption. Benzene does not absorb wavelengths longer than $1.1\text{x}10^{-5}$ inches (in) (275 nanometers [nm]).[8]

In laboratory evaluation, benzene is predicted to form phenols and ring cleavage products when reacted with OH, and to form quinone and ring cleavage products when reacted with aromatic hydrogen.[6] Other products that are predicted to form from indirect reactions with benzene in the atmosphere include aldehydes, peroxides, and epoxides. Photodegradation of NO_2 produces atomic oxygen, which can react with atmospheric benzene to form phenols.[9]

3.2 OVERVIEW OF PRODUCTION AND USE

During the eighteenth century, benzene was discovered to be a component of oil, gas, coal tar, and coal gas. The commercial production of benzene from coal carbonization began in the United States around 1941. It was used primarily as feedstock in the chemical manufacturing industry.[10] For United States industries, benzene is currently produced in the United States, the Virgin Islands, and Puerto Rico by 26 companies at

36 manufacturing facilities.[11] The majority of benzene production facilities in the United States are found in the vicinity of crude oil sources, predominantly located around the Texas and Louisiana Gulf coast. They are also scattered throughout Kentucky, Pennsylvania, Ohio, Illinois, and New Jersey.[11]

Domestic benzene production in 1992 was estimated at 2,350 million gallons (gal) (8,896 million L).[11] Production was expected to increase by approximately 3 to 3.5 percent per year through 1994. Exports of benzene in 1993 were about 23 million gal (87 million L), around 1 percent of the total amount produced in the United States.[12]

Benzene is produced domestically by five major processes.[12] Approximately 45 percent of the benzene consumed in the United States is produced by the catalytic reforming/separation process.[11] With this process, the naphtha portion of crude oil is mixed with hydrogen, heated, and sent through catalytic reactors.[13] The effluent enters a separator while the hydrogen is flashed off.[13] The resulting liquid is fractionated and the light ends (C_1 to C_4) are split. Catalytic reformate, from which aromatics are extracted, is the product.[13]

Approximately 22 percent of the benzene produced in the United States is derived from ethylene production.[11] Pyrolysis gasoline is a by-product formed from the steam cracking of natural gas concentrates, heavy naphthas, or gas oils to produce ethylene.[14]

Toluene dealkylation or toluene disproportionation processes account for another 25 percent of the United States production of benzene.[11] Toluene dealkylation produces benzene and methane from toluene or toluene-rich hydrocarbons through cracking processes using heat and hydrogen. The process may be either fixed-bed catalyst or thermal. Toluene disproportionation produces benzene and xylenes as co-products from toluene using similar processes.[15]

Three percent of benzene produced in the United States is derived from coke oven light oil distillation at coke by-product plants.[11] Light oil is recovered from coke oven gas, usually by continuous countercurrent absorption in a high-boiling liquid from which it is stripped by steam distillation.[9] A light oil scrubber or spray tower removes the light oil from coke oven gas.[10] Benzene is recovered from the light oil by a number of processes, including fractionating to remove the lighter and heavier hydrocarbons, hydrogenation, and conventional distillation.

Finally, about 2 percent of benzene produced in the United States is derived as a coproduct from xylene isomerization.[11] Figure 3-1 presents a simplified production and use tree for benzene. Each major production process is shown, along with the percent of benzene derived from each process. The primary uses of benzene and the percentage for each use are also given in the figure.

The major use of benzene is still as a feedstock for chemical production, as in the manufacture of ethylbenzene (and styrene). In 1992, the manufacture of ethylbenzene (and styrene) accounted for 53 percent of benzene consumption.[12] Ethylbenzene is formed by reacting benzene with ethylene and propylene using a catalyst such as anhydrous aluminum chloride or solid phosphoric acid.[8] Styrene is the product of dehydrogenation of ethylbenzene.[9]

Twenty-three percent of the benzene supply is used to produce cumene.[12] Cumene is produced from benzene alkylation with propylene using solid phosphoric acid as a catalyst.[7] Cumene is oxidized to produce phenols and acetone.[12] Phenol is used to make resins and resin intermediates for epoxies and polycarbonates, and caprolactam for nylon.[12] Acetone is used to make solvents and plastics.[16]

Cyclohexane production accounts for 13 percent of benzene use.[12] Cyclohexane is produced by reducing benzene hydrogenated vapors using a nickel catalyst at 392°F (200°C). Almost all of cyclohexane is used to make nylon or nylon intermediates.[17]

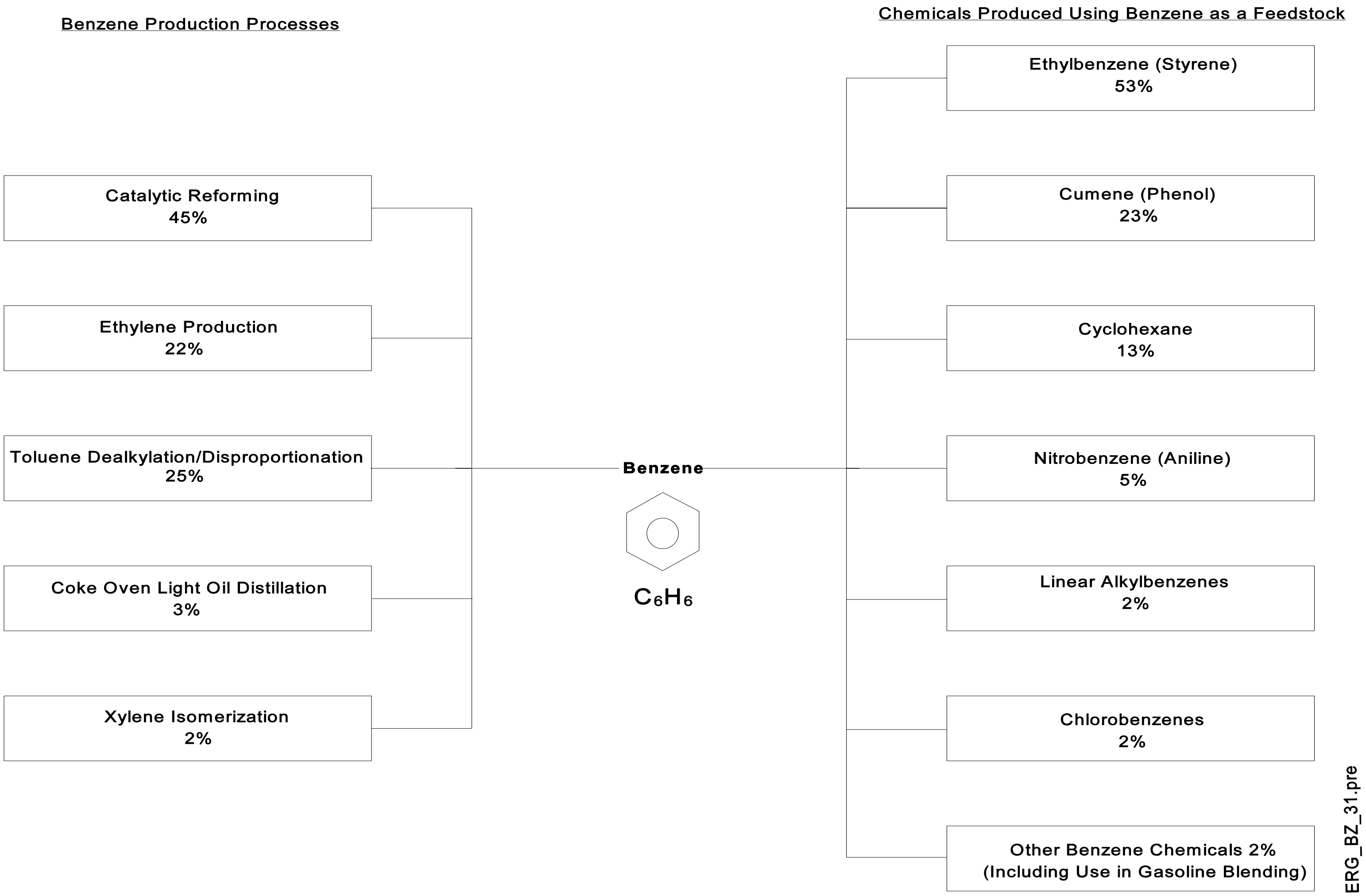


Figure 3-1. Production and Use Tree for Benzene

Source: References 11 and 12.

The production of nitrobenzene, from which aniline is made, accounts for 5 percent of benzene consumption. Nitrobenzene is produced by the nitration of benzene with a concentrated acid mixture of nitric and sulfuric acid. Nitrobenzene is reduced to form aniline.[10] Aniline, in turn, is used to manufacture isocyanates for polyurethane foams, plastics, and dyes.[18]

Chlorobenzene production accounts for 2 percent of benzene use. The halogenation of hot benzene with chlorine yields chlorobenzene. Monochlorobenzene and dichlorobenzene are produced by halogenation with chlorine using a molybdenum chloride catalyst.[19]

The remainder of the benzene produced is consumed in the production of other chemicals. Other benzene-derived chemicals include linear alkylbenzene, resorcinol, and hydroquinone.

Though much of the benzene consumed in the United States is used to manufacture chemicals, another important use is in gasoline blending. Aromatic hydrocarbons, including benzene, are added to vehicle fuels to enhance octane value. As lead content of fuels is reduced, the amount of aromatic hydrocarbons is increased to maintain octane rating, such that the benzene content in gasoline was increased in recent years.[4] The concentration of benzene in refined gasoline depends on many variables, such as gasoline grade, refinery location and processes, and crude source.[6] The various sources of benzene emissions associated with gasoline marketing are discussed in Section 6.0, and benzene emissions associated with motor vehicles are discussed in Section 8.0 of this document.

3.3 OVERVIEW OF EMISSIONS

Sources of benzene emissions from its production and uses are typical of those found at any chemical production facility:

- Process vents;

- Equipment leaks;
- Waste streams (secondary sources);
- Transfer and storage; and
- Accidental or emergency releases.

These sources of benzene emissions are described in Sections 4.0 and 5.0 of this document.

Miscellaneous sources of benzene including oil and gas production, glycol dehydrators, petroleum refineries, gasoline marketing, POTWs, landfills, and miscellaneous manufacturing processes are addressed in Section 6.0. Combustion sources emitting benzene are addressed in Section 7.0. Section 8.0 presents a discussion of benzene emissions from mobile sources. Recent work by the EPA Office of Mobile Sources on benzene in vehicle exhaust resulted in revised emission factors.[20] For off-road vehicles, EPA has also completed a recent study to estimate emissions.

SECTION 4.0

EMISSIONS FROM BENZENE PRODUCTION

This section presents information on the four major benzene production source categories that may discharge benzene air emissions. The four major processes for producing benzene are:

- Catalytic reforming/separation;
- Toluene dealkylation and disproportionation;
- Ethylene production; and
- Coke oven light oil distillation.

For each of these production source categories, the following information is provided in the sections below: (1) a brief characterization of the national activity in the United States, (2) a process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed. Table 4-1 lists U. S. producers of benzene and the type of production process used.[11]

Following the discussion of the major benzene production source categories, Section 4.5 contains a discussion of methods for estimating benzene emissions from process vents, equipment leaks, storage tanks, wastewater, and transfer operations. These emissions estimation methods are discussed in general terms and can be applied to the source categories in this section as well as the source categories in Section 5.0.

TABLE 4-1. BENZENE PRODUCTION FACILITIES

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Amerada Hess Corporation	St. Croix, Virgin Islands	75 (284)	Catalytic reformate;
Hess Oil Virgin Islands Corporation, subsidiary			toluene; no captive use
American Petrofina, Incorporated	Port Arthur, Texas	33 (125)	Catalytic reformate; partly captive
Fina Oil and Chemical Company, subsidiary		31 (117)	Toluene; partly captive
Amoco Corporation	Texas City, Texas	85 (322)	Catalytic reformate; partly captive
Amoco Oil Company, subsidiary		25 (95)	Pyrolysis gasoline; partly captive
		12 (45)	Xylene isomerization
Aristech Chemical Corporation	Clairton, Pennsylvania	45 (170)	Coke-oven light oil
Ashland Oil, Incorporated	Catlettsburg, Kentucky	55 (208)	Coke-oven light oil; captive
Ashland Chemical Company, division		2 (8)	Catalytic reformate; captive
Petrochemicals Division			
Atlantic Richfield Corporation	Channelview, Texas	90 (341)	Pyrolysis gasoline; captive
Lyondell Petrochemical Company, subsidiary	Houston, Texas	35 (132)	Catalytic reformate; no captive use
		15 (57)	Toluene; no captive use

(continued)

TABLE 4-1. CONTINUED

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
BP Oil	Alliance, Louisiana	18 (68)	Catalytic reformate; no captive use
		47 (178)	Toluene
	Lima, Ohio	35 (132)	Catalytic reformate; no captive use
		80 (303)	Toluene
Chevron Corporation	Philadelphia, Pennsylvania	24 (91)	Catalytic reformate; captive
Chevron Chemical Company, subsidiary		21 (79)	Toluene; captive
Aromatics and Derivatives Division	Port Arthur, Texas	42 (159)	Catalytic reformate; partly captive
		24 (91)	Pyrolysis gasoline; partly captive
		35 (132)	Toluene; partly captive
Citgo Petroleum Corporation	Corpus Christi, Texas	55 (208)	Catalytic reformate; captive
		23 (87)	Toluene
Coastal Eagle Point Oil Co.	Westville, New Jersey	15 (57)	Catalytic reformate
Coastal Refining and Marketing, Inc.	Corpus Christi, Texas	50 (189)	Toluene; captive use
		7 (26)	Catalytic reformate
Dow Chemical U.S.A.	Freeport, Texas	25 (95)	Pyrolysis gasoline; captive
	Plaquemine, Louisiana	80 (303)	Pyrolysis gasoline; captive
		120 (454)	Toluene; captive

(continued)

TABLE 4-1. CONTINUED

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Exxon Corporation Exxon Chemical Company, division Exxon Chemical Americas	Corpus Christi, Texas	50 (189)	Pyrolysis gasoline
		30 (114)	Toluene
	Baton Rouge, Louisiana	50 (189)	Catalytic reformate
		30 (114)	Pyrolysis gasoline; no captive use
	Baytown, Texas	75 (284)	Catalytic reformate; no captive use
		20 (76)	Pyrolysis gasoline
		20 (76)	Xylene isomerization
		23 (87)	Toluene
Huntsman Chemical Corporation	Bayport, Texas	15 (57)	Toluene; captive
Kerr-McGee Corporation Southwestern Refining Company, Incorporated, subsidiary	Corpus Christi, Texas	17 (64)	Catalytic reformate; no captive use
Koch Industries, Incorporated Koch Refining Company, subsidiary	Corpus Christi, Texas	25 (95)	Catalytic reformate; captive
		55 (208)	Toluene; captive
		10 (38)	Xylene isomerization
		50 (189)	Toluene
Mobil Corporation Mobil Oil Corporation Mobil Chemical Company, division Petrochemicals Division U.S. Marketing and Refining Division	Beaumont, Texas	90 (341)	Catalytic reformate; no captive use
		10 (38)	Pyrolysis gasoline
		20 (76)	Catalytic reformate; no captive use
	Chalmette, Louisiana		

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Occidental Petroleum Corporation Petrochemicals Olefins and Aromatics Division	Chocolate Bayou, Texas	60 (227) 40 (151)	Pyrolysis gasoline Toluene
Phibro Energy USA, Inc.	Houston, Texas	5 (19)	Catalytic reformate; no captive use
Phillips Petroleum Company Chemicals Division Olefins and Cyclics Branch	Sweeny, Texas	11 (42)	Catalytic reformate; captive
Phillips Puerto Rico Core, Incorporated, subsidiary	Guayama, Puerto Rico	35 (132) 48 (182)	Catalytic reformate; captive Toluene; captive
Shell Oil Company Shell Chemical Company, division	Deer Park, Texas	75 (284) 80 (303)	Catalytic reformate; partly captive Pyrolysis gasoline; partly captive
	Wood River, Illinois	50 (189)	Catalytic reformate; no captive use
Sun Company, Incorporated Sun Refining and Marketing Company, Incorporated, subsidiary	Marcus Hook, PA	26 (98) 11 (42)	Catalytic reformate; no captive use Toluene; no captive use
	Toledo, Ohio	19 (72)	Catalytic reformate

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Texaco, Incorporated	El Dorado, Kansas	15 (57)	Catalytic reformate; captive
Texaco Chemical Company, subsidiary	Port Arthur, Texas	46 (174)	Catalytic reformate; captive
		20 (76)	Pyrolysis gasoline; captive
The UNO-VEN Company	Lemont, Illinois	12 (45)	Catalytic reformate
		7 (26)	Coke-oven light oil; no captive
USX Corporation	Lake Charles, Louisiana	55 (208)	Catalytic reformate; captive
Marathon Oil Company, subsidiary	Texas City, Texas	7 (26)	Toluene
Marathon Petroleum Company, subsidiary			
TOTAL		2,350(8,896)	

Source: Reference 11.

[a] Captive means used for subsequent processes on site.

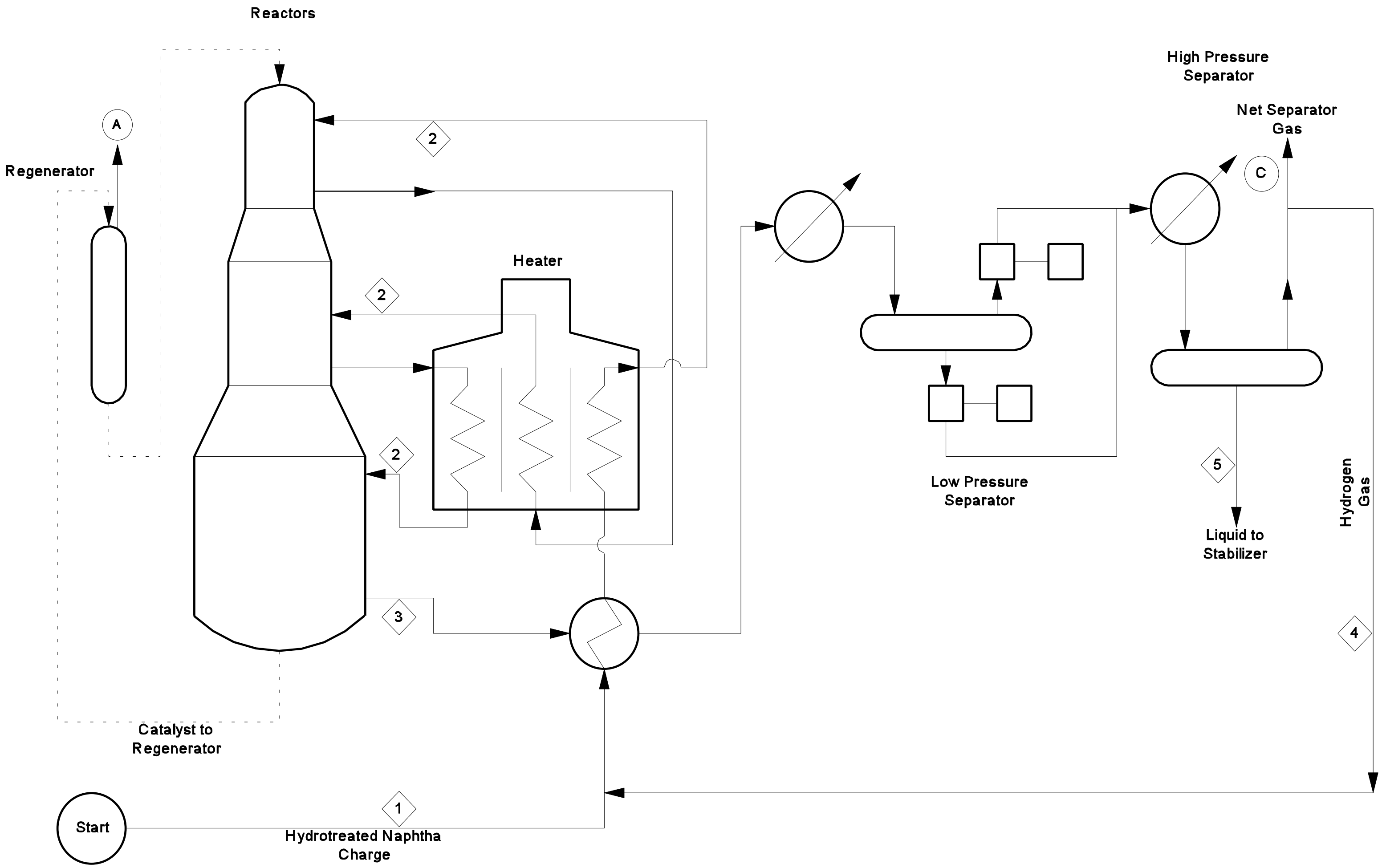
Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel. Reference SRI '93 indicates these data reflect changes made in product locations as of January 1993.

4.1 CATALYTIC REFORMING/SEPARATION PROCESS

Production of benzene by reforming/separation is associated with the production of toluene and xylene (BTX plants). Catalytic reforming is used to prepare high-octane blending stocks for gasoline production and for producing aromatics as separate chemicals. The reforming process, shown in Figure 4-1,[22] accounts for about 45 percent of all benzene produced in the United States.[12] In the following description of the reforming process, potential emission points are identified; however, not all of the emission points discussed in this section are always present at plants using this production process. Some companies have indicated that they have closed systems; others have indicated that process vent emissions are well-controlled by flares or scrubbers.[22]

4.1.1 Process Description for Catalytic Reforming/Separation

The reforming process used at BTX plants (shown in Figure 4-1) can greatly increase the aromatic content of petroleum fractions by such reactions as dehydrogenation, isomerization and dehydrogenation, or cyclization. The usual feedstock in this process is a straight-run, hydrocracked, thermally cracked, or catalytically cracked naphtha. After the naphtha is hydrotreated to remove sulfur (Stream 1), it is mixed with recycled hydrogen (Stream 4) and heated. This feed (Stream 2) is sent through catalytic reactors in which the catalyst, usually platinum or rhenium chloride, converts paraffins to aromatic compounds. The product stream (Stream 3) consists of excess hydrogen and a reformate rich in aromatics. Products from the reactor (Stream 3) are fed to the separation section, which separates the hydrogen gas from the liquid product. The hydrogen gas can be recycled to the reactor (Stream 4). The liquid product from the separator (Stream 5) is fed to a stabilizer (not shown in the figure).[22] The stabilizer is a fractionator in which more volatile, light hydrocarbons are removed from the high-octane liquid product. The liquid is then sent to a debutanizer (not shown in the figure). Aromatics (benzene, toluene, and mixed xylenes) are then extracted from the stabilized reformate.[22]



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-1. Universal Oil Products Platforming (Reforming) Process

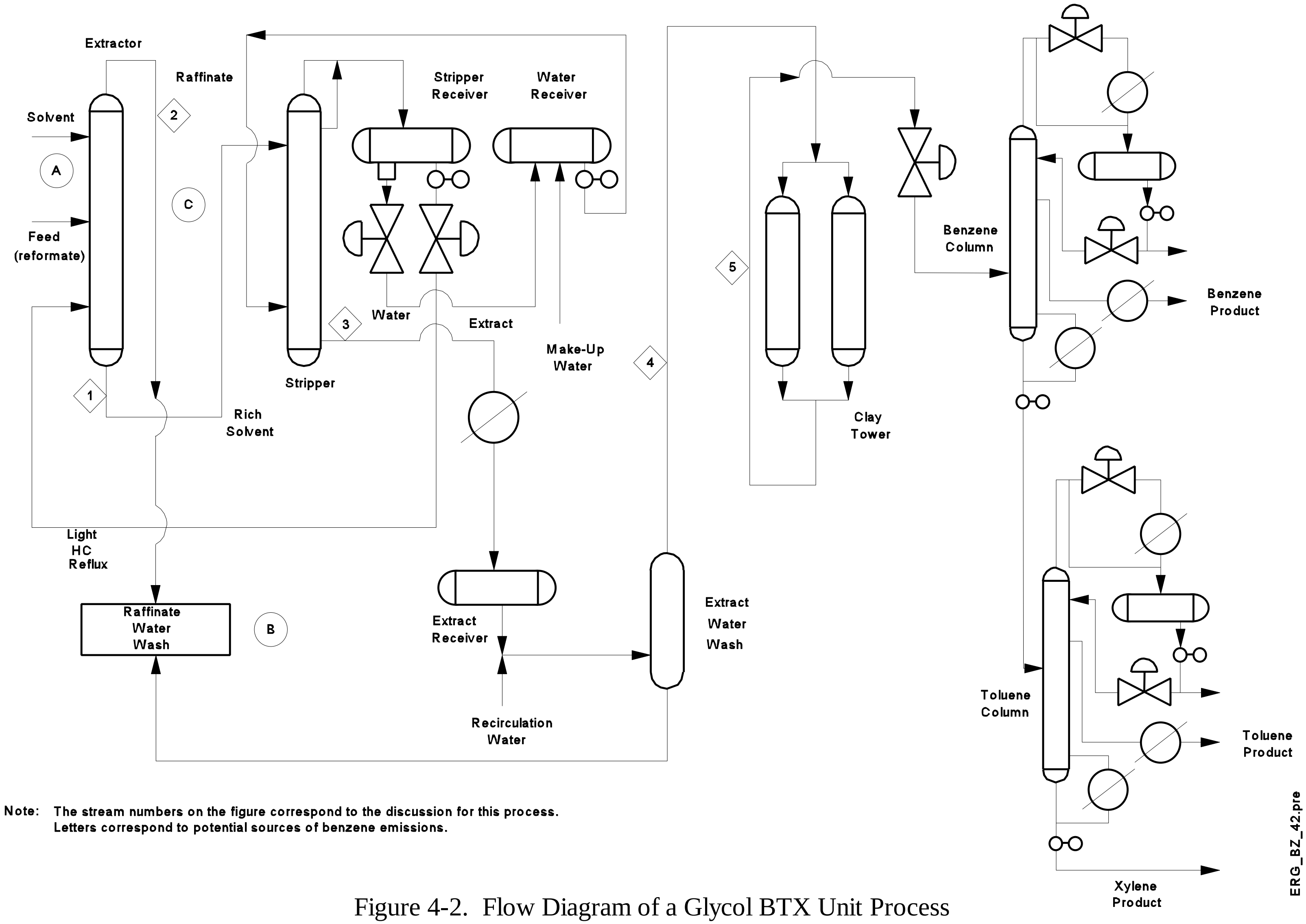
Source: Reference 22.

Numerous solvents are available for the extraction of aromatics from the stabilized reformate stream. Glycols (tetraethylene glycol) and sulfolane (1,1-tetrahydrothiophene dioxide) are most commonly used. The processes in which these solvents are used are similar, so only the glycol process is described here. In the glycol process shown in Figure 4-2, aromatics are separated from the reformate in the extractor.[22] The raffinate (stream 2) is water-washed and stored. The dissolved aromatics extract (Stream 1) is steam-stripped and the hydrocarbons separated from the solvent. The hydrocarbon stream (Stream 3) is water-washed to remove remaining solvent and is then heated and sent through clay towers to remove olefins (Stream 4). Benzene, toluene, and xylene (Stream 5) are then separated by a series of fractionation steps.[22]

4.1.2 Benzene Emissions from Catalytic Reforming/Separation

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the catalytic reforming/separation process is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points from this process, the reader is referred to Section 4.5 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

A literature search, a review of materials in the docket (A-79-27) for some National Emission Standards for Hazardous Air Pollutants (NESHAP) efforts on benzene, and information provided by the benzene production industry revealed no source-specific emission factors for benzene from catalytic reforming/separation.[22] However, information provided by the benzene production industry indicates that BTX is commonly produced in closed systems, and that any process vent emissions are well-controlled by flares and/or scrubbers. (See Section 4.5 of this chapter for a discussion of control devices.)[22] Furthermore, some descriptive data were found, indicating that benzene may be emitted from the



Note: The stream numbers on the figure correspond to the discussion for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-2. Flow Diagram of a Glycol BTX Unit Process

Source: Reference 22.

catalytic/reforming process during catalyst regeneration or replacement, during recycling of hydrogen gas to the reformer, and from the light gases taken from the separator. These potential emission points are labeled as A, B, and C, respectively, in Figure 4-1.

One general estimate of the amount of benzene emitted by catalytic reforming/separation has been reported in the literature. In this reference, it was estimated that 1 percent of total benzene produced by catalytic reforming is emitted.[23]

Benzene may be emitted from separation solvent regeneration, raffinate wash water, and raffinate in association with the separation processes following catalytic reforming. These potential sources are shown as A, B, and C, respectively, in Figure 4-2. However, no specific data were found showing emission factors or estimates for benzene emissions from these potential sources. One discussion of the Sulfolane process indicated that 99.9-percent recovery of benzene was not unusual. Therefore, the 0.1 percent unrecovered benzene may be a rough general estimate of the benzene emissions from separation processes.[23]

4.2 TOLUENE DEALKYLATION AND TOLUENE DISPROPORTIONATION PROCESS

Benzene can also be produced from toluene by hydrodealkylation (HDA) or disproportionation. The amount of benzene produced from toluene depends on the overall demand and price for benzene because benzene produced by HDA costs more than benzene produced through catalytic reforming or pyrolysis gasoline.[24] At present, benzene production directly from toluene accounts for almost 30 percent of total benzene produced.[11] Growth in demand for toluene in gasoline (as an octane-boosting component for gasoline blending) appears to be slowing because of increased air quality legislation to remove aromatics from gasoline. (At present, gasoline blending accounts for 30 percent of the end use of toluene.) If toluene is removed from the gasoline pool to any great extent, its value is expected to drop because surpluses will occur. In such a scenario, increased use of toluene to produce benzene by HDA or disproportionation would be expected.[24] At present, production of benzene by the HDA and disproportionation processes accounts for 50 percent of toluene end use.

4.2.1 Toluene Dealkylation

Process Description

Hydrodealkylation of toluene can be accomplished through thermal or catalytic processes.[25] The total dealkylation capacity is almost evenly distributed between the two methods.[10] As shown in Figure 4-3, pure toluene (92 to 99 percent) or toluene (85 to 90 percent) mixed with other heavier aromatics or paraffins from the benzene fractionation column is heated together with hydrogen- containing gas to 1,346°F (730°C) at a specified pressure (Stream 1) and is passed over a dealkylation catalyst in the reactor (Stream 2). Toluene reacts with the hydrogen to yield benzene and methane. The benzene may be separated from methane in a high-pressure separator (Stream 3) by flashing off the methane-containing gas.[25]

The product is then established (Stream 4), and benzene is recovered by distillation in the fractionalization column (Stream 5).[10] Recovered benzene is sent to storage (Stream 6). Unreacted toluene and some heavy aromatic by-products are recycled (Stream 7). About 70 to 85 percent conversion of toluene to benzene is accomplished per pass through the system, and the ultimate yield is 95 percent of the theoretical yield. Because there is a weight loss of about 23 percent, the difference in toluene and benzene prices must be high enough to justify use of the HDA process.

Benzene Emissions

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the toluene dealkylation process was reviewed. No source-specific emission factors were found for benzene emissions from its production through dealkylation of toluene. The reader is referred to Section 4.5 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

Potential sources of emissions from the dealkylation process include the separation of benzene and methane, distillation, catalyst regeneration, and stabilization.[23] These potential sources are shown as emission points A, B, C, and D respectively, in Figure 4-3.[10,15,25]

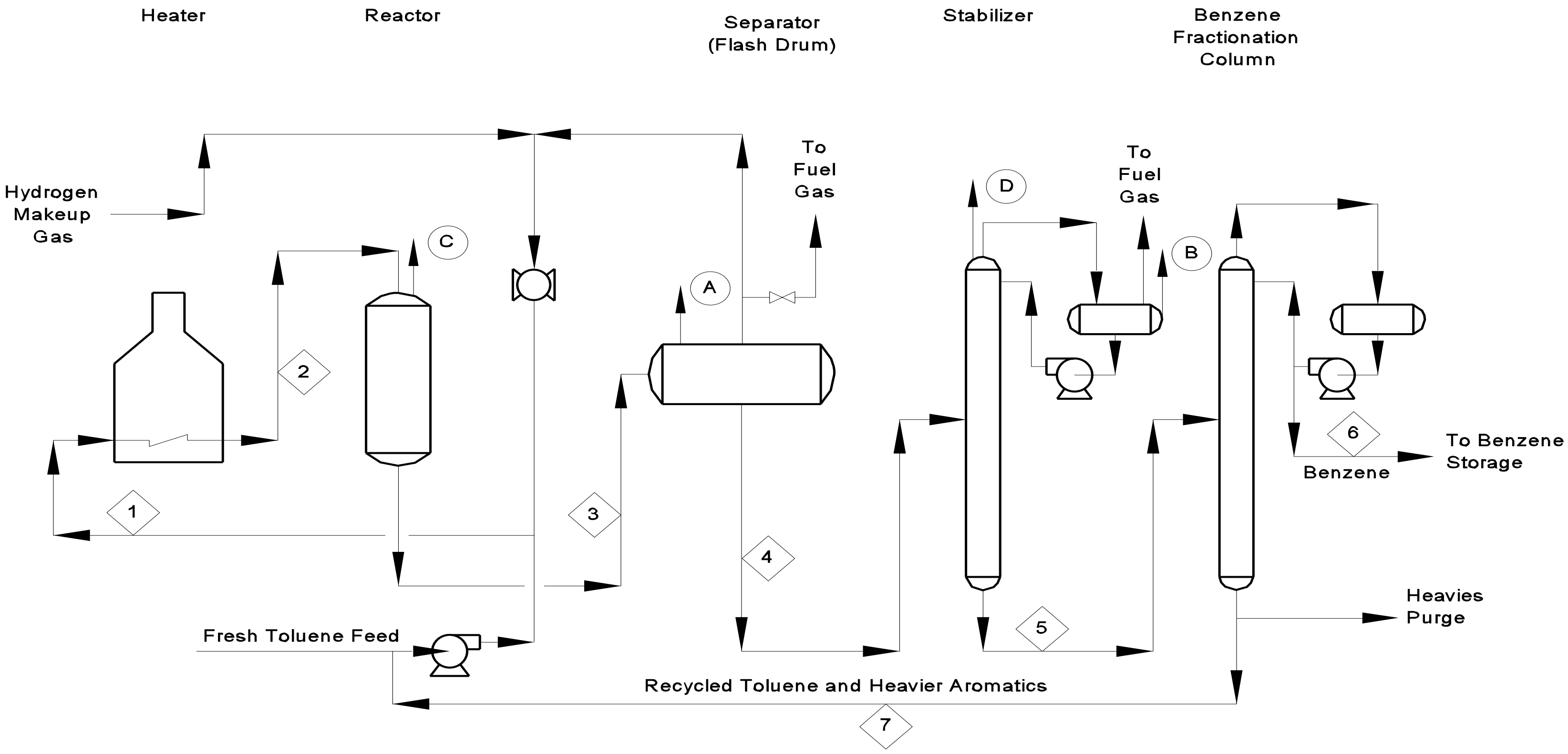
4.2.2 Toluene Disproportionation

Process Description

Toluene disproportionation (or transalkylation) catalytically converts two molecules of toluene to one molecule each of benzene and xylene.[24] As shown in Figure 4-4, the basic process is similar to toluene hydrodealkylation, but can occur under less severe conditions.[15,26] Transalkylation operates at lower temperatures, consumes little hydrogen, and no loss of carbon to methane occurs as with HDA.[24] Toluene material is sent to a separator for removal of off-gases (Stream 3). The product is then established (Stream 4) and sent through clay towers (Stream 5). Benzene, toluene, and xylene are recovered by distillation, and unreacted toluene is recycled (Stream 6). Note that if benzene is the only product required, then HDA is a more economical and feasible process.[27]

Benzene Emissions

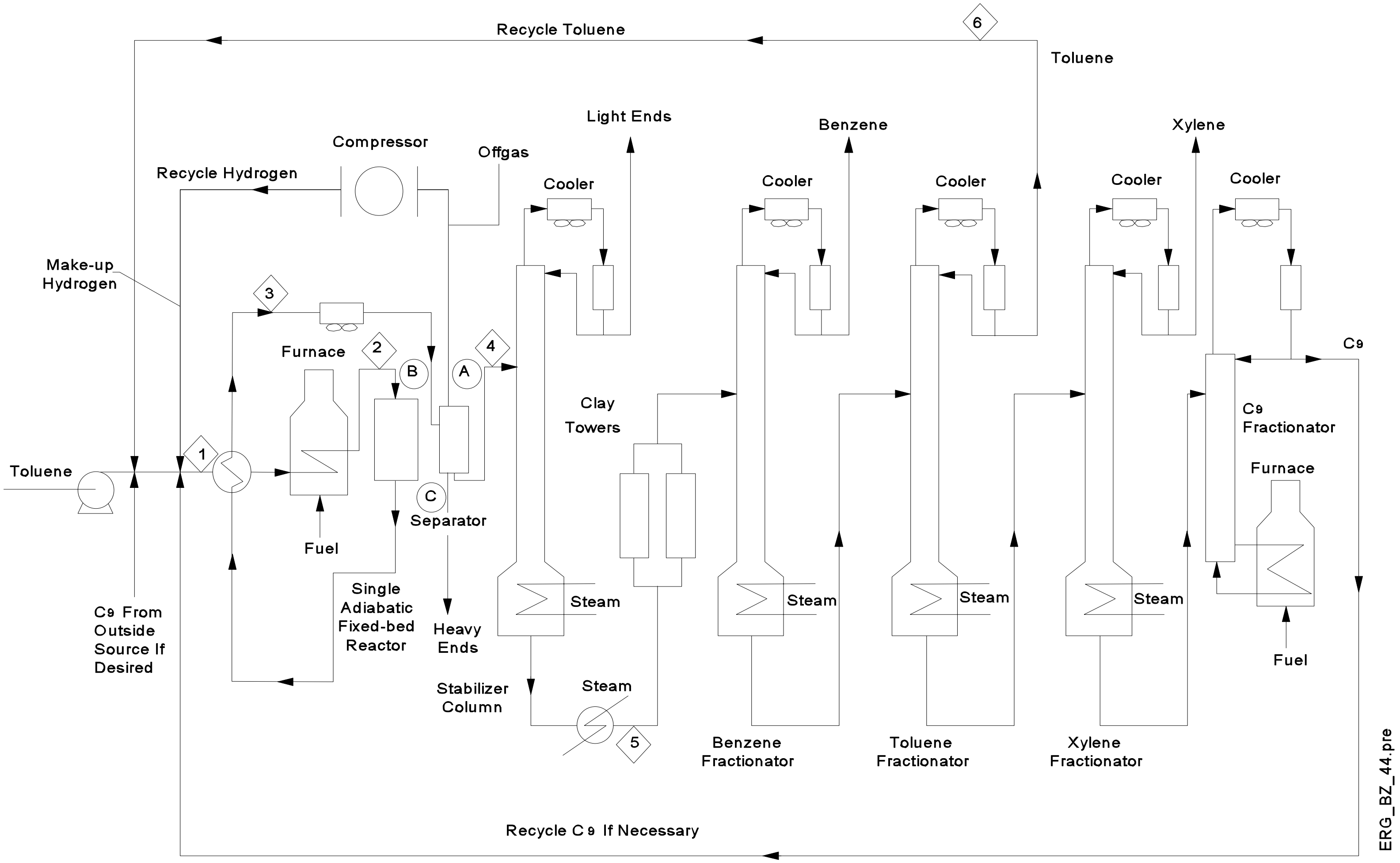
No specific emission factors were found for benzene emissions from its production via toluene disproportionation. Potential sources of benzene emissions from this process are associated with the separation of benzene and xylene, catalyst regeneration, and heavy hydrocarbons that do not break down.[23] These potential sources are shown as points A, B, and C, respectively, in Figure 4-4.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-3. Process Flow Diagram of a Toluene Dealkylation Unit

Source: References 10, 15, and 25.



Note: Stream numbers correspond to the discussion in the text for this process. Letters represent potential sources of benzene emissions.

Figure 4-4. Toluene Disproportionation Process Flow Diagram (Tatoray Process)

Source: References 15 and 26.

4.3 ETHYLENE PRODUCTION

4.3.1 Process Description

Ethylene is produced through pyrolysis of natural gas concentrates or petroleum fractions such as naphthas and atmospheric gas oils.[28] Pyrolysis gasoline is a liquid by-product formed as part of the steam-cracking process. The liquid pyrolysis gasoline is rich in benzene. Ethylene plants of the same production capacity, but using different feedstocks (ethane/propane versus naphthas/gas oils), will produce different amounts of pyrolysis gasoline with different benzene concentrations. For example, an ethylene plant producing 1 billion pounds (453.5 gigagrams [Gg]) of ethylene per year from ethane will produce about 16,097,023 lbs (7.3 Gg) pyrolysis gasoline with about 7,497,244 lbs (3.4 Gg) benzene in the pyrolysis gasoline.[28] A plant producing the same amount of ethylene from atmospheric gas oils will produce about 754,134,509 lbs (342 Gg) of pyrolysis gasoline containing 213,450,937 lbs (96.8 Gg) benzene.[28]

Because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from the pyrolysis gasoline. Table 4-1 lists facilities reported to recover benzene from pyrolysis gasoline. However, benzene can be emitted from ethylene plants that produce pyrolysis gasoline but do not recover benzene. Table 4-2 lists ethylene producers and their locations. To locate most of the potential sources of benzene from ethylene/pyrolysis gasoline plants, information is included here on ethylene/pyrolysis gasoline production, as well as information on recovery of benzene from pyrolysis gasoline. But because ethylene plants using naphthas/gas oils as feedstocks produce more pyrolysis gasoline and more often treat the gasoline prior to storage, these types of plants are emphasized in the following discussion.

Reference 28 provides more detailed information on ethylene plants using natural gas concentrates as feedstocks. In general, natural gas-using plants are less complex than naphtha-using plants. The potential emissions sources of benzene at the two types of

TABLE 4-2. ETHYLENE PRODUCERS - LOCATION AND CAPACITY

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Atlantic Richfield Company			
Lyondell Petrochemical Company, subsidiary	Channelview, Texas	3,360 (1,524)	Partly captive
The BF Goodrich Company			
BF Goodrich Chemical Group	Calvert City, Kentucky	350 (159)	Merchant
Chemicals & Speciality Products Group	Alvin, Texas	2,384 (1,081)	Mostly merchant
Chevron Corporation			
Chevron Chemical Company, subsidiary			
Olefins and Derivatives Division	Cedar Bayou, Texas	1,450 (658)	Mostly captive
	Port Arthur, Texas	1,250 (567)	Mostly captive use at Orange, Texas
Dow Chemical U.S.A.	Freeport, Texas	2,050 (930)	Captive
	Plaquemine, Louisiana	2,300 (1,043)	Captive
Du Pont			
Du Pont Chemicals	Orange, Texas	1,050 (476)	Captive
Eastman Chemical Company			
Texas Eastman Company	Longview, Texas	1,400 (635)	Mostly Captive

(continued)

TABLE 4-2. CONTINUED

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Exxon Chemical Company			
Exxon Chemical Americas	Baton Rouge, Louisiana	1,775 (805)	Captive
	Baytown, Texas	2,100 (953)	Some captive use at Mont Belvieu, Texas
Javelina Gas Processing	Corpus Christi, Texas	180 (82)	Recovered from gas by-products of local refineries; merchant
Koch Industries, Inc.			
Koch Refining Company, subsidiary	Corpus Christi, Texas	24 (11)	Captive
Mobil Oil Corporation			
Mobil Chemical Company, division	Beaumont, Texas	1,100 (499)	Mostly captive
Petrochemicals Division	Houston, Texas	500 (227)	Mostly captive
Occidental Petroleum Corporation			
Petrochemicals			
Olefins & Aromatics Division	Chocolate Bayou, Texas	1,100 (499)	Mostly captive
	Corpus Christi, Texas	1,700 (771)	Mostly captive
	Lake Charles, Louisiana	750 (340)	Captive
Phillips Petroleum Company			
Chemicals Division	Sweeny, Texas	2,550 (1,157)	Partly captive
Olefins and Cyclics Branch			

(continued)

TABLE 4-2. CONTINUED

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Quantum Chemical Corp. USI Division	Clinton, Iowa	900 (408)	Captive
	Deer Park, Texas	1,500 (680)	Captive
	Morris, Illinois	1,000 (454)	Captive
Rexene Corporation	Odessa, Texas	500 (228)	Partly captive
Shell Oil Company Shell Chemical Company, division	Deer Park, Texas	1,900 (862)	Partly merchant
	Noroco, Louisiana	2,560 (1,161)	Partly captive
Sun Refining and Marketing Co.	Brandenburg, Kentucky	NA	Captive
	Claymont, Delaware	250 (113)	Partly captive
Sweeny Olefins Limited Partnership	Sweeny, Texas	1,500 (680)	Merchant
Texaco Chemical Company	Port Arthur, Texas	1,150 (522)	Some captive use at Port Neches
	Port Neches, Texas	350 (159)	Captive
Union Carbide Corporation Industrial Chemicals Division	Seadrift, Texas	880 (399)	Captive
	Taft, Louisiana	1,405 (637)	Captive
	Texas City, Texas	1,400 (635)	Mostly captive

(continued)

TABLE 4-2. CONTINUED

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Union Texas Petroleum/BASF Corporation/GE Petrochemicals, Inc. Chemical Company	Geismar, Louisiana	1,160 (526)	Captive
Vista Chemical Company	Lake Charles, Louisiana	920 (417)	Mostly captive
Westlake Petrochemicals Corporation	Sulphur, Louisiana	1,000 (454)	Mostly captive
TOTAL		45,798 (20,774)	

Source: Reference 11.

[a] Captive means used for subsequent processes on site. Merchant means sold as a final product.

NA = not available

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as throughput and control measures; and should be determined through direct contacts with plant personnel. Data represent producers, locations, and capacities as of January 1993.

plants are similar, with smaller amounts of benzene being emitted from natural gas concentrate-using plants.

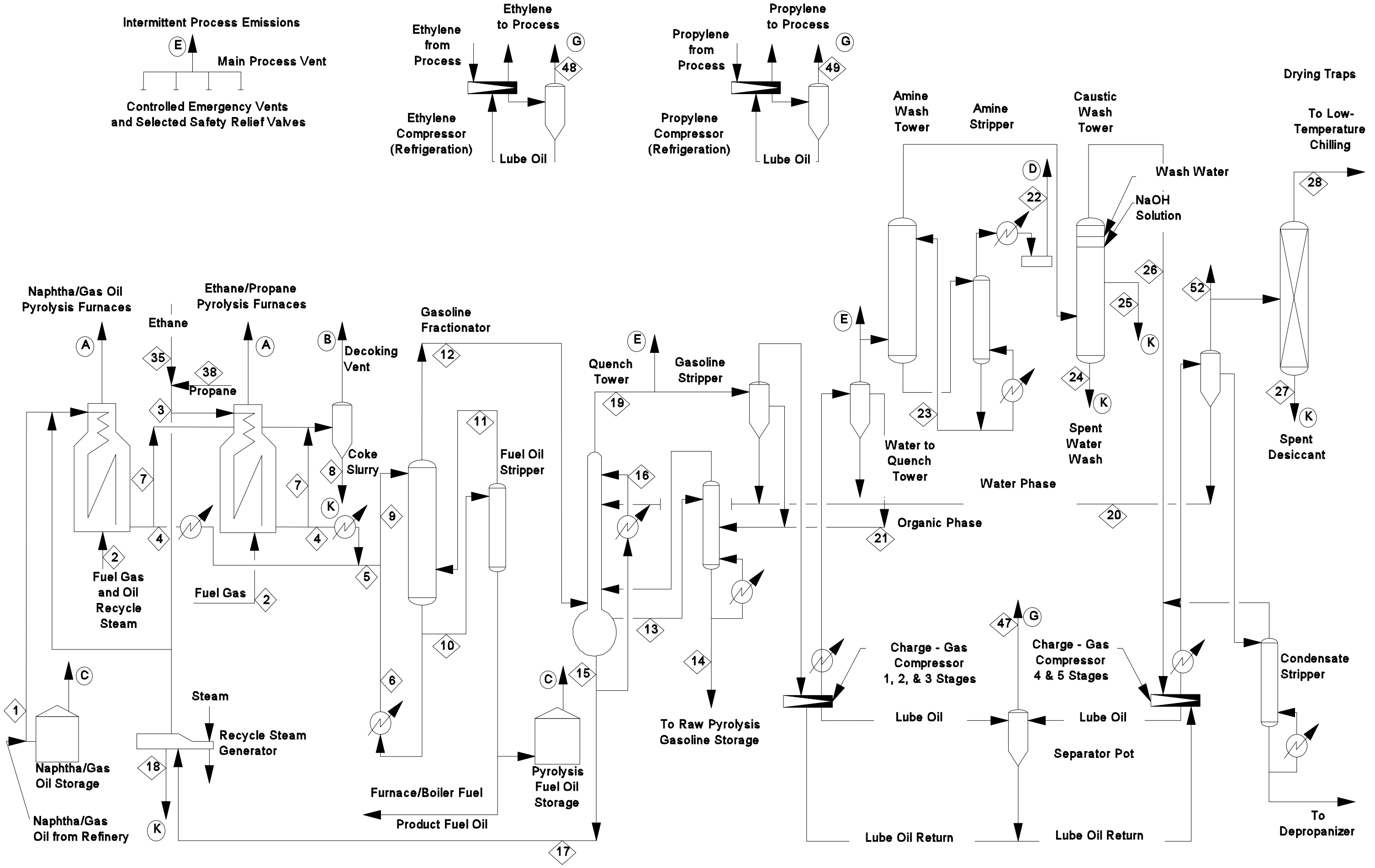
Ethylene/Pyrolysis Gasoline Production

A process flow diagram for a plant producing ethylene from naphtha and/or gas oil is shown in Figure 4-5. Many older facilities use larger numbers of compressors (in parallel) than are shown in the flow diagrams in Figure 4-5. For reference, Table 4-3 lists stream descriptions and corresponding stream numbers in Figure 4-5. The description of the process is taken almost entirely from Reference 28.

Naphtha and/or gas oil (Stream 1), diluted with steam, is fed in parallel to a number of gas- or oil-fired tubular pyrolysis furnaces. The fuel gas and oil (Stream 2) for these furnaces are supplied from gas and oil fractions removed from the cracked gas in later separation steps. Ethane and propane, which are present in the cracked gas and are separated in later distillation steps (Streams 35 and 38), are combined and recycled (Stream 3) through a separate cracking furnace. The resulting cracked gas is combined with the cracked gas from the naphtha/gas-oil furnaces (Stream 5). The flue gas from the pyrolysis furnaces is vented (Vent A on Figure 6).

During operation, coke accumulates on the inside walls of the reactor coils, and each furnace must be periodically taken out of service for removal of the accumulated coke. Normally, one furnace is out of service for decoking at all times. Decoking is accomplished by passing steam and air through the coil while the furnace is maintained at an elevated temperature, effectively burning the carbon out of the coil. While a furnace is being decoked, the exhaust is diverted (Stream 7) to an emissions control device (Vent B) whose main function is to reduce particulate emissions. The collected particles are removed as a slurry (Stream 8).

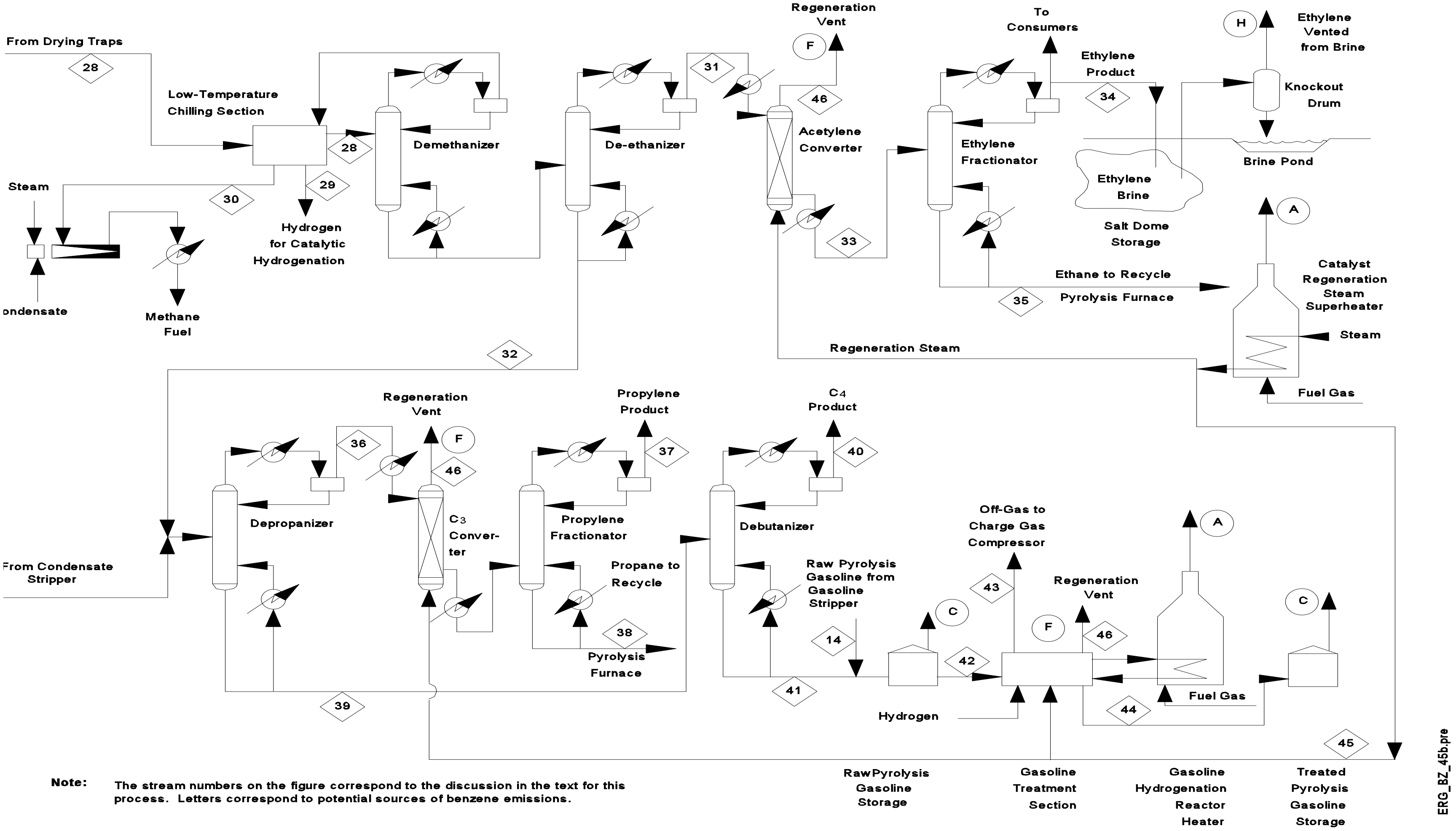
The cracked gas (Stream 4) leaving the pyrolysis furnaces is rapidly cooled (quenched) to 482 to 572°F (250 to 300°C) by passing it through transfer-line exchangers,



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-5. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds

Source: Reference 28.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-5. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds, continued

Source: Reference 28.

TABLE 4-3. STREAM DESIGNATIONS FOR FIGURE 4-5, PRODUCTION OF ETHYLENE FROM NAPHTHA AND/OR GAS-OIL FEEDS

Stream Number	Stream Description
1	Naphtha or gas oil feed
2	Fuel gas and oil
3	Ethane/propane recycle stream
4	Cracked gas
5	Cracked gas
6	Recycled pyrolysis fuel oil from gasoline fractionator
7	Furnace exhaust
8	Slurry of collected furnace decoking particles
9	Quenched cracked gas
10	Surplus fuel oil
11	Light fractions
12	Overheads from gasoline fractionator
13	Condensed organic phase
14	Raw pyrolysis gasoline to intermediate storage
15	Water phase (saturated with organics) from quench tower
16	Recycled water phase from heat exchangers
17	Surplus water from quench tower
18	Wastewater blowdown from recycle steam generator
19	Overheads from quench tower
20	Water condensed during compression
21	Organic fractions condensed during compression
22	Acid gas stripped in amine stripper
23	Diethanolamine (DEA)
24	Liquid waste stream from caustic wash tower
25	Liquid waste stream from caustic wash tower
26	Process gas stream from caustic wash tower
27	Solid waste stream from drying traps

(continued)

TABLE 4-3. CONTINUED

Stream Number	Stream Description
28	Process gas
29	Hydrogen rich stream from demethanizer
30	Methane rich stream from demethanizer
31	C_2 components from de-ethanizer
32	C_3 and heavier components from de-ethanizer
33	Hydrogenated acethylene from acetylene convertor
34	Overheads from ethylene fractionator
35	Ethane to recycle pyrolysis furnace
36	Overheads from depropanizer
37	Propylene (purified)
38	Propane to ethane/propane pyrolysis furnace
39	C_4 and heavier components to debutanizer
40	Overheads from debutanizer
41	C_5 and heavier components from debutanizer
42	Combined C_5 components and gasoline stripper bottoms fractions
43	Light ends to cracked gas compressor
44	C_5 and heavier components
45	Superheated stream
46	Stream and hydrocarbons
47	Organic vapor from separator pot
48	Organic vapor from separator pot
49	Organic vapor from separator pot

which end pyrolysis and simultaneously generate steam. The streams from the transfer-line exchangers (Stream 5) are combined and further quenched by the injection of recycled pyrolysis fuel oil from the gasoline fractionator (Stream 6).

The remaining operations shown in Figure 4-5 are required for separation of the various product fractions formed in the cracking of gas oil and/or naphtha; for removal of acid gases (primarily hydrogen sulfide [H_2S]) and carbon dioxide (CO_2) and water; and for hydrogenation of acetylene compounds to olefins or paraffins.

The quenched cracked gas (Stream 9) passes to the gasoline fractionator, where pyrolysis fuel oil is separated. Most of the fuel oil passes through water-cooled heat exchangers and is recycled (Stream 6) to the preceding oil-quenching operation. The surplus fuel oil (Stream 10), equivalent to the quantity initially present in the cracked gas, passes first to the fuel oil stripper, where light fractions are removed, and then to fuel oil storage. The light fractions (Stream 11) removed in the fuel oil stripper are recycled to the gasoline fractionator. The gasoline fractionator temperatures are well above the vaporization temperature of water, and the contained water remains as superheated steam, with the overhead stream containing the lighter cracked-gas components.

The overhead stream from the gasoline fractionator (Stream 12) passes to the quench tower, where the temperature is further reduced, condensing most of the water and part of the C_5 and heavier compounds. The condensed organic phase (Stream 13) is stripped of the lighter components in the gasoline stripper and is passed to raw pyrolysis gasoline intermediate storage (Stream 14). Most of the water phase, which is saturated with organics, is separated in the quench tower (Stream 15), passed through water-cooled heat exchangers (Stream 16), and then recycled to the quench tower to provide the necessary cooling. The surplus water (Stream 17), approximately equivalent to the quantity of steam injected with the pyrolysis furnace feed, passes to the dilution steam generator, where it is vaporized and recycled as steam to the pyrolysis furnaces. Blowdown from the recycle steam generator is removed as a wastewater stream (Stream 18).

On leaving the quench tower, the pyrolysis gas is compressed to about 3.5 mPa in five stages.[29] The overhead stream from the quench tower (Stream 19) passes to a centrifugal charge-gas compressor (first three stages), where it is compressed. Water (Stream 20) and organic fractions (Stream 21) condensed during compression and cooling are recycled to the quench tower and gasoline stripper.

Lubricating oil (seal oil) discharged from the charge-gas compressor is stripped of volatile organics in a separator pot before the oil is recirculated. The organic vapor is vented to the atmosphere (Vent G). Similar separator pots separate volatile organics from lubricating oil from both the ethylene and propylene refrigeration compressors (Streams 48 and 49).

Following compression, acid gas (H_2S and CO_2) is removed by absorption in diethanolamine (DEA) or other similar solvents in the amine wash tower followed by a caustic wash step. The amine stripper strips the acid gas (Stream 22) from the saturated DEA and the DEA (Stream 23) is recycled to the amine wash tower. Very little blowdown from the DEA cycle is required.

The waste caustic solution, blowdown from the DEA cycle, and wastewater from the caustic wash tower are neutralized, stripped of acid gas, and removed as liquid waste streams (Streams 24 and 25). The acid gas stripped from the DEA and caustic waste (Stream 22) passes to an emission control device (Vent D), primarily to control H_2S emissions.

Following acid gas removal, the remaining process gas stream (Stream 26) is further compressed and passed through drying traps containing a desiccant, where the water content is reduced to the low level necessary to prevent ice or hydrate formation in the low-temperature distillation operations. The drying traps are operated on a cyclic basis, with periodic regeneration necessary to remove accumulated water from the desiccant. The desiccant is regenerated with heated fuel gas and the effluent gas is routed to the fuel system. Fouling of the desiccant by polymer formation necessitates periodic desiccant replacement, which results in the generation of a solid waste (Stream 27). However, with a normal desiccant service life of possibly several years, this waste source is relatively minor.

With the exception of three catalytic hydrogenation operations, the remaining process steps involve a series of fractionations in which the various product fractions are successively separated.

The demethanizer separates a mixture of hydrogen and methane from the C_2 and heavier components of the process gas (Stream 28). The demethanizer overhead stream (hydrogen and methane) is further separated into hydrogen-rich and methane-rich streams (Streams 29 and 30) in the low-temperature chilling section. The methane-rich stream is used primarily for furnace fuel. Hydrogen is required in the catalytic hydrogenation operations.

The de-ethanizer separates the C_2 components (ethylene, ethane, and acetylene) (Stream 31) from the C_3 and heavier components (Stream 32). Following catalytic hydrogenation of acetylene to ethylene by the acetylene converter (Stream 33), the ethylene-ethane split is made by the ethylene fractionator. The overhead from the ethylene fractionator (Stream 34) is removed as the purified ethylene product, and the ethane fraction (Stream 35) is recycled to the ethane/propane cracking furnace. For the separation of binary mixtures with close boiling points, such as in the ethylene-ethane fractions, open heat pumps are thermodynamically the most attractive. Both heating and cooling duties have to be incorporated into the cascade refrigeration system for optimum energy utilization.[29]

The de-ethanizer bottoms (C_3 and heavier compounds) (Stream 32) pass to the depropanizer, where a C_3-C_4 split is made. The depropanizer overhead stream (primarily propylene and propane) (Stream 36) passes to a catalytic hydrogenation reactor (C_3 converter), where traces of propadiene and methyl acetylene are hydrogenated. Following hydrogenation, the C_3 fraction passes to the propylene fractionator, where propylene is removed overhead as a purified product (Stream 37). The propane (Stream 38) is recycled to the ethane/propane pyrolysis furnace.

The C_4 and heavier components (Stream 39) from the depropanizer pass to the debutanizer, where a C_4-C_5 split is made. The overhead C_4 stream (Stream 40) is removed as feed to a separate butadiene process.

The stream containing C_5 and heavier compounds from the debutanizer (Stream 41) is combined with the bottoms fraction from the gasoline stripper as raw pyrolysis gasoline. The combined stream (Stream 42) is hydrogenated in the gasoline treatment section. Following the stripping of lights (Stream 43), which are recycled to the cracked-gas compressor, the C_5 and heavier compounds (Stream 44) are transferred to storage as treated pyrolysis gasoline. This stream contains benzene and other aromatics formed by pyrolysis.

The three catalytic hydrogenation reactors for acetylene, C_3 compounds, and pyrolysis gasoline all require periodic regeneration of the catalyst to remove contaminants. The catalyst is generally regenerated every four to six months. At the start of regeneration, as superheated steam (Stream 45) is passed through a reactor, a mixture of steam and hydrocarbons leaving the reactor (Stream 46) is passed to the quench tower. After sufficient time has elapsed for stripping of organics (approximately 48 hours), the exhaust is directed to an atmospheric vent (Vent F) and a steam-air mixture is passed through the catalyst to remove residual carbon. This operation continues for an additional 24 to 48 hours. The presence of air during this phase of the regeneration prevents the vented vapor from being returned to the process.

Because the olefins and di-olefins present in pyrolysis gasoline are unstable in motor gasoline and interfere with extraction of aromatics, they are hydrogenated prior to extraction of aromatics.[10] Also, as mentioned before, because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from the pyrolysis gasoline.

Recovery of Benzene from Pyrolysis Gasoline

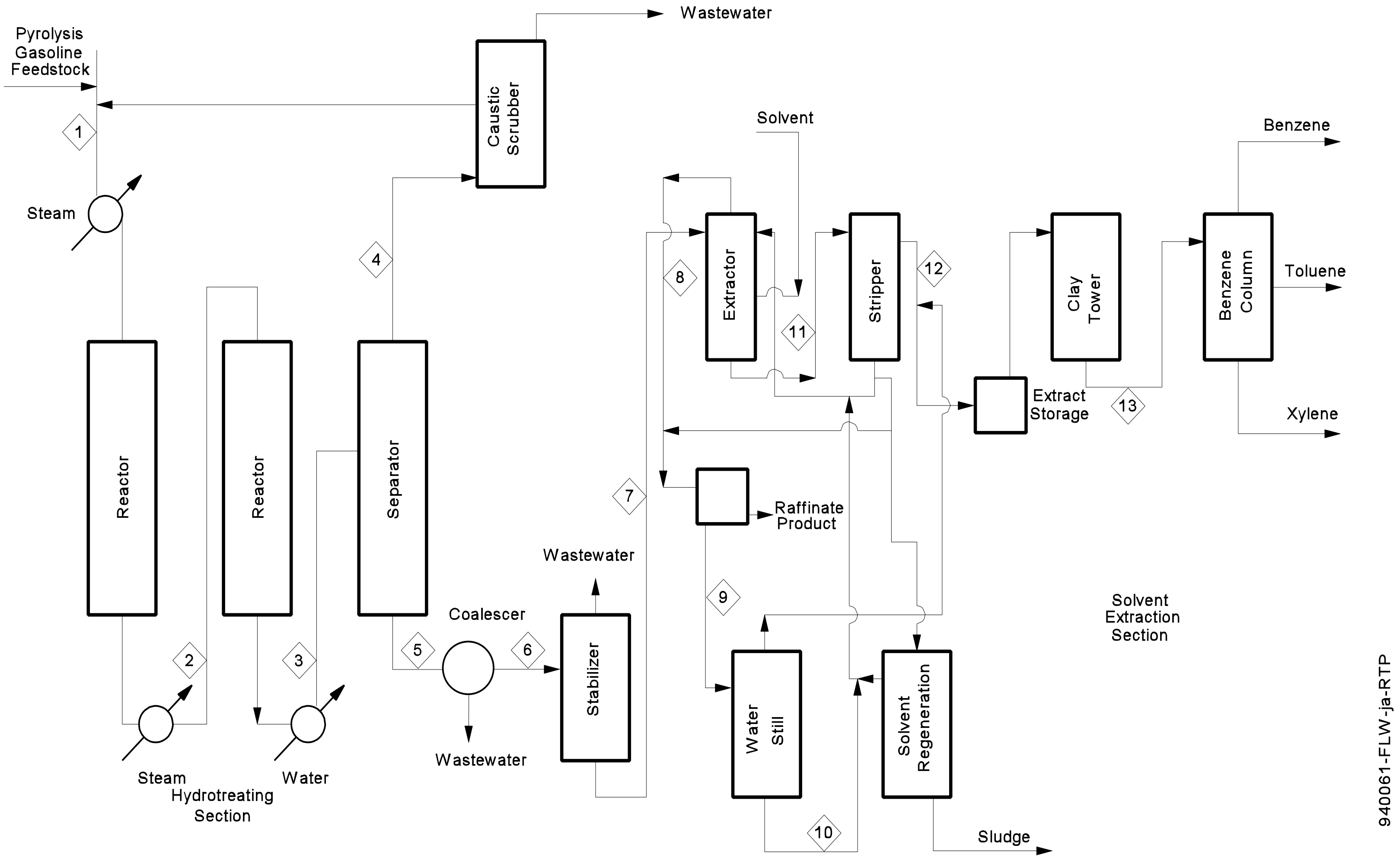
A process flow diagram for a plant producing benzene, toluene, and xylenes by hydrogenation of pyrolysis gasoline is presented in Figure 4-6. Pyrolysis gasoline is fed with make-up hydrogen into the first stage hydrogenation reactor (Stream 1), where olefins are hydrogenated. The reaction conditions are mild (104 to 203°F [40 to 95°C] and 147 to 588 lb/in^2 [10 to 40 atmospheres pressure]).[10]

The catalyst in the first stage reactor (nickel or palladium) requires more frequent regeneration than most refinery catalysts because of the formation of gums. Catalyst may be regenerated about every 4 months and coke is burned off every 9 to 12 months.[10,30]

From the first reactor, the hydrogenated di-olefins and olefins are sent to a second reactor (Stream 2). Reactor effluent is then cooled and discharged into a separator (Stream 3). Part of the gas stream from the separator is recycled back to the reactor (Stream 4) after being scrubbed with caustic solution. The liquid phase from the separator is sent to a coalescer (Stream 5), where water is used to trap particles of coke formed in the reactor.[30] Next, the light hydrocarbons are removed from the liquid in the stabilizer (Stream 6). At this point, the process becomes similar to the solvent extraction of reformate in the catalytic reforming of naphtha. The stabilized liquid is extracted with a solvent, usually Sulfolane or tetraethylene glycol (Stream 7).

The raffinate (Stream 8) contains paraffins and may be sent to a cracking furnace to produce olefins.[30] The solvent may be regenerated (Streams 9 and 10). Dissolved aromatics (benzene, toluene, and xylene) are separated from the solvent by distillation (Stream 11) and sent through clay towers (Stream 12). Individual components (benzene, toluene, and xylene) are finally separated (Stream 13) and sent to storage.

The above process may vary among facilities. For example, Stream 1 may be passed over additional catalyst, such as cobalt molybdenum, after being passed over a nickel or



Note: No data were available concerning benzene emission points. Likely emission points include reactor vents, compressors, and any vents on the benzene column.

Figure 4-6. Production of BTX by Hydrogenation of Pyrolysis Gasoline

Source: Reference 30.

palladium catalyst. Also, the olefins produced from the raffinate stream (Stream 8) may be added to a gasoline process or sold as a reformer stock.[31]

4.3.2 Benzene Emissions from Ethylene Plants and Benzene Recovery from Pyrolysis Gasoline

Production of ethylene from naphtha/gas oil does not produce large quantities of volatile organic compounds (VOC) or benzene emissions from process vents during normal operations.[28] Emission factors for benzene from sources at ethylene plants are shown in Table 4-4. The chief source of benzene emissions during normal operations is the charge gas compressor lubricating oil vent (Stream 47, Vent G in Figure 4-5). The emission factors in Table 4-4 were developed from data supplied by ethylene manufacturers.

Most benzene emissions from ethylene plants are intermittent and occur during plant startup and shutdown, process upsets, and emergencies (Vent E). For example, benzene may be emitted from pressure relief devices, during intentional venting of off-specification materials, or during depressurizing and purging of equipment for maintenance.[28] Charge gas compressor and refrigeration compressor outages are also potential sources. Emissions from these compressors are generally short term in duration, but pollutants may be emitted at a high rate.

In general, intermittent emissions and emissions from all pressure relief devices and emergency vents are routed through the main process vent (Vent E in Figure 4-5). The vent usually is controlled. The relief valve from the demethanizer is usually not routed to the main vent, but the valve is operated infrequently and emits mainly hydrogen and methane.[28]

Potential sources of benzene such as flue gas from the cracking furnace (Vent A), pyrolysis furnace decoking (Vent B), acid gas removal (Vent D), and hydrogenation catalyst regeneration (Vent F) generally are not significant sources.[28] Flue gas normally contains products of hydrogen and methane combustion. Emissions from pyrolysis furnace decoking consist of air, steam, CO_2, CO, and particles of unburned carbon.[28] Emissions from

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[a]

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)	Factor Rating
3-01-197-45 Ethylene Manufacturing-Compressor Lube Oil Vent	Compressor Lube Oil Vents	Uncontrolled	0.0006 (0.0003)	U
	Single Compressor Train	Uncontrolled	0.0004 (0.0002)	U
	Dual Compressor Train	Uncontrolled	0.0008 (0.0004)	U
3-01-197-42 Ethylene Manufacturing - Pyrolysis Furnace Decoking	Pyrolysis Furnace Decoking		No benzene emissions	
3-01-197-43 Ethylene Manufacturing-Acid Gas Removal	Acid Gas Removal		No benzene emissions	
3-01-197-44 Ethylene Manufacturing - Catalyst Regeneration	Catalyst Regeneration		No benzene emissions	
3-01-197-XX Ethylene Manufacturing - Secondary Sources	Secondary Wastewater Treatment	Uncontrolled	0.0434 (0.0217)	U
3-01-197-49 Ethylene Manufacturing - Equipment Leak Emissions	Equipment Leak Emissions	Detection/ Correction of leaks	See Section 4.5.2	
		Uncontrolled	See Section 4.5.2	

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[a]

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)	Factor Rating
3-01-197-XX Ethylene Manufacturing-Intermittent Emissions	Intermittent Emissions[c]			
	Single Compressor Train	Flare	0.1584-0.0316 (0.0792-0.0158)	U
		Uncontrolled	1.584 (0.7919)	U
	Dual Compressor Train	Flare	0.0202-0.004 (0.0101-0.002)	U
		Uncontrolled	0.2022 (0.1011)	U

[a] Data are for a hypothetical plant using 50 percent naphtha/50 percent gas oil as feed and having an ethylene capacity of 1,199,743 lb/yr (544.2 Gg/yr).

[b] Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylene produced.

[c] Intermittent emissions have been reported from the activation of pressure relief devices and the depressurization and purging of equipment for maintenance purposes.

acid gas removal are H_2S, SO_2, and CO_2; these emissions are generally controlled to recover H_2S as sulfur or convert H_2S to SO_2. As discussed earlier, catalyst regeneration is infrequent and no significant concentrations of benzene have been reported as present in the emissions.[28]

Equipment leak benzene emissions at ethylene plants may originate from pumps, valves, process sampling, and continuous process analysis. Refer to Section 4.5.2 of this document, for information on emission estimates procedures, and available emission factors. Regarding equipment leak component counts, totals of 377 and 719 valves for benzene vapor and benzene liquid service respectively had been reported for ethylene plants.[32] Storage of ethylene in salt domes is not a potential source of benzene emissions because the ethylene generally does not contain benzene.

The emission factor for benzene from storage vessels shown in Table 4-4 was derived from AP-42 equations.[33] No supporting data showing how the equations were applied were provided by the emission factor reference.

Secondary emissions include those associated with handling and disposal of process wastewater. The emission factor in Table 4-4 was derived from estimates of wastewater produced and the estimated percent of the volatile organic compounds (VOC) emitted from the wastewater that is benzene.

No data were available concerning benzene emissions from recovering benzene from pyrolysis gasoline. Likely sources include reactor vents, compressors, and any vents on the benzene column (Figure 4-6).

The primary control techniques available for intermittent emissions of benzene (pressure relief valves, emergency vents) are flaring and combustion within industrial waste boilers. Other control methods are not as attractive because the emissions are infrequent and of short duration. The estimated control efficiency of flares is 98 percent or greater[34] while control efficiencies for industrial waste boilers vary depending upon design and operation.[28]

For additional discussion on flares and industrial waste boilers as control methods, see Section 4.5.1. One ethylene producer that provided a process description stated that all process vents are connected to flares. However, it was not possible to determine how prevalent such systems are for ethylene production.[35]

Equipment leak emissions may be controlled by inspection/maintenance plans or use of equipment such as tandem seal pumps. For additional discussion on equipment leak emissions, see Section 4.5.2. Emissions from sampling lines can be controlled by piping sample line purge gas to the charge gas compressor or to a combustion chamber. Streams from process analyzers may be controlled in the same manner.[28]

The primary means of controlling emissions from pyrolysis gasoline or naphtha feedstock storage is floating roof tanks. Emissions can be reduced by 85 percent when internal floating roof devices are used.[28] For additional discussion on storage tank emissions, see Section 4.5.3.

4.4 COKE OVEN AND COKE BY-PRODUCT RECOVERY PLANTS

Most coke is produced in the U.S. using the by-product recovery process. In 1994, there was one plant that used a “nonrecovery” process. This section will focus on the by-product recovery process because there are so few nonrecovery facilities in operation.[296]

4.4.1 Process Description

Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil at coke by-product recovery plants. Light oil is a clear yellow-brown oil that contains coke oven gas components with boiling points between 32 and 392°F (0 and 200°C).[26] Most by-product recovery plants recover light oil, but not all plants refine it. About 3.4 to 4.8 gal (13 to 18 liters [L]) of light oil can be recovered from the coke oven gas evolved in coke ovens producing 0.91 ton (1 megagram [Mg]) of furnace coke (3 to 4 gal/ton [10.3 to 13.7 L/Mg]). Light oil itself is 60 to 85 percent benzene.[37]

The coke by-product industry recovers various components of coke oven gas including:

- Coal tar, a feedstock for producing electrode binder pitch, roofing pitch, road tar, and numerous basic chemicals;
- Light oil, a source of benzene and other light aromatic chemicals;
- Ammonia or ammonium sulfate, for agriculture and as chemical feedstocks;
- Sulfur, a basic chemical commodity;
- Naphthalene, used primarily as an intermediate in the production of organic chemicals; and
- Coke oven gas, a high-quality fuel similar to natural gas.[38]

Because it is contained in the coke oven gas, benzene may be emitted from processes at by-product recovery plants that do not specifically recover or refine benzene. Table 4-5 lists coke oven batteries with by-product recovery plants in the United States.[36] Figure 4-7 shows a process flow diagram for a representative coke by-product recovery plant.[37,39] The figure does not necessarily reflect any given plant, nor does it include all possible operations that could be found at a given facility. The number of units and the types of processes used varies among specific plants. For example, naphthalene recovery is not practiced at all plants, and some plants do not separate benzene from the light oil. Therefore, it is advisable to contact a specific facility to determine which processes are used before estimating emissions based on data in this document.

Coal is converted to coke in coke ovens. About 99 percent of the U.S. production of coke uses the slot oven process, also referred to as the Kopper-Becker by-product coking process; the other 1 percent is produced in the original beehive ovens.

TABLE 4-5. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES

Plant (Location)	Battery Identification Number
ABC Coke (Tarrant, AL)	A 5 6
Acme Steel (Chicago, IL)	1 2
Armco, Inc. (Middletown, OH)	1 2 3
Armco, Inc. (Ashland, KY)	3 4
Bethlehem Steel (Bethlehem, PA)	A 2 3
Bethlehem Steel (Burns Harbor, IN)	1 2
Bethlehem Steel (Lackawanna, NY)	7 8
Citizens Gas (Indianapolis, IN)	E H 1
Empire Coke (Holt, AL)	1 2
Erie Coke (Erie, PA)	A B
Geneva Steel (Provo, UT)	1 2 3 4
Gulf States Steel (Gadsden, AL)	2 3

(continued)

TABLE 4-5. CONTINUED

Plant (Location)	Battery Identification Number
Inland Steel (East Chicago, IN)	6 7 9 10 11
Koppers (Woodward, AL)	1 2A 2B 4A 4B 5
LTV Steel (Cleveland, OH)	6 7
LTV Steel (Pittsburgh, PA)	P1 P2 P3N P3S P4
LTV Steel (Chicago, IL)	2
LTV Steel (Warren, OH)	4
National Steel (Ecorse, MI)	5
National Steel (Granite City, IL)	A B
New Boston Coke (Portsmouth, OH)	1
Sharon Steel (Monessen, PA)	1B 2
Shenango (Pittsburgh, PA)	1 4
Sloss Industries (Birmingham, AL)	3 4 5
Toledo Coke (Toledo, OH)	C
Tonawanda Coke (Buffalo, NY)	1

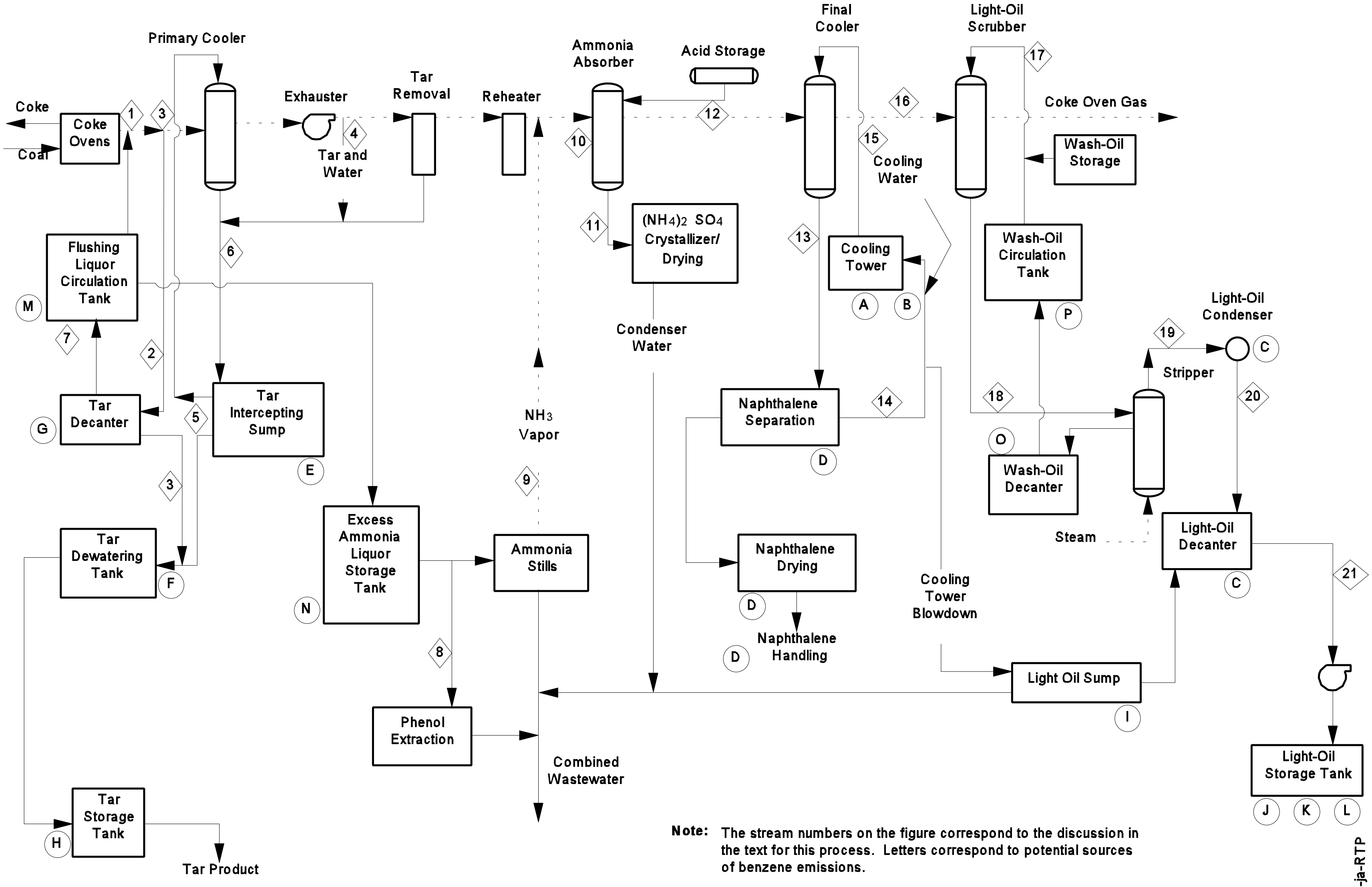
(continued)

TABLE 4-5. CONTINUED

Plant (Location)	Battery Identification Number
USX (Clairton, PA)	1
	2
	3
	7
	8
	9
	13
	14
	15
	19
	20
	B
USX (Gary, IN)	23
	5
	7
Wheeling-Pittsburgh (East Steubenville, WV)	1
	2
	3
	8

Source: Reference 36.

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These operating plants and locations were current as of April 1, 1992.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-7. Coke Oven By-Product Recovery, Representative Plant

Source: Reference 37 and 39.

Each oven has 3 main parts: coking chambers, heating chambers, and regenerative chambers. All of the chambers are lined with refractory (silica) brick. The coking chamber has ports in the top for charging of the coal.[22]

Each oven is typically capable of producing batches of 10 to 55 tons (9.1 to 49.9 Mg) of coke product. A coke oven battery is a series of 20 to 100 coke ovens operated together, with offtake flues on either end of the ovens to remove gases produced. The individual ovens are charged and discharged at approximately equal time intervals during the coke cycle. The resulting constant flow of evolved gas from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. Process heat comes from the combustion of gases between the coke chambers. Approximately 40 percent of cleaned oven gas (after the removal of its byproducts) is used to heat the coke ovens. The rest is either used in other production processes related to steel production or sold. Coke oven gas is the most common fuel for underfiring coke ovens.[22] The coking time affects the type of coke produced. Furnace coke results when coal is coked for about 15 to 18 hours. Foundry coke, which is less common and is of higher quality (because it is harder and less readily ignited), results when coal is coked for about 25 to 30 hours.[37]

The coking process is actually thermal distillation of coal to separate volatile and nonvolatile components. Pulverized coal is charged into the top of an empty, but hot, coke oven. Peaks of coal form under the charging ports and a leveling bar smoothes them out. After the leveling bar is withdrawn, the topside charging ports are closed and the coking process begins.

Heat for the coke ovens is supplied by a combustion system under the coke oven. The gases evolved during the thermal distillation are removed through the offtake main and sent to the by-product recovery plant for further processing.

After coking is completed (no volatiles remain), the coke in the chamber is ready to be removed. Doors on both sides of the chamber are opened and a ram is inserted into the chamber. The coke is pushed out of the oven in less than 1 minute, through the coke guide and into a quench car. After the coke is pushed from the oven, the doors are cleaned and repositioned. The oven is then ready to receive another charge of coal.

The quench car carrying the hot coke moves along the battery tracks to a quench tower where approximately 270 gallons of water per ton of coke (1,130 L of water per Mg) are sprayed onto the coke mass to cool it from about 2000 to 180°F (1100 to 80°C) and to prevent it from igniting. The quench car may rely on a movable hood to collect particulate emissions, or it may have a scrubber car attached. The car then discharges the coke onto a wharf to drain and continue cooling. Gates on the wharf are opened to allow the coke to fall onto a conveyor that carries it to the crushing and screening station. After sizing, coke is sent to the blast furnace or to storage.

As shown in Figure 4-7, coke oven gas leaves the oven at about 1292°F (700°C) and is immediately contacted with flushing liquor (Stream 1). The flushing liquor reduces the temperature of the gas and acts as a collecting medium for condensed tar. The gas then passes into the suction main. About 80 percent of the tar is separated from the gas in the mains as “heavy” tar and is flushed to the tar decanter (Stream 2).[37] Another 20 percent of the tar is “light” tar, which is cleaner and less viscous, and is condensed and collected in the primary cooler.[39] Smaller amounts of “tar fog” are removed from the gas by collectors (electrostatic precipitators or gas scrubbers) (Stream 4).[37] Light tar and tar fog is collected in the tar intercept sump (stream 6) and is routed to the tar decanter (Stream 5).

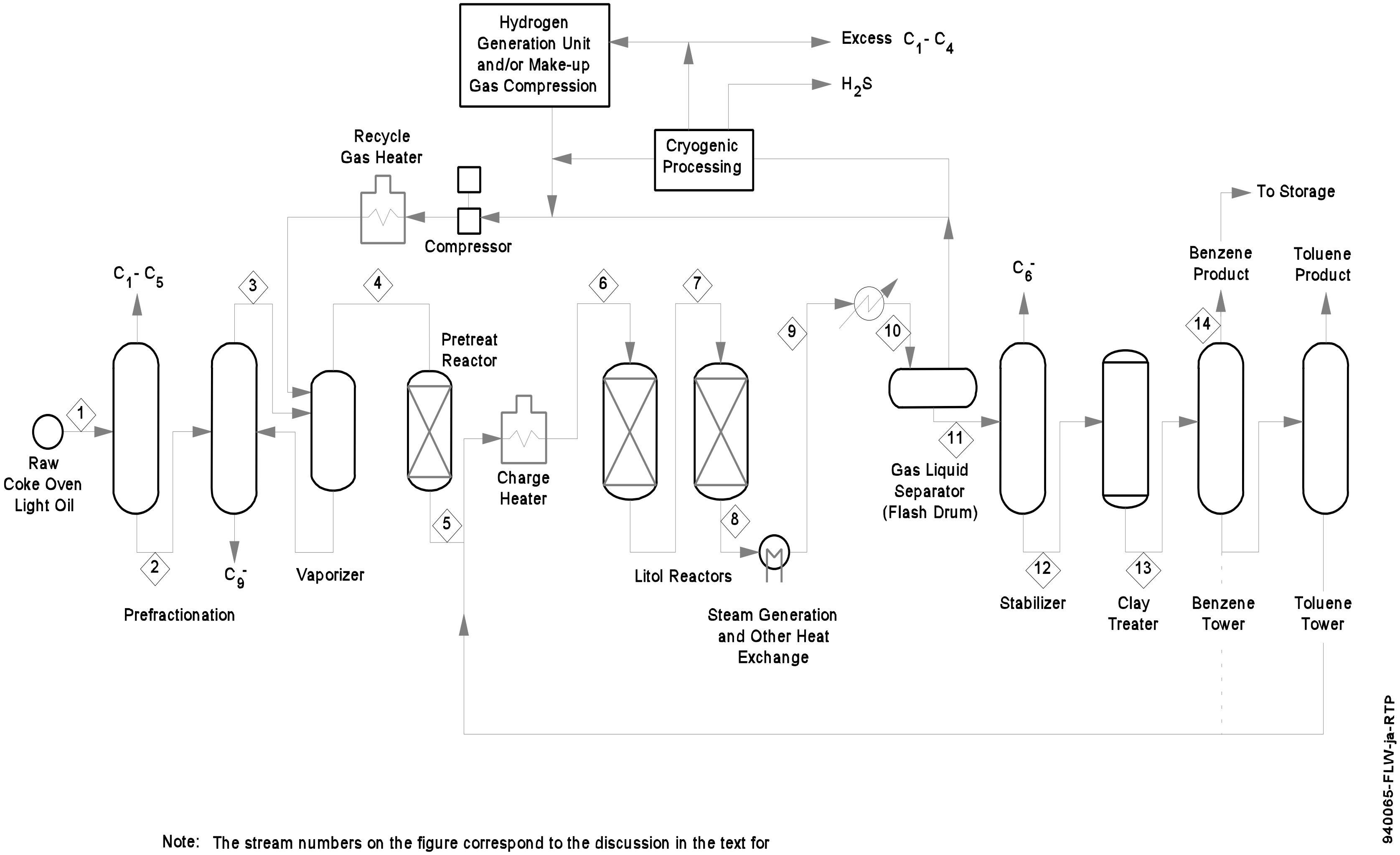
Depending on plant design, the heavy and light tar streams (Streams 2 and 5) may be merged or separated. The tar is separated from the flushing liquor by gravity in the tar decanter. Recovered flushing liquor is returned to the Flushing Liquor Circulation Tank (Stream7) and re-used. Tar from the decanter is further refined in the tar dewater tank

(Stream 3). Tar may be sold to coal tar refiners or it may be refined further on site. Tar and tar products are stored on site in tanks.

Wastewater processing can recover phenol (Stream 8) and ammonia, with the ammonia routinely being reinjected into the gas stream (Stream 9). Ammonia salts or ammonia can be recovered by several processes. Traditionally, the ammonia-containing coke oven gas is contacted with sulfuric acid (Stream 10), and ammonium sulfate crystals are recovered (Stream 11). The coke oven gas from which tar and ammonia have been recovered is sent to the final cooler (Stream 12). The final cooler is generally a spray tower, with water serving as the cooling medium.[37]

Three types of final coolers and naphthalene recovery technologies are currently used: (1) direct cooling with water and naphthalene recovery by physical separation, (2) direct cooling with water and naphthalene recovery in the tar bottom of the final cooler, and (3) direct cooling with wash oil and naphthalene recovery in the wash oil.[37] Most plants use direct water final coolers and recover naphthalene by physical separation.[37] In this method, naphthalene in the coke oven gas is condensed in the cooling medium and separated by gravity (Stream 13). After the naphthalene is separated, the water is sent to a cooling tower (Stream 14) and recirculated to the final cooler (Stream 15). The coke oven gas that leaves the final cooler is sent to the light oil processing segment of the plant (Stream 16).

As shown in Figure 4-7, light oil is primarily recovered from coke oven gas by continuous countercurrent absorption in a high-boiling liquid from which it is stripped by steam distillation.[10] Coke oven gas is introduced into a light oil scrubber (Stream 16). Packed or tray towers have been used in this phase of the process, but spray towers are now commonly used.[10] Wash oil is introduced into the top of the tower (Stream 17) and is circulated through the contacting stages of the tower at around 0.11 to .019 gal/ft^3 (1.5 to 2.5 liters per cubic meter [L/m3]) of coke oven gas.[39] At a temperature of about 86°F (30°C), a light oil scrubber will remove 95 percent of the light oil from coke oven gas. The



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-8. Litol Process Flow Diagram

Source: References 40 and 41.

benzene-containing wash oil is steam-stripped (Stream 18) to recover the light oil.[39] Steam and stripped vapors are condensed and separated (Streams 19 and 20). The light oil is sent to storage (Stream 21).[37,39]

To recover the benzene present in the light oil, processes such as Litol (licensed by Houdry) or Hydeal (licensed by UOP) are used. Figure 4-8 shows a process diagram of the Litol process. The following discussion of the Litol process is drawn from two published descriptions of the process.[40,41]

The light oil is prefractionated (Stream 1) to remove the C_5 and lighter fractions, and the C_9 and heavier fractions (Stream 2). The remaining "heart cut" is sent to a vaporizer, where it contacts gas with a high hydrogen content (Stream 3). The light oil and hydrogen then flow to a pretreat reactor (Stream 4), where styrene, di-olefins, and some sulfur compounds are hydrogenated (at about 572°F [300°C]). The partially hydrogenated stream is heated by the charge heater to the temperature required for the main reactor (Stream 5).

The stream is then sent through a set of fixed-bed (Litol) reactors (Streams 6 and 7), where all remaining sulfur compounds are converted to H_2S and organics are dehydrogenated or dealkylated. The reactor effluent is cooled by post-reactor exchangers (Streams 8 and 9). At the flash drum, aromatics are condensed and separated from the gas stream (Stream 10). At the stabilizer, additional gas is removed, resulting in a hot liquid fuel for clay treatment (Stream 11). The clay treater removes the last trace of unsaturates from the aromatics (Stream 12). Conventional distillation yields pure benzene followed by pure toluene (Stream 13). Benzene product may then be sent to storage (Stream 14).[40,41]

4.4.2 Benzene Emissions

Benzene may be emitted from many points in a coke and coke by-product plant; emissions are not limited to the benzene recovery section of the process. The coke ovens themselves are potential sources of benzene emissions from the charging operation, leaking coke oven doors, topside port lids and offtake systems on the topside of the battery, collecting mains, and bypass/bleeder stacks.[36]

During charging, moist coal contacts the hot oven floor and walls and, as a result, the release of volatile components begins immediately. Control of charging emissions is more dependent on operating procedures than on equipment. Control options include staged charging, sequential charging, and use of wet scrubbers on larry cars (the mobile hoppers that discharge the coal).

Staged charging involves pouring coal into the coke ovens so that an exit space for the generated gases is constantly maintained.[42] The hoppers delivering the coal are discharged such that emissions are contained in the ovens and collecting mains by steam aspiration. Generally, a maximum of two hoppers are discharging at the same time.

In sequential charging, the first hoppers are still discharging when subsequent hoppers begin discharging coal. As with staged charging, the coke ovens are under aspiration in sequential charging. The sequential charging procedure is designed to shorten the charging time.

In the use of wet scrubbers on larry cars, the scrubber emissions are contained by hoods or shrouds that are lowered over the charging ports.

Another potential source of benzene emissions at coke ovens is leaking doors. The doors are sealed before the coking process begins. Some doors have a flexible metal band or rigid knife edge as a seal. The seal is formed by condensation of escaping tars on the door's metal edge. Other doors are sealed by hand by troweling a mixture into the opening between the coke oven door and door frame. After the coking process is complete, the doors are opened to push the coked coal out into special railroad cars called quench cars for transport to the quench tower. Quenched coke is then discharged onto a “coke wharf” to allow quench water to drain and to let the coke cool. Control techniques for leaking doors include oven door seal technology, pressure differential devices, hoods/shrouds over the doors, and the use of more efficient operating/maintenance procedures.[42]

Oven door seal technology relies on the principle of producing a resistance to the flow of gases out of the coke oven. This resistance may be produced by a metal-to-metal seal, a resilient soft seal, or a luted seal (applying a slurry mixture of clay, coal, and other materials). Small cracks and defects in the seal allow pollutants to escape from the coke oven early in the cycle. The magnitude of the leak is determined by the size of the opening, the pressure drop between the oven and the atmosphere, and the composition of the emissions.

The effectiveness of a pressure differential control device depends on the ability of the device to reduce or reverse the pressure differential across any defects in the door seal. These systems either provide a channel to permit gases that evolve at the bottom of the oven to escape to the collecting main, or the systems provide external pressure on the seal through the use of steam or inert gases.

Oven door emissions also can be reduced by collecting the leaking gases and particulates and subsequently removing these pollutants from the air stream. A suction hood above each door with a wet electrostatic precipitator for fume removal is an example of this type of system.

Other control techniques rely on operating and maintenance procedures rather than only hardware. Operating procedures for emission reduction could include changes in the oven cycle times and temperatures, the amount and placement of each charge, and any adjustments of the end-door while the oven is on line. Maintenance procedures include routine inspection, replacement, and repair of control devices and doors.

Topside leaks are those occurring from rims of charging ports and standpipe leaks on the top of the coke oven. These leaks are primarily controlled by proper maintenance and operating procedures that include:[42]

- Replacement of warped lids;
- Cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seats;
- Patching or replacing cracked standpipes;
- Sealing lids after a charge or whenever necessary with lute; and
- Sealing cracks at the base of a standpipe with lute.

Luting mixtures are generally prepared by plant personnel according to formulas developed by each plant. The consistency (thickness) of the mixture is adjusted to suit different applications.

There are few emission factors specifically for benzene emissions at coke ovens. One test that examined emissions of door leaks detected benzene in the emissions.[42] The coke oven doors being tested were controlled with a collecting device, which then fed the collected emissions to a wet electrostatic precipitator. Tests at the precipitator inlet showed benzene concentrations of 1.9×10^{-7} to 6.2×10^{-7} lb/ft^3 (1 to 3 parts per million [ppm] or about 3 to 10 milligrams per cubic meter [Mg/m3]). These data translated into an estimated benzene emission factor of 1.3 lb to 5.3 lb (0.6 to 2.4 kilograms [kg]) benzene per hour of operation for coke oven doors. In addition to coke oven door emissions, benzene may also be emitted from the coke oven bypass stack at a rate of 22 lbs/ton of coal charged (11,000 g/Mg) uncontrolled, 0.22 lbs/ton of coal charged (110 g/Mg) controlled with flare.[296] No additional emission factors for benzene and coke ovens were found in the literature. However, an analysis of coke oven gas indicated a benzene content of 1.3×10^{-3} to 2.2×10^{-3} lb/ft^3 (21.4 to 35.8 grams per cubic meter [g/m^3]).

Other potential sources of benzene emissions associated with the by-product recovery plant are given in Table 4-6, along with emission factors.[37,43]

Equipment leaks may also contribute to benzene emissions. Emission factors for pumps, valves, etc., at furnace coke and foundry coke by-product recovery plants are shown in Tables 4-7 and 4-8, respectively.[37,43] The following paragraphs describe the potential sources of benzene emissions listed in Tables 4-6, 4-7, and 4-8. Emission sources and control technologies are described in groups of related processes, beginning with the final cooling unit.

The final cooling unit itself is not a source of benzene because coolers are closed systems. However, the induced-draft cooling towers used in conjunction with direct-water and tar-bottom final coolers are potential sources of benzene. Benzene can be condensed in the direct-contact cooling water, and in the cooling tower, lighter components (such as benzene) will be stripped from the recirculating cooling water. The emission factor of 0.54 pound per ton (lb/ton) (270 g/Mg) coke shown in Table 4-6 was based on actual measurements of benzene concentrations and volumetric gas flow rates taken from source testing reports.[37]

Use of a wash oil final cooler effectively eliminates the benzene emissions associated with direct water or tar bottom coolers because the wash oil is cooled by an indirect heat exchanger, thereby eliminating the need for a cooling tower.[37] Wash oil is separated after it leaves the heat exchanger and recirculates back through the circulation tank to the final cooler.

Coke by-product recovery plants may recover naphthalene by condensing it from the coke oven gas and separating it from the cooling water by flotation. Benzene may be emitted from most naphthalene separation and processing operations.[37] Vapors from naphthalene separation tanks have been reported to contain benzene, benzene homologs, and other aromatic hydrocarbons.[37] The emission factors for naphthalene separation and

TABLE 4-6. SUMMARY OF BENZENE EMISSION FACTORS FOR FURNACE AND FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

SCC and Description	Emissions Source[a]	Control Device	Emission Factor lb/ton (g/Mg)[b]		Factor Rating
			Furnace Coke	Foundry Coke	
3-03-003-15 By-Product Coke - Gas By-Product Plant	Cooling Tower				
	- Direct Water (A)[c]	Uncontrolled	0.54 (270)	0.40 (200)	E
	- Tar bottom (B)[c]	Uncontrolled	0.14 (70)	0.10 (51)	E
	Light-Oil Condenser Vent (C)	Uncontrolled	0.18 (89)	0.096 (48)	E
		Gas Blanketing	3.6×10^{-3} (1.8)	1.9×10^{-3} (0.97)	E
	Naphthalene Separation and Processing (D)	Uncontrolled	0.22 (110)	0.16 (80)	E
		Activated Carbon	7.0×10^{-4} (0.35)	5.0×10^{-4} (0.25)	E
	Tar-Intercepting Sump (E)	Uncontrolled	0.019 (9.5)	0.009 (4.5)	E
	Tar Dewatering (F)	Uncontrolled	0.042 (21)	0.020 (9.9)	E
		Gas Blanketing	8.4×10^{-4} (0.45)	4×10^{-4} (0.2)	E

(continued)

TABLE 4-6. CONTINUED

SCC and Description	Emissions Source[a]	Control Device	Emission Factor lb/ton (g/Mg)[b]		Factor Rating
			Furnace Coke	Foundry Coke	
	Tar Decanter (G)	Uncontrolled	0.11 (54)	0.05 (25)	E
		Gas Blanketing	22×10^{-3} (1.1)	1.0×10^{-3} (0.5)	E
	Tar Storage (H)	Uncontrolled	0.013 (6.6)	6.2×10^{-3}	E
		Gas Blanketing	7.6×10^{-4} (0.38)	3.6×10^{-4} (0.18)	E
	Light-Oil Sump (I)	Uncontrolled	0.03 (15)	0.016 (8.1)	E
		Gas Blanketing	6×10^{-4} (0.3)	3.2×10^{-4} (0.16)	E
	Light-Oil Storage (J)	Uncontrolled	0.012 (5.8)	6.2×10^{-3} (3.1)	E
		Gas Blanketing	2.4×10^{-4} (0.12)	1.2×10^{-4} (0.06)	E
	BTX Storage (K)[d]	Uncontrolled	0.012 (5.8)	6.2×10^{-3} (3.1)	E
		Gas Blanketing	2.4×10^{-4} (0.12)	1.2×10^{-4} (0.06)	E
	Benzene Storage (L)[d]	Uncontrolled	0.0116 (5.8)	6.2×10^{-3} (3.1)	E
		Gas Blanketing	2.4×10^{-4} (0.12)	1.2×10^{-4} (0.06)	E

(continued)

TABLE 4-6. CONTINUED

SCC and Description	Emissions Source[a]	Control Device	Emission Factor lb/ton (g/Mg)[b]		Factor Rating
			Furnace Coke	Foundry Coke	
	Flushing-Liquor Circulation Tank (M)	Uncontrolled	0.026 (13)	0.019 (9.5)	E
		Gas Blanketing	5.2 x 10^{-4} (0.26)	3.8 x 10^{-4} (0.19)	E
	Excess-Ammonia Liquor Tank (N)	Uncontrolled	2.8 x 10^{-3}	2.0 x 10^{-3}	E
		Gas Blanketing	5.6 x 10^{-5} (0.028)	4.0 x 10^{-5} (0.020)	E
	Wash-Oil Decanter (O)	Uncontrolled	7.6 x 10^{-3} (3.8)	4.2 x 10^{-3} (2.1)	E
		Gas Blanketing	1.5 x 10^{-4} (0.076)	8.2 x 10^{-5} (0.041)	E
	Wash-Oil Circulation Tank (P)	Uncontrolled	7.6 x 10^{-3} (3.8)	4.2 x 10^{-3} (2.1)	E
		Gas Blanketing	1.5 x 10^{-4} (0.076)	8 .2 x 10^{-5} (0.041)	E

Source: Reference 296.

[a] Source identification letters correspond to locations identified in Figure 4-7.
[b] Emission factors are expressed as g benzene emitted per Mg coke produced.
[c] Usually only smaller plants use direct-water final cooler; all final coolers are shown as one unit in Figure 4-7.
[d] Not all plants separate BTX or benzene. Therefore, all product storage is indicated in one box on the diagram in Figure 4-7.

TABLE 4-7. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FURNACE COKE BY-PRODUCT RECOVERY PLANTS

				Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)		Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
3-03-003-15 By-Product Coke - Gas By-Product Recovery	Valves	Uncontrolled		0.4 (0.18)	0.49 (0.22)	U
		Quarterly inspection	(63)	0.15 (0.07)	0.18 (0.08)	U
		Monthly inspection	(72)	0.11 (0.05)	0.13 (0.06)	U
		Use sealed bellows valves	(100)	--	--	
	Pumps	Uncontrolled		4.2 (1.9)	5.1 (2.3)	U
		Quarterly inspection	(71)	1.2 (0.55)	1.5 (0.67)	U
		Monthly inspection	(83)	0.71 (0.32)	0.86 (0.39)	U
		Use dual mechanical seals	(100)	--	--	
	Exhausters	Uncontrolled		0.62 (0.28[c])	0.62 (0.28[c])	U
		Quarterly inspection	(55)	0.29 (0.13)	0.29 (0.13)	U
		Monthly inspection	(64)	0.22 (0.10)	0.22 (0.10)	U
		Use degassing reservoir vents	(100)	--	--	
	Pressure Relief Devices	Uncontrolled		6.0 (2.7)	7.5 (3.4)	U
		Quarterly inspection	(44)	3.3 (1.5)	4.2 (1.9)	U
		Monthly inspection	(52)	2.9 (1.3)	3.5 (1.6)	U
		Use rupture disk system	(100)	--	--	
	Sampling Connections	Uncontrolled		0.55 (0.25)	0.68 (0.31)	U
		Closed-purge sampling	(100)	--	--	

(continued)

TABLE 4-7. CONTINUED

			Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)	Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
	Open-ended Lines	Uncontrolled	0.084 (0.038)	0.104 (0.047)	U
		Plug or cap (100)	--	--	

Source: Reference 37.

[a] Factors are based on the total VOC emissions from petroleum refineries and the percent of benzene in light oil and refined benzene.
[b] Factors are expressed as lb emitted per source day (kg benzene emitted per source day).
[c] Emission factors are presented for two different types of coke by-product recovery plants, but are not representative of any particular plant.

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

			Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)	Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
3-03-003-15 By-Product Coke - Gas By-Product Recovery	Valves	Uncontrolled	0.35 (0.16)	0.44 (0.20)	U
		Quarterly inspection (63)	0.13 (0.06)	0.15 (0.07)	U
		Monthly inspection (72)	0.09 (0.04)	0.13 (0.06)	U
		Use sealed bellows valves (100)	--	--	
	Pumps	Uncontrolled	3.7 (1.7)	4.6 (2.1)	U
		Quarterly inspection (71)	1.1 (0.5)	1.3 (0.6)	U
		Monthly inspection (83)	0.66 (0.3)	0.88 (0.4)	U
		Use dual mechanical seals (100)	--	--	
	Exhausters	Uncontrolled	0.55 (0.25)	0.55 (0.25)	U
		Quarterly inspection (55)	0.24 (0.11)	0.24 (0.11)	U
		Monthly inspection (64)	0.20 (0.09)	0.20 (0.09)	U
		Use degassing reservoir vents (100)	--	--	
	Pressure Relief Devices	Uncontrolled	5.5 (2.5)	6.8 (3.1)	U
		Quarterly inspection (44)	3.1 (1.4)	3.7 (1.7)	U
		Monthly inspection (52)	2.6 (1.2)	3.3 (1.5)	U
		Use rupture disk system (100)	--	--	
	Sampling Connections	Uncontrolled	0.51 (0.23)	0.62 (0.28)	U
		Plug or cap (100)	--	--	

(continued)

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

			Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)	Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
	Open-ended Lines	Uncontrolled	0.077 (0.035)	0.95 (0.043)	U
		Closed-purge sampling (100)	--	--	

Source: Reference 37.

[a] Factors for foundry coke are drawn from Reference 43.
[b] Factors are expressed in terms of lb (kg) of benzene emitted per source day.
[c] Emission factors are presented for two different types of foundry coke by-product recovery plants, but are not representative of any particular plant.

"--" = Data not available.

processing shown in Table 4-6 are based on source testing data from a flotation unit, drying tank, and melt pit at a coke by-product recovery plant.[37]

Benzene may also be emitted from the light oil plant, which includes the light-oil condenser vent, light oil decanter, storage tank, intercepting sumps, the wash-oil decanter, wash-oil circulation tank(s), and BTX storage. A control technique required by the benzene NESHAP is the use of gas blanketing with clean coke oven gas from the gas holder (or battery underfire system).[44] With this technology, a positive (or negative) pressure blanket of clean coke oven gas is piped to the light oil plant and the enclosed sources are connected to the blanketing line. Using a series of piping connections and flow inducing devices (if necessary), vapor emissions from the enclosed sources are transported back into the clean gas system (the coke-oven battery holder, the collecting main, or another point in the by-product recovery process).

Ultimate control of the vapors is accomplished by the combustion of the coke oven gas.[37] Such systems are currently in use at some by-product recovery plants and reportedly have operated without difficulty. Examples of gases that may be used as the gas blanket include dirty or clean coke gas, nitrogen, or natural gas.[37] The control efficiency is estimated to be 98 percent.[37,44] The control technique required by the benzene NESHAP for the light oil sump is a tightly fitting, gasketed cover with an estimated 96-percent efficiency.[44] The emission factors for benzene sources in the light oil plant shown in Table 4-6 are based on source tests.[37]

Sources of benzene emissions from tar processing include the tar decanter, the tar-intercepting sump, tar dewatering and storage, and the flushing-liquor circulation tank. Emission factors for these sources are shown in Table 4-6.

Benzene emissions from the tar decanter are sensitive to two operating practices: residence time in the separator and optimal heating of the decanter.[37] These two variables should be kept in mind when using the emission factors presented in Table 4-6.

Benzene is emitted from tar decanters through vents. Coke oven gas can be mechanically entrained with the tar and liquor that are fed into the decanter. Because tar is fed into the decanter at a slightly higher pressure, the coke oven gas will build up in the decanter if it is not vented.[37] Emissions were measured at tar decanters at several locations in the United States and the emission factor shown in Table 4-6 is the average of the test values.[37]

The water that separates from the tar in the decanter is flushing liquor, which is used to cool the gas leaving the coke oven. Excess flushing liquor is stored in the excess ammonia liquor tank. Benzene may be emitted from the flushing liquor circulation tank and the excess ammonia liquor tank. The emission factor of 0.026 lb benzene/ton (13 g benzene/Mg) coke produced was derived from a source test of fugitive emissions from a primary cooler condensate tank. It was assumed that the condensate tank was similar in design and in liquids stored as the ammonia liquor and the flushing liquor circulation tanks.[296] The actual benzene emission rate from the flushing liquor circulation tank and excess ammonia liquor tank depends on the number of tanks, the number of vents, and the geometry of the tanks.[37]

The tar-intercepting sump is a type of decanter that accepts light tar and condensate from the primary cooler. Some of this condensate may be used to make up flushing liquor and some may be forwarded to ammonia recovery.[37] No significant benzene emissions have been identified from the recovery of ammonia, but benzene can be emitted from the intercepting sump. An emission factor of 0.019 lb/ton (9.5 g benzene/Mg) coke was reported in the literature.[296]

Tar dewatering may be accomplished by steam heating or centrifugal separation or a combination of the two methods. Use of centrifugal separation will probably not be a source of benzene emissions directly, but benzene may be emitted as a fugitive emission if storage vessels are used.[39] In steam heating, benzene could be driven off in the vapors. The emission factor for tar dewatering in Table 4-6 was derived by averaging three factors (0.082, 0.019, and 0.0258 lb benzene/ton coke [41, 9.5, and 12.9 g benzene/Mg coke]) based on source tests at tar dewatering tanks.[37] Gas blanketing is the control technology required by the benzene NESHAP for tar processing.

The final source of benzene emissions at coke by-product recovery plants is leaks from equipment such as pumps, valves, exhausters, pressure relief devices, sampling connection systems, and open-ended lines. Emission factors are shown in Tables 4-7 and 4-8 and are based on emission factors from a comprehensive survey of petroleum refineries and the percent of benzene in the liquid associated with each type of equipment.[37] Two different sets of emission factors are presented, one set for a plant practicing light oil and BTX recovery and one set for a plant producing refined benzene in addition to light oil. Emission factors for exhausters were derived by multiplying the VOC emission factor for compressors in hydrogen service and refineries by 0.235, the measured ratio of benzene to nonmethane hydrocarbons present in the coke oven gas at the exhausters.[37]

To control benzene emissions from process vessels, storage tanks, and tar-interrupting sumps as required by the benzene NESHAP, all openings must be enclosed or sealed. All gases must be routed to a gas collection system (or similar configuration) where the benzene in the gas will be removed or destroyed. Alternately, the gases may be routed through a closed vent system to a carbon absorber or vapor incinerator that is at least 98 percent efficient. See Section 4.5 for a discussion of these types of process control devices.[44] The control techniques required by the benzene NESHAP to control benzene emissions from equipment leaks are presented in Table 4-9.

For the nonrecovery process, benzene emissions for coal charging are 3.6×10^{-5} lb/ton of coal charged (1.8×10^{-2} g/Mg). Emissions from pushing and quenching are expected to be similar to those from the by-product recovery process. Additional benzene emissions occur from the combustion stack of nonrecovery batteries at the rate of 5.1×10^{-4} lb/ton of coal charged (0.26 g/Mg).[296]

TABLE 4-9. TECHNIQUES TO CONTROL BENZENE EMISSIONS FROM EQUIPMENT LEAKS REQUIRED BY THE BENZENE NESHAP FOR COKE BY-PRODUCT RECOVERY PLANTS

Emission Points	Control Technique (% efficiency)
Pumps	Monthly Inspection[a] (83)
	Dual Mechanical Seals (100)
Valves	Monthly Inspection[a] (73)
	Sealed-Bellows Valves (100)
Exhausters	Quarterly Inspections[a] (55)
	Degassing Reservoir Vents (100)
Pressure-Relief Devices	Rupture Disc System (100)
Sampling Connection Systems	Closed-Purge Sampling (100)
Open-Ended Lines	Cap or Plug (100)

Source: Reference 44.

[a] Inspection and maintenance programs include tightening seals, replacing manufacturing equipment, etc.

4.5 METHODS FOR ESTIMATING BENZENE EMISSIONS FROM EMISSION SOURCES

In this section, the sources of benzene emissions from process vents, equipment leaks, storage tanks, wastewater, and transfer operations are summarized, along with the types of controls currently available for use in the industry. In addition, an overview of methods for estimating uncontrolled and controlled emissions of benzene is presented where available. Current Federal regulations applicable to these benzene emission sources are identified. The information provided in this section is applicable to benzene production facilities (discussed earlier in this chapter) as well as to facilities that use benzene as a feedstock to produce cyclic intermediates (discussed in Chapter 5.0).

4.5.1 Process Vent Emissions, Controls, and Regulations

Benzene emissions can occur from any process vent in any chemical production operation that manufactures or uses benzene. Section 4.0 of this document contains a discussion of chemical operations that manufacture benzene, whereas Section 5.0 contains a discussion of chemical operations that use benzene as feedstock. Chemical operations that emit benzene include air oxidation processes, reactor processes, and distillation operations. In air oxidation processes, one or more chemicals are reacted with oxygen supplied as air or air enriched with oxygen to create a product. With reactor processes, one or more chemicals are reacted with another chemical (besides oxygen) and chemically altered to create one or more new products. In distillation, one or more inlet feed streams is separated into two or more outlet product streams, each product stream having component concentrations different from those in the feed streams. During separation, the more volatile components are concentrated in the vapor phase and the less volatile components in the liquid phase.[45]

Calculations for estimating emissions from any of these three processes are specific to the type of vent stream and the type of control in place.

Two general types of methods are used for controlling benzene emissions from process vents: recovery devices and combustion devices. Examples of each type of control device that can be used to comply with air pollution control standards, along with its estimated control efficiency, are summarized in Tables 4-10 and 4-11 and discussed briefly below.[45] The reader should keep in mind that the most appropriate recovery control device, as well as its effectiveness, is highly dependent upon flow rate, concentration, chemical and physical properties of the vent stream, contaminants present, and stream temperature. To achieve optimal control efficiency with recovery devices, several stream characteristics must remain within a certain range. Combustion control devices are less dependent upon these process and vent stream characteristics; however, combustion temperature and stream flow must remain within a certain range to ensure complete combustion.[46]

TABLE 4-10. CONTROL TECHNOLOGIES THAT FORM THE BASIS OF AIR POLLUTION CONTROL STANDARDS

Type	Control Levels Achievable	Design Conditions to Meet Control Level	Comments
Flares	≥ 98%	• Flame present at all times - monitor pilot • Non-assisted Flares - >200 Btu/scf heating value, and 60 ft/sec (18 m/sec) maximum exit velocity • Air and Steam Assisted Flares - >300 Btu/scf heating value, and maximum exit velocity based on Btu content formula	• Destroys rather than recovers organics • Smoking allowed for 5 min/2 hr • Not used on corrosive streams
Industrial Boilers/Process Heaters	≥ 98%	• Vent stream directly into flame	• Destroys rather than recovers organics
Thermal Oxidation	≥ 98%, or 20 ppm	• 1600°F (871°C) Combustion temperature • 0.75 sec. residence • For halogenated streams 2000°F (1093°C), 1.0 sec. and use a scrubber on outlet • Proper mixing	• Destroys rather than recovers organics • May need vapor holder on intermittent streams
Adsorption	≥ 95%	• Adequate quantity and appropriate quality of carbon • Gas stream receives appropriate conditioning (cooling, filtering) • Appropriate regeneration and cooling of carbon beds before breakthrough occurs	• Most efficient on streams with low relative humidity (<50 percent). • Recovers organics

Source: Reference 45.

TABLE 4-11. OTHER CONTROL TECHNOLOGIES THAT CAN BE USED TO MEET STANDARDS

Type	Estimated Control Level	Critical Variables That Affect Control Level	Comments
Catalytic Oxidation	up to 98%	• Dependent on compounds, temp. and catalyst bed size	• Destroys rather than recovers organics • Technical limitations include particulate or compounds that poison catalysts
Absorption	50 to 95%	• Solubility of gas stream in the absorbent • Good contact between absorbent and gas stream	• Appropriate absorbent needed may not be readily available • Disposal of spent absorbent may require special treatment procedures, and recovery of organic from absorbent may be time consuming • Preferable on concentrated streams
Condensation	50 to 95%	• Proper design of the heat exchanger • Proper flow and temperature of coolant	• Preferable on concentrated streams • Recovers organics

Source: Reference 45.

Three types of recovery devices have been identified for controlling benzene emissions: condensation, absorption, and adsorption. With a condensation-type recovery device, all or part of the condensible components of the vapor phase are converted to a liquid phase. Condensation occurs as heat from the vapor phase is transferred to a cooling medium. The most common type of condensation device is a surface condenser, where the coolant and vapor phases are separated by a tube wall and never come in direct contact with each other. Efficiency is dependent upon the type of vapor stream entering the condenser and the flow rate and temperature of the cooling medium. Condenser efficiency varies from 50 to 95 percent. Stream temperature and the organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.[46]

In absorption, one or more components of a gas stream are selectively transferred to a solvent liquid. Control devices in this category include spray towers, venturi scrubbers, packed columns, and plate columns. Absorption efficiency is dependent upon the type of solvent liquid used, as well as design and operating conditions. Absorption is desirable if there is a high concentration of compound in the vent stream that can be recovered for reuse. For example, in the manufacture of monochlorobenzene, absorbers are used to recover benzene for reuse as a feedstock.[46] Stream temperature, specific gravity (the degree of adsorbing liquid saturation), and the organic concentration level must remain within a certain range to ensure optimal control efficiency.[46] Absorbers are generally not used on streams with VOC concentrations below 300 ppmv.[45] Control efficiencies vary from 50 to 95 percent.[45]

In adsorption, the process vent gas stream contains a component (adsorbate) that is captured on a solid-phase surface (adsorbent) by either physical or chemical adsorption mechanisms. Carbon adsorbers are the most commonly used adsorption method. With carbon adsorption, the organic vapors are attracted to and physically held on granular activated carbon through intermolecular (van der Waals) forces. The two adsorber designs are fixed-bed and fluidized-bed. Fixed-bed adsorbers must be regenerated periodically to desorb the collected organics. Fluidized-bed adsorbers are continually regenerated.[46]

Adsorption efficiency can be 95 percent for a modern, well-designed system. Removal efficiency depends upon the physical properties of the compounds in the offgas, the gas stream characteristics, and the physical properties of the adsorbent. Stream mass flow during regeneration, the temperature of the carbon bed, and organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.[46] Adsorbers are not recommended for vent streams with high VOC concentrations.[45]

Four types of combustion devices are identified for control of benzene emissions from process vents: flares, thermal oxidizers, boilers and process heaters, and catalytic oxidizers. A combustion device chemically converts benzene and other organics to CO_2 and water. If combustion is not complete, the organic may remain unaltered or be converted to another organic chemical, called a product of incomplete combustion. Combustion temperature and stream flow must remain within a certain range to ensure complete combustion.[46]

A flare is an open combustion process that destroys organic emissions with a high-temperature oxidation flame. The oxygen required for combustion is provided by the air around the flame. Good combustion is governed by flame temperature, residence time of the organics in the combustion zone, and turbulent mixing of the components to complete the oxidation reaction. There are two main types of flares: elevated and ground flares. A combustion efficiency of at least 98 percent can be achieved with such control.[46]

A thermal oxidizer is usually a refractory-lined chamber containing a burner (or set of burners) at one end. The thermal oxidation process is influenced by residence time, mixing, and temperature. Unlike a flare, a thermal oxidizder operates continuously and is not suited for intermittent streams. Because it operates continuously, auxiliary fuel must be used to maintain combustion during episodes in which the organic concentration in the process vent stream is below design conditions. Based on new technology, it has been determined that all new thermal oxidizers are capable of achieving at least 98 percent destruction efficiency or a 20 parts per million by volume (ppmv) outlet concentration, based on operation at 870°C (1,600°F) with a 0.75-second residence time.[46]

Industrial boilers and process heaters can be designed to control organics by combining the vent stream with the inlet fuel or by feeding the stream into the boiler or stream through a separate burner. An industrial boiler produces steam at high temperatures. A process heater raises the temperature of the process stream as well as the superheating steam at temperatures usually lower than those of an industrial boiler. Greater than 99 percent control efficiency is achievable with these combustion devices.[46]

By using catalysts, combustion can occur at temperatures lower than those used in thermal incineration. A catalytic oxidizer is similar to a thermal incinerator except that it incorporates the use of a catalyst. Combustion catalysts include platinum, platinum alloys, copper oxide, chromium, and cobalt. Catalytic oxidizers can achieve destruction efficiencies of 98 percent or greater.[46]

Biofiltration is another type of VOC control. In biofiltration, process exhaust gases are passed through soil on compost beds containing micro organisms, which convert VOC to carbon dioxide, water, and mineral salts.[47]

Table 4-12 presents a comparison of the VOC control technologies (excluding combustion) that are discussed in this section.[47]

Process vents emitting benzene and other VOC that are discussed in Sections 4.1 through 4.4 and in Section 5.0 are affected by one or more of the following six Federal regulations:

1. “National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry,” promulgated April 22, 1994.[48]
2. “National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries,” promulgated August 18, 1995.[49]

TABLE 4-12. COMPARISON OF VOC CONTROL TECHNOLOGIES

Control Technology	Applicable Concentration Range, ppm	Capacity Range, cfm	Removal Efficiency	Secondary Wastes	Advantages	Limitations and Contradictions
Thermal Oxidation	100-2,000	1,000-500,000	95-99+%	Combustion products	Up to 94% energy recovery is possible.	Halogenated compounds may require additional control equipment downstream. Not recommended for batch operations.
Catalytic Oxidation	100-2,000	1,000-100,000	90-95%	Combustion products	Up to 70% energy recovery is possible.	Thermal efficiency suffers with swings in operating conditions. Halogenated compounds may require additional control equipment downstream. Certain compounds can poison the catalyst (lead, arsenic, phosphorous, chlorine, sulfur, particulate matter).
Condensation	>5,000	100-20,000	50-90%	Condensate	Product recovery can offset annual operating costs.	Not recommended for materials with boiling point <100°F. Condensers are subject to scale buildup which can cause fouling.
Carbon Adsorption	20-5,000	100-60,000	90-98%	Spent carbon; collected organic	Product recovery can offset annual operating costs. Can be used as a concentrator in conjunction with another type of control device. Works well with cyclic processes.	Not recommended for streams with relative humidity <50%. Ketones, aldehydes, and esters clog the pores of the carbon, decreasing system efficiency.

(continued)

TABLE 4-12. CONTINUED

Control Technology	Applicable Concentration Range, ppm	Capacity Range, cfm	Removal Efficiency	Secondary Wastes	Advantages	Limitations and Contradictions
Absorption	500-5,000	2,000-100,000	95-98%	Wastewater; Captured particulate	Product recovery can offset annual operating costs.	Might require exotic scrubbing media. Design could be difficult in the event of lack of equilibrium data. Packing is subject to plugging and fouling if particulates are in the gas stream. Scale formation from adsorbent/adsorber interaction can occur.
Biofiltration	0-1,000	<90,000	80-99%	Disposal of spent compost beds.	Efficient for low concentration streams. Low operating costs.	Large amount of space may be required. Microorganisms are effective only in the 50 to 100°F temperature range and may be killed if proper bed moisture content and pH is not maintained.

Source: Reference 47.

3. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Air Oxidation," promulgated July 1, 1994.[50]

4. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Distillation Operations," promulgated July 1, 1994.[51]

5. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Reactor Processes," promulgated July 1, 1994.[52]

6. "National Emission Standards for Benzene Emissions from Coke By-Product Recovery Plants, promulgated October 27, 1993."[53]

In general, for the affected facilities subject to these six regulations, use of the recovery devices and combustion devices discussed above is required. Tables 4-10 and 4-11 present a summary of those controls and the required operating parameters and monitoring ranges needed to ensure that the required control efficiency is being achieved.

4.5.2 Equipment Leak Emissions, Controls, and Regulations

Equipment leak emissions occur from process equipment components whenever the liquid or gas streams leak from the equipment. Equipment leaks can occur from the following components: pump seals, process valves, compressor seals and safety relief valves, flanges, open-ended lines, and sampling connections. The following approaches for estimating equipment leak emissions are presented in the EPA publication *Protocol for Equipment Leak Emission Estimates*:[54]

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches differ in complexity; however, greater complexity usually yields more accurate emissions estimates.

The simplest method, the average emission factor approach, requires that the number of each component type be known. For each component, the benzene content of the stream and the time the component is in service are needed. This information is then multiplied by the EPA's average emission factors for the SOCMI shown in Table 4-13.[54] Refinery average emission factors are shown in Table 4-14; marketing terminal average emission factors are shown in Table 4-15; and oil and gas production average emission factors are shown in Table 4-16.[54] This method is an improvement on using generic emissions developed from source test data, inventory data, and/or engineering judgement. However, this method should only be used if no other data are available because it may result in an overestimation or underestimation of actual equipment leak emissions. For each component, estimated emissions are calculated as follows:

$$\left[\begin{array}{c}\text{No. of}\\ \text{equipment}\\ \text{components}\end{array}\right] \text{ x } \left[\begin{array}{c}\text{Weight \%}\\ \text{benzene}\\ \text{in the stream}\end{array}\right] \text{ x } \left[\begin{array}{c}\text{Component-}\\ \text{specific}\\ \text{emission factor}\end{array}\right] \text{ x } \left[\begin{array}{c}\text{No. hr/yr in}\\ \text{benzene service}\end{array}\right]$$

To obtain more accurate equipment leak emission estimates, one of the more complex estimation approaches should be used. These approaches require that some level of emissions measurement for the facility's equipment components be collected. These are described briefly, and the reader is referred to the EPA protocol document for the calculation details.

The screening ranges approach (formerly known as the leak/no leak approach) is based on a determination of the number of leaking and non-leaking components. This approach may be applied when screening data are available as either "greater than or equal to 10,000 ppmv" or as "less than 10,000 ppmv." Emission factors for these two ranges of screening values are presented in Table 4-17 for SOCMI screening; Table 4-18 for refinery screening, Table 4-19 for marketing terminal screening, and Table 4-20 for oil and gas production screening.[54]

TABLE 4-13. SOCMI AVERAGE TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR EQUIPMENT LEAK EMISSIONS[a]

Equipment Type	Service	Emission Factor[b] lb/hr/source (kg/hr/source)
Valves	Gas	0.01313 (0.00597)
	Light liquid	0.00887 (0.00403)
	Heavy liquid	0.00051 (0.00023)
Pump seals[c]	Light liquid	0.0438 (0.0199)
	Heavy liquid	0.01896 (0.00862)
Compressor seals	Gas	0.502 (0.228)
Pressure relief valves	Gas	0.229 (0.104)
Connectors	All	0.00403 (0.00183)
Open-ended lines	All	0.0037 (0.0017)
Sampling connections	All	0.0330 (0.0150)

Source: Reference 54.

[a] The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI average emission factors.
[b] These factors are for total organic compound emission rates.
[c] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

The EPA correlation approach offers an additional refinement to estimating equipment leak emissions by providing an equation to predict mass emission rate as a function of screening value for a specific equipment type. The EPA correlation approach is preferred when actual screening values are available. Correlation operations for SOCMI, refinery, marketing terminals, and oil and gas production along with respective correlation curves are provided in Reference 54.

The unit-specific correlation approach requires the facility to develop its own correlation equations and requires more rigorous testing, bagging, and analyzing of equipment leaks to determine mass emission rates.

Appendix A of the EPA protocol document provides example calculations for each of the approaches described above.

TABLE 4-14. REFINERY AVERAGE EMISSION FACTORS

Equipment type	Service	Emission Factor (kg/hr/source)[a]
Valves	Gas	0.0268
	Light Liquid	0.0109
	Heavy Liquid	0.00023
Pump seals[b]	Light Liquid	0.114
	Heavy Liquid	0.021
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.16
Connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.0150

Source: Reference 54.

[a] These factors are for non-methane organic compound emission rates.
[b] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

Although no specific information on controls of fugitive emissions used by the industry was identified, equipment components in benzene service will have some controls in place. Generally, control of fugitive emissions will require the use of sealless or double mechanical seal pumps and an inspection and maintenance program, as well as replacement of leaking valves and fittings. Typical controls for equipment leaks are listed in Table 4-21.[55] Some leakless equipment is available, such as leakless valves and sealless pumps.[55]

Equipment leak emissions are regulated by the National Emission Standard for Equipment Leaks (Fugitive Emission Sources) of Benzene promulgated in June 6, 1984.[56] This standard applies to sources that are intended to operate in benzene service, such as pumps, compressors, pressure relief devices, sampling connection systems, open-ended valves or lines, valves, flanges and other connectors, product accumulator vessels, and control devices or systems required by this subpart.

TABLE 4-15. MARKETING TERMINAL AVERAGE EMISSION FACTORS

Equipment Type	Service	Emission Factor (kg/hr/source)[a]
Valves	Gas	1.3×10^{-5}
	Light Liquid	4.3×10^{-5}
Pump seals	Gas	6.5×10^{-5}
	Light Liquid	5.4×10^{-4}
Others (compressors and others)[b]	Gas	1.2×10^{-4}
	Light Liquid	1.3×10^{-4}
Fittings (connectors and flanges)[c]	Gas	4.2×10^{-5}
	Light Liquid	8.0×10^{-6}

Source: Reference 54.

[a] These factors are for total organic compound emission rates (including non-VOC such as methane and ethane).

[b] The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

[c] "Fittings" were not identified as flanges or non-flanged connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

Each owner or operator subject to Subpart J shall comply with the requirement of the National Emission Standard for Equipment Leaks promulgated in June 6, 1984.[57] The provisions of this subpart apply to the same sources mentioned above that are intended to operate in volatile hazardous air pollutant (VHAP) service. Benzene is a VHAP.

The SOCMI New Source Performance Standards promulgated in October 18, 1983[58] also apply to equipment leak emissions. These standards apply to VOC emissions at affected facilities that commenced construction, modification, or reconstruction after January 5, 1981.

Equipment leak emissions from Coke by-product recovery plants are regulated by the National Emission Standard for Benzene Emissions from Coke By-Product Recovery Plants promulgated in September 14, 1989.[53] These standards apply to the same sources (equipment leak components) as indicated in Subpart J, and V of Part 61.

TABLE 4-16. OIL AND GAS PRODUCTION OPERATIONS AVERAGE EMISSION FACTORS (kg/hr/source)

Equipment Type	Service[a]	Emission Factor (kg/hr/source)[b]
Valves	Gas	4.5×10^{-3}
	Heavy Oil	8.4×10^{-6}
	Light Oil	2.5×10^{-3}
	Water/Oil	9.8×10^{-5}
Pump seals	Gas	2.4×10^{-3}
	Heavy Oil	NA
	Light Oil	1.3×10^{-2}
	Water/Oil	2.4×10^{-5}
Others[c]	Gas	8.8×10^{-3}
	Heavy Oil	3.2×10^{-5}
	Light Oil	7.5×10^{-3}
	Water/Oil	1.4×10^{-2}
Connectors	Gas	2.0×10^{-4}
	Heavy Oil	7.5×10^{-6}
	Light Oil	2.1×10^{-4}
	Water/Oil	1.1×10^{-4}
Flanges	Gas	3.9×10^{-4}
	Heavy Oil	3.9×10^{-7}
	Light Oil	1.1×10^{-4}
	Water/Oil	2.9×10^{-6}
Open-ended lines	Gas	2.0×10^{-3}
	Heavy Oil	1.4×10^{-4}
	Light Oil	1.4×10^{-3}
	Water/Oil	2.5×10^{-4}

Source: Reference 54.

[a] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50 percent, from the point of origin to the point where the water content reaches 99 percent. For water streams with a water content greater than 99 percent, the emission rate is considered negligible.

[b] These factors are for total organic compound emission rates (including non-VOC such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[c] The "other" equipment type was derived from compressors, diaphrams, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

TABLE 4-17. SOCMI SCREENING VALUE RANGE TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR EQUIPMENT LEAK EMISSIONS[a]

Equipment Type	Service	≥10,000 ppmv Emission Factor[b] lb/hr/source(kg/hr/source)	<10,000 ppmv Emission Factor[b] lb/hr/source(kg/hr/source)
Valves	Gas	0.1720 (0.0782)	0.000288 (0.000131)
	Light liquid	0.1962 (0.0892)	0.000363 (0.000165)
	Heavy liquid	0.00051 (0.00023)	0.00051 (0.00023)
Pump seals[c]	Light liquid	0.535 (0.243)	0.00411 (0.00187)
	Heavy liquid	0.475 (0.216)	0.00462 (0.00210)
Compressor seals	Gas	3.538 (1.608)	0.1967 (0.0894)
Pressure relief valves	Gas	3.720 (1.691)	0.0983 (0.0447)
Connectors	All	0.249 (0.113)	0.0001782 (0.0000810)
Open-ended lines	All	0.02629 (0.01195)	0.00330 (0.00150)

Source: Reference 54.

[a] The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI ≥ 10,000/< 10,000 ppmv emission factors.

[b] These factors are for total organic compound emission rates.

[c] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE 4-18. REFINERY SCREENING RANGES EMISSION FACTORS

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/hr/source)[a]	<10,000 ppmv Emission Factor (kg/hr/source)[a]
Valves	Gas	0.2626	0.0006
	Light Liquid	0.0852	0.0017
	Heavy Liquid	0.00023	0.00023
Pump seals[b]	Light Liquid	0.437	0.0120
	Heavy Liquid	0.3885	0.0135
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.0375	0.00006
Open-ended lines	All	0.01195	0.00150

Source: Reference 54.

[a] These factors are for non-methane organic compound emission rates.
[b] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

The hazardous organic NESHAP (or HON) equipment leak provisions promulgated on April 22, 1994, affect chemical production processes.[59,60] The HON provisions apply to new and existing facilities and specify a control level of 90 percent.

The petroleum refineries NESHAP equipment leak provisions promulgated on August 18, 1995 affects petroleum refinery process units. The petroleum refinery provisions apply to new and existing facilities.

4.5.3 Storage Tank Emissions, Controls, and Regulations

A possible source of benzene emissions from chemical production operations that produce or use benzene are storage tanks that contain benzene. Emissions from storage tanks include "working losses" and "breathing losses." Working losses are emissions that occur while a tank is being filled (filling the tank with liquid forces organic vapors out of the tank). Breathing losses are emissions that result from expansion due to temperature changes (a higher

TABLE 4-19. MARKETING TERMINAL SCREENING RANGES EMISSION FACTORS

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/hr/source)[a]	<10,000 ppmv Emission Factor (kg/hr/source)[a]
Valves	Gas	NA	$1.3x10^{-5}$
	Light Liquid	$2.3x10^{-2}$	$1.5x10^{-5}$
Pump seals	Light Liquid	$7.7x10^{-2}$	$2.4x10^{-4}$
Others (compressors and others)[b]	Gas	NA	$1.2x10^{-4}$
	Light Liquid	$3.4x10^{-2}$	$2.4x10^{-5}$
Fittings (connectors and flanges)[c]	Gas	$3.4x10^{-2}$	$5.9x10^{-6}$
	Light Liquid	$6.5x10^{-3}$	$7.2x10^{-6}$

Source: Reference 54.

[a] These factors are for total organic compound emission rates (including non-VOC such as methane and ethane). "NA" indicates that not enough data were available to develop the indicated emission factors.

[b] The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

[c] "Fittings" were not identified as flanges or connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

ambient temperature heats the air inside the tank, causing the air to expand and forcing organic vapors out of the tank). The calculations to estimate working and breathing loss emissions from storage tanks are complex and require knowledge of a number of site-specific factors about the storage tank for which emissions are being estimated. Equations for estimating emissions of organic compounds from storage tanks are provided in the EPA document entitled *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 7.[33]

Benzene emissions from storage tanks may be reduced with control equipment and by work practices. Various types of control equipment may be used to reduce organic emissions, including (1) storing the liquid in a storage tank with a floating deck (i.e., an internal-floating-roof tank or external-floating-roof tank), (2) equipping floating decks with additional devices to reduce emissions (e.g., applying sealing mechanisms around the perimeter of the floating deck, welding the deck seams, installing gaskets around openings and in closure devices on the floating deck), and (3) venting air emissions from a fixed-roof storage tank to a control device (e.g., a closed-vent system and a carbon adsorber, condenser, or flare). Work

TABLE 4-20. OIL AND GAS PRODUCTION OPERATIONS SCREENING RANGES EMISSION FACTORS

Equipment Type	Service[a]	≥10,000 ppmv Emission Factor (kg/hr/source)[b]	10,000 ppmv Emission Factor (kg/hr/source)[b]
Valves	Gas	$9.8x10^{-2}$	$2.5x10^{-5}$
	Heavy Oil	NA	$8.4x10^{-6}$
	Light Oil	$8.7x10^{-2}$	$1.9x10^{-5}$
	Water/Oil	$6.4x10^{-2}$	$9.7x10^{-6}$
Pump seals	Gas	$7.4x10^{-2}$	$3.5x10^{-4}$
	Heavy Oil	NA	NA
	Light Oil	$1.0x10^{-1}$	$5.1x10^{-4}$
	Water/Oil	NA	$2.4x10^{-5}$
Others[c]	Gas	$8.9x10^{-2}$	$1.2x10^{-4}$
	Heavy Oil	NA	$3.2x10^{-5}$
	Light Oil	$8.3x10^{-2}$	$1.1x10^{-4}$
	Water/Oil	$6.9x10^{-2}$	$5.9x10^{-5}$
Connectors	Gas	$2.6x10^{-2}$	$1.0x10^{-5}$
	Heavy Oil	NA	$7.5x10^{-6}$
	Light Oil	$2.6x10^{-2}$	$9.7x10^{-6}$
	Water/Oil	$2.8x10^{-2}$	$1.0x10^{-5}$
Flanges	Gas	$8.2x10^{-2}$	$5.7x10^{-6}$
	Heavy Oil	NA	$3.9x10^{-7}$
	Light Oil	$7.3x10^{-2}$	$2.4x10^{-6}$
	Water/Oil	NA	$2.9x10^{-6}$
Open-ended lines	Gas	$5.5x10^{-2}$	$1.5x10^{-5}$
	Heavy Oil	$3.0x10^{-2}$	$7.2x10^{-6}$
	Light Oil	$4.4x10^{-2}$	$1.4x10^{-5}$
	Water/Oil	$3.0x10^{-2}$	$3.5x10^{-6}$

Source: Reference 54.

[a] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50 percent, from the point of origin to the point where the water content reaches 99 percent. For water streams with a water content greater than 99 percent, the emission rate is considered negligible.

[b] These factors are for total organic compound emission rates (including non-VOC such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[c] The "other" equipment type was derived from compressors, diaphrams, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

TABLE 4-21. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

Equipment Component (Emission Source)	Control Technique	Percent Reduction[a]
Pump Seals:		
Packed and Mechanical	Seal area enclosure vented to a combustion device	100
	Monthly LDAR[b]	69
	Quarterly LDAR	45
Double Mechanical[c]	N/A[d]	--
Compressors	Vent degassing reservoir to combustion device	100
Flanges	None available	0
Valves:		
Gas	Monthly LDAR	87
	Quarterly LDAR	67
Liquid	Monthly LDAR	84
	Quarterly LDAR	61
Pressure Relief Devices		
Gas	Monthly LDAR	50
	Quarterly LDAR	44
	Rupture Disk	100
Sample Connections	Closed-purge sampling	100
Open-Ended Lines	Caps on open ends	100

Source: Reference 55.

[a] If a negative reduction for a control technique was indicated, zero was used.

[b] LDAR = Leak detection and repair, at a leak definition of 10,000 ppmv.

[c] Assumes the seal barrier fluid is maintained at a pressure above the pump stuffing box pressure and the system is equipped with a sensor that detects failure of the seal and/or barrier fluid system.

[d] N/A - Not applicable. There are no VOC emissions from this component.

practices that reduce organic emissions include keeping manholes and other access doors gasketed and bolted unless in use.

The control efficiencies achieved by the various types of control equipment vary. Storage tanks with internal or external floating roofs will have varying emission control efficiencies depending on the type of floating deck and seal mechanism used, as well as various other factors. The control efficiency achieved by closed-vent systems and control devices also varies, depending on the type and specific design of the control device used. For information on the control efficiencies associated with specific control devices, refer to Tables 4-10 and 4-11. The control devices applicable to reducing process vent emissions listed in these tables are also applicable to storage tanks.

Storage tanks containing benzene and other organic compounds are regulated by the four following Federal rules:

1. "National Emission Standard for Benzene Emissions from Benzene Storage Vessels;"[61]
2. "Standards of Performance for Volatile Organic Liquid Storage Vessels for which Construction, Reconstruction, or Modification Commenced after July 23, 1984;"[62]
3. "National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater;"[63] and
4. "National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries."[49]

In combination, these four regulations generally require new and existing facilities subject to the rules to store benzene in an internal-floating-roof storage tank, an external-floating-roof storage tank, or a fixed-roof storage tank with a closed-vent system and control device that reduces emissions by 95 percent for a new facility, or 90 percent for an existing facility. Additionally, the four regulations include requirements for specific seal mechanisms and gaskets to be utilized on a floating roof, as well as certain work practices.

4.5.4 Wastewater Collection and Treatment System Emissions, Controls, and Regulations

A possible source of benzene emissions from chemical production operations that use benzene are wastewater collection and treatment systems that handle wastewater containing benzene. Benzene emissions from wastewater collection systems can originate from various types of equipment including wastewater tanks, surface impoundments, containers, drain systems, and oil-water separators. Emissions also originate from wastewater treatment systems. Equations for estimating emissions of organic compounds from wastewater collection and treatment systems are provided in the EPA document *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 4.[64]

Two control strategies can be applied to benzene emissions from wastewater. The first control strategy is waste minimization through process modifications, modification of operating practices, preventive maintenance, recycling, or segregation of waste streams. The second control strategy is to reduce the benzene content of the wastewater through treatment before the stream contacts ambient air. A complete strategy for reducing the benzene content of the wastewater includes: (1) suppression of emissions from collection and treatment system components by hard piping or enclosing the existing wastewater collection system up to the point of treatment, (2) treatment of the wastewater to remove benzene, and (3) treatment of residuals. Residuals include oil phases, condensates, and sludges from nondestructive treatment units.[65] This section will discuss the second control strategy of reducing benzene emissions by suppression and treatment.

The benzene emissions from wastewater collection and treatment systems can be controlled either by hard piping or by enclosing the transport and handling system from the point of wastewater generation until the wastewater is treated to remove or destroy the organic compounds. Suppression techniques can be broken down into four categories: collection system controls, roofs, floating membranes, and air-supported structures. These techniques can be applied to drain systems, tanks, containers, surface impoundments, and oil-water separators. Suppression of benzene emissions merely keeps the organic compounds in the wastewater until they reach the next potential benzene emission source. Therefore, these techniques are not effective unless the benzene emissions are suppressed until the wastewater reaches a treatment device where the organic compounds are either removed or destroyed. Also, work practices, such as leak detection and repair, must be used to maintain equipment effectiveness.[65]

Treatment techniques that can be used to remove or destroy benzene are steam stripping and air stripping (removal) and biological treatment (destruction). Steam and air stripping accomplish removal by stripping benzene out of the wastewater into a gas stream, which must then be controlled and vented to the atmosphere. Biological treatment destroys benzene by using microorganisms to biodegrade the benzene in the process of energy and biomass production.

Add-on controls serve to reduce benzene emissions by destroying or extracting benzene from gas phase vent streams before it is discharged to the atmosphere. Add-on controls are applicable to vents associated with collection and treatment covers, such as drain covers, fixed roofs, and air-supported structures, and with organic compound removal devices, such as air strippers and steam strippers. Add-on controls for benzene emissions are classified into four broad categories: adsorption, combustion, condensation, and absorption. The type of add-on control best suited for a particular wastewater emission source depends on the size of the source and the characteristics of the wastewater in the source.[65]

The control efficiencies associated with the various types of suppression, treatment, and add-on control equipment vary. Estimating the control efficiency of emissions suppression techniques for wastewater collection systems (e.g., water seals, covers, floating roofs, and submerged fill pipes) is complex, and equations for estimating emissions from these sources are not readily available. The control efficiency associated with use of a fixed-roof or gasketed cover and a closed-vent system routed to a control device would be equivalent to the efficiency achieved by the control device. Refer to Tables 4-10 and 4-11 for a listing of control devices applicable to wastewater systems. Additionally, the control efficiencies associated with steam and air strippers and biological treatment units vary, depending on the design of the systems. Refer to the discussion below for the specific control efficiencies associated with steam strippers and biological treatment units that would be designed to comply with existing Federal regulations.

Wastewater streams containing benzene are Federally regulated by the following rules:

1. "National Emission Standard for Benzene Waste Operations;"[66]
2. "National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater" (HON);[63] and
3. "National Emission Standards for Hazardous Air Pollutants at Petroleum Refineries."[49]

The rules regulate benzene emissions from wastewater collection and treatment systems, and apply to new and existing facilities. Chemical production processes subject to the regulations would be required to apply many of the controls specified above for both wastewater collection and waste water treatment systems.

The rules require specific suppression equipment (e.g., roofs) and work practices (e.g., leak detection and repair) rather than specifying a suppression control efficiency that must be achieved. For add-on control devices (e.g., incinerators, adsorbers) to destroy organics vented from collection and treatment equipment, both rules require 95 percent efficiency.

For treatment, the National Emission Standard for Benzene Waste Operations[66] and the National Petroleum Refinery NESHAP[49] do not require specific treatment equipment. Instead, the rule requires the treatment process to achieve either removal or destruction of benzene in the waste system by 99 percent, or removal of benzene to less than 10 parts per million by weight (ppmw). However, the technology basis for the 99 percent efficiency standard is steam stripping.

The HON offers several different wastewater treatment compliance options. These options include concentration-based limits, pollutant reduction percentages, and an equipment standard. The equipment standard is a steam stripper with specific design criteria that would result in a 99 percent reduction in benzene emissions. The HON also allows facilities to comply with the treatment standard by using biological treatment units that achieve a 95 percent reduction of total organic hazardous air pollutants in the wastewater. (Benzene is one of the hazardous air pollutants).

4.5.5 Product Loading and Transport Operations Emissions, Controls, and Regulations

Although pipeline transfer of raw materials and products is widely used in the different industries, shipment by tank cars, tank trucks, ships, and barges is also common. The product loading and transportation of chemicals and petroleum liquids represent potential sources of evaporation losses.

Emissions from the above sources are due to loading losses, ballasting losses, and transit losses. Refer to Section 6.3 (Gasoline Marketing) of this document for information on emission factors and equations to estimate emissions from loading and transport operations, as well as information on control technology.

The HON regulates organic hazardous air pollutants (HAP) emissions from product loading and transport operations.[59,63] The National Emission Standard for Benzene Emissions from Benzene Transfer Operations also regulates benzene transfer emissions.[67]

SECTION 5.0

EMISSIONS FROM MAJOR USES OF BENZENE

The largest portion of benzene produced is used in the production of ethylbenzene/styrene. Other major chemicals for which benzene is used as a feedstock include cyclohexane, cumene, phenol, nitrobenzene, and linear alkylbenzene. For each of these emission sources, the following information is provided in the sections below: (1) a brief characterization of the national activity in the United States, (2) a process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed.

Emission factors are presented, as available. The reader is advised to contact the specific source in question to verify the nature of the process, production volume, and control techniques used before applying any of the emission factors presented in this report.

Other minor chemicals where benzene is used as a feedstock include resorcinol, benzophenone, hydroquinone, anthraquinone, biphenyl, and benzene sulfonic acid.[68] These chemical processes are discussed briefly in this section. Although benzene has been used in the past as a feedstock in the production of maleic anhydride, all capacity for producing maleic anhydride in the United States is now n-butane based; therefore, the process for producing maleic anhydride from benzene is not included in this section.

5.1 ETHYLBENZENE AND STYRENE PRODUCTION

Ethylbenzene is a liquid at standard conditions, with a boiling point of 277 °F (136°C) and a vapor pressure of 1,284 Pa (0.0126 atm).[69] About 50 percent of the U.S. production of benzene is used to produce ethylbenzene. The ethylbenzene industry is closely tied to the styrene industry because styrene is produced exclusively from ethylbenzene. There can be approximately a 0.3 percent by weight carry-over of benzene into ethylbenzene and styrene.[9] Additionally, some benzene is reformed in the production of styrene. Ethylbenzene production processes and uses thereby constitute a major potential source of benzene emissions, particularly because styrene production is anticipated to experience continued growth. Ethylbenzene demand is expected to show growth of only 2.5 to 3.5 percent per year over the next several years.[70]

Ethylbenzene is used almost exclusively to produce styrene. Some ethylbenzene is used as a solvent (often replacing xylene) and in the production of some dyes.[71] Total ethylbenzene production capacity is currently 13,874 million pounds per year (lb/yr) (6,293 kg/yr).[11] Approximately 95 percent of this capacity is based on benzene alkylation, with the remainder based on extraction from mixed xylene streams. Most styrene is produced by two methods: hydrogenation of ethylbenzene (89 percent) and peroxidation of ethylbenzene with subsequent hydration (11 percent). The latter process can also co-produce propylene oxide. A third process, converting ethylbenzene isothermally to styrene, was developed in Europe. To date, no U.S. facilities report using this method.

Another method that co-produces both ethylbenzene and styrene has been patented.[72] In this process, toluene and light alkanes other than ethane are reacted at 1,832 to 2,192 °F (1,000 to 1,200°C) and then gradually cooled to produce an 80 percent ethylbenzene/12 percent styrene product with a mass of about 25 percent by weight of the toluene reactant. These products can be separated by distillation, and the ethylbenzene either recycled, sold, or converted to styrene by another process--dehydrogenation or peroxidation. This process is not reported to be in use at this time.

Table 5-1 lists U.S. producers of ethylbenzene and styrene.[11,69,73] Most facilities produce both ethylbenzene and styrene on site, thus reducing shipping and storage. Only one styrene production site does not have ethylbenzene production capacity. Four ethylbenzene production sites do not have styrene production capacity. Ethylbenzene from mixed xylene separation is generally shipped or supplemented with another ethylbenzene source for styrene production. Only one site uses the peroxidation process to produce styrene. Table 5-1 also gives the latest facility capacity.

5.1.1 Process Description for Ethylbenzene and Styrene Production Using Benzene Alkylation and Ethylbenzene Dehydrogenation

Most ethylbenzene production is integrated with the dehydrogenation process to produce styrene; therefore, these processes are described together. The primary reactions are (1) catalytic alkylation of benzene with ethylene to produce ethylbenzene, and (2) catalytic dehydrogenation of ethylbenzene to produce styrene.

A process flow diagram including the basic operations that may be used in the production of ethylbenzene by benzene alkylation with ethylene is shown in Figure 5-1.[14,74]

The first step in the process is the drying of benzene to remove water from both feed and recycled benzene. An emission source in this process is the vent from the benzene drying column (Vent B).[69]

The dry benzene (Stream 1) is fed to the alkylation reactor along with ethylene, aluminum chloride catalyst, and recycled polyethylbenzenes. The reactor effluent (Stream 2) goes to a settler, where crude ethylbenzene is decanted and the heavy catalyst-complex layer is recycled to the reactor. Any inert gases fed with the ethylene or produced in the alkylation reactor, along with some unreacted benzene, other organics, and hydrogen chloride, are exhausted from the reactor or from the treating section (Vent A). Reactor vent gas is generally routed through a condenser and scrubbers in the alkylation reaction section (not shown on the

TABLE 5-1. U.S. PRODUCERS OF ETHYLBENZENE AND STYRENE

		Ethylbenzene		Styrene	
Company	Location	Process	Capacity million lb (million kg)	Process	Capacity million lb (million kg)
Amoco Chemical Company	Texas City, TX	NA	908[a] (412)	C[b]	800[a] (363)
ARCO Chemical Company	Channelview, TX	NA	2789[a] (1265)	D[b]	2525[a] (1145)
	Monarca, PA		220 (100)	---	---
Chevron Chemical Company	St. James, LA	NA	1700[a] (771)	C[b]	1525[a] (692)
Cos-Mar, Inc.	Carville, LA	A[c]	2200[a,d] (998)	C[b]	1900[a] (862)
Deltech Corporation	Baton Rouge, LA	NA	694[a,e] (315)	---	---
Dow Chemical U.S.A.	Freeport, TX	A[c]	1750[a] (794)	C[b]	1420[a] (644)
Huntsman Chemical Corporation	Bayport, TX	NA	1240[a] (562)	C[b]	1250[a] (567)
Koch Refining Company	Corpus Christi, TX	65% A[c] 35% B[c]	100[a] (45)	---	---
Phibro Energy USA, Inc.	Houston, TX	NA	25[a] (11)	---	---
Rexene Corporation	Odessa, TX	NA	350[a] (159)	C[b]	320[a] (145)
Sterling Chemicals, Inc.	Texas City, TX	NA	1750[a] (794)	C[b]	1600[a] (726)
Westlake Styrene Corporation	Lake Charles, LA	NA	368[a] (167)	---	---
	Sulphur, LA	---	---	C[b]	353[a] (160)

(continued)

TABLE 5-1. CONTINUED

Source: References 11, 69, and 73.

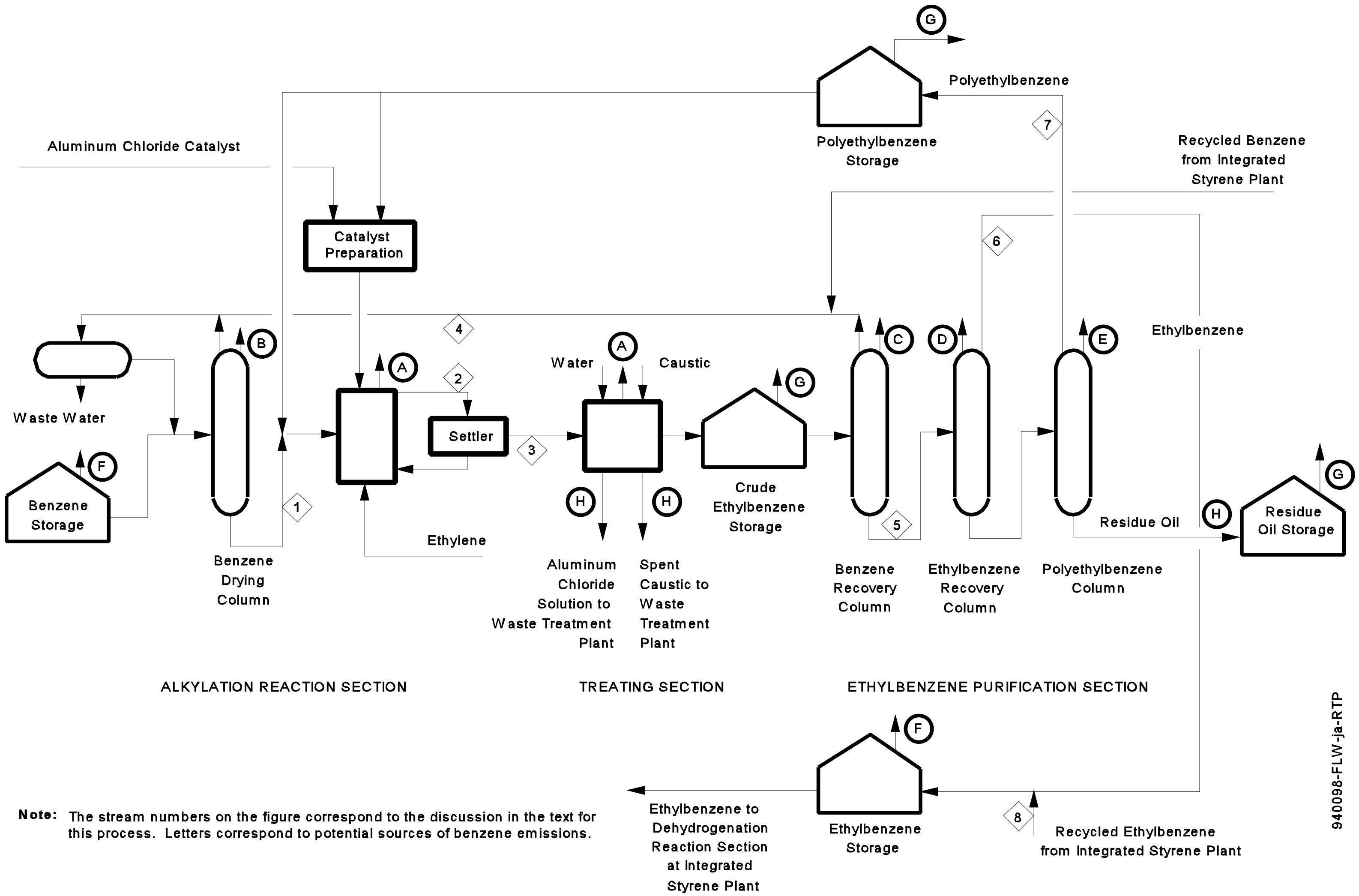
[a] Reference 11.
[b] Reference 73.
[c] Reference 69.
[d] Capacity does not include an excess capacity of 500 million pounds (227 million kg) of capacity on standby.
[e] Plant is on standby.

NA = Not available.

A = Benzene Alkylation (ethylbenzene production)
B = Xylene Separation (ethylbenzene production)
C = EB Hydrogenation (styrene production)
D = EB Peroxidation and Dehydration (styrene production)

"--" = means that the plant does not make this product.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contact with plant personnel. These data for producers and locations were current as of January 1993.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-1. Basic Operations that may be used in the Production of Ethylbenzene by Benzene Alkylation with Ethylbenzene

Source: References 14 and 74.

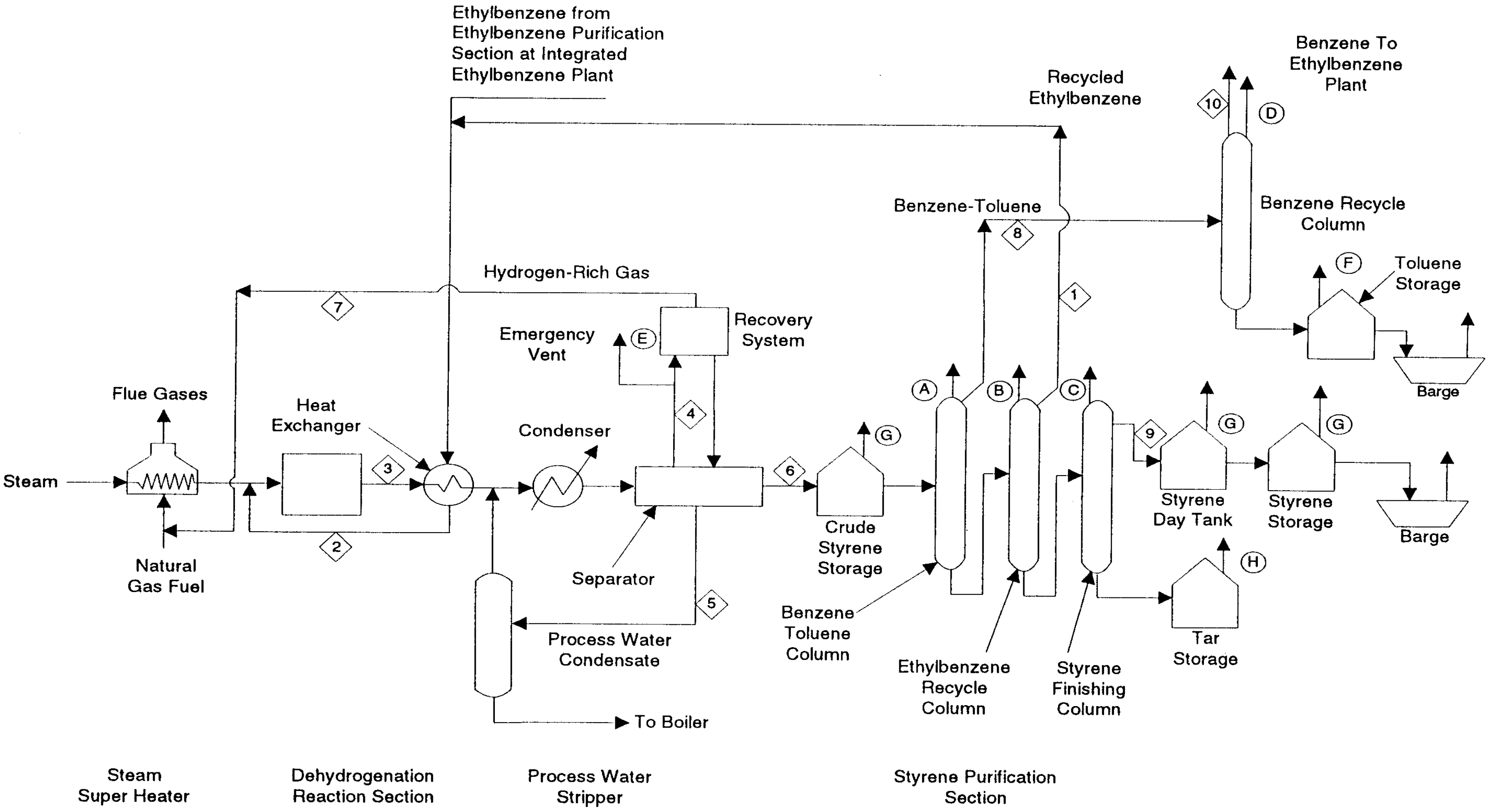
figure) to recover aromatics and to remove hydrogen chloride (HCl) before the remaining inert gases are vented.[69]

The crude ethylbenzene (Stream 3) from the settler is washed with water and caustic to remove traces of chlorides and then fed to the ethylbenzene purification section. The crude ethylbenzene contains 40 to 55 percent benzene, 10 to 20 percent polyethylbenzene (PEB), and high-boiling point materials. The first step in purification is separation of recycled benzene (Stream 4) from the crude ethylbenzene in the benzene recovery column. In the second step, the product ethylbenzene (Stream 5) is separated from the heavier hydrocarbons in the ethylbenzene recovery column. The heavier hydrocarbons are distilled in the polyethylbenzene column to separate the polyethylbenzenes, which are recycled (Stream 7), from the residue oil.[69] Emission points in the purification section include vents from the benzene and ethylbenzene recovery columns (Vent C and D, respectively) and the polyethylbenzene column (Vent E).[69]

Fresh ethylbenzene (Stream 6) from the ethylbenzene purification section is combined with recycled ethylbenzene (Stream 8) from the styrene purification section at the integrated styrene plant and is stored for use as an intermediate for making styrene.[69] Other emission points from the process including storage tanks, are shown in Figure 5-1.

A process flow diagram including the basic operations that may be used in the production of styrene by ethylbenzene dehydrogenation is shown in Figure 5-2.[69,74]

Fresh ethylbenzene from the ethylbenzene purification section (ethylbenzene plant) is combined with recycled ethylbenzene (Stream 1) from the styrene purification section. The purified ethylbenzene is preheated in a heat exchanger. The resultant vapor (Stream 2) is then mixed continuously with steam at 1,310°F (710°C) in the dehydrogenation reactor, which contains one of several catalysts. The reaction product (Stream 3) then exits through the heat exchanger and is further cooled in a condenser, where water and crude styrene vapors are condensed.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-2. Basic Operations that may be used in the Production of Styrene by Ethylbenzene Dehydrogenation

Source: References 14 and 74.

The hydrogen-rich process gas is recovered and used as a fuel (Stream 7) and the process water is purified in a stripper and recycled to the boiler. The remaining crude styrene liquid (Stream 6) goes to a storage tank. Benzene and toluene (Stream 8) are removed from the crude styrene in the benzene/toluene column. They are then typically separated by distillation. The toluene is sold and the benzene is returned to ethylbenzene production section (Stream 10), or it may also be sold. Next, the ethylbenzene column removes ethylbenzene, which is directly recycled (Stream 1). Tars are removed and the product styrene (Stream 9) emerges from the styrene finishing column. In some facilities, an ethylbenzene/benzene/toluene stream is separated from the crude styrene initially and then processed separately.

Emission points in this process include vents from the columns for the styrene purification section between the separator and the recovery sections. These include the benzene toluene column (Vent A), the ethylbenzene recycle column (Vent B) and the emergency vent in the styrene finishing column (Vent C). Other emission points from the process including storage tanks and barge loading are shown in Figure 5-2.

5.1.2 Process Description for Ethylbenzene Production from Mixed Xylenes

Ethylbenzene can also be extracted from mixed xylene streams. Proportionately, however, very little ethylbenzene is produced in this fashion. The two major sources of ethylbenzene containing xylenes are catalytic reformate from refineries, and pyrolysis gasoline from ethylene production (see process description for ethylene production in Section 4.3). The amount of ethylbenzene available is dependent on upstream production variables. The ethylene separation occurs downstream of the benzene production. For this reason, the ethylbenzene produced by this process is not considered a source of benzene emissions. Instead, benzene emissions from the entire process train are considered to be emissions from benzene production and are included elsewhere in this document (Section 4.0).

When combined with the dehydrogenation process previously described to produce styrene (Figure 5-2), the process is similar except that the benzene recycling (Stream 10 in Figure 5-2) cannot be reused directly.

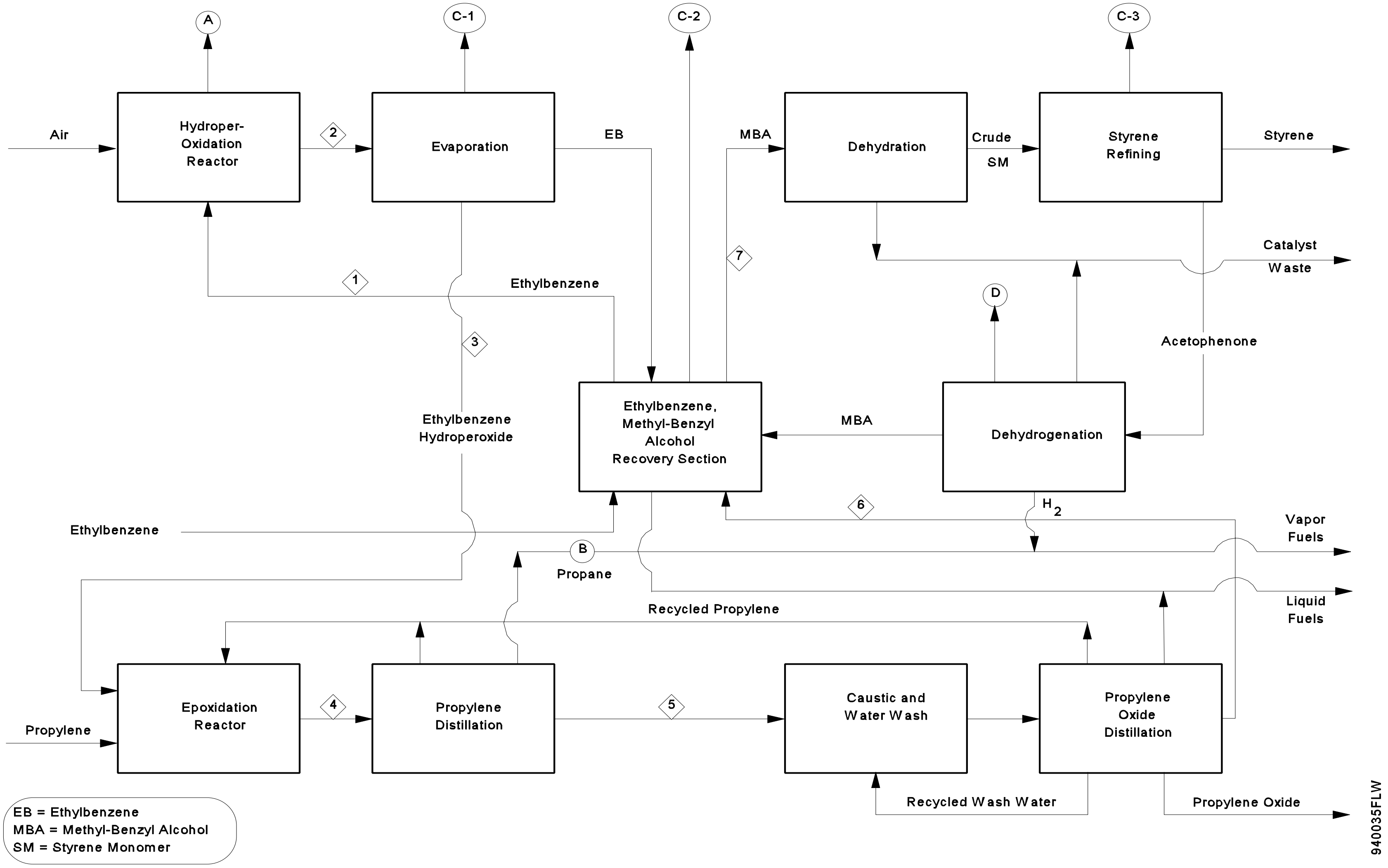
5.1.3 Process Description for Styrene Production from Ethylbenzene Hydroperoxidation

Presently, only one U.S. facility uses the hydroperoxidation process to produce styrene. Figure 5-3 shows a process flow diagram. The four major steps are described below.

Ethylbenzene (Stream 1) is oxidized with air to produce ethylene hydroperoxide (Stream 2) and small amounts of α-methyl-benzyl alcohol and acetophenone. The exit gas (principally nitrogen) is cooled and scrubbed to recover aromatics before venting. Unreacted ethylbenzene and low-boiling contaminants are removed in an evaporator. Ethylbenzene is then sent to the recovery section to be treated before reuse.

Ethylbenzene hydroperoxide (Stream 3) is combined with propylene over a catalyst mixture and high pressures to produce propylene oxide and acetophenone. Pressure is then reduced and residual propylene and other low-boiling compounds (Stream 4) are separated by distillation. The vent stream containing propane and some propylene can be used as a fuel. Propylene is recycled to the epoxidation reactor. The crude epoxidate (Stream 5) is treated to remove acidic impurities and residual catalyst material and the resultant epoxidate stream is distilled to separate the propylene oxide product for storage.

Residual water and propylene are recycled to the process train and liquid distillate is recovered as a fuel. The organic layer is routed (Stream 6) to the ethylbenzene and α-methyl-benzyl alcohol recovery section. Distillation removes any remaining ethylbenzene. Organic waste streams are separated from the α-methyl-benzyl alcohol and acetophenone organic waste liquids are used as fuel.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-3. Ethylbenzene Hydroperoxidation Process Block Diagram

Source: Reference 74.

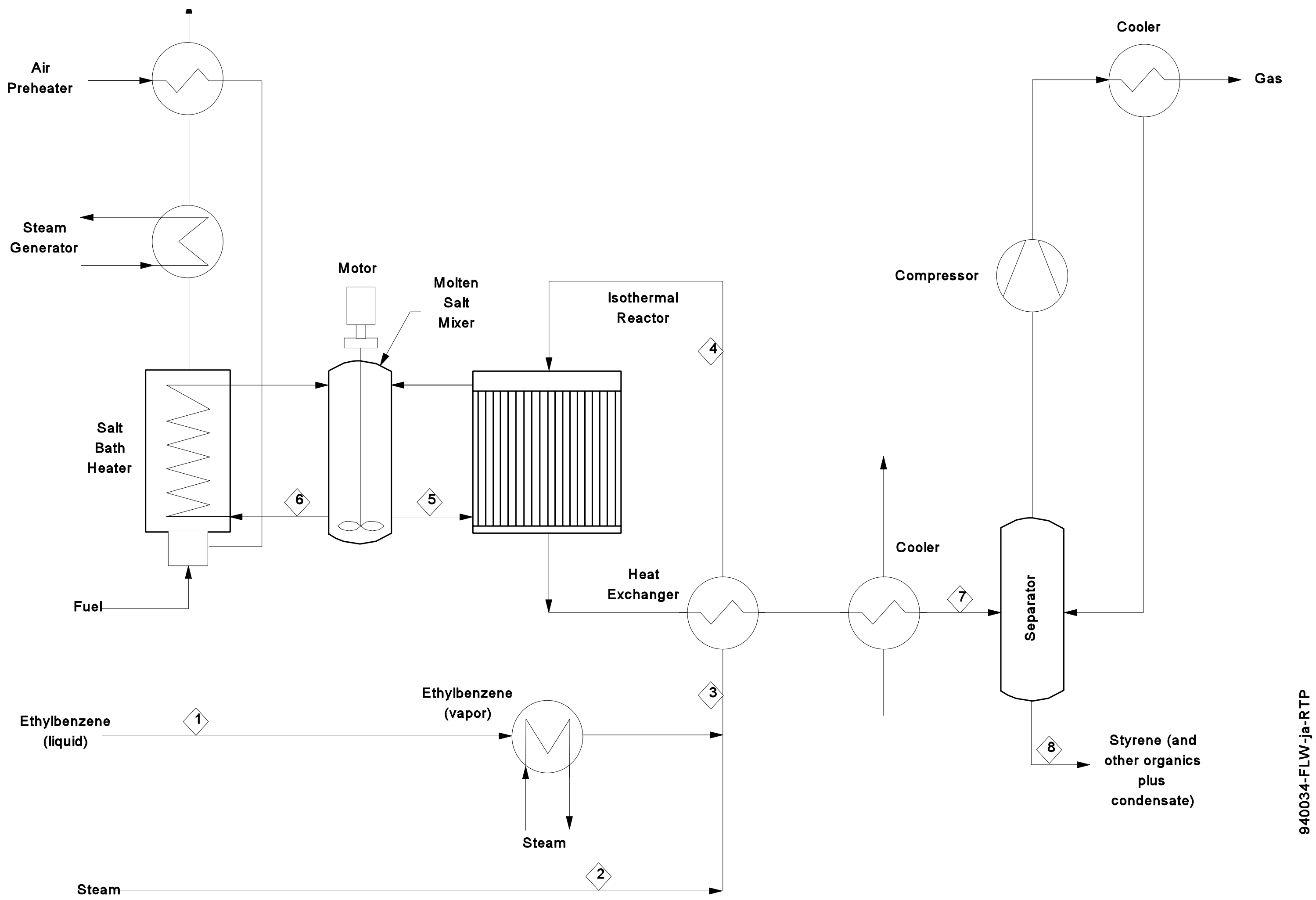
The mixed stream of α-methyl-benzyl alcohol and acetophenone (Stream 7) is then dehydrated over a solid catalyst to produce styrene. Residual catalyst solids and high-boiling impurities are separated and collected for disposal. The crude styrene goes to a series of distillation columns, where the pure styrene monomer product is recovered. The residual organic stream contains crude acetophenone, catalyst residue, and various impurities. This mixture is treated under pressure with hydrogen gas to convert the acetophenone to α-methyl-benzyl alcohol. Catalyst waste is separated from the α-methyl-benzyl alcohol, which is returned to the recovery section for processing and reuse. Hydrogen and organic vapors are recovered for use as fuel.

5.1.4 Process Description for Styrene Production by an Isothermal Process

Ethylbenzene may also be converted to styrene by an isothermal process (Figure 5-4). Liquid ethylbenzene is vaporized by condensing steam in a heat exchanger (Stream 1). Process steam (Stream 2) is then introduced into the ethylbenzene stream and the feed mixture is superheated (Stream 3) before it enters the molten-salt reactor (Stream 4) (see Figure 5-4).[75]

In the reactor, the ethylbenzene/steam mixture passes through the tubes, where it comes into contact with the catalyst and is dehydrogenated. Heat for the dehydrogenation reaction is supplied by molten salt (preferably a mixture of sodium carbonate, lithium carbonate, and potassium carbonate) surrounding the tubes (Stream 5). The reactor is maintained at a uniform wall temperature by circulating the molten-salt mixture through the heat exchanger of a fired heater (Stream 6).[75]

The reaction products are cooled and condensed in a separator (Stream 7). The liquid phase is a mixture of organic products: styrene, unreacted ethylbenzene, and small quantities of benzene, toluene, and high-boiling compounds. Styrene (Stream 8) is separated from the other liquid constituents, which then are recovered and recycled.[75]



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-4. Isothermal Processing of Styrene

Source: Reference 75.

The gas phase from the condensation step in the separator consists mainly of hydrogen, with small quantities of CO_2, CO, and methane. After these gases are compressed, they are cooled. Condensible products from this final cooling stage are then recovered and recycled to the separator. When hydrogen-rich offgas is used as fuel for the heater of the molten-salt reactor, the fuel requirement for this stage of the process is zero.[75]

5.1.5 Benzene Emissions from Ethylbenzene and Styrene Production via Alkylation and Dehydrogenation

Emission Estimates from Ethylbenzene Production and Dehydrogenation to Styrene

Emission factors have been developed based on an uncontrolled 300-million-kg/yr capacity integrated ethylbenzene/styrene production plant. Major process emission sources are the alkylation reactor area vents (Vent A in Figure 5-1), atmospheric and pressure column vents (Vents B, C, and D in Figure 5-1), vacuum column vents (Vent B in Figure 5-2), and the hydrogen separation vent (Stream 7 in Figure 5-2). Emission factors from these sources are given in Table 5-2.[69,74] The first four process vent streams in Table 5-2 are low-flow, high-concentration streams. The hydrogen separation stream (Stream 7 in Figure 5-2) is high-flow, low-concentration. Other emission sources listed in Table 5-2 include storage losses and shipment losses (Vent G). Fugitive emissions from valves and other equipment leaks are not indicated in Figure 5-1 or 5-2.

Reactor area vents remove various inerts plus entrained aromatics (benzene). Inerts include nitrogen or methane used in pressure control, unreacted ethylene, reaction byproducts, and ethylene feed impurities. In typical plants using liquid-phase aluminum chloride catalyst with high-purity ethylene, vent streams are usually cooled and scrubbed to recover aromatics. In plants using the newer solid support catalysts of the UOP or Mobil/Badger process, reactor vent flow rates are very high because of the low-purity ethylene feed. Process economics requires that these vent gases be burned as fuel.

TABLE 5-2. EMISSION FACTORS FOR ETHYLBENZENE/STYRENE PRODUCTION VIA ALKYLATION AND DEHYDROGENATION

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating
3-01-169-02 Ethylbenzene Manufacturing - Alkylation Reactor Vent	Alkylation Reactor Vent	Process Heater	0.0006 (0.0003)	U
		Uncontrolled	0.6[b] (0.3)	U
3-01-169-03 Ethylbenzene Manufacturing - Benzene Drying Column	Atmospheric/Pressure Column Vents[d]	Flare	0.024[b] - 0.96[d] (0.012 - 0.48)	U
		Uncontrolled	2.4[b] (1.2)	U
3-01-169-04 Ethylbenzene Manufacturing - Benzene Recovery Column				
3-01-169-05 Ethylbenzene Manufacturing - Ethylbenzene Recovery Column				
3-01-169-06 Ethylbenzene Manufacturing - Polyethylbenzene Recovery Column	Other Vacuum Vents[e]	Flare	0.0010[b] - 0.004[d] (0.005 - 0.002)	U
		Uncontrolled	0.10[b] (0.05)	U
3-01-206-02 Styrene Manufacturing - Benzene Recycle Column				
3-01-206-03 Styrene Manufacturing - Styrene Purification Vents				
3-01-206-XX Styrene Manufacturing -Benzene - Toluene Vacuum Vent	Benzene-Toluene Vacuum Vent	Flare	0.06[b] - 2.4[d] (0.03 - 1.2)	U
		Uncontrolled	6.0[b] (3.0)	U

(continued)

TABLE 5-2. CONTINUED

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating
3-01-206-XX Styrene Manufacturing - Hydrogen Separation Vent	Hydrogen Separation Vent	Flare	0.00006[b] - 0.0024[d] (0.00003 -0.0012)	U
		Uncontrolled	0.006[d] (0.003)	U
3-01-169-80/3-01-206-80 Ethylbenzene/Styrene Manufacturing - Equipment Leaks	Equipment Leaks	Detection and Correction Uncontrolled	See Section 4.5.2	
4-07-196-XX/4-07-196-13 Ethylbenzene/Styrene Manufacturing - Storage and Handling	Storage and Handling	Floating Roof, Vented to Flare, Refrigerated Vent Condenser, and Uncontrolled	See Section 4.5.3	

[a] Emission factors are for a model plant with capacity 661 million lbs (300 million kg) per year. Actual emission factors may vary with throughput and control measures and should be determined through direct contacts with plant personnel. Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylbenzene/styrene produced.[69]

[b] Reference 74.

[c] Includes the following vents: benzene drying column, benzene recovery column, and ethylbenzene recovery column.

[d] Reference 69.

[e] Includes the following vents: polyethylbenzene recovery column at ethylbenzene plants; and benzene recycle column and styrene purification vents at styrene plants.

Atmospheric and column vents remove non-combustibles in the column feeds, light aliphatic hydrocarbons, and any entrained aromatics. The benzene drying column also removes impurities in the benzene feed. Most emissions occur in the first column of the distillation train (benzene recovery column in Figure 5-1).

Vacuum column vents remove air that leaks into the column, light hydrocarbons and hydrogen formed in dehydrogenation, non-combustibles in the column feed, and entrained aromatics. Most emissions occur on the benzene/toluene column (vent A in Figure 5-2). Uncontrolled distillation vents emit 4.2×10^{-3} lb hydrocarbons/lb styrene (4.2×10^{-3} kg hydrocarbons/kg styrene) in one plant where the hydrocarbons are benzene and toluene. Another condenser controlled vent emits 0.4×10^{-3} lb benzene/lb styrene (0.4×10^{-3} kg benzene/kg styrene).[9]

Following dehydrogenation, a hydrogen-rich gas (Stream 4 in Figure 5-2) containing methane, ethane, ethylene, CO_2, CO, and aromatics is normally cooled and compressed to recover aromatics. The stream should be vented to the atmosphere (Vent E in Figure 5-2) only during startup, shutdown, and recovery section compressor outages. Some plants may also vent this stream to a flare. Flares are an efficient (99 percent) emission control only when flare diameter and gas flow are closely matched for optimum turbulence and mixing. Emissions can be better controlled when the stream is routed to a manifold and burned with other fuels.

Stripper vents have been reported to emit 0.032 lb ethylbenzene/lb styrene (32 g ethylbenzene/kg styrene).[9] This corresponds to 9.6×10^{-6} lb benzene/lb styrene (9.6×10^{-3} g benzene/kg styrene). Benzene in shipping and storage (Vent F in Figure 5-1) must also be considered as a source if benzene is not produced on site (in which case these emissions would be considered part of the benzene production process).

Benzene Emissions from Styrene Production Using Ethylbenzene Hydroperoxidation

Only one U.S. facility currently reports using this method. Emission estimates presented in this section are based on a capacity of 1200 million lb styrene/yr (544 million kg styrene/yr).

The three main process emission sources are the ethylbenzene oxidation reactor vent (A in Figure 5-3), the propylene recycle purge vent (B), and the vacuum column vents (C) and (D). Propane vapor (B) is considered a fuel if it is not vented to the atmosphere. Of these sources, only the vacuum vents are large benzene emitters. These emissions result from benzene impurities in the ethylbenzene feed, which may result in minor side reactions in the process train.

The ethylbenzene oxidation reactor vent (A) releases CO, light organics, entrained aromatics with nitrogen, oxygen, and CO_2. The vent gas is scrubbed with oil and water for a 99 percent removal efficiency for organics. The resulting vent stream contains approximately 35 ppm benzene (0.11 mg benzene/l) or 15.9 lb benzene/hr (7.2 kilograms benzene per hour [kg/hr]).[74]

The propylene recycle vent (B) releases propane, propylene, ethane, and other impurities. No flow volume data are available but, based on a similar procedure in high-grade propylene production, this stream is a high-Btu gas and would be used as a fuel. No significant benzene emissions are expected.[74]

The ethylbenzene hydroperoxidation process contains numerous vacuum columns and evaporators. Vents on these operations (C-1 to C-3) release inerts and light organics dissolved in the column feeds, nitrogen used for process pressure control, and entrained aromatics. A combined vent flow is reported to be 264,200 gal/hr (1.0×10^6 l/hr) containing about 60 lbs benzene/hr (27 kg benzene/hr).[74]

The dehydrogenation vent (D in Figure 5-3) may be an emergency pressure vent similar to the separation vent (C in Figure 5-2). No specific information is available on storage, transport, or fugitive emissions for this process.

5.1.6 Control Technology for Ethylbenzene/Styrene Processes

Control methods for the two ethylbenzene/styrene processes in use in the United States include condensation, adsorption, flaring, and combustion in boilers or other process heaters. Controls for fugitive emissions from storage tanks, equipment leaks, and others include the use of floating-roof tanks and leak detection/correction programs. No information is available on control methods specific to the two processes mentioned in this report but not in use in the United States.

Condensers may be used to control benzene emissions associated with ethylbenzene/styrene production. The control efficiency of a condenser is determined by the temperature and pressure at which the condenser operates and by the concentration and vapor pressure of the organics in the vent stream. At typical pressures of 1 to 3 atmospheres and coil temperatures of 36 to 41 °F (2 to 5°C), condensers can achieve 80 to 90 percent benzene reduction when used on vent streams at 70 to 100 percent saturation in benzene at 104 to 122 °F (40 to 50°C).[74] Higher efficiencies become prohibitively expensive.

Condensers have limited use in handling high-volume streams, short duration emergency releases, or cyclic releases such as from the hydrogen separation vent. Furthermore, condensers are inefficient at low saturations such as with the alkylation reactor vents and the column vents of Figure 5-1.

In an ethylbenzene/styrene plant, a packed tower can be used to remove benzene. PEB and various ethylbenzene produced during benzene alkylation are good absorbers of benzene and are normally recycled. This system is unsuitable, however, for handling high-volume or intermittent releases of gases beyond the tower design capabilities.

Absorption systems can maintain 80 to 99 percent benzene removal efficiencies for both saturated and unsaturated benzene streams, depending on the tower design and operating variables.

Flare systems can control some streams for which condensation or absorption is not suitable. Flares can efficiently handle highly saturated streams such as from the alkylation vents. They can also control upset releases and other irregular releases, although efficiency can be variable. The major difficulty here occurs in manifolding. High-nitrogen or other low- or non-combustible gases may also be problematic. Consequently, there are no conclusive data on flare efficiency. Limited data show benzene destruction efficiencies ranging from 60 to 99 percent. A properly designed flare system must account for a range of flow and gas composition as well as the potential for explosion.

Use of vent gases as a fuel combined with regular process fuel is advantageous because vent flow variations can be better accounted for. Also, better gas/air mixing occurs along the entire flare front. As with flares, however, manifolding to ensure optimal combustion characteristics is the major technical problem. Process pressure variations and the possibility of emergency releases are complicating factors.

5.2 CYCLOHEXANE PRODUCTION

About 15 percent of the U.S. supply of benzene is used to produce cyclohexane.[10] Table 5-3 lists the location and current capacity for U.S. cyclohexane producers.[11] Two basic methods are used to produce cyclohexane: hydrogenation of benzene and petroleum liquid separation. Most of the cyclohexane produced domestically is produced through hydrogenation of benzene. The following discussions of these two processes are taken from Reference 76.

TABLE 5-3. U.S. PRODUCERS OF CYCLOHEXANE

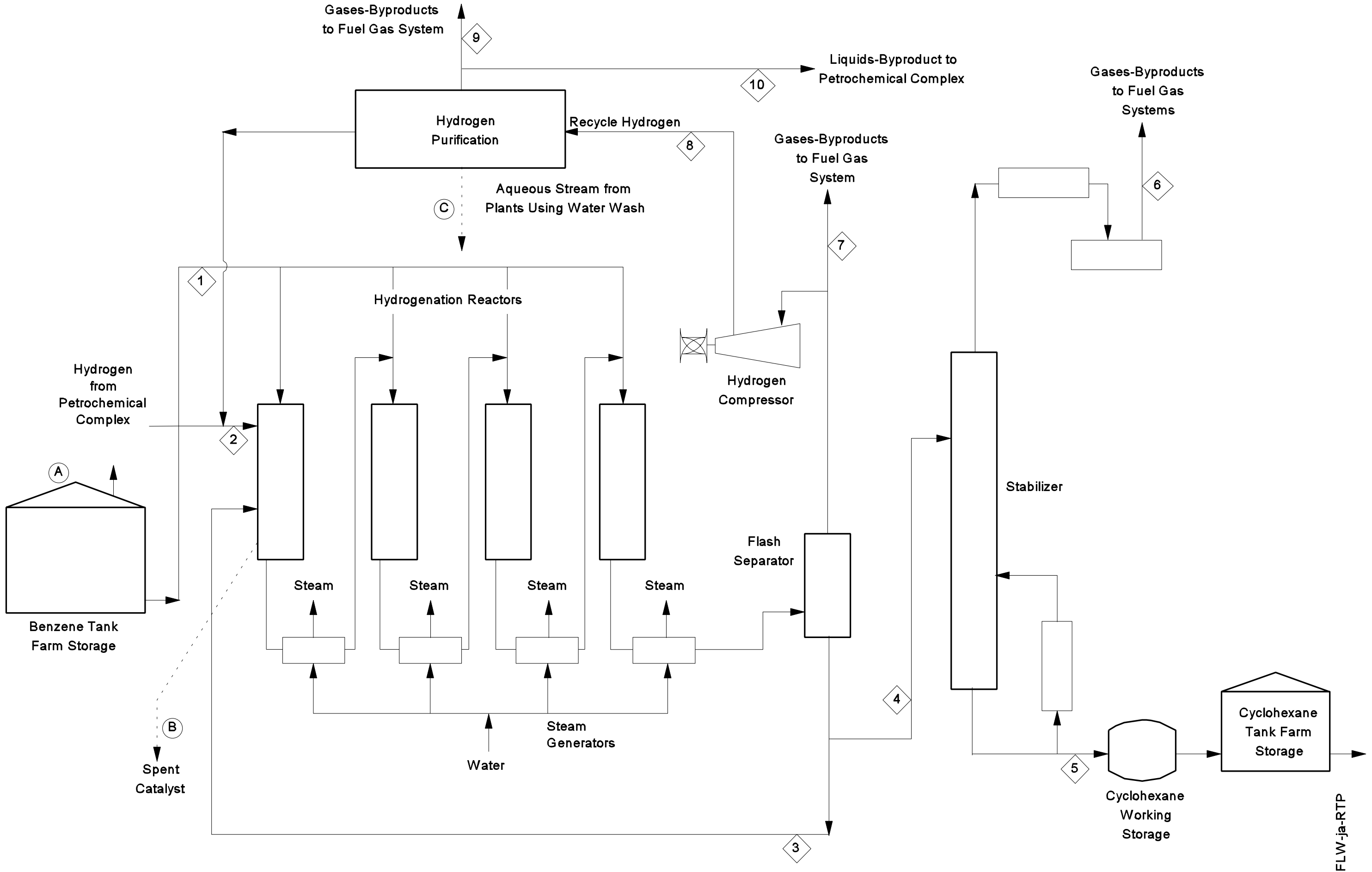
Company	Location	Annual Capacity millions of gal (l)
Chevron Chemical Company	Port Arthur, TX	38 (144)
Phillips Petroleum Company		
Specialty Chemicals Branch	Borger, TX	35 (132)
Olefins and Cyclics Branch	Sweeny, TX	90 (341)
Phillips Puerto Rico Core, Inc.	Guayama, PR	100 (379)
Texaco Chemical Company	Port Arthur, TX	75 (284)
CITGO Petroleum Corporation	Corpus Christi, TX	30 (114)
TOTAL		368 (1,393)

Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These plant locations and capacities were current as of January 1, 1993.

5.2.1 Process Description for Cyclohexane Production via Benzene Hydrogenation

Figure 5-5 shows a model flow diagram for the manufacture of cyclohexane by benzene hydrogenation.[76] High-purity benzene (Stream 1) is fed to the catalytic reactors in parallel and hydrogen (Stream 2) is fed into the reactors in series. Part of the cyclohexane separated in the flash separator is recycled (Stream 3) and fed to the reactors in series. Recycling helps to control the reactor temperature, because the reaction is highly exothermic. The temperature is also controlled by generating steam, which is used elsewhere in the petrochemical complex. Both platinum and nickel catalysts are used presently to produce cyclohexane.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-5. Process Flow Diagram for Cyclohexane Production Using the Benzene Hydrogenation Process

Source: Reference 76.

After leaving the flash separator, the cyclohexane (Stream 4) is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons, and soluble hydrogen gas from the cyclohexane product. These impurities (Stream 6) are routed to the fuel-gas storage system for the facility and used as fuel in process heaters. Cyclohexane (Stream 5) purified in the stabilizer may be greater than 99.9 percent pure. The residual benzene content is typically less than 0.0042 lb/gal (500 mg/l). This pure product is stored in large tanks prior to shipment.

Gas from the flash separator, largely hydrogen, is not pure enough for direct reuse. Therefore, the stream (8) is purified before being recycled to (Stream 2) the reactor. Typical processes used for hydrogen purification are absorption and stripping of the hydrogen gas and cryogenic separation. Some plants use a combination of the two processes. Organic liquids (Stream 10) that are separated from the hydrogen in the hydrogen purification unit are sent to other petroleum processing units in the petrochemical complex. The separated gases (Stream 9) are used as fuel gas.

Depending on the type of hydrogen purification used, inert impurities present in the gas from the flash separator can be purged from the system before the gas enters the hydrogen purification equipment. This stream (7) is sent to the fuel gas system.

5.2.2 Benzene Emissions from Cyclohexane Production via Benzene Hydrogenation

There are no process emissions during normal operation.[76] During shutdowns, individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams, the concentration of benzene in the process equipment is low; therefore, few or no benzene emissions would be expected during a shutdown.[76]

Equipment leak emissions from process pumps, valves, and compressors may contain benzene or other hydrocarbons. Storage of benzene (Vent A in Figure 5-5) may also contribute to benzene emissions.

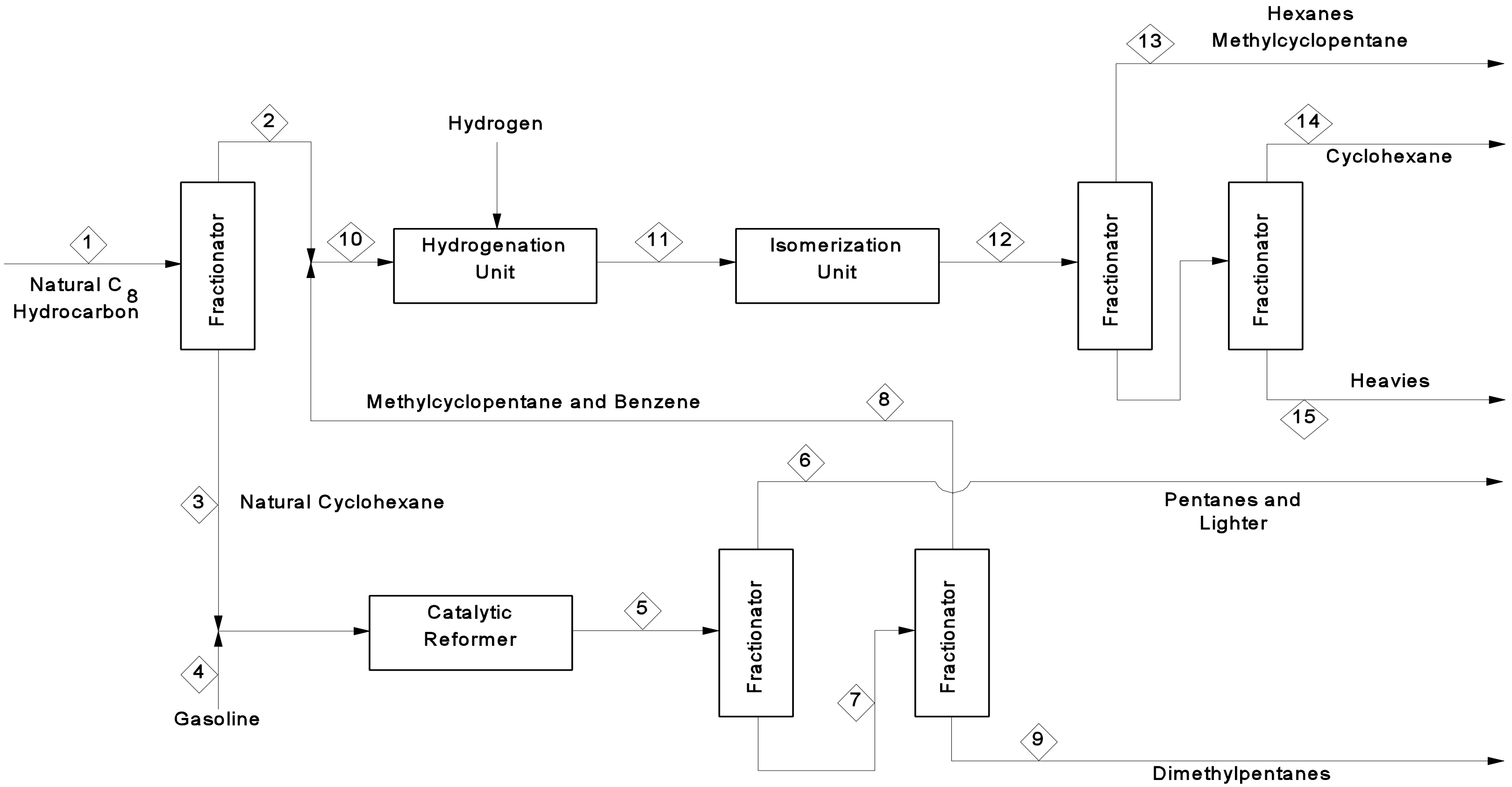
Other potential sources of emissions are catalyst handling (B) and absorber wastewater (C) (when an aqueous solution is used to purify the recycled hydrogen). Caution is taken to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[76]

5.2.3 Process Description for Cyclohexane Production via Separation of Petroleum Fractions

Cyclohexane may also be produced by separation of select petroleum fractions. The process used to recover cyclohexane in this manner is shown in Figure 5-6.[76] A petroleum fraction rich in cyclohexane (Stream 1) is fed to a distillation column, in which benzene and methylcyclopentane are removed (Stream 2) and routed to a hydrogenation unit. The bottoms (Stream 3) from the column containing cyclohexane and other hydrocarbons are combined with another petroleum stream (4) and sent to a catalytic reformer, where the cyclohexane is converted to benzene. The hydrogen generated in this step may be used in the hydrogenation step or used elsewhere in the petrochemical complex.

The benzene-rich stream (5) leaving the catalytic reformer is sent to a distillation column, where compounds that have vapor pressure higher than benzene (pentanes, etc.) are removed (Stream 6) and used as byproducts. The benzene-rich stream (7) that is left is sent to another distillation column, where the benzene and methylcyclopentane (Stream 8) are removed. The remaining hydrocarbons (largely dimethylpentanes) are used elsewhere in the petrochemical complex as byproducts (Stream 9).

Stream 8 (benzene and methylcyclopentane) is combined with Stream 2 and sent to a hydrogenation unit (Stream 10). Hydrogen is fed to this unit and the benzene is converted to cyclohexane. Isomers of cyclohexane, such as methylcyclopentane, are converted to cyclohexane in an isomerization unit (Stream 11) and the effluent from this equipment (Stream 12) is separated in a final distillation step. Pure cyclohexane (Stream 14) is separated from isomers of cyclohexane (Stream 13) and compounds with lower vapor pressures (Stream 15).



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-6. Process Flow Diagram for Cyclohexane from Petroleum Fractions

Source: Reference 76.

5.2.4 Benzene Emissions from Cyclohexane Production via Separation of Petroleum Fractions

There are no process emissions during normal operation.[76] During emergency shutdowns, individual equipment vents are opened as required.

Equipment leaks can be sources of benzene, cyclohexane, methane, or other petroleum compound emissions. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Equipment leak losses have special significance because of the high diffusivity of hydrogen at elevated temperatures and pressures and the extremely flammable nature of the liquid and gas processing streams.[77] No specific emission factors or component counts (valves, flanges, etc.) were found for benzene associated with equipment leak emissions at these plants.

A potential source of benzene emissions is catalyst handling. Special efforts are made to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[76] No emission factors were found for benzene as related to catalyst handling.

5.3 CUMENE PRODUCTION

In the United States, all commercial cumene is produced by the reaction of benzene with propylene. Typically, the catalyst is phosphoric acid, but sulfuric acid or aluminum chloride may be used. Additionally, various new processes based on solid zeolite catalysts were introduced during 1993; however, information about these new processes is limited, and they are not discussed in this section. The location and capacities of U.S. producers of cumene are provided in Table 5-4.[11,78]

TABLE 5-4. U.S. PRODUCERS OF CUMENE

Plant	Location	Annual Capacity million lb (million kg)	Notes
Ashland Chemical Company	Catlettsburg, KY	550 (249)	Cumene is sold
BTL Specialty Resins Corporation	Blue Island, IL	120 (54)	Captive for phenol and acetone
Chevron Chemical Company	Philadelphia, PA	450 (204)	Cumene is sold
	Port Arthur, TX	450 (204)	Cumene is sold
Citgo Petroleum Corp. (Champlin)	Corpus Christi, TX	825 (374)	--
Coastal Refining	Westville, NJ	150 (68)	Cumene is sold
Georgia Gulf Corporation	Pasadena, TX	1,420 (644)	Some cumene transferred to company's phenol/acetone plant
Koch Refining Company	Corpus Christi, TX	750 (340)	Cumene is sold
Shell Chemical Company	Deer Park, TX	900 (408)	Captive for phenol/acetone
Texaco Chemical Company	El Dorado, KS	135 (61)	Captive for phenol/acetone

Source: References 11 and 78.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current list and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These locations, producers, and capacities were current as of November 1993.

5.3.1 Process Descriptions for Cumene Production by Alkylating Benzene with Propylene

Cumene is present in crude oils and refinery streams. However, all commercial cumene is produced by the reaction of benzene and propylene.

Benzene and propylene are reacted at elevated temperatures and pressures in the presence of an acidic catalyst. A simplified equation for this reaction is as follows:

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(propylene)}}{CH_2CHCH_3} \xrightarrow{\text{[catalyst]}} \underset{\text{(cumene)}}{(CH_3)_2CHC_6H_5}$$

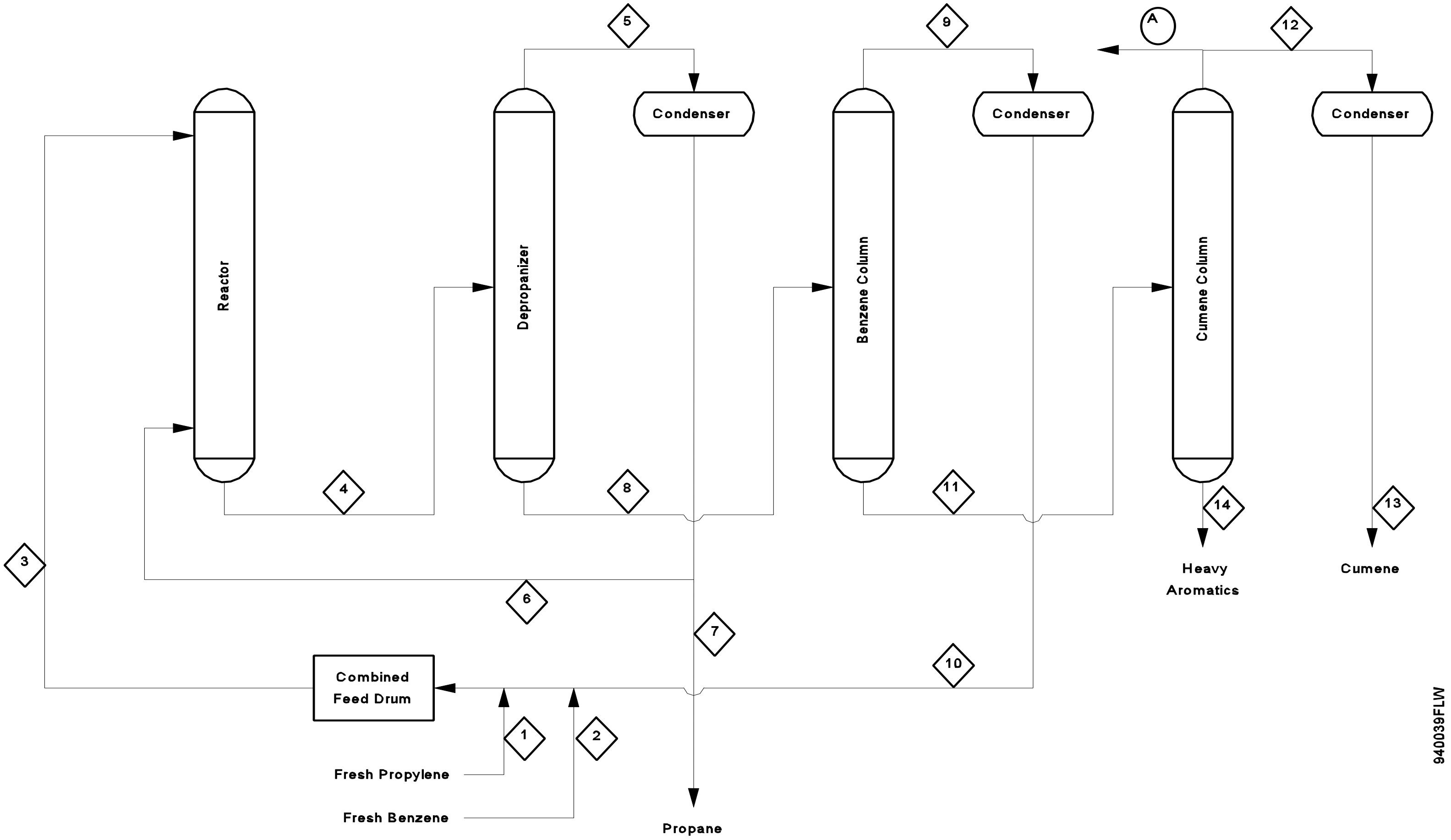
The exothermic reaction is typically conducted using solid phosphoric acid as a catalyst, but the reaction may also be conducted using aluminum chloride or sulfuric acid as the catalyst. The aluminum chloride and sulfuric acid processes are similar; therefore, the sulfuric acid process is not described here.[79]

Solid Phosphoric Acid Catalyst Process

Figure 5-7 is a typical flow diagram for the manufacture of cumene by the process using phosphoric acid as the catalyst support.[80] Solid phosphoric acid is the most favored catalyst system for manufacturing cumene and is a selective alkylation catalyst that promotes the alkylation of benzene with propylene in a vapor-phase system.[79]

Because the catalyst is selective, propylene feedstock for this process does not have to be thoroughly refined before use. Crude propylene streams (Stream 1) from refinery crackers that are fractionated to about 70 percent propylene can be used without further purification. The benzene (Stream 2) used in this process does not have to be dried before use because the catalyst system requires small amounts of water vapor in the reactor stream to activate the catalyst.[79]

Propylene and benzene (Streams 1 and 2) are combined in a feed drum and then fed (Stream 3) to a reactor containing the phosphoric acid catalyst. The feed ratio is normally at least four moles of benzene per mole of propylene. An excess of benzene is maintained in order to inhibit side reactions. The propylene is completely consumed. From the reactor, the byproducts, unreacted material, and product are separated by distillation. The reaction products (Stream 4) are sent to a depropanizers where residual hydrocarbons (mostly propane) are removed. The propane (Stream 5) is sent through a condenser, after which some of the



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-7. Process for the Manufacture of Cumene Using Solid Phosphoric Acid Catalyst

Source: Reference 80.

recovered propane is recycled to the reactor (Stream 6) for cooling. The remainder (Stream 7) can be returned to a refinery for use as feedstock or fuel gas.[79]

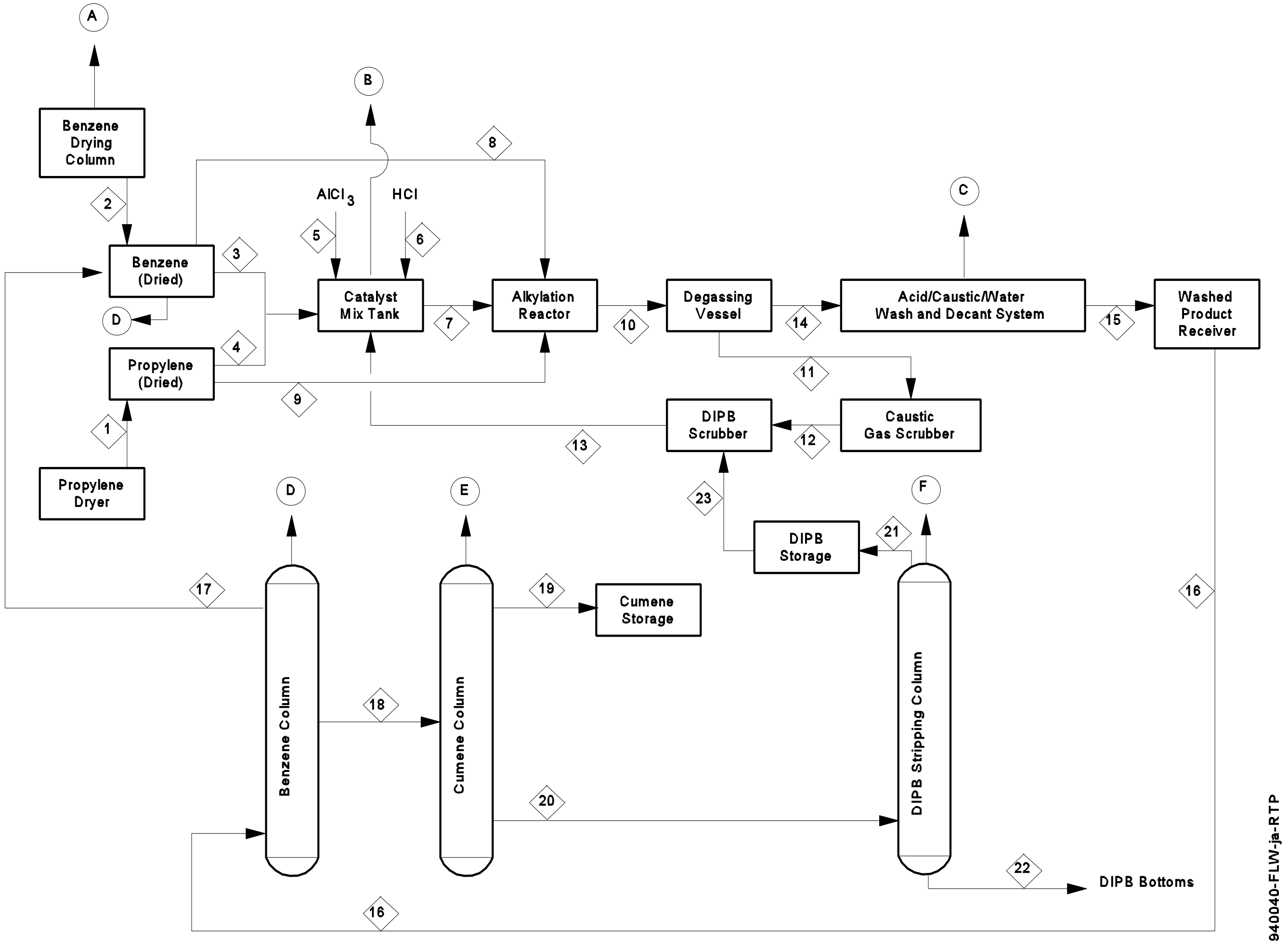
Unpurified product from the depropanizer (Stream 8) is sent to the benzene distillation column, where unreacted benzene is recovered overhead (Stream 9), sent through a condenser, and recycled to the feed drum (Stream 10). From the bottom of the benzene column (Stream 11), the crude product is sent to the cumene distillation column, where the high-purity cumene is separated from heavy aromatics and then condensed (Stream 12) and stored (Stream 13). The bottoms (compounds of relatively lower volatility) from cumene distillation (Stream 14) contain primarily diisopropylbenzene and are sent to a refinery or used as fuel gas.[79]

The cumene distillation column is normally operated slightly above atmospheric pressure and is padded with methane (or nitrogen) to protect the cumene from contact with the air. As the pressure fluctuates, a pressure-control valve relieves excess pressure on this system by bleeding off a mixture of methane (or nitrogen) and cumene vapor (Vent A).[79]

Aluminum Chloride Catalyst Process

The production of cumene using an aluminum chloride catalyst is similar to that using a solid phosphoric acid catalyst. The aluminum chloride method requires additional equipment to dry recycled streams and to neutralize reaction products. Figure 5-8 shows a typical process diagram for cumene manufacture using aluminum chloride as the alkylation catalyst. Aluminum chloride is a much more active and much less selective alkylation catalyst than solid phosphoric acid.[79]

The aluminum chloride used as a catalyst in this process is received and handled as a dry powder. To prevent undesirable side reactions, the propylene used with this catalyst system must be of chemical grade (95 percent pure) and must contain no more than minute amounts of other olefins such as ethylene and butylene. This propylene feedstock must also be



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-8. Process for the Manufacture of Cumene Using Aluminum Chloride Catalyst

Source: Reference 80.

dried and treated (Stream 1) to remove any residual organic sulfur compounds. The benzene used in this process must be azeotropically dried (Stream 2) to remove dissolved water. The azeotrope drying distillation generates a vent gas (Vent A) that is rich in benzene.[79]

Benzene and propylene (Streams 3 and 4) are fed to a catalyst mix tank, where the aluminum chloride powder (Stream 5) is added. This mixture is treated with HCl gas (Stream 6) to activate the catalyst. The catalyst preparation operation generates a vent gas consisting of inert gases and HCl gas saturated with vapors of benzene and diisopropylbenzene. A scrubber is typically used to absorb the HCl gas and the residual vapors are then vented (Vent B). The resulting catalyst suspension (Stream 7) and additional dried benzene (Stream 8) are fed to the alkylation reactor as liquids, and additional dried propylene (Stream 9) is introduced into the bottom of the reactor. The feed ratio to the alkylation reactor is maintained at or above four moles of benzene per mole of propylene to inhibit side reactions.[79]

The crude reaction mixture from the alkylation reactor (Stream 10) is sent to a degassing vessel, where hydrocarbons such as propane are released from solution (Stream 11). This vapor stream is scrubbed with a weak caustic solution and then fed (Stream 12) to the diisopropylbenzene (DIPB) scrubber, where the hydrocarbon vapor is recontacted with DIPB to extract residual unreacted propylene. The stream containing the propylene (Stream 13) is sent to the catalyst mix tank.[79]

The degassed product (Stream 14) is sent to the acid wash tank, where it is contacted with a weak acid solution that breaks down the catalyst complex and dissolves the aluminum chloride in the water layer. The crude product from the acid wash tank is sent to a decanter tank, where the water is removed. The product is then sent to a caustic wash tank, where any residual acid in the product is extracted and neutralized. The product is decanted again to remove water and then enters a water wash tank, where it is mixed with fresh process water. This process water extracts and removes any residual salt or other water soluble material from the product. The product from the water wash tank is sent to a third decanter tank, where the crude product and water settle and separate.[79]

The entire wash-decanter system is tied together by one common vent-pad line that furnishes nitrogen for blanketing this series of tanks. A pressure control valve on the end of the vent-pad manifold periodically releases vent gas (Vent C) as levels rise and fall in the various tanks of the wash-decanter system. The vent gas is saturated with water vapor and hydrocarbon vapor (principally benzene) as contained VOC.[79]

The washed and decanted product (Stream 15) is stored in a washed-product receiver tank. The crude product from the washed-product tank (Stream 16) is sent to a recovery column, where the excess benzene is stripped out. The recovered benzene (Stream 17) is returned to the benzene feed tank. The vent line associated with the benzene recovery column and with the benzene receiver tank releases some vent gas (Vent D). This vapor is principally inert gas saturated with benzene vapor as contained VOC.[79]

The crude cumene (Stream 18) is sent to the cumene distillation column for distillation of the cumene product. The cumene product (Stream 19) is then stored for sale or in-plant use. The cumene distillation column and the associated cumene receiver tank are operated above atmospheric pressure and are blanketed with nitrogen (or methane) to protect the cumene from reacting with oxygen in the air and forming cumene hydroperoxide. The vent line associated with the cumene distillation column and with the cumene receiver tank releases some vent gas (Vent E). This vent gas is nitrogen (or methane) saturated with cumene vapor as the contained VOC.[79]

The bottoms from the cumene distillation column contain a small amount of cumene, along with mixed isomers of diisopropylbenzene and a small amount of higher-boiling alkylbenzenes and miscellaneous tars. The bottoms stream (Stream 20) is sent to a DIPB stripping column, where DIPB is recovered and then stored (Stream 21). This stripping column is normally operated under vacuum because of the high-boiling points of the DIPB isomers. The vacuum system on the stripping column draws a vent stream from the column condenser, and this vent stream is air (or inert gas) saturated with cumene and DIPB vapors as the contained VOC. Depending on the design and operation of the vacuum system for the column, part or all of the vent gas could be discharged to the atmosphere (Vent F).[79]

The bottoms from the DIPB stripper (Stream 22) are stored in a receiver tank and then sent to waste disposal for use as a fuel. The recycle DIPB (Stream 23) is sent to the DIPB scrubber, where it is used to absorb residual propylene from the propane waste gas stream. This recycle DIPB eventually returns to the alkylation reactor, where it is transalkylated with excess benzene to generate additional cumene.[79]

5.3.2 Benzene Emissions From Cumene Production

Information related to benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with cumene production is presented below. Where a literature review has revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points, the reader is referred to Section 5.10 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

Benzene Emissions from the Solid Phosphoric Acid Catalyst Process

In the solid phosphoric acid process, potential process vent emissions of benzene may be associated with the cumene column vent (Vent A in Figure 5-7). Using methane to pressurize the system, the process operates at a pressure slightly higher than atmospheric pressure to make sure that no air contacts the product.[80] The methane is eventually vented to the atmosphere, carrying with it other hydrocarbon vapors.[80]

No specific emission factors were found for benzene emissions from the cumene column. One factor for total VOC emissions indicated that 0.015 lb (0.03 kg) of total VOC are emitted per ton (Mg) of cumene produced, and that benzene constituted a “trace amount” of the hydrocarbons in the stream.[80] One cumene producer has indicated that it uses a closed system (all process vents are served by a plant flare system). Thus, it is possible that there are no process vent emissions occurring directly from the production of cumene, although there may be emissions from the flares.[79]

Benzene Emissions from the Aluminum Chloride Catalyst Process

Process vent emissions of benzene from the production of cumene using an aluminum chloride catalyst are associated with the benzene drying column (Vent A in Figure 5-8), the scrubber or the catalyst mix tank (Vent B), the wash-decanter system (Vent C), the benzene recovery column (Vent D), the cumene distillation system (Vent E), and the DIPB stripping system (Vent F).[80] No specific emission factors were located for benzene emissions from these sources. However, as presented in Table 5-5, one reference provided total VOC emission factors and estimates of benzene percent composition of the emissions.[3,80] The percent (weight) of benzene may be used along with a cumene production volume to calculate an estimate of benzene emissions from these sources. The control technique most applicable to these sources is flaring, with an estimated efficiency of at least 98 percent (see Section 4.5.1 of this chapter for further discussion of this control device).

5.4 PHENOL PRODUCTION

Most U.S. phenol (97 percent) is produced by the peroxidation of cumene, a process in which cumene hydroperoxide (CHP) is cleaved to yield acetone and phenol, as well as recoverable by-products α-methylstyrene (AMS) and acetophenone. Phenol is also produced by toluene oxidation and distillation from petroleum operations.[81,82] Table 5-6 shows the locations, capabilities, and production methods of the phenol producers in the United States.[11,81,83] Because benzene may be present in the feedstock, it may be emitted during production of phenol.

TABLE 5-5. SUMMARY OF EMISSION FACTORS FOR CUMENE PRODUCTION AT ONE FACILITY USING THE ALUMINUM CHLORIDE CATALYST

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a,b]	Factor Rating
3-01-156-02 Cumene Manufacturing - Benzene Drying Column	Process Vent	Uncontrolled	4.00×10^{-2} (2.00×10^{-2})	U
		Flare	2.00×10^{-3} (1.00×10^{-3})	U
3-01-156-03 Cumene Manufacturing - Catalyst Mix Tank Scrubber Vent	Process Vent	Uncontrolled	3.18×10^{-1} (1.59×10^{-1})	U
		Flare	1.59×10^{-2} (7.95×10^{-3})	U
3-01-156-04 Cumene Manufacturing - Wash-Decant System Vent	Process Vent	Uncontrolled	1.57×10^{-2} (7.85×10^{-3})	U
		Flare	7.84×10^{-4} (3.92×10^{-4})	U
3-01-156-05 Cumene Manufacturing - Benzene Recovery Column	Process Vent	Uncontrolled	3.40×10^{-2} (1.70×10^{-2})	U
		Flare	1.70×10^{-3} (8.50×10^{-4})	U

Source: References 3 and 80.

[a] Factors are expressed as lb (kg) benzene emitted per ton (Mg) cumene produced.

[b] Derived by multiplying the total VOC emission factor by percent of benzene in the stream.

TABLE 5-6. U.S PRODUCERS OF PHENOL

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Allied-Signal, Inc. Engineering Materials Sector	Philadelphia, PA	810 (367)	Cumene peroxidation
Aristech Chemical Corporation	Haverhill, OH	630 (286)	Cumene peroxidation
BTL Specialty Resins Corporation	Blue Island, IL	90 (41)	Cumene peroxidation
Dakota Gasification Company	Beulah, ND	50 (23)	Petroleum and coal tar
Dow Chemical U.S.A.	Oyster Creek, TX	550 (249)	Cumene peroxidation
General Electric Company GE Plastics	Mount Vernon, IN	640 (290)	Cumene peroxidation
Georgia Gulf Corporation	Pasadena, TX	160 (73)	Cumene peroxidation
	Plaquemine, LA	440 (200)	Cumene peroxidation
Kalama Chemical, Inc.	Kalama, WA	70 (32)	Toluene oxidation
Merichem Company	Houston, TX	35 (16)	Petroleum and coal tar
PMC, Inc.	Santa Fe Springs, CA	8 (3.6)	Petroleum and coal tar
Shell Chemical Company Shell Chemical Company, Division	Deer Park, TX	600 (272)	Cumene peroxidation
Stimson Lumber Company Northwest Petrochemical Corporation, Division	Anacortes, WA	<5 (<2.3)	Petroleum

(continued)

TABLE 5-6. CONTINUED

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Texaco, Inc. Texaco Chemical Company, Subsidiary	El Dorado, KS	95 (43)	Cumene peroxidation
TOTAL		<3,398 (<1,541)	

Source: References 11, 81, and 83.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of November 1993.

In the process involving peroxidation of cumene, acetone and phenol are produced by the peroxidation of cumene followed by cleavage of the resulting CHP. The two basic reactions for this process are as follows:[80]

$$\underset{\text{(cumene)}}{C_6H_5CH(CH_3)_2} + \underset{\text{(air)}}{O_2} \rightarrow \underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2}$$

$$\underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2} \xrightarrow[\text{(acid)}]{[H_2SO_4]} \underset{\text{(acetone)}}{CH_3COCH_3} + \underset{\text{(phenol)}}{C_6H_5OH}$$

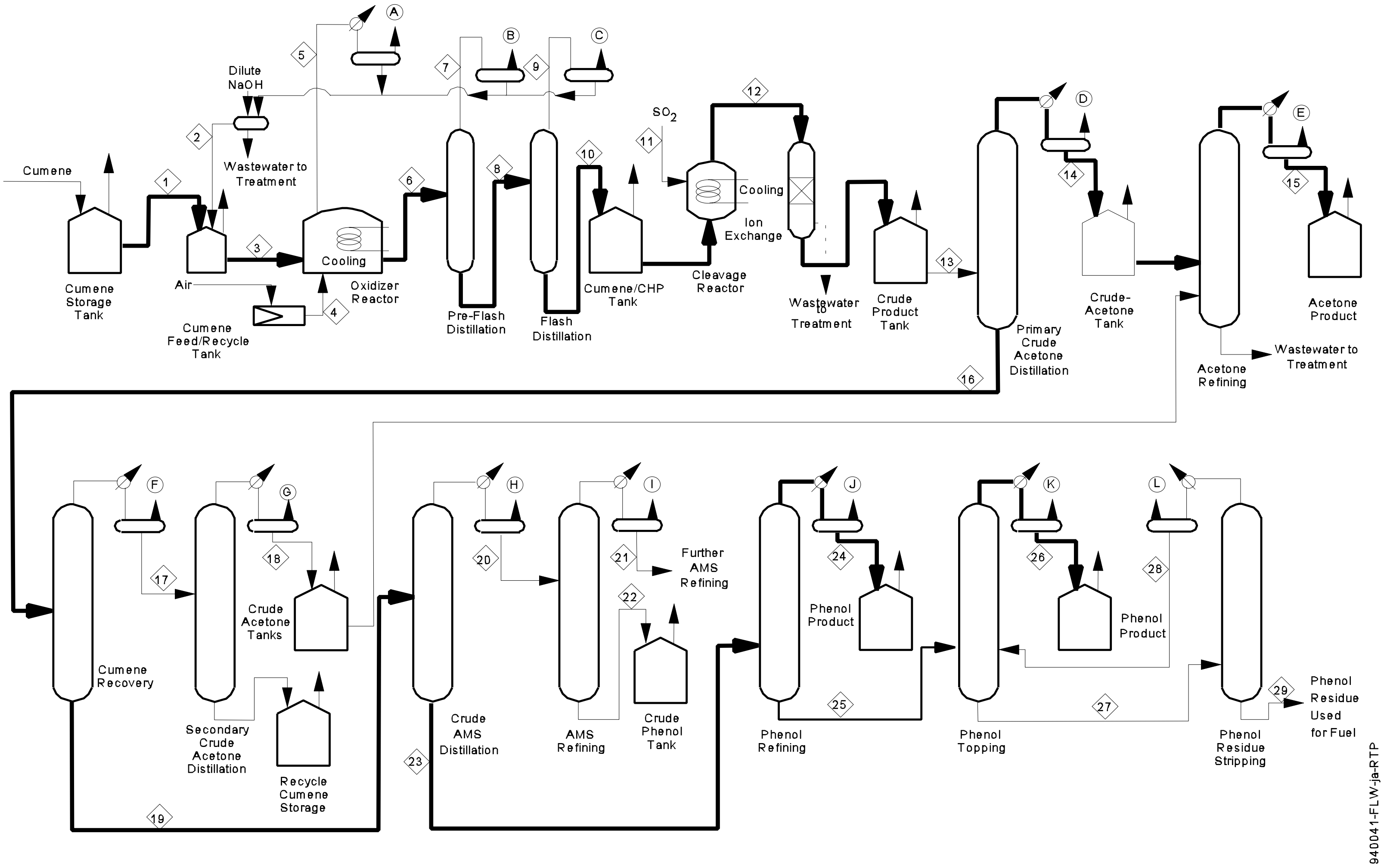
5.4.1 Phenol Production Techniques

There are two technologies for producing phenol by the peroxidation of cumene--one licensed by Allied Chemical and the other licensed by Hercules. The major differences between the Allied and Hercules processes involve the operating conditions of the peroxidation reaction and the method of neutralization of the acid in the cleavage product. These differences affect plant design primarily in the peroxidation and cleavage-product neutralization steps, in the location of process emission points, and in the potential quantity of process emissions. These two process types are discussed below.[80]

In addition to the two cumene peroxidation processes, phenol is produced by the oxidation of toluene. This process is described below; however, the description is brief because of limited available information on the process.

Allied Process

Figure 5-9 shows a typical flow diagram for the manufacture of phenol by the Allied process.[79] Cumene (Stream 1), manufactured on site or shipped to the site, and recycle cumene (Stream 2) are combined (Stream 3) and fed with air (Stream 4) to the multiple-reactor system, where cumene is oxidized to form CHP. Substantial quantities of cumene (Stream 5) are carried out of the reactors with the spent air to a refrigerated vent system, where part of the



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-9. Flow Diagram for Phenol Production from Cumene Using the Allied Process

Source: Reference 79.

cumene is recovered and recycled.[80] Uncondensed vapors, including organic compounds, are vented (Vent A).

The reaction product (Stream 6), containing primarily cumene and CHP, is vacuum flashed first in the pre-flash distillation column and then (Stream 8) in the flash distillation column to remove most of the cumene, which is recycled (Streams 7 and 9). Uncondensed vapors, including organic compounds, are vented (Vents B and C). The concentrated CHP (Stream 10) flows through the CHP concentrate tank to the cleavage reactor, where the CHP is cleaved to acetone and phenol by the addition of SO_2 (Stream 11). The cleavage product (Stream 12) is neutralized in ion-exchange columns and fed through the crude-product surge tank (Stream 13) to a multi-column distillation system.[80,84,85]

In the primary crude acetone distillation column, acetone and lower-boiling impurities such as acetaldehyde and formaldehyde are distilled overhead. This product (Stream 14) is condensed and flows through the crude acetone surge tank to the acetone refining column, where the acetone is distilled overhead. Acetone product is condensed (Stream 15) and sent to storage. Uncondensed vapors, including organic compounds, are vented from the condensers after both the primary crude acetone and acetone refining columns (Vents D and E).[80,84]

The compounds of relatively lower volatility (bottoms) from the primary crude acetone column (Stream 16) are distilled in the cumene recovery column to remove residual cumene. The overheads from the cumene recovery column are sent through a condenser (Stream 17) and into a secondary crude acetone distillation column to further remove acetone from the residual cumene. The residual cumene (i.e., the bottoms from the secondary crude acetone column) is stored for recycling.[80] The uncondensed vapors from the condensers, following both the cumene recovery column and secondary crude acetone column are vented (Vents F and G). The condensed overheads from the secondary crude acetone column (Stream 18) are fed through a crude acetone surge tank back to the acetone refining column.

Some facilities using this process may not incorporate the secondary crude acetone distillation column, which is utilized both to further recover acetone product and to reduce organic emissions from the storage tanks containing the recycle cumene. Some processes store the condensed product from the overhead of the cumene recovery column as the recycle cumene (Stream 17).

The bottoms from the cumene recovery column (Stream 19) contain primarily phenol, AMS, acetophenone, and other organics with higher boiling points than phenol. This stream is fed to the crude AMS distillation column. The crude AMS distillation column overhead stream (Stream 20) is condensed and sent to the AMS refining column. Uncondensed vapors from the condenser after the crude AMS distillation column are vented (Vent H). The stream entering the AMS refining column undergoes distillation to refine out AMS. The refined overhead stream is condensed (Stream 21) and sent to additional columns (not shown) for further refining.

The uncondensed vapors from the condenser following the AMS refining column are vented (Vent I). The bottoms from the AMS refining column (Stream 22) are stored in a crude phenol tank. The phenol in this storage tank is either sold as crude product or is fed to the phenol refining column for further refining. Crude phenol from the bottom of the crude AMS column (Stream 23) flows to the phenol refining column, where phenol is distilled overhead, condensed, (Stream 24), and fed to phenol product storage tanks. The uncondensed vapors from the condenser following the phenol refining column are vented (Vent J).[80,84,85]

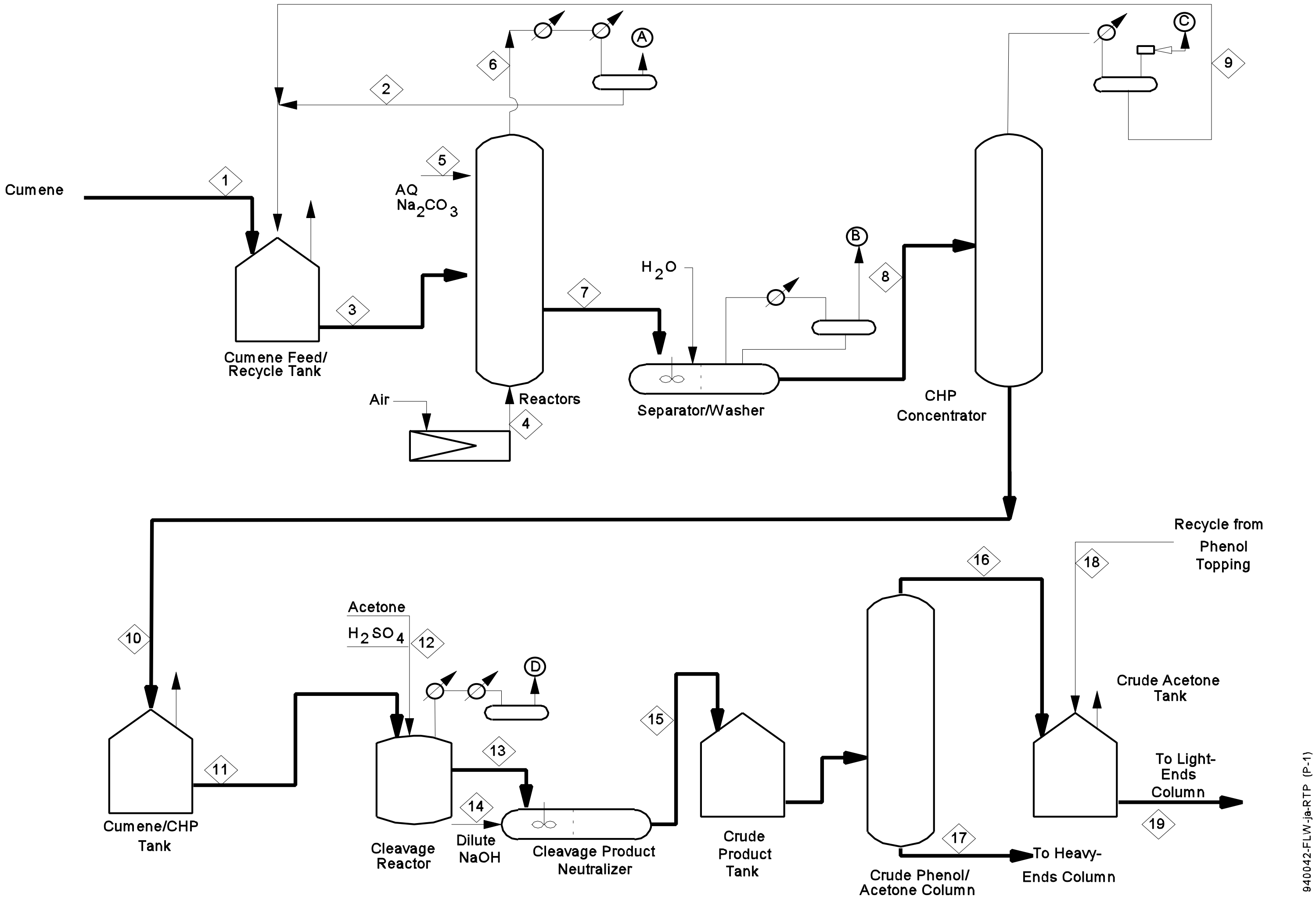
The bottoms from the phenol refining column (Stream 25) are further processed to recover phenol. The bottoms are sent to a phenol topping column, from which the overhead stream is condensed (Stream 26) and fed to phenol product storage. Uncondensed vapors from the condenser after the phenol topping column are vented (Vent K). The bottoms from the phenol topping column (Stream 27) are fed to a phenol residue stripping column, which removes phenol residue in the bottoms (Stream 29). The phenol residue may be used as fuel for on-site industrial boilers. The overheads from the phenol residue stripping column are condensed (Stream 28) and fed back to the phenol topping column to further recover phenol product. The uncondensed vapors from the condenser following the phenol residue stripping column are vented (Vent L).[84,85]

The phenolic wastewater generated by the Allied process (e.g., generated by recovery devices, such as condensers and scrubbers) is fed through distillation columns to further recover acetone and phenol products. This batch distillation cycle, which is not a continuous process, is not shown in Figure 5-9. Phenolic wastewater is fed through a dephenolizer (i.e., a steam stripping process) and one or two batch distillation columns. The recovered product is crude phenol or acetol phenol.[84-86]

Hercules Process

Figure 5-10 shows a typical flow diagram for the manufacture of acetone and phenol by the Hercules process.[79] Cumene from storage (Stream 1) and recycle cumene (Streams 2 and 9) are combined (Stream 3) and then fed with air (Stream 4) to the multiple-reactor system. Additionally, an aqueous sodium carbonate solution (Stream 5) is fed to the reactor system to promote the peroxidation reaction. In the reactor system, cumene is peroxidized to cumene hydroperoxide. Unreacted cumene is carried out of the reactors with the spent air (Stream 6) to a refrigerated vent system, where part of the cumene is recovered and recycled (Stream 2). Uncondensed vapors are vented (Vent A).[80]

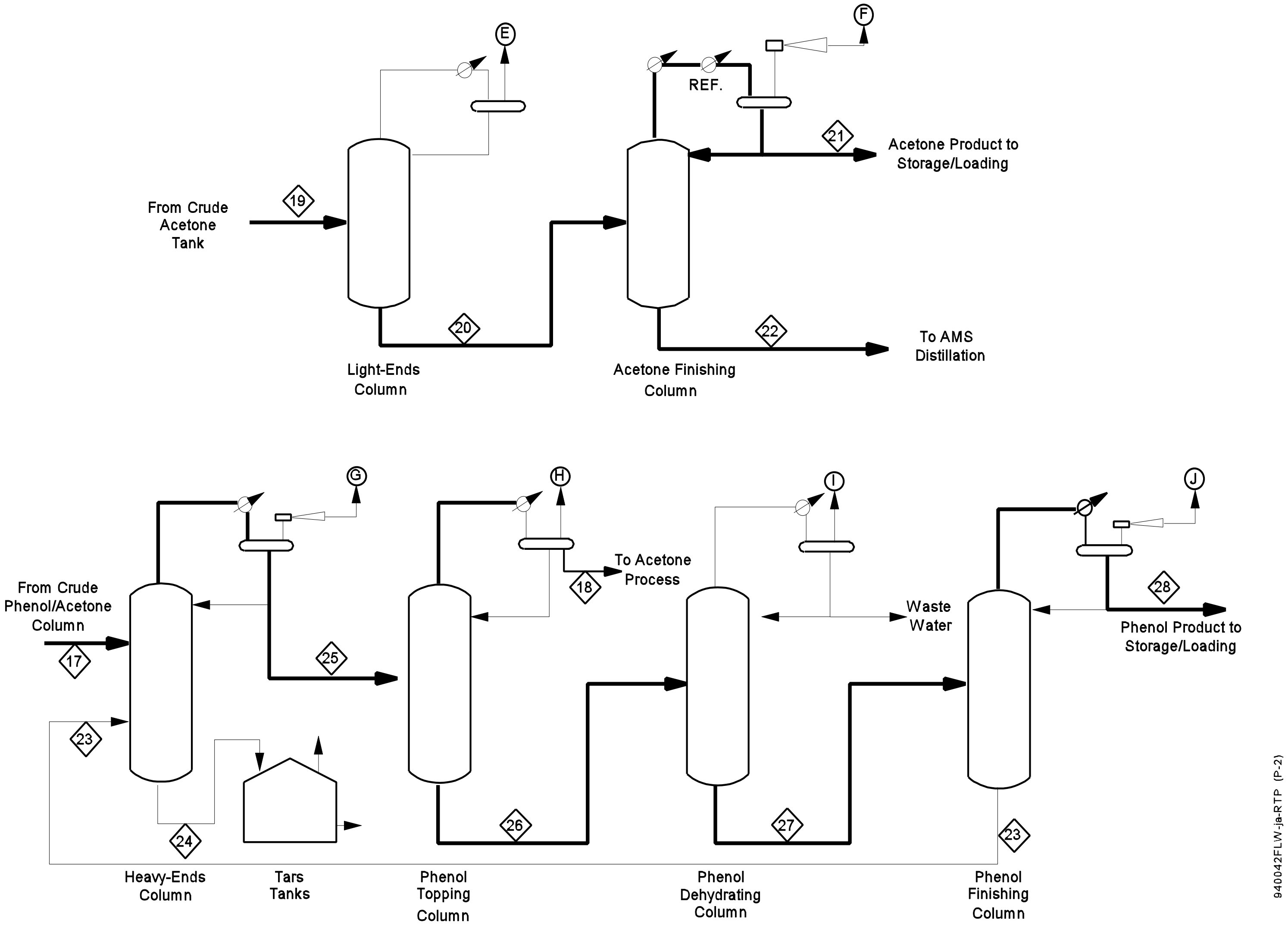
The oxidation reaction product (Stream 7) flows into a separator to remove spent carbonate solution and then is washed with water to remove remaining carbonate and other soluble components. The air stream removed is sent to a condenser from which uncondensed vapors are vented (Vent B). The washed product (Stream 8) is fed to a distillation column operated under vacuum, where the cumene hydroperoxide is separated from the cumene. The overheads from the CHP concentrator are condensed and the recovered



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. Flow Diagram for Phenol Production Using the Hercules Process

Source: Reference 79.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. (Continued)

cumene (Stream 9) is recycled. The uncondensed vapors from the condenser are vented (Vent C).

The concentrated CHP (Stream 10) is transferred through a surge tank to the cleavage reactor (Stream 11). Sulfuric acid, diluted to 5 to 10 percent with acetone (Stream 12), is added to catalyze the decomposition of CHP to acetone and phenol.[80] Uncondensed vapors captured from the cleavage reactor are vented (Vent D). Excess acid in the cleaved mixture (Stream 13) is neutralized with sodium hydroxide solution (Stream 14). The neutralized product (Stream 15) flows through the crude-product surge tank to a multi-column distillation train to produce product-grade acetone, phenol, and AMS.[80]

The crude product is separated in the first distillation column into a crude acetone fraction (Stream 16) and a crude phenol stream (Stream 17). The crude acetone (Stream 16) is combined with recycled hydrocarbons from the phenol topping column (Stream 18) and fed through a surge tank to the light-ends column (Stream 19) to strip low-boiling hydrocarbon impurities, such as acetaldehyde and formaldehyde, which are vented to the atmosphere (Vent E).

The bottoms stream from the light-ends column (Stream 20) is fed to the acetone finishing column, where the acetone is distilled overhead, condensed (Stream 21), and sent to day tanks and subsequently to acetone product storage and loading. Uncondensed vapors are vented (Vent F). The bottoms stream (Stream 22) is processed to produce AMS (not shown).[80]

The crude phenol stream (Stream 17) and the bottoms from the phenol finishing column (Stream 23) are fed to the heavy-ends column and distilled under vacuum to separate tars (Stream 24) from the impure phenol stream (Stream 25).[80] Uncondensed vapors from the condenser following the heavy-ends column are vented (Vent G).

The impure phenol is fed to the phenol topping column to remove hydrocarbons such as cumene and AMS. The overhead stream from the phenol topping column (Stream 18) may be condensed and recycled to the light-ends column of the acetone process for removal of residual acetone, cumene, and AMS. The uncondensed vapors from the condenser following the phenol topping column are vented (Vent H). The phenolic stream (Stream 26) is then fed to a dehydrating column, where water is removed overhead as a phenol/water azeotrope. Uncondensed vapors are vented (Vent I).[80]

The dried phenol stream (Stream 27) is distilled under vacuum in the phenol finishing column to separate product-quality phenol (Stream 28) from higher boiling components (Stream 23), which are recycled to the heavy ends column. Uncondensed vapors from the condenser after the phenol finishing column are vented (Vent J). The product-quality phenol is stored in tanks for subsequent loading.[80]

Toluene Oxidation Process

In this process, toluene is oxidized by air to benzoic acid. Following separation, the benzoic acid is catalytically converted to phenol.

5.4.2 Benzene Emissions from Phenol Production

Information related to benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with phenol production is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points, the reader is referred to Section 5.10 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these types of emission points.

“Spent air” from the oxidizer reactor (Vent A, Figure 5-9) is the largest source of benzene emissions at phenol production plants utilizing the Allied process.[87] Table 5-7 provides uncontrolled and controlled (i.e., thermal oxidizer) emission factors from the oxidizer

TABLE 5-7. SUMMARY OF EMISSION FACTORS FOR PHENOL PRODUCTION BY THE PEROXIDATION OF CUMENE

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating	Reference
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Uncontrolled[b]	4.00×10^{-3} (2.00×10^{-3})	U	3
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Thermal Oxidizer	1.16×10^{-4} (5.82×10^{-5})	D	88, 89

[a] Factors are expressed in lb (kg) benzene emitted for ton (Mg) cumene produced.

[b] Measured at post oxidizer condenser vent.

reactor vent from the phenol production process based on the peroxidation of cumene.[88,89] Charcoal adsorption is the most commonly used method to control emissions from the oxidizer reactor vent; however, condensation, absorption, and thermal oxidation have also been used.[90] Recovery devices (i.e., one or more condensers and/or absorbers) are the most commonly used methods to recover product and control emissions from the cleavage (Vent D, Figure 5-9) and product purification distillation columns; however, adsorption and incineration have also been used for emissions reduction.[81,90]

5.5 NITROBENZENE PRODUCTION

Benzene is a major feedstock in commercial processes used to produce nitrobenzene. Approximately 5 percent of benzene production in the United States is used in the production of nitrobenzene.[12] In these processes, benzene is directly nitrated with a mixture of nitric acid, sulfuric acid, and water.

As of February 1991, five companies were producing nitrobenzene in the United States.[91] Their names and plant locations are shown in Table 5-8.[11] In addition to these plants, plans are underway for Miles and First Chemical to start up a possible 250-million-pound (113.4-Gg) aniline plant, along with feedstock nitrobenzene, at Baytown, Texas.[92]

A discussion of the nitrobenzene production process, potential sources of benzene emissions, and control techniques is presented in this section. Unless otherwise referenced, the information that follows has been taken directly from Reference 93.

5.5.1 Process Descriptions for Continuous Nitration

Nitrobenzene is produced by a highly exothermic reaction in which benzene is reacted with nitric acid in the presence of sulfuric acid. Most commercial plants use a continuous

TABLE 5-8. PRODUCERS OF NITROBENZENE

Company	Location	Capacity in million lb/yr (million kg/yr)
Rubicon, Inc.	Geismar, LA	550 (250)
First Chemical Corporation	Pascagoula, MS	536 (244)
E.I. duPont de Nemours and Company, Inc.	Beaumont, TX	350 (160)
BASF Corporation (Polymers Division Urethanes)	Geisman, LA	250 (110)
Miles, Inc. (Polymers Division Polyurethane)	New Martinsville, WV	100 (45)
TOTAL		1,786 (809)

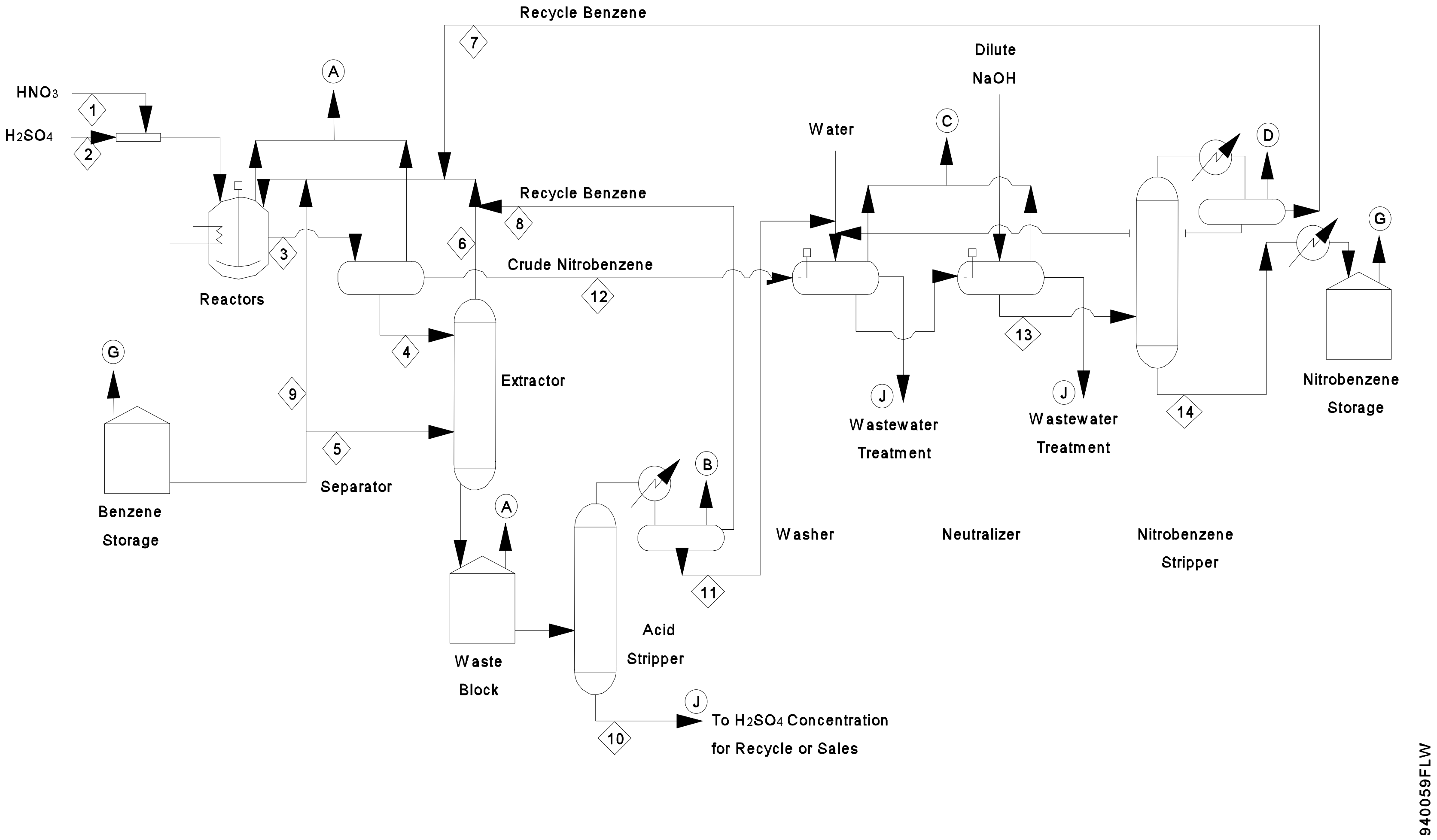
Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and location were current as of January 1993.

nitration process, where benzene and the acids are mixed in a series of continuous stirred-tank reactors. A flow[94] diagram of the basic continuous process is shown in Figure 5-11.[93]

As shown in the figure, nitric acid (Stream 1) and sulfuric acid (Stream 2) are mixed before flowing into the reactor. Benzene extract (Stream 6), two recovered and recycled benzene streams (Streams 7 and 8), and as much additional benzene (Stream 9) as is required are combined to make up the benzene charge to the reactor.

For the process depicted here, nitration occurs at 131°F (55°C) under atmospheric pressure. Cooling coils are used to remove the heat generated by the reaction.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-11. Process Flow Diagram for Manufacture of Nitrobenzene

Following nitration, the crude reaction mixture (Stream 3) flows to the decanter, where the organic phase of crude nitrobenzene is separated from the aqueous waste acid. The crude nitrobenzene (Stream 12) subsequently flows to the washer and neutralizer, where mineral (inorganic) and organic acids are removed. The washer and neutralizer effluent are discharged to wastewater treatment. The organic layer (Stream 13) is fed to the nitrobenzene stripper, where water and most of the benzene and other low-boiling-point components are carried overhead. The organic phase carried overhead is primarily benzene and is recycled (Stream 7) to the reactor. The aqueous phase (carried overhead) is sent to the washer. Stripped nitrobenzene (Stream 14) is cooled and then transferred to nitrobenzene storage.

The treatment, recycling, or discharge of process streams is also shown in the flow diagram. Aqueous waste acid (Stream 4) from the decanter flows to the extractor, where it is denitrated. There, the acid is treated with fresh benzene from storage (Stream 5) to extract most of the dissolved nitrobenzene and nitric acid. The benzene extract (Stream 6) flows back to the nitrating reactor, whereas the denitrated acid is stored in the waste acid tank.

Benzene is commonly recovered from the waste acid by distillation in the acid stripper. The benzene recovered is recycled (Stream 8), and water carried overhead with the benzene is forwarded (Stream 11) to the washer. The stripped acid (Stream 10) is usually reconcentrated on site but may be sold.[93]

Typically, many of the process steps are padded with nitrogen gas to reduce the chances of fire or explosion. This nitrogen padding gas and other inert gases are purged from vents associated with the reactor and separator (Vent A in Figure 5-11), the condenser on the acid stripper (Vent B), the washer and neutralizer (Vent C), and the condenser on the nitrobenzene stripper (Vent D).

5.5.2 Benzene Emissions from Nitrobenzene Production

Benzene emissions may occur at numerous points during the manufacture of nitrobenzene. These emissions may be divided into four types: process emissions, storage emissions, equipment leak emissions, and secondary emissions.

Process emissions occur at the following four gas-purge vents: the reactor and separator vent (A), the acid stripper vent (B), the washer and neutralizer vent (C), and the nitrobenzene stripper vent (D). The bulk of benzene emissions occur from the reactor and separator vent. This vent releases about three times the level of benzene released from Vents B and D (Figure 5-11), and about 120 times that released from Vent C. For all of these vents, the majority of VOC emissions is in the form of benzene. Benzene accounts for 99, 100, 76, and 99 percent of total VOC emissions from Vents A, B, C, and D, respectively. Table 5-9 shows estimated emission factors for benzene from these sources.[93]

Other emissions include storage, equipment leak, and secondary emissions. Storage emissions (G) occur from tanks storing benzene, waste acid, and nitrobenzene. Equipment leak emissions of benzene can occur when leaks develop in valves, pump seals, and other equipment. Leaks can also occur from corrosion by the sulfuric and nitric acids and can hinder control of fugitive emissions.

Secondary emissions can result from the handling and disposal of process waste liquid. Three potential sources of secondary benzene emissions (J) are the wastewater from the nitrobenzene washer, waste caustic from the nitrobenzene neutralizer, and waste acid from the acid stripper. Where waste acid is not stripped before its sale or reconcentration, secondary emissions will be significantly affected (increased) unless the reconcentration process is adequately controlled.

Table 5-9 gives benzene emission factors before and after the application of possible controls for two hypothetical plants using the continuous nitration process. The two

TABLE 5-9. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL NITROBENZENE PRODUCTION PLANTS

SCC and Description	Emissions Source[a]	Control Device	Emission Factor in lb/ton (g/kg)[b]	Factor Rating
3-01-195-01 Nitrobenzene - General	Small Benzene Storage[c] (Point G)	Uncontrolled	0.156 (0.078)[d]	U
			0.154 (0.077)[e]	U
3-01-195-01 Nitrobenzene - General	Benzene Storage[c] (Point G)	Uncontrolled	0.566 (0.283)[d]	U
			0.562 (0.281)[e]	U
		Internal Floating Roof	0.085 (0.0425)[d,e]	U
3-01-195-01 Nitrobenzene - General	Secondary (Point J)	Uncontrolled	0.20 (0.10)[d,e]	U
3-01-195-01 Nitrobenzene - General	Total	Uncontrolled	4.9 (2.45)[d]	U
			4.4 (2.19)[e]	U
		Vent Adsorber	0.78 (0.39)[d]	U
			0.64 (0.32)[e]	U
		Thermal Oxidizer	0.44 (0.22)[d]	U
			0.52 (0.26)[e]	U
3-01-195-03 Nitrobenzene - Acid Stripper Vent	Waste-Acid Stripper (Point B)	Uncontrolled	0.034 (0.170)[d,e]	U
3-01-195-04 Nitrobenzene - Washer/Neutralizer Vent	Wash and Neutralization (Point C)	Uncontrolled	0.0162 (0.0081)[d,e]	U
		Vent Adsorber	0.155 (0.0776)[d,e]	U

(continued)

TABLE 5-9. CONTINUED

SCC and Description	Emissions Source[a]	Control Device	Emission Factor in lb/ton (g/kg)[b]	Factor Rating
3-01-195-05 Nitrobenzene - Nitrobenzene Stripper Vent	Nitrobenzene Stripper (Point D)	Uncontrolled	0.34 (0.170)[d,e]	U
		Thermal Oxidizer	0.0288 (0.0144)[d,e]	U
3-01-195-06 Nitrobenzene - Waste Acid Storage	Waste Acid Storage (Point G)	Uncontrolled	0.102 (0.051)[d,e]	U
			0.96 (0.048)[d,e]	U
3-01-195-80 Nitrobenzene - Equipment Leak Emissions	Process Pumps and Valves[f]	Uncontrolled	1.26 (0.63)[d]	U
			0.76 (0.38)[e]	U
		LD&R plus mechanical seals	0.33 (0.165)[d]	U
			0.198 (0.099)[e]	U

Source: Reference 93.

[a] Emission points refer to Figure 5-11.

[b] Factors are expressed as lb (g) benzene emitted per ton (kg) nitrobenzene produced.

[c] Storage emission factors are based on these tank parameters:

For 198 million lb/yr (90,000 Mg/yr) Model Plant

	Tank Size ft^3 (m^3)	Turnovers/Year	Bulk Liquid Temperature °F (°C)
Benzene (large tank)	100,292 (2,840)	24	68 (20)
Benzene (small tank)	10,029 (284)	236	68 (20)

For 331 million lb/yr (150,000 Mg/yr) Model Plant

	Tank Size ft^3 (m^3)	Turnovers/Year	Bulk Liquid Temperature °F (°C)
Benzene (large tank)	160,035 (4,730)	24	68 (20)
Benzene (small tank)	16,704 (473)	236	68 (20)

(continued)

TABLE 5-9. CONTINUED

[d] Emission factor for a hypothetical 198 million lb/yr (90,000 Mg/yr) capacity plant.

[e] Emission factor for a hypothetical 331 million lb/yr (150,000 Mg/yr) capacity plant.

[f] Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility. All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in this table are based on the factors given in Section 4.5.2.

plants differ in capacity; one produces 198 million lb/yr (90,000 Mg/yr) and the other 331 million lb/yr (150,000 Mg/yr) of nitrobenzene. Both plants use a vent absorber or thermal oxidizer to control process emissions in conjunction with waste-acid storage and small benzene storage emissions.

The values presented for the main benzene storage emissions were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof tank emissions by 85 percent. The values presented for controlled equipment leak emissions are based on the assumption that leaks from valves and pumps, resulting in concentrations greater than 10,000 ppm on a volume basis, are detected, and that appropriate measures are taken to correct the leaks.

Secondary emissions and nitrobenzene storage emissions are assumed to be uncontrolled. Uncontrolled emission factors are based on the assumptions given in the footnotes to Table 5-9. The total controlled emission factors for these hypothetical plants range from 0.44 to 0.78 lb/ton (0.22 to 0.39 kg/Mg). Actual emissions from nitrobenzene plants would be expected to vary, depending on process variations, operating conditions, and control methods.[93]

A variety of control devices may be used to reduce emissions during nitrobenzene production, but insufficient information is available to determine which devices nitrobenzene producers are using currently. Process emissions may be reduced by vent absorbers, water scrubbers, condensers, incinerators, and/or thermal oxidizers.

Storage emissions from the waste-acid storage tank and the small benzene storage tank can be readily controlled in conjunction with the process emissions. (A small storage tank contains approximately one day's supply of benzene; the larger tank is the main benzene storage tank.) In contrast, emissions from the main benzene storage tanks are controlled by using floating-roof storage tanks.

Equipment leak emissions are generally controlled by leak detection and repair, whereas secondary emissions are generally uncontrolled.

5.6 ANILINE PRODUCTION

Almost 97 percent of the nitrobenzene produced in the United States is converted to aniline.[91] Because of its presence as an impurity in nitrobenzene, benzene may be emitted during aniline production. Therefore, a brief discussion of the production of aniline from nitrobenzene and its associated benzene emissions is included in this document.

Table 5-10 lists the U.S. producers of aniline and the production method.[11] The main derivative of aniline (75 percent) is p.p.-methylene diphenyl diisocyanate (MDI). The growth outlook for aniline is expected to remain strong because of its continued use in housing and automobile parts.[95]

5.6.1 Process Descriptions for Aniline Production for Nitrobenzene

A process flow diagram of the most widely used process for manufacturing of aniline--by hydrogen reduction of nitrobenzene--is shown in Figure 5-12.[96] As shown in the figure, nitrobenzene (Stream 1) is vaporized and fed with excess hydrogen (Stream 2) to a fluidized-bed reactor. The product gases (Stream 3) are passed through a condenser. The condensed materials are decanted (Stream 4), and non-condensible materials are recycled to the reactor (Stream 5). In the decanter, one phase (Stream 6) is crude aniline and the other is an aqueous phase (Stream 7).

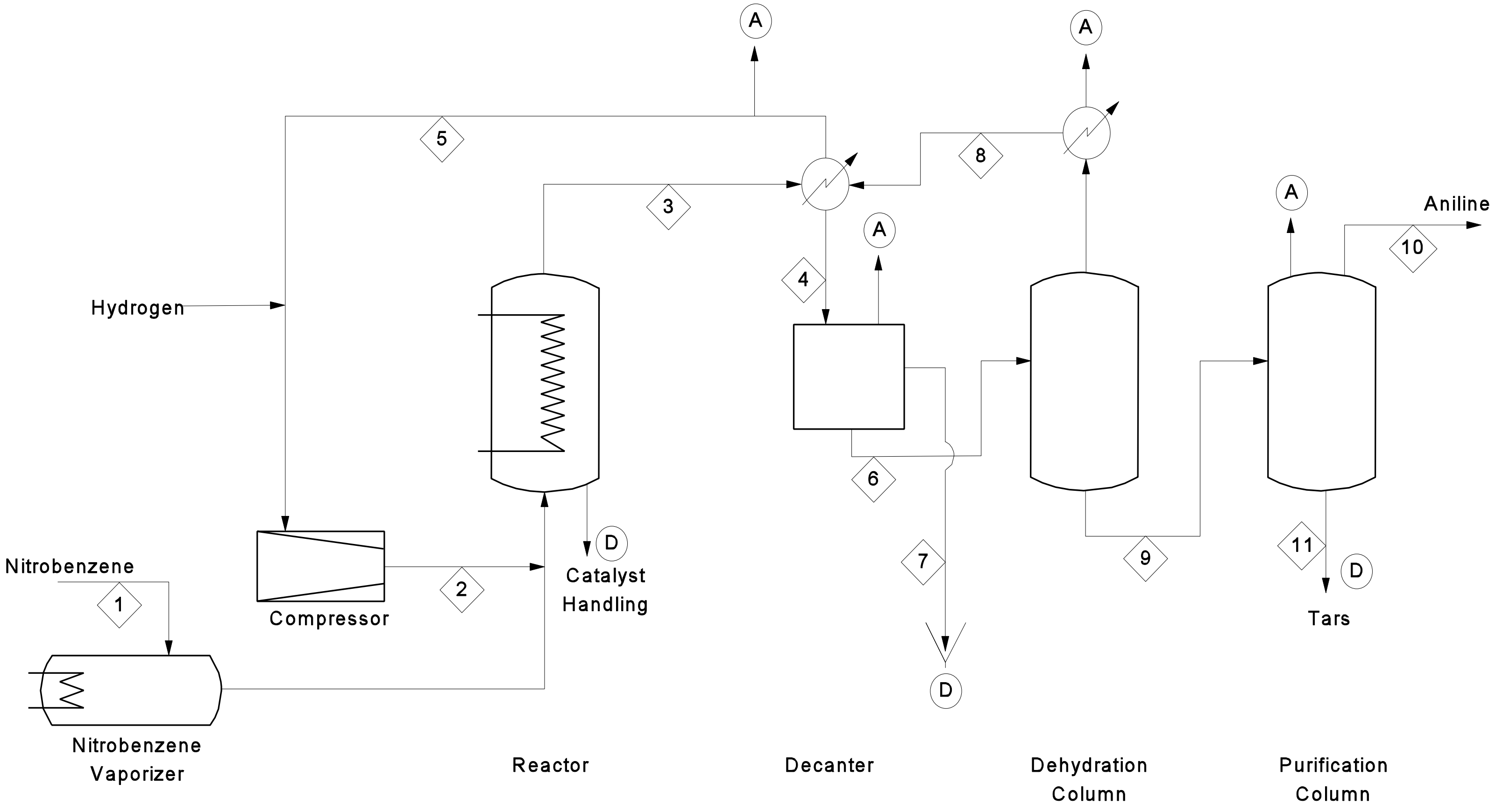
The crude aniline phase is routed to a dehydration column that operates under vacuum. Aniline is recovered from the aqueous phase by stripping or extraction with nitrobenzene. Overheads from the dehydration column (Stream 8) are condensed and recycled to the decanter. The bottoms from the dehydration column (Stream 9), which contain aniline,

TABLE 5-10. U.S. PRODUCERS OF ANILINE

Facility	Location	Annual Capacity in million gal/yr (million kg/yr)	Process and Remarks
Aristech Chemical Corporation	Haverhill, OH	200 (90)	Ammonolysis of phenol (Halcon process)
E.I. duPont de Nemours and Company, Inc.			
duPont Chemicals	Beaumont, TX	260 (120)	Hydrogen reduction of nitrobenzene
First Chemical Corporation	Pascagoula, MS	275 (130)	Hydrogen reduction of nitrobenzene
ICI American Holdings, Inc. and Uniroyal, Inc. Affiliate			
Rubicon, Inc.	Geismar, LA	400 (180)	Hydrogen reduction of nitrobenzene
Miles, Inc.			
Polymers Polyurethane Division	New Martinsville, WV	40 (20)	Nitrobenzene (acid-iron reduction process)
BASF Corporation Polymers Division Urethanes	Geismar, LA	190 (90)	
TOTAL		1,365 (630)	

Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of January 1, 1993.



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Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-12. Flow Diagram for Manufacture of Aniline

Source: Reference 96.

are sent to the purification column. Overheads (Stream 10) from the purification column contain the aniline product, while the bottoms (Stream 11) contain tars.

Fourteen percent of current aniline production (produced by Miles, Inc.) involves an acid-iron reduction process where iron oxide is created as a co-product. Nitrobenzene is reacted with iron and dilute hydrochloric acid at reflux. When the reaction is complete, the aniline-water mixture is separated from the iron-hydroxide sludge and the heavier aniline layer is removed and vacuum distilled to yield purified aniline.[18]

5.6.2 Benzene Emissions from Aniline Production

Process emissions of benzene typically originate from the purging of non-condensibles during recycle to the reactor and purging of inert gases from separation and purification equipment (Vent A in Figure 5-12).[9]

Only one emission factor was found for benzene emissions from aniline production. For process vents (Vent A), an uncontrolled emission factor of 0.0114 lb benzene/ton aniline produced (0.0057 kg/Mg) was reported in the literature.[96] The SCC code for this emission point is 3-01-034-03: Aniline-Reactor Recycle Process Vent. No details of the emission factor derivation were provided, other than it was based on data provided by an aniline producer, so it was assigned a U rating.

Control techniques available for emissions associated with the purging of equipment vents include water scrubbing and thermal oxidation.[96] No data were found to indicate the efficiencies of these control devices for benzene emissions. The reader is urged to contact specific production facilities before applying the emission factor given in this report to determine exact process conditions and control techniques.

5.7 CHLOROBENZENE PRODUCTION

The most important chlorobenzenes for industrial applications are monochlorobenzene (MCB), dichlorobenzene (DCB), and trichlorobenzene (TCB). Therefore, this section focuses on benzene emissions associated with production of these three types of chlorobenzenes. Table 5-11 lists the U.S. producers of MCB, DCB, and TCB. The producing companies' capabilities are flexible, such that different chlorobenzenes may be isolated, depending on market demand. DCBs and TCBs are produced in connection with MCB. The relative amounts of the products can be varied by process control.[97]

5.7.1 Process Description for Chlorobenzene Production by Direct Chlorination of Benzene

The most widely used process for the manufacture of chlorobenzenes is direct chlorination of benzene in the presence of ferric chloride catalyst to produce MCB and DCB. HCl is a by-product. The two major isomers of DCB are ortho and para. As chlorination continues, tri-, tetra-, penta-, and, finally, hexachlorobenzenes are formed. However, TCB is the only one of the more highly chlorinated products found in significant amounts.

Basic operations that may be used in the continuous production of MCB are shown in Figure 5-13.[19] The process begins with a series of small, externally cooled cast iron or steel vessels containing the catalyst (which may consist of Rashing rings of iron or iron wire). Chlorine is supplied into each vessel through suitably positioned inlets to maintain a large benzene-to-chlorine reaction at all points along the reaction stream. The temperature is held between 68 to 104°F (20 to 40°C) to minimize the production of DCBs, which form at higher temperatures. Dry benzene (Stream 1) and dried recycled benzene (Stream 2) are introduced into the reactor, which produces an overhead gas (Stream 3).

The gas stream (containing HCl, unreacted chlorine, inert gases from the chlorine feed, benzene, and other VOC) is sent to an organic absorber, where benzene and

TABLE 5-11. U.S. PRODUCERS OF MONO-, DI-, AND TRICHLOROBENZENE

Company	Location	Product	Annual Capacity million lb (million kg)
Monsanto Company Chemical Group	Sauget, IL	Monochlorobenzene	176 (80)
		o-Dichlorobenzene	11 (5)
		p-Dichlorobenzene	22 (10)
PPG Industries, Inc. Chemical Group	Natrium, WV	Monochlorobenzene	45 (20)
		o-Dichlorobenzene	20 (9)
		p-Dichlorobenzene	30 (14)
Standar Chlorine Chemical Company, Inc.	Delaware City, DE	Monochlorobenzene	150 (68)
		o-Dichlorobenzene	50 (23)
		p-Dichlorobenzene	75 (34)
		1,2,3-Trichlorobenzene	NA
		1,2,4-Trichlorobenzene	NA
Southland Corporation Chemical Division	Great Meadows, NJ	1,3,5-Trichlorobenzene	NA

Source: Reference 11.

NA = Not available

Note: This is a list of major facilities producing mono-, di-, and trichlorobenzene. The list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel. The data on producers and locations were current as of January 1993.

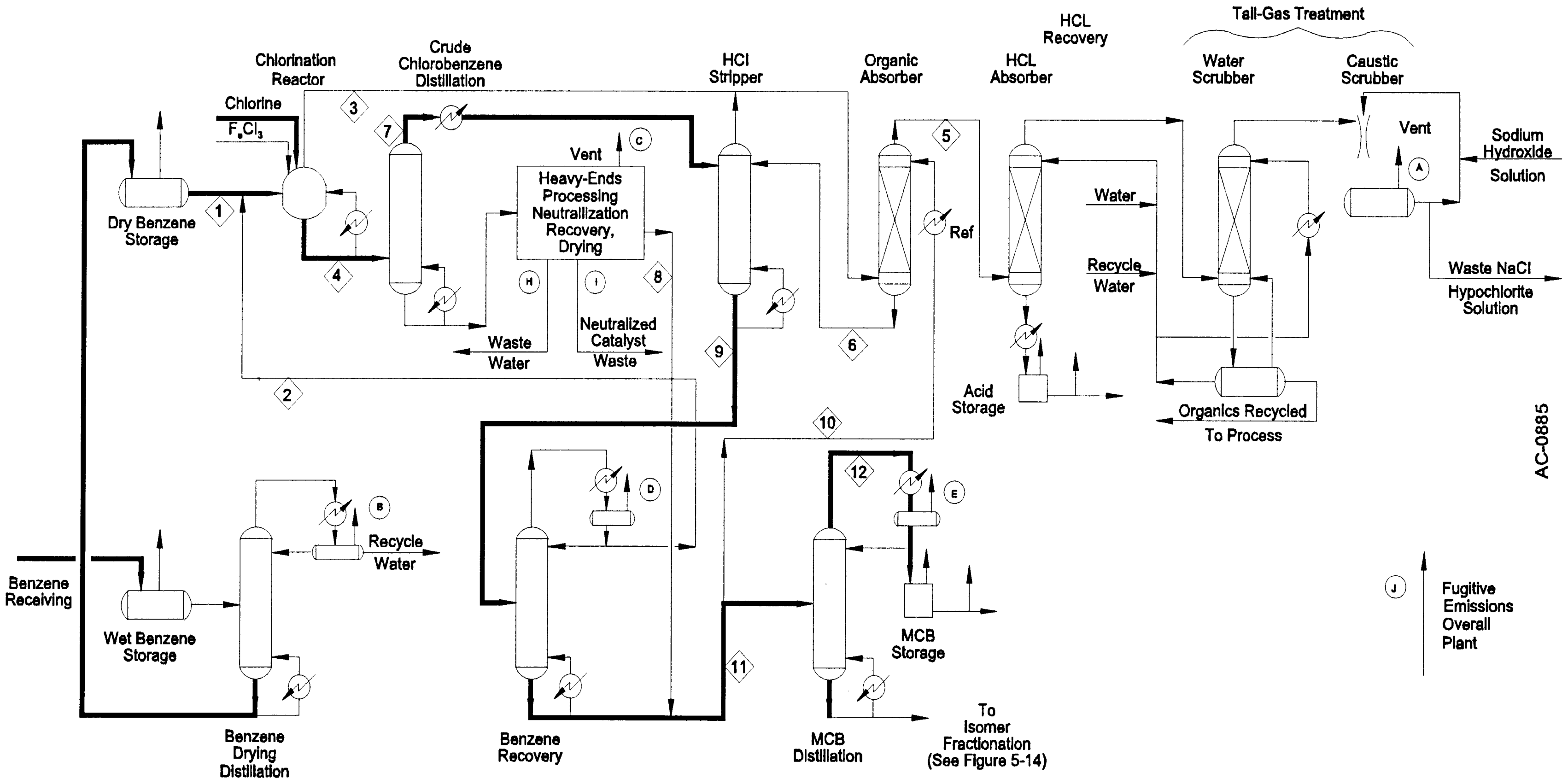


Figure 5-13. Monochlorobenzene Continuous Production Process Diagram

Source: Reference 19.

other VOC are removed. The bottoms from the organic absorber (Stream 6) flow to the HCl stripper for recovery of HCl. The overhead gas (Stream 5) is sent to HCl absorption. By-product HCl is then removed in the HCl absorber, where it is saturated by washing with a refrigerated solvent (e.g., o-DCB) or low vapor pressure oil, and then recovered in wash towers as commercially usable hydrochloric acid.[98]

Crude reaction liquid product (Stream 4) enters the crude chlorobenzene distillation column, which produces overheads (Stream 7) that contains most of the chlorobenzenes, unreacted benzene, and some HCl, and a bottom stream from which catalyst and other byproducts are separated (Stream 8) and processed for reuse. The overheads (Stream 7) pass through an HCl stripper and into a benzene recovery column (Stream 9). Part of the subsequent benzene-free stream (Stream 10) is returned to the organic absorber; the remainder (Stream 11) enters the MCB distillation column. The overhead MCB distillation product (Stream 12) is then stored and the bottom stream containing DCB and TCB isomers is processed.[98]

Figure 5-14 presents basic operations that may be used to produce o- and p-DCB and TCB. In a continuation of the production of MCB, o- and p-DCB can be separated by fractional distillation. Isomer fractionation yields p-DCB (with traces of o-DCB and m-DCB), which enters the overhead (Stream 1); the o-DCB enters the bottoms (Stream 2). The o-DCB bottoms (Stream 2) undergoes fractional distillation and produces an o-DCB overhead (Stream 3), which is sent to storage, and bottoms (Stream 4), which is further processed to yield TCBs.[98]

The crude p-DCB with other trace isomers (Stream 5) is purified by batch crystallization. Part of the purified p-DCB (Stream 6) is sent to liquid storage. The remainder (Stream 7) undergoes freezing, crushing, screening, and packing of p-DCB crystals. The mother liquor from crystallization (Stream 8) is sent to DCB solvent-grade fractionalization, where it is separated into solvent grade o-DCB (Stream 9) and p-DCB (Stream 10) and stored.[98]

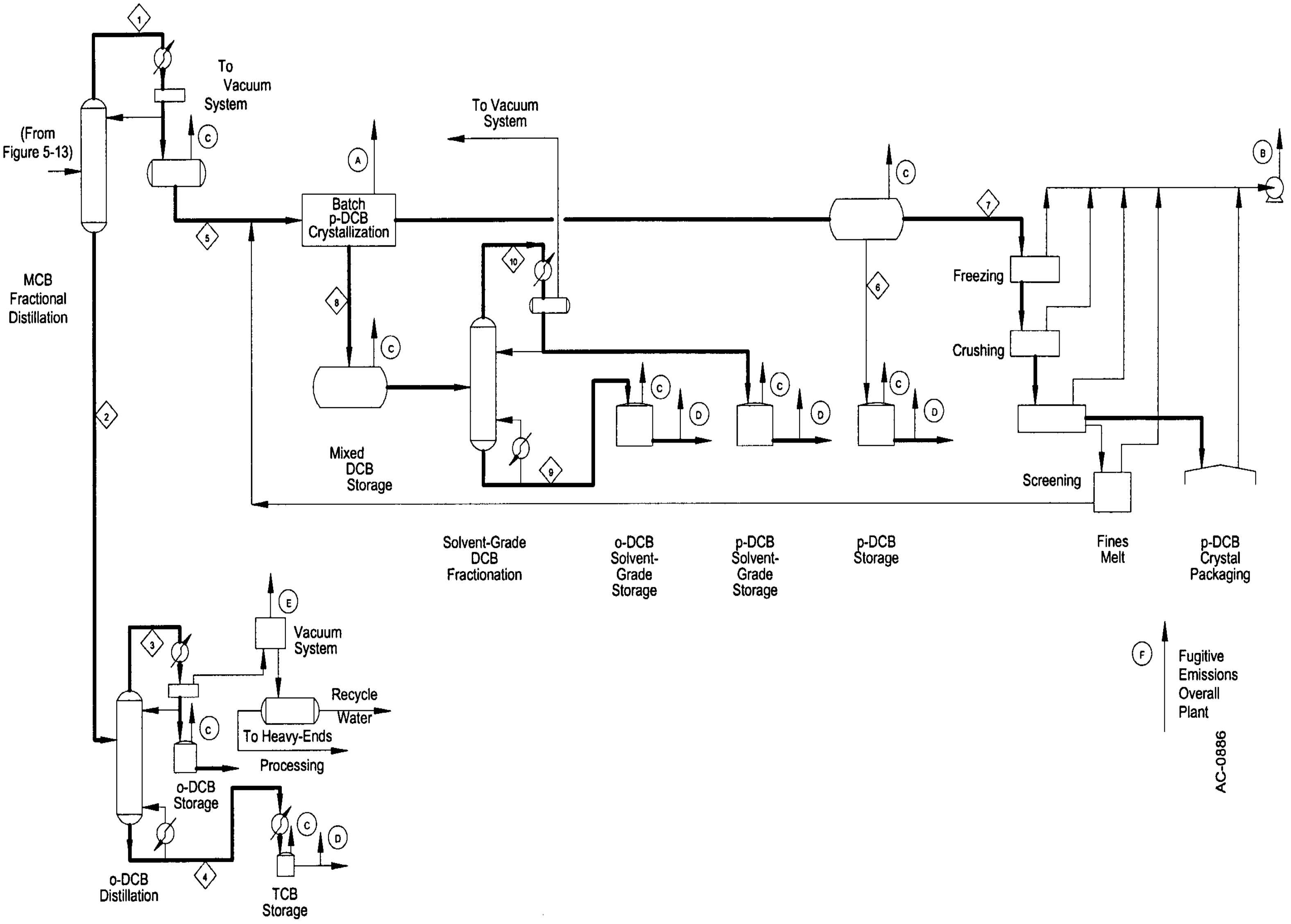


Figure 5-14. Dichlorobenzene and Trichlorobenzene Continuous Production Diagram

Source: Reference 19.

The isolation of m-DCB from mixed DCB streams is not economical, because it usually occurs at a level of 1 percent or less. Metadichlorobenzene is sold with other isomers as mixed chlorobenzenes.[98]

Other processes that are most often used in the production of MCB are the batch and Rashing methods.[98] Other TCB production processes are the reaction of α, β, or γ-benzene hexachloride with alcoholic potash, the dehalogenation of α-benzene hexachloride with pyridine, and the reaction of α-benzene hexachloride with calcium hydroxide to form primarily 1,2,4-TCB.[19]

5.7.2 Benzene Emissions from Chlorobenzene Production

The primary source of benzene emissions during MCB production is the tail gas treatment vent of the tail gas scrubber (Vent A in Figure 5-13). Usually, this vent does not have a control device.[19] Other potential sources of benzene emissions are atmospheric distillation vents from the benzene drying column, heavy-ends processing, the benzene recovery column, and MCB distillation (Vents B, C, D, E in Figure 5-13, respectively), equipment leak emissions, emissions from benzene storage, and secondary emissions from wastewater.[19]

Table 5-12 presents estimated controlled and uncontrolled emission factors for benzene emissions from the tail gas treatment vent, atmospheric distillation vents, equipment leak emissions, and benzene storage.[19] The point source factors are based on emissions reported to EPA in response to information requests and trip reports.[19] For information on emission factors for estimating equipment leak and storage tank emissions refer to Sections 4.5.2 and 4.5.3 respectively of this document. As noted in Table 5-12, carbon adsorption is an appropriate control technology for control of emissions from tail gas treatment and distillation column vents. The control technique applicable to process equipment leak emissions is an inspection/maintenance program for pumps, valves, and flanges. Internal floating roof tanks may be used to control benzene emissions resulting from benzene storage.[19]

TABLE 5-12. EMISSION FACTORS FOR CHLOROBENZENE PRODUCTION BY DIRECT CHLORINATION OF BENZENE

SCC and Description	Emissions Source	Contol Device	Emission Factor in lb/ton (kg/Mg)[a,b]	Factor Rating
3-01-301-01 Chlorobenzene Manufacturing - Tail-gas Scrubber	Tail-gas Scrubber Treatment	Carbon Adsorption	0.0134 (0.0067)	U
		Uncontrolled	1.04 (0.52)	U
3-01-301-02 Chlorobenzene Manufacturing - Benzene Dry Distillation	Atmospheric Distillation Vents[c]	Carbon Adsorption	0.0084 (0.0042)	U
		Uncontrolled	0.64 (0.32)	U
3-01-301-04 Chlorobenzene Manufacturing - Heavy Ends Processing				
3-01-301-05 Chlorobenzene Manufacturing - Monochlorobenzene Distillation				
3-01-301-03 Chlorobenzene Manufacturing - Benzene Recovery	Atmospheric Distillation Vent - Benzene Recovery	Carbon Adsorption	0.00104 (0.00052)	U
		Uncontrolled	0.08 (0.04)	U
3-01-3-1080 Chlorobenzene Manufacturing - Equipment Leaks	Equipment Leaks	Detection and Repair of Major Leaks	See Section 4.5.2	
		Uncontrolled	See Section 4.5.2	

(continued)

TABLE 5-12. CONTINUED

SCC and Description	Emissions Source	Contol Device	Emission Factor in lb/ton (kg/Mg)[a,b]	Factor Rating
4-07-196-01 Organic Chemical Storage - Benzene Storage	Benzene Storage Vessel	Internal Floating Roof	See Section 4.5.3	
		Uncontrolled	See Section 4.5.3	

Source: Reference 19.

[a] Emission factors are expressed as lb (kg) benzene emitted per ton (Mg) chlorobenzene product produced.

[b] These emission factors are based on a hypothetical plant producing 74,956 tons (68 Gg) monochlorobenzene, 13,669 tons (12.4 Gg) o-dichlorobenzene, and 17,196 tons (15.6 Gg) p-dichlorobenzene. The reader is urged to contact a specific plant as to process, products made, and control techniques used before applying these emission factors.

[c] Includes the following vents: benzene dry distillation, heavy ends processing, and monochlorobenzene distillation.

5.8 LINEAR ALKYLBENZENE PRODUCTION

Approximately 2 percent of the benzene produced in the United States is used in the production of linear alkylbenzene (LAB). LAB (or linear alkylate) improves the surfactant performance of detergents. The primary end use for LAB is in the production of linear alkylbenzene sulfonates (LAS). Because of their water-soluble properties, LAS are used extensively in powdered home laundry products (over 50 percent of LAS produced) and in heavy-duty liquid products.[99]

Alkyl benzene sulfonates with highly branched C_{12} side chains possess excellent detergent properties, and they have also been used in the past in formulating detergents. However, in recent years, LAS have essentially replaced all branched alkylbenzene sulfonates in detergent formulations in the United States because of environmental considerations. LAB is extensively degraded (>90 percent) by microorganisms in sewage plants after a relatively short period of time. In comparison, the highly branched alkyl benzene sulfonates have a much lower biological degradability.[100] Dodecylbenzene and tridecylbenzene are the two most common LABs. The locations of the LAB producers in the United States are shown in Table 5-13.[11,101]

In the United States, LAB is produced using two different processes. Vista's Baltimore plant uses a monochloroparaffin LAB production process. Vista's Lake Charles plant and Monsanto's Alvin plant use an olefin process, wherein hydrogen fluoride serves as a catalyst. Approximately 64 percent of LAB is produced by the olefin process. The paraffin chlorination process accounts for about 36 percent of LAB production. Both processes are described in the following sections.

5.8.1 Process Description for Production of LAB Using the Olefin Process

Production of LAB using the olefin process consists of two steps: a dehydrogenation reaction and an alkylation reaction. The C_{10} to C_{14} linear paraffins are

TABLE 5-13. U.S. PRODUCERS OF LINEAR ALKYLBENZENE (DETERGENT ALKYLATES)

Company	Location	Annual Capacity million lb/yr (million kg/yr)	Process
Linear Alkylbenzene (Dodecyclbenzene and tridecyclbenzene)			
Monsanto Company Chemical Group	Alvin, TX	330 (150)	Internal olefins--HFl; merchant
Vista Chemical Company	Baltimore, MD	300 (140)	Monochloroparaffin, merchant and captive
	Lake Charles, LA	210 (95)	Internal olefins--HFl; merchant and captive
Linear Alkylbenzene (except dodecyl and tridecyl)			
Phillips 66 Company	NA	NA	---
TOTAL		840 (385)	

Source: References 11 and 101.

NA = Not available

Note: This is a list of major facility that produce linear alkylbenzene. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel. These data for producers and locations were current as of January 1993.

dehydrogenated to n-olefins, which are reacted with benzene under the influence of a solid, heterogenous catalyst (such as hydrogen fluoride [HFl]) to form LAB. The discussion of LAB production using the olefin process is taken from references 102 and 103.

First, n-paraffins are transferred from bulk storage to the linear paraffin feed tank in Stream 1 (Figure 5-15.)[103] The paraffins are heated to the point of vaporization (Stream 2) and passed through a catalyst bed in the Pacol reactor (Stream 3), where the feed is dehydrogenated to form the corresponding linear olefins by the following reaction:

$$R_1 - CH_2 - CH_2 - R_2 \text{--->} R_1\,CH = CH - R_2 + H_2$$

The resulting olefins contain from 10 to 30 percent α-olefins, and a mixture of internal olefins, unreacted paraffins, some diolefins, and lower-molecular-weight "cracked materials." The gas mixture is quickly quenched with a cold liquid stream as it exits to process thermally-promoted side reactions (Stream 4). The hydrogen-rich offgases (e.g., hydrogen, methane, ethane, etc.) are then separated from the olefin liquid phases (Stream 5). The gas is used as process fuel (Stream 6) or vented to a flare stack.

Di-olefins in the Pacol separator liquid are selectively converted back to mono-olefins in the Define reactor (Stream 7). The effluent from the reactor is routed to a stripper (Stream 8), where light ends are removed (Stream 9). The olefin-paraffin mixture (Stream 10) is then alkylated with benzene (Stream 11) in the fixed-bed reactor to be blended with a HFl catalyst. The blend is held at reaction conditions long enough for the alkylation reaction to go to completion as follows:

$$R_1CH = CHR_2 + C_6H_6 \text{ ---> } R_1CH_2 - CHR_2$$

Product from the reactor flows to the benzene stripping column (Stream 12) for separation and recycle of unreacted benzene to the fixed-bed reactor (Stream 13). The liquid HFl is also separated and recycled to the alkylation vessel to be mixed with fresh HFl.

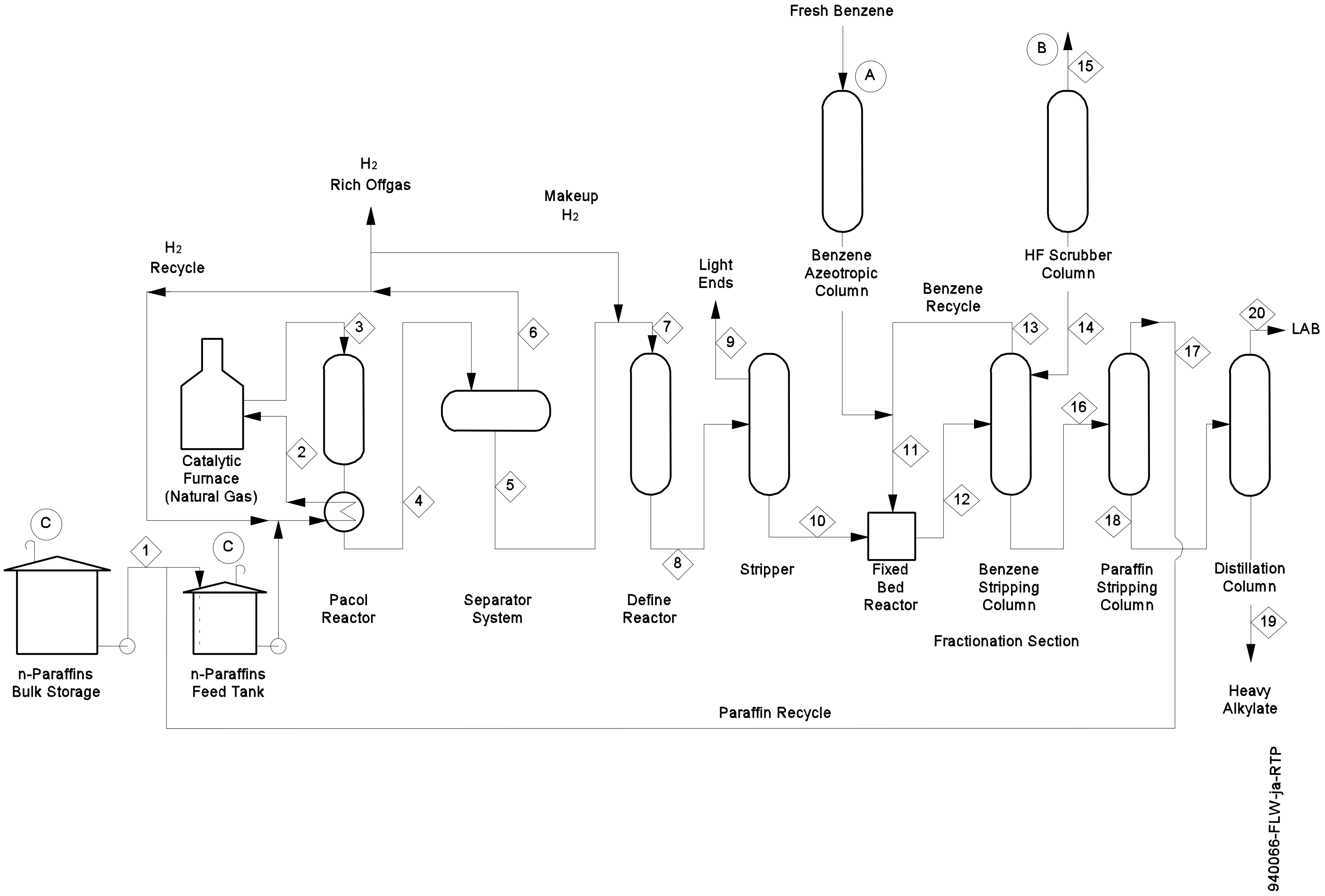


Figure 5-15. Linear Alkybenzene Production Using the Olefin Process

Source: Reference 103.

Following benzene stripping, a lime water solution is then fed into the HFl scrubber column (Stream 14) to neutralize the HFl. The solution is filtered (Stream 15); the wastewater is routed to the treatment facility and the solids are transferred to a landfill. Unreacted paraffins are separated in the paraffin stripping column (Stream 16) and recycled to the Pacol reactor (Stream 17). The last distillation column purifies the main LAB (Stream 18). Heavy alkylate byproducts are stored (Stream 19) and the pure LAB is transferred to storage tanks (Stream 20) awaiting sale.

5.8.2 Benzene Emissions from LAB Production Using the Olefin Process

Benzene emissions from the LAB olefin process are shown in Table 5-14.[102] The two major sources of emissions are the benzene azeotropic column (Vent A) and the HFl scrubber column controlling emissions from the benzene stripping column (Vent B). Some benzene can be emitted through the HFl scrubber column. Inert gases and air venting from the unit, temperature, and purge rate of the scrubber can influence the amount of volatiles emitted. These gases are usually sent to a flare. The control for both of these emissions is use as fuel. Benzene emissions can also occur from benzene storage tanks and equipment leaks. Refer to Section 4.5 for a discussion of benzene emissions from these sources.

5.8.3 Process Description for Production of LAB Using the Chlorination Process

The LAB chlorination process consists of two sequential reactions. In the first step, n-paraffins are chlorinated to monochlorinated n-paraffins. In the second reaction, benzene and crude secondary alkyl chlorides (chloroparaffins) are blended with an aluminum chloride catalyst to form crude LAB. The following discussion of LAB production using the chlorination process is taken from references 100 and 102.

As shown in Figure 5-16, n-paraffins (alkanes) (Stream 1) are reacted with liquid chlorine (Stream 2) in a series of UV-catalyzed chlorination reactors.[100] The n-paraffins

TABLE 5-14. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL LINEAR ALKYLBENZENE PLANT USING THE OLEFIN PROCESS

SCC and Description	Emissions Source	Control Device	Emission Factor lb/ton (g/Mg)[a,b]	Factor Rating
3-01-211-02 Linear Alkylbenzene - Benzene Drying	Benzene Azeotropic Column Vent (Point A)[c]	Uncontrolled	7.4×10^{-3} (3.7)	U
		Used as fuel	1.5×10^{-6} (7.4×10^{-4})	U
3-01-211-03 Linear Alkylbenzene HFl Scrubber Vent	Hydrogen Fluoride Scrubber Column Vent (Point B)[c]	Uncontrolled	0.022 (11)	U
		Used as fuel	4.4×10^{-6} (2.2×10^{-3})	U
		Flare	2.2×10^{-3} (1.1)	U

Source: Reference 102.

[a] Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant.
[b] Emission factors refer to lb (g) benzene emitted per ton (Mg) LAB produced by the olefin process.
[c] Letters refer to vents designated in Figure 5-15.

Note: Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

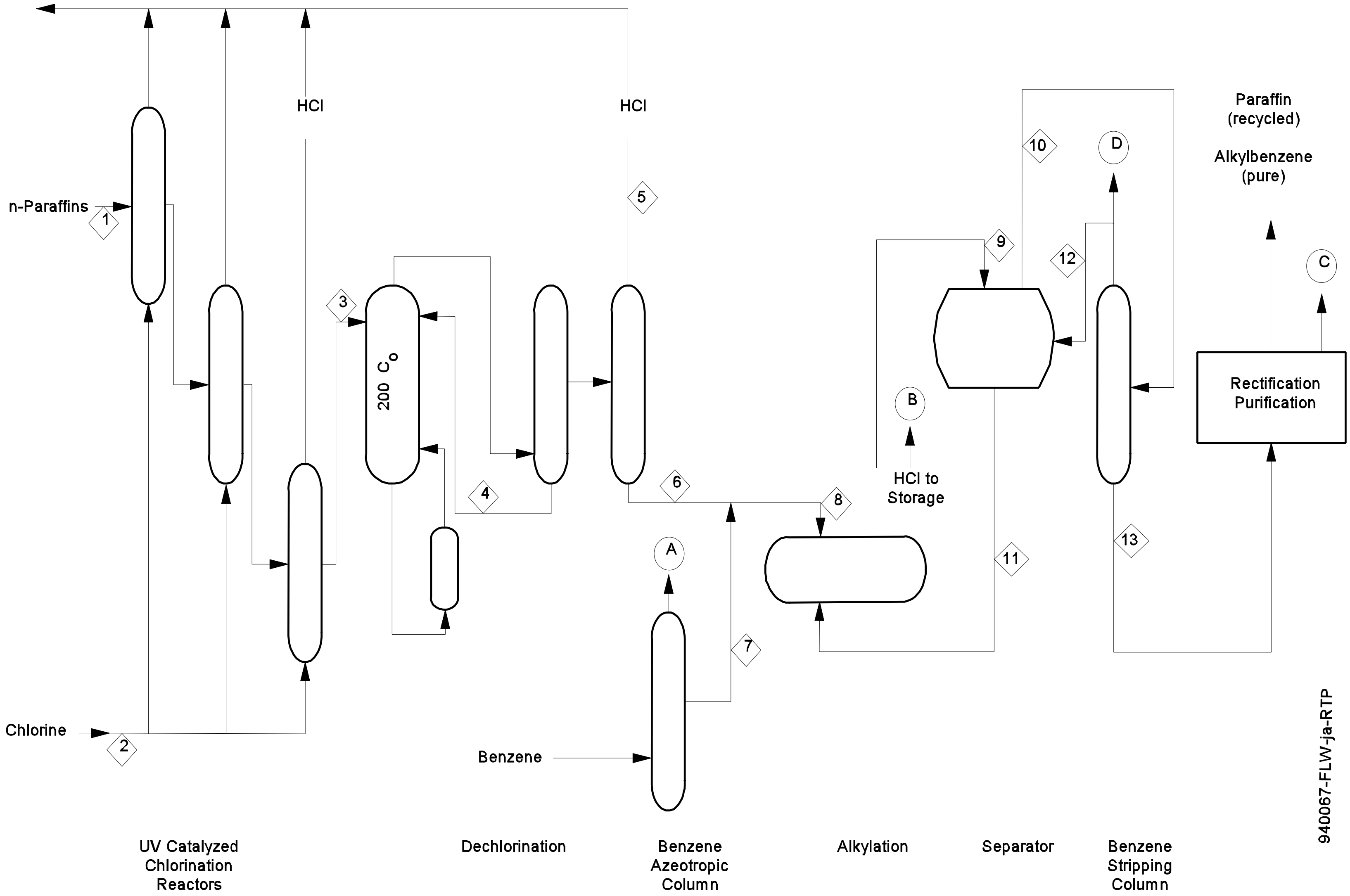
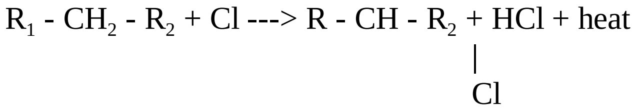


Figure 5-16. Production of Linear Alkybenzenes via Chlorination

Source: Reference 100.

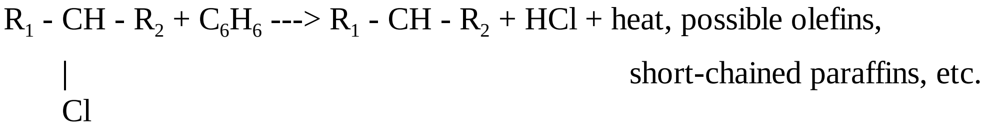
are converted at 212°F (100°C) to a mixture of about 35 percent chlorinated paraffins, and the remainder to paraffins and HCl as shown in the following reaction:



$$R_1 - CH_2 - R_2 + Cl \longrightarrow R - \underset{\substack{|\\ Cl}}{CH} - R_2 + HCl + \text{heat}$$

Following this reaction, dehydrochlorination (elimination of HCl) of the monochloroalkanes takes place at 392 to 752°F (200 to 300°C) over an iron catalyst to form olefins (linear alkenes with internal double bonds) (Stream 3). It is necessary to remove all chlorinated paraffins (such as dichloroalkenes) from the process stream because they form other products besides LAB. Therefore, the remaining chlorinated paraffins are dehydrochlorinated to give tar-like products that are easily separated and recycled back to the reactor (Stream 4). HCl is also removed from the mixture (Stream 5), leaving a mixture of only olefins and paraffins for the alkylation reaction.[100]

This olefin-paraffin mixture (Stream 6) is combined with benzene from storage that has been dried in a benzene azeotropic column (Stream 7). These two streams are combined in an alkylation reactor with an aluminum chloride catalyst at 122°F (50°C) (Stream 8). The subsequent reaction produces LAB, illustrated below:



$$R_1 - \underset{\substack{|\\ Cl}}{CH} - R_2 + C_6H_6 \longrightarrow R_1 - CH - R_2 + HCl + \text{heat, possible olefins, short-chained paraffins, etc.}$$

At this point, HCl gas and some fugitive volatile organics given off during the reaction are treated with adsorbers and excess HCl is routed to storage (Vent B). Next, the LAB (Stream 9) is routed to a separator where hydrolysis is performed in the presence of HFl at 50°F (10°C) to separate crude LAB and the organics (benzene, tar, etc.) (Stream 10) from the catalyst sludge (Stream 11). Benzene is recovered in the benzene stripping column and recycled back to the reactor (Stream 12).

The resulting paraffin-alkylate mixture (Stream 13) is sent through rectification and purification (which includes washing and decanting) to yield pure alkylbenzene and paraffin, which can be recycled as feedstock.[100]

5.8.4 Benzene Emissions from LAB Production Using the Chlorination Process

Benzene emissions using the LAB chlorination process are shown in Table 5-14. The four major points of benzene emissions are listed below. Emission factors for these points also are presented in Table 5-15.[102]

One emission point is the benzene azeotropic column vent, which serves to dry the benzene before it enters the alkylation reactor. Some benzene emissions can escape from the vent in the column (Vent A). The quantity of escaping emissions is dependent on the dryness of the benzene and the design of the column condenser.

A second emission point is the hydrochloric acid adsorber vent. Following the alkylation reaction, the HCl gas and fugitive volatile organics are treated by absorbers. Most of the product goes to hydrochloric acid storage, but some is vented off (Vent B). The amount of benzene emissions given off here is dependent on the fluid temperature in the absorber and the vapor pressure of the mixed absorber fluid.

The third type of emission point is the atmospheric wash decanter vents. In the final purification/rectification stage, the crude LAB is washed with alkaline water to neutralize it. Benzene emissions can escape from these atmospheric washer vents (Vent C).

Finally, in the benzene stripping column, benzene is recovered and returned to the benzene feed tank. Residual inert gases and benzene emissions can occur at this point (Vent D). The amount of benzene in the stream depends on the quantity of inert gases and the temperature and design of the reflux condenser used.

TABLE 5-15. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL LINEAR ALKYLBENZENE PLANT USING THE CHLORINATION PROCESS

SCC and Description	Emissions Source	Control Device	Emission Factor in lb/ton (g/Mg)[a]	Factor Rating
3-01-211-02 Linear Alkylbenzene-Benzene Drying	Benzene Azeotropic Column Vent (Point A)[c]	Uncontrolled	7.4×10^{-3} (3.7)	U
		Used as fuel	1.5×10^{-6} (7.4×10^{-4})	U
3-01-211-23 Linear Alkylbenzene - HCl Adsorber Vent	Hydrochloric Acid Adsorber Vent (Point B)[c]	Uncontrolled	0.5 (250)	U
		Used as fuel	1×10^{-4} (0.05)	U
3-01-211-24 Linear Alkylbenzene - Atmospheric Wash/Decanter Vent	Atmospheric Wash/Decanter Vent (Point C)[c]	Uncontrolled	0.0246 (12.3)	U
		Used as a fuel	5×10^{-6} (2.5×10^{-3})	U
3-01-211-25 Linear Alkylbenzene - Benzene Strip Column	Benzene Stripping Column Vent (Point D)[c]	Uncontrolled	7.4×10^{-3} (3.7)	U
		Used as a fuel	1.48×10^{-6} (7.4×10^{-4})	U

Source: Reference 102.

[a] Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant.

[b] Emission factors refer to lb (g) benzene emitted per ton (Mg) LAB produced by the chlorination process.

[c] Letters refer to vents designated in Figure 5-16.

Note: Any given LAB olefin producing plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

The most frequently applied control option for all of these sources is to use the emissions for fuel.

5.9 OTHER ORGANIC CHEMICAL PRODUCTION

Several additional organic chemicals that are produced using benzene as a feedstock are believed to have benzene emissions. These chemicals include hydroquinone, benzophenone, benzene sulfonic acid, resorcinol, biphenyl, and anthraquinone.[68] A brief summary of the producers, end uses, and manufacturing processes for these chemicals is given below. No emissions data were available for these processes.

5.9.1 Hydroquinone

The primary end use of hydroquinone is in developing black-and-white photographic film (46 percent). A secondary end use is as a raw material for rubber antioxidants (31 percent).[104]

A technical grade of hydroquinone is manufactured using benzene and propylene as raw materials by Goodyear Tire and Rubber Company in Bayport, TX, 11 million lb/yr (5 million kg/yr) and by the Eastman Chemical Company, Tennessee Eastman Division, in Kingsport, Tennessee, 26 million lb/yr (12 million kg/yr).[11,101]

In this process, benzene and recycled cumene are alkylated with propylene in the liquid phase over a fixed-bed silica-alumina catalyst to form a mixture of diisopropylbenzene isomers. The meta isomer is transalkylated with benzene over a fixed bed silica-alumina catalyst to produce cumene for recycle. The para isomer is hydroperoxidized in the liquid phase, using gaseous oxygen, to a mixture of diisopropylbenzene hydroperoxide isomers. The mono isomer is recycled to the hydroperoxidation reactor. The diisopropylbenzene hydroperoxide is cleaved in the liquid phase with sulfuric acid to hydroquinone and acetone. Acetone is produced as a co-product.[104]

5.9.2 Benzophenone

Benzophenone (diphenylketone) is used as an intermediate in organic synthesis, and as an odor fixative. Derivatives are used as ultraviolet (UV) absorbers, such as in the UV curing of inks and coatings.[105] Benzophenone is also used as flavoring, soap fragrance, in pharmaceuticals, and as a polymerization inhibitor for styrene. Nickstadt-Moeller, Inc., in Ridgefield, New Jersey, and PMC, Inc., PMC Specialties Group Division in Chicago, Illinois, produce a technical grade of benzophenone.[11] Benzophenone is also produced by Upjohn Company, Fine Chemicals.[101] Benzophenone is produced by acylation of benzene and benzyl chloride.[68]

5.9.3 Benzene Sulfonic Acid

Benzene sulfonic acid is used as a catalyst for furan and phenolic resins and as a chemical intermediate in various organic syntheses including the manufacture of phenol and resorcinol.[105,106] Benzene sulfonic acid is manufactured by sulfonation--reacting benzene with fuming sulfuric acid.[106] Burroughs Wellcome in Greenville, North Carolina; CL Industries, Inc., in Georgetown, Illinois; and Sloss Industries Corporation in Birmingham, Alabama, produce benzene sulfonic acid.[11]

5.9.4 Resorcinol

Resorcinol is produced by INDSPEC Chemical Corporation in Petrolia, Pennsylvania.[11] Resorcinol is produced by fusing benzene-m-disulfonic acid with sodium hydroxide. Resorcinol is used in manufacturing resorcinol-formaldehyde resins, dyes, and pharmaceuticals. It is also used as a cross-linking agent for neoprene, as a rubber tackifier, in adhesives for wood veneers and runner-to-textiles composites, and in the manufacture of styphnic acid and cosmetics.[106]

5.9.5 Biphenyl

Biphenyl (diphenyl or phenylbenzene) is produced by Chemol Co. in Greensboro, North Carolina; Koch Refining Co. in Corpus Christi, Texas; Monsanto Co. in Anniston, Alabama; Sybron Chemical Inc., in Wellford, South Carolina; and Chevron Chemical Co. of Chevron Corp.[11,101] One method for producing biphenyl is by dehydrogenation--slowly passing benzene through a red-hot iron tube.[106]

Biphenyl is used in organic synthesis, as a heat-transfer agent, as a fungistat in packaging citrus fruit, in plant disease control, in the manufacture of benzidine, and as a dyeing assistant for polyesters.[106] In 1991, 8,976 tons (8,143 Mg) of biphenyl were sold.[101]

5.9.6 Anthraquinone

Anthraquinone is manufactured by heating phthalic anhydride and benzene in the presence of aluminum chloride and dehydrating the product. Anthraquinone is used as an intermediate for dyes and organics, as an organic inhibitor, and as a bird repellent for seeds.

5.10 BENZENE USE AS A SOLVENT

Benzene has been used historically as an industrial solvent. Because benzene is readily soluble in a variety of chemicals (including alcohol, ether, and acetone), it has commonly been used as an agent to dissolve other substances. As an industrial solvent, benzene application has included use as an azeotropic agent, distilling agent, reaction solvent, extracting solvent, and recrystallizing agent. However, benzene use as an industrial solvent has been steadily declining over the last few years because of its adverse health effects and increased regulation. The Occupational Safety and Health Administration has cited health risk to workers from exposure to benzene, and EPA has classified benzene as a Group A chemical, a known human carcinogen.[107]

Source categories that currently use benzene as a solvent include pharmaceutical manufacturing; general organic synthesis; alcohol manufacturing; caprolactam production, and plastics, resins, and synthetic rubber manufacturing. Benzene is also used in small quantities (generally less than 0.1 percent) in solvents used in the rubber tire manufacturing industry; however, the amount of emissions generated is variable depending on the amount of solvent used.[108]

Facilities in the above-listed source categories indicate that they plan to eliminate benzene solvent use in the next few years.[107] Facilities have been experimenting with substitutes, such as toluene, cyclohexane, and monochlorobenzene. However, those facilities that continue to use benzene indicate that they have been unable to identify a solvent substitute as effective as benzene.[109]

Several facilities in the source categories listed above reported benzene emissions in the 1992 TRI. These facilities and their locations are included in Table 5-16.

Emissions of benzene from solvent used in the manufacture and use of pesticides, use of printing inks, application of surface coatings, and manufacture of paints are believed to be on the decline or discontinued.[107,110] However, several facilities in these source categories reported benzene emissions in the 1992 TRI.[111] These facilities and their locations are also included in Table 5-16.[111]

Benzene continues to be used in alcohol manufacture as a denaturant for ethyl alcohol. It is also used as an azeotropic agent for dehydration of 95 percent ethanol and 91 percent isoproponal.[109] Companies currently producing these alcohols are presented in Table 5-17.[11,111]

Benzene is also used as a solvent to extract crude caprolactam.[112] The three major caprolactam facilities currently operating in the United States are listed in

TABLE 5-16. PARTIAL LIST OF MANUFACTURERS IN SOURCE CATEGORIES WHERE BENZENE IS USED AS A SOLVENT

Solvent Use Source Category	Location
Plastics Materials and Resins	
Amoco Chemical Co.	Moundville, AL
Arizona Chemical Co.	Gulfport, MS
Chemfax Inc.	Gulfport, MS
Exxon Chemical Americas Baton Rouge Resin Finishing	Baton Rouge, LA
Formosa Plastics Corp.	Point Comfort, TX
Lawter Intl. Inc. Southern Resin Division	Moundville, AL
Neville Chemical Co.	Pittsburgh, PA
Quantum Chemical Corp. La Porte	La Porte, TX
Quantum Chemical Corp. USI Division	Clinton, IA
Rexene Corp. Polypropylene Plant	Odessa, TX
Union Carbide Chemicals & Plastics Co. Texas City Plant	Texas City, TX
Pharmaceutical Manufacturing	
Warner-Lambert Co. Parke Davis Division	Holland, MI
Pesticides and Agricultural Chemicals	
Rhone-Poulenc Ag Co.	Institute, WV
Agribusiness Maketers, Inc.	Baton Rouge, LA
Commercial Printing (Gravure)	
Piedmont Converting, Inc.	Lexington, NC

(continued)

TABLE 5-16. CONTINUED

Solvent Use Source Category	Location
Paints and Allied Products	
BASF Corporation Inks & Coating Division	Greenville, OH
St. Louis Paint Manufacturing Co., Inc.	St. Louis, MS
Synthetic Rubber	
DuPont Pontchartrain Works	La Place, LA
DuPont Beaumont Plant	Beaumont, TX

Source: Reference 111.

TABLE 5-17. U.S. PRODUCERS OF ETHANOL OR ISOPROPANOL

Facility	Location	Annual Capacity million gal (million L)
Ethanol		
Archer Daniels Midland Company ADM Corn Processing Division	Cedar Rapids, IA	700 (2,650)
	Clinton, IA	
	Decatur, IL	
	Peoria, IL	
	Walhalla, ND	11 (42)
Biocom USA Ltd.	Jennings, LA	40 (151)
Cargill, Incorporated Domestic Corn Milling Division	Eddyville, IA	30 (113)
Chief Ethanol Fuels Inc.	Hastings, NB	14 (53)
Eastman Chemical Company Texas Eastman Division	Longview, TX	25 (95)
Georgia-Pacific Corporation Chemical Division	Bellingham, WA	12 (45)
Giant Refining Co.	Portales, NM	10 (38)
Grain Processing Corporation	Muscatine, IA	60 (227)
High Plains Corp.	Colwich, KS	15 (57)
Hubinger-Roquette Americas, Inc.	Keokuk, IA	11 (42)
Midwest Grain Products, Inc.	Atchison, KS	22 (83)
	Pekin, IL	19 (72)
Minnesota Corn Processors	Columbus, NB	NA
	Marshall, MN	28 (106)
New Energy Company of Indiana	South Bend, IN	70 (265)
Pekin Energy Company	Pekin, IL	80 (303)
Quantum Chemical Corp. USI Division	Tuscola, IL	68 (257)
South Point Ethanol	South Point, OH	60 (227)
A. E. Staley Manufacturing Company Sweetner Business Group Ethanol Division	Loudon, TN	60 (227)

(continued)

TABLE 5-17. CONTINUED

Facility	Location	Annual Capacity million gal (million L)
Ethanol (continued)		
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	123 (466)
	TOTAL	1,458 (5,519)
Isopropanol		
Exxon Chemical Company Exxon Chemical Americas	Baton Rouge, LA	650 (2,460)
Lyondell Petrochemical Company	Channelview, TX	65 (246)
Shell Chemical Company	Deer Park, TX	600 (2,271)
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	530 (2,006)
	TOTAL	1,845 (6,984)

Source: References 11 and 111.

[a] Emissions listed are those reported in the 1992 TRI.

NA = Not available

-- = no emissions reported

Table 5-18.[11,111] Of the three facilities, DSM and BASF use benzene as a solvent, and Allied Signal produces benzene as a co-product.[113]

Benzene is also used as a solvent in the blending and shipping of aluminum alkyls.[113]

Emission points identified for solvent benzene are process vents, dryer vents, and building ventilation systems.[107] As shown in Table 5-19, only one emission factor was identified for any of the solvent use categories.[114] The emission factor presented is for the vacuum dryer vent controlled with a venturi scrubber in pharmaceutical manufacturing.

TABLE 5-18. U.S. PRODUCERS OF CAPROLACTAM

Facility	Location	Annual Capacity million lb (million kg)	Raw Material
Allied-Signal, Inc. Engineered Materials Sector	Hopewell, VA	660 (299)	Phenol
BASF Corporation Chemicals Division Fiber Raw Materials	Freeport, TX	420 (191)	Cyclohexane
DSM Chemicals North America, Inc.	August, GA	360 (163)	Cyclohexane
	TOTAL	1,440 (653)	

Source: References 11 and 111.

[a] Emissions listed are those reported in the 1992 TRI.

"--" = no emissions reported.

TABLE 5-19. SUMMARY OF EMISSION FACTORS FOR BENZENE USE AS A SOLVENT

SCC and Description	Emissions Source	Control Device	Emission Factor[a] lb/1,000 gal (g/L)	Factor Rating
3-01-060-01 Pharmaceuticals - General Process - Vacuum Dryers	Vacuum Dryer Vent	Venturi Scrubber (99.10% efficiency)	2.1 (0.25)	B

Source: Reference 114.

[a] Factor is expressed as lb (kg) benzene emitted per 1,000 gal (L) pharmaceutical product produced.

SECTION 6.0
EMISSIONS FROM OTHER SOURCES

The following activities and manufacturing processes (other than benzene production or use of benzene as a feedstock) were identified as additional sources of benzene emissions: oil and gas wellheads, petroleum refineries, glycol dehydrators, gasoline marketing, publicly owned treatment works (POTWs), landfills, pulp and paper manufacturing, synthetic graphite manufacturing, carbon black manufacturing, rayon-based carbon manufacturing, aluminum casting, asphalt roofing manufacturing, and use of consumer products and building supplies.

For each of these categories, the following information is provided in the sections below: (1) a description of the activity or process, (2) a brief characterization of the national activity in the United States, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed.

6.1 OIL AND GAS WELLHEADS

6.1.1 <u>Description of Oil and Gas Wellheads</u>

Oil and gas production (through wellheads) delivers a stream of oil and gas mixture and leads to equipment leak emissions. Emissions from the oil and gas wellheads, including benzene, are primarily the result of equipment leaks from various components at the wellheads (valves, flanges, connections, and open-ended lines). Component configurations for wellheads can vary significantly.

Oil and gas well population data are tracked by State and Federal agencies, private oil and gas consulting firms, and oil and gas trade associations. In 1989 a total of 262,483 gas wells and 310,046 oil wells were reported in the United States.[115,116] Reference 117 presents a comprehensive review of information sources for oil and gas well count data. The activity factor data are presented at four levels of resolution: (1) number of wells by county, (2) number of wells by State, (3) number of fields by county, and (4) number of fields by State.

6.1.2 Benzene Emissions from Oil and Gas Wellheads

Emissions from oil and gas wellheads can be estimated using the average emission factor approach as indicated in the EPA Protocol for Equipment Leak Emission Estimates.[54] This approach allows the use of average emission factors in combination with wellheads-specific data. These data include: (1) number of each type of components (valves, flanges, etc.), (2) the service type of each component (gas, condensate, mixture, etc.), (3) the benzene concentration of the stream, and (4) the number of wells.

A main source of data for equipment leak hydrocarbon emission factors for oil and gas field operations is an API study[118] developed in 1980.

Average gas wellhead component count has been reported as consisting of 11 valves, 50 screwed connections, 1 flange, and 2 open-ended lines.[119] No information was found concerning average component counts for oil wellheads.

Benzene and total hydrocarbons equipment leak emission factors from oil wellheads are presented in Table 6-1.[120] These emission factors were developed from

TABLE 6-1. BENZENE AND TOTAL HYDROCARBONS EQUIPMENT LEAK EMISSION FACTORS FOR OIL WELLHEAD ASSEMBLIES[a]

				Emission Factor		
SCC Number	Description	Emission Source	Emission level[b]	Total Hydrocarbons lb/hr/wellhead (kg/hr/wellhead)	Benzene lb/hr/wellhead (kg/hr/wellhead)	Emission Factor Rating
3-10-001-01	Oil wellheads[c]	Equipment leaks	1	3.67×10^{-2} (1.65×10^{-2})	1.27×10^{-7} (5.77×10^{-8})	D
			2	6.53×10^{-3} (2.97×10^{-3})	3.9×10^{-8} (1.77×10^{-8})	D
			3	9.74×10^{-4} (4.43×10^{-4})	6.25×10^{-9} (2.84×10^{-9})	D
			4	3.48×10^{-4} (1.58×10^{-4})	NA	D
			5	1.06×10^{-4} (4.82×10^{-5})	NA	D

Source: Reference 120.

[a] Over 450 accessible production wellhead assemblies were screened, and a total of 28 wellhead assemblies were selected for bagging. The oil production facilities included in this study are located in California.

[b] The concentration ranges applicable to the 5 emission levels developed were as follows: level 1-->10,000 ppm at two or more screening points or causing instrument flameout; level 2--3,000 to 10,000 ppm; level 3--500 to 3,000 ppm; level 4--50 to 500 ppm; level 5--0 to 50 ppm.

[c] Field wellhead only. Does not include other field equipment (such as dehydrators, separators, inline heaters, treaters, etc.).

NA = Not available.

screening and bagging data obtained in oil production facilities located in California.[120] Over 450 accessible production wellhead assemblies were screened, and a total of 28 wellhead assemblies were selected for bagging. For information about screening and bagging procedures refer to Reference 54.

The composition of gas streams varies among production sites. Therefore, when developing benzene emission estimates, the total hydrocarbons emission factors should be modified by specific benzene weight percent, if available.

Benzene constituted from less than 0.1 up to 2.3 percent weight of total non-methane hydrocarbons (TNMHC) for water flood wellhead samples from old crude oil production sites in Oklahoma. Also, benzene constituted approximately 0.1 percent weight of TNMHC for gas driven wellhead samples.[121] The VOC composition in the gas stream from old production sites is different than that from a new field. Also, the gas-to-oil ratio for old production sites may be relatively low.[121] The above type of situations should be analyzed before using available emission factors.

6.2 GLYCOL DEHYDRATION UNITS

Glycol dehydrators used in the petroleum and natural gas industries have only recently been discovered to be an important source of volatile organic compound (VOC) emissions, including benzene, toluene, ethylbenzene, and xylene (BTEX). Natural gas is typically dehydrated in glycol dehydration units. The removal of water from natural gas may take place in field production, treatment facilities, and in gas processing plants. Glycol dehydration units in field production service have smaller gas throughputs compared with units in gas processing service. It has been estimated that between 30,000 and 40,000 glycol dehydrating units are in operation in the United States.[122] In a survey conducted by the Louisiana Department of Environmental Quality, triethylene glycol (TEG) dehydration units accounted for approximately 95 percent of the total in the United States, with ethylene glycol (EG) and diethylene glycol (DEG) dehydration units accounting for approximately 5 percent.[123]

Data on the population and characteristics of glycol dehydration units nationwide is limited. Demographic data has been collected by Louisiana Department of Environmental Quality, Texas Mid-Continent Oil and Gas Association and Gas Processors Association, Air Quality Service of the Oklahoma Department of Health (assisted by the Oklahoma Mid-Continent Oil and Gas Association), and Air Quality Division of the Wyoming Department of Environmental Quality.[124] Table 6-2 presents population data and characteristics of glycol dehydration units currently available.[124]

6.2.1 Process Description for Glycol Dehydration Units

The two basic unit operations occurring in a glycol dehydration unit are absorption and distillation. Figure 6-1 presents a general flow diagram for a glycol dehydration unit.[125] The "wet" natural gas (Stream 1) enters the glycol dehydrator through an inlet separator that removes produced water and liquid hydrocarbons. The gas flows into the bottom of an absorber (Stream 2), where it comes in contact with the "lean" glycol (usually triethylene glycol [TEG]). The water and some hydrocarbons in the gas are absorbed by the glycol. The "dry" gas passes overhead from the absorber through a gas/glycol exchanger (Stream 3), where it cools the incoming lean glycol. The gas may enter a knock-out drum (Stream 4), where any residual glycol is removed. From there, the dry natural gas goes downstream for further processing or enters the pipeline.

After absorbing water from the gas in the absorber, the "rich" glycol (Stream 5) is preheated, usually in the still, and the pressure of the glycol is dropped before it enters a three-phase separator (Stream 6). The reduction in pressure produces a flash gas stream from the three-phase separator. Upon exiting the separator (Stream 7), the glycol is filtered to remove particles. This particular configuration of preheat, flash, and filter steps may vary from unit to unit. The rich glycol (Stream 8) then passes through a glycol/glycol exchanger for further preheating before it enters the reboiler still.

TABLE 6-2. GLYCOL DEHYDRATION UNIT POPULATION DATA

Survey	Service	No. of Units		
		Total	Capacity ≤ 10 MMscfd	Capacity > 10 MMscfd
Texas Mid-Continent Oil and Gas Association (TMOGA) and Gas Processors Association (GPA) Survey[a]	Production	618	556	62
	Gas Processing	206	103	103
	Pipeline	192	144	48
	Total	1016	803	213
Louisiana Department of Environmental Quality (LDEQ) Survey[b]	Ethylene Glycol	12	0	12
	Triethylene Glycol	191	96	95
	Total	203	96	107
Oklahoma Mid-Continent Oil and Gas Association (OKMOGA) Survey[c]	Total	1,333	NR	NR
Wyoming Department of Environmental Survey[d]	Total	1,221	1,185	36

Source: Reference 124.

[a] The survey only covers some companies; therefore it should not be considered a complete listing of units in Texas.
[b] The survey was only directed to units > 5 MMscfd; therefore it should not be considered a complete listing of units in Louisiana.
[c] The survey only covers dehydrator units for eight companies; therefore it should not be considered a complete listing of units in Oklahoma.
[d] The survey covered 50 companies owning and/or operating glycol units in Wyoming.

NR = Not reported.

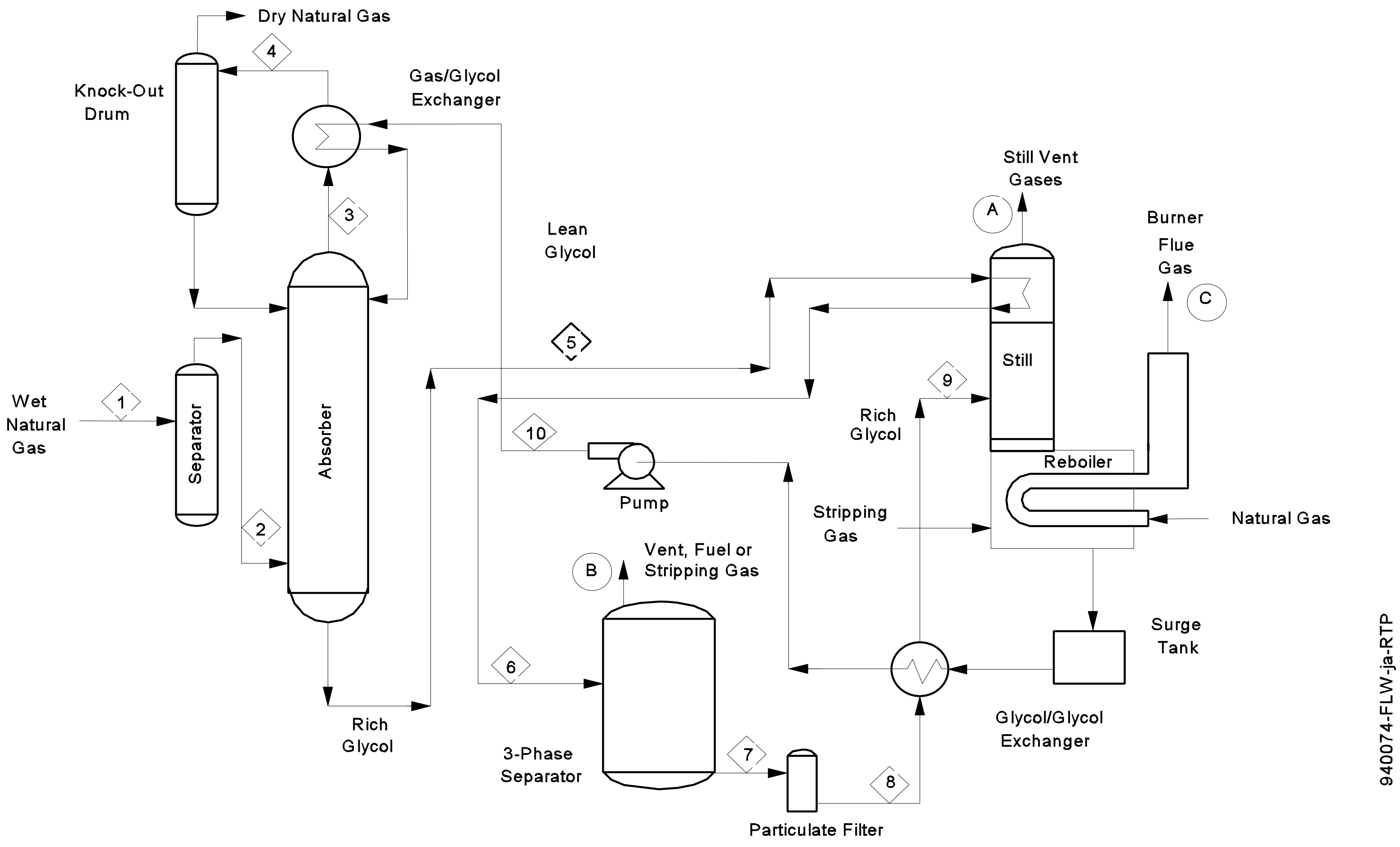


Figure 6-1. Flow Diagram for Glycol Dehydration Unit

Source: Reference 125.

Then, the rich glycol enters the reboiler still (Stream 9) (operating at atmospheric pressure), where the water and hydrocarbons are distilled (stripped) from the glycol making it lean. The lean glycol is pumped back to absorber pressure and sent to the gas/glycol exchanger (Stream 10) before entering the absorber to complete the loop.

6.2.2 Benzene Emissions from Glycol Dehydration Units

The primary source of VOC emissions, including BTEX, from glycol dehydration units is the reboiler still vent stack (Vent A).

Because the boiling points of BTEX range from 176°F to 284°F (80 to 140°C), they are not lost to any large extent in the flash tank but are separated from the glycol in the still. These separations in the still result in VOC emissions that contain significant quantities of BTEX.[126]

Secondary sources of emissions from glycol dehydration units are the phase separator vent (Vent B) and the reboiler burner exhaust stack (Vent C).

Most glycol units have a phase separator between the absorber and the still to remove dissolved gases from the warm rich glycol and reduce VOC emissions from the still. The gas produced from the phase separator can provide the fuel and/or stripping gas required for the reboiler.

A large number of small glycol dehydration units use a gas-fired burner as the heat source for the reboiler. The emissions from the burner exhaust stack are considered minimal and are typical of natural gas combustion sources.

Reboiler still vent data have been collected by the Louisiana Department of Environmental Quality,[123] and the Ventura County (California) Air Pollution Control District.[127] Table 6-3 presents emission factors for both triethylene glycol (TEG) units and

TABLE 6-3. REACTIVE ORGANIC COMPOUNDS (ROCs)[a] AND BTEX EMISSION FACTORS FOR GLYCOL DEHYDRATION UNITS

SCC Number	SCC and Description	Emissions Source	Control Device	Emission Factor	Emission Factor Rating
3-10-003-01	Glycol dehydration units TEG units	Reboiler Still Vent	None	34×10^{2} lb/yr of ROC/MMscfd[b] (54.46×10^{3} kg/yr of ROC/MMscmd)	U
			None	18.6×10^{2} lb/yr of BTEX/MMscfd[b] (29.79×10^{3} kg/yr of BTEX/MMscmd)	U
			None	32.4×10^{2} lb/yr of ROC/MMscfd[c] (51.90×10^{3} kg/yr of ROC/MMscmd)	U
3-10-003-XX	Glycol dehydration units EG units	Reboiler Still Vent	None	54.0×10^{1} lb/yr of ROC/MMscfd[b] (8.65×10^{3} kg/yr of ROC/MMscmd)	U
			None	24×10^{1} lb/yr of BTEX/MMscfd[b] (3.84×10^{3} kg/yr of BTEX/MMscmd)	U
			None	74.0×10^{1} lb/yr of ROC/MMscfd[c] (11.85×10^{3} kg/yr of ROC/MMscmd)	U

[a] ROC are defined as total non-methane and ethane hydrocarbons.
[b] Louisiana DEQ emission factor from glycol dehydration unit survey.
[c] Ventura County (California) Air Pollution Control District emission factor from one source test.

MMscfd = Million standard cubic feet per day.
MMscmd = Million standard cubic meter per day.

ethylene glycol (EG) units based on the natural gas throughput of the gas treated. The emission factors developed from the LDEQ study were based on responses from 41 companies and 208 glycol dehydration units. The Ventura County, California, factors include testing results at two locations (one for TEG and one for EG). The amount of produced gas treated is thought to be the most important because it largely determines the size of the glycol system.[127] However, the data base does not show a strong correlation because other variables with countervailing influences were not constant.[127] VOC and BTEX emissions from glycol units vary depending upon the inlet feed composition (gas composition and water content) as well as the configuration, size, and operating conditions of the glycol unit (i.e., glycol type, pump type and circulation rate, gas and contactor temperatures, reboiler fire-cycles, and inlet scrubber flash tank efficiencies).[129]

The speciation of Total BTEX for TEG units reported by the LDEQ in their study indicated the following composition (% weight): benzene (35); toluene (36); ethylbenzene (5); and xylene (24). For EG units, the following compositions were reported: benzene (48); toluene (30); ethylbenzene (4); and xylene (17). Note that the BTEX composition of natural gas may vary according to geographic areas. Limited information/data on the BTEX composition is available.

Four methods for estimating emissions have been reported for glycol dehydration units: (1) rich/lean glycol mass balance, (2) inlet/outlet gas mass balance, (3) unconventional stack measurements (total-capture condensation, and partial stack condensation/flow measurement), and (4) direct stack measurements (conventional stack measurements, and novel stack composition/flow measurement).[129]

Sampling of the rich/lean glycol then estimating emissions using mass balance has been the selected method for measuring emissions to date. The Louisiana Department of Environmental Quality requested emission estimates using reboiler mass balances on the rich/lean glycol samples.

Based upon a set of studies conducted by Oryx Energy Co as part of a task force for the Oklahoma-Kansas Midcontinent Oil & Gas Association, rich/lean glycol mass balance is a highly convenient, cost effective method for estimating air emissions from glycol dehydration units.[129] The following conclusions were addressed in reference 129 regarding this method: (a) good estimates of BTEX can be obtained from rich/lean glycol mass balance, (b) the rich/lean glycol mass balance BTEX estimates are in excellent agreement with total capture condensation method, and (c) rich/lean glycol mass balance is a more reproducible method for emission estimations than nonconventional stack methods. Note that conventional stack methods cannot be used on the stacks of glycol dehydration units because they are too narrow in diameter and have low flow rates.

An industry working group consisting of representatives from the American Petroleum Institute, Gas Processors Association, Texas-Midcontinent Oil & Gas Association, Louisiana Mid-Continent Oil and Gas Association, and GRI is conducting field evaluation experiments to determine appropriate and accurate sampling and analytical methods to calculate glycol dehydration unit emissions.[125] GRI has developed a computer tool, entitled GRI-GLYCalc, for estimating emissions from glycol dehydrators. The U.S. EPA has performed their own field study of GRI-GLYCalc and has recommended that it be included in EPA guidance for State/local agency use for development of emission inventories.[130]

Atmospheric rich/lean glycol sampling is being evaluated as a screening technique in the above working group program. The goal is to compare these results to the stack and other rich/lean results and determine if a correction factor can be applied to this approach.[125]

A second screening technique under study is natural gas sampling and analysis combined with the software program GRI-GLYCalc© to predict emissions. Table 6-4 shows the inputs required of the user and also shows the outputs returned by GRI-GLYCalc©.[132]

TABLE 6-4. GLYCOL DEHYDRATION EMISSION PROGRAM INPUTS AND OUTPUTS

Inputs	Units
Gas Flow Rate	MMscfd
Gas Composition	Volume percent for C_1-C_6 hydrocarbons and BTEX compounds
Gas Pressure	psig
Gas Temperature	°F
Dry Gas Water Content[a]	lbs/MMscf
Number of Equilibrium Stages[a]	Dimensionless
Lean Glycol Circulation	gpm
Lean Glycol Composition	Weight % H_2O
Flash Temperature[c]	°F
Flash Pressure[c]	psig
Gas-Driven Pump Volume Ratio[c]	acfm gas/gpm glycol

Outputs	Units
BTEX Mass Emissions	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Other VOC Emissions	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Flash Gas Composition	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Dry Gas Water Content[b]	lbs/MMscf
Number of Equilibrium Stages[b]	Dimensionless

Source: Reference 132.

[a] Specify <u>one</u> of these inputs.
[b] Dry Gas Water Content is an output if the Number of Equilibrium Stages is specified and vice versa.
[c] Optional

6.2.3 Controls and Regulatory Analysis

Controls applicable to glycol dehydrator reboiler still vents include hydrocarbon skimmers, condensation, flaring, and incineration. Hydrocarbon skimmers use a three-phase separator to recover gas and hydrocarbons from the liquid glycol prior to its injection into the reboiler. Condensation recovers hydrocarbons from the still vent emissions, whereas flaring and incineration destroy the hydrocarbons present in the still vent emissions.

For glycol dehydrators it has been determined by the Air Quality Service, Oklahoma State Department of Health that the Best Available Control Technology (BACT) could include one or more of the following: (1) substitution of glycol, (2) definition of specific operational parameters, such as the glycol circulation rate, reduction of contactor tower temperature, or increasing temperature in the three-phase separator, (3) flaring/incineration, (4) product/vapor recovery, (5) pressurized tanks, (6) carbon adsorption, or (7) change of desiccant system.[128]

The Air Quality Division, Wyoming Department of Environmental Quality has stated that facilities will more than likely be required to control emissions from glycol dehydration units. The Division has determined and will accept the use of condensers in conjunction with a vapor recovery system, incinerator, or a flare as representing BACT.[133]

Most gas processors have begun to modify existing glycol reboiler equipment to reduce or eliminate VOC emissions. Some strategies and experiences from one natural gas company are presented in Reference 124. For other control technologies refer to Reference 134.

Glycol dehydration units are subject to the NSPS for VOC emissions from equipment leaks for onshore natural gas processing plants promulgated in June 1985.[135] The NSPS provides requirements for repair schedules, recordkeeping, and reporting of equipment leaks.

The Clean Air Act Amendments (CAAA) of 1990 resulted in regulation of glycol dehydration units. Title III of the CAAA regulates the emissions of 188 hazardous air pollutants (HAPs) from major sources and area sources. Title III has potentially wide-ranging effects for glycol units. The BTEX compounds are included in the list of 188 HAPs and may be emitted at levels that would cause many glycol units to be defined as major sources and subject to Maximum Achievable Control Technology (MACT).[125]

Currently, the MACT standard for the oil and natural gas production source category, which includes glycol dehydration units, is being developed under authority of Section 112(d) of the 1990 CAAA and is scheduled for promulgation in May, 1999.

In addition to the federal regulations, many states have regulations affecting glycol dehydration units. The State of Louisiana has already regulated still vents on large glycol units, and its air toxics rule may affect many small units. Texas, Oklahoma, Wyoming, and California are considering regulation of BTEX and other VOC emissions from dehydration units.[125]

6.3 PETROLEUM REFINERY PROCESSES

6.3.1 Description of Petroleum Refineries

Crude oil contains small amounts of naturally occurring benzene. One estimate indicates that crude oil consists of 0.15 percent benzene by volume.[136] Therefore, some processes and operations at petroleum refineries may emit benzene independent of specific benzene recovery processes. Appendix B (Table B-1) lists the locations of petroleum refineries in the U.S. As of January 1995, there were 173 operational petroleum refineries in the United States, with a total crude capacity of 15.14 million barrels per calendar day.[137,138] The majority of refinery capacity is located in Texas, Louisiana, and California. Significant refinery capacities are also found in the Chicago, Philadelphia, and Puget Sound areas. A flow diagram of processes likely to be found at a model refinery is shown in Figure 6-2.[139] The arrangement of these processes varies among refineries, and few, if any, employ all of these processes.

Processes at petroleum refineries can be grouped into five types: (1) separation processes, (2) conversion processes, (3) treating processes, (4) auxiliary processes and operation, and (5) feedstock/product storage and handling. These are discussed briefly below.

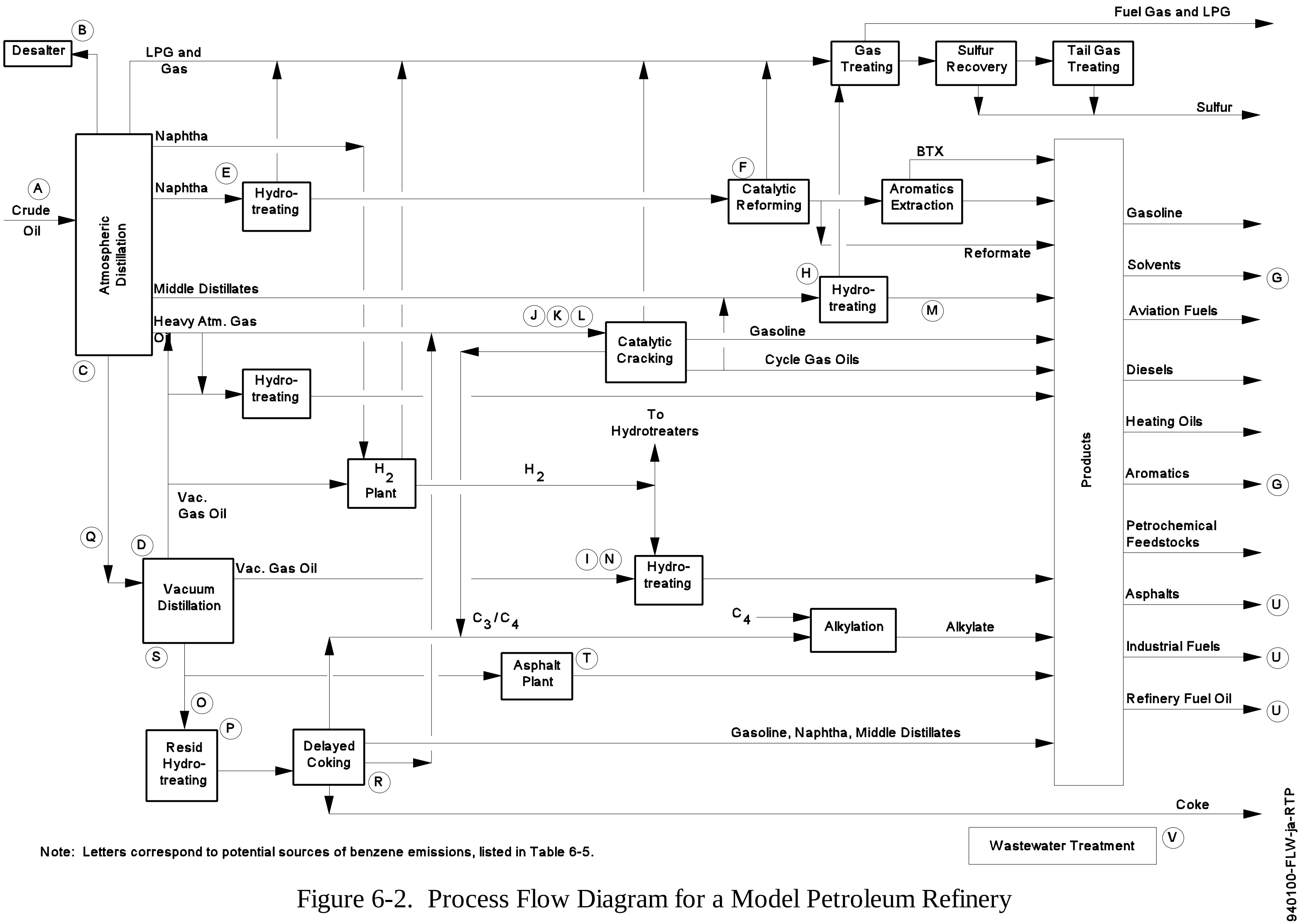
The first phase in petroleum refining operations is the separation of crude oil into its major constituents using four separation processes: (1) desalting, (2) atmospheric distillation, (3) vacuum distillation, and (4) light ends recovery.

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions using one or more of the following conversion processes: (1) catalytic cracking (fluidized-bed and moving-bed), (2) thermal processes (coking, and visbreaking), (3) alkylation, (4) polymerization, (5) isomerization, and (6) reforming.

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products. Among the treating processes are (1) hydrotreating, (2) chemical sweetening, (3) deasphalting, and (4) asphalt blowing.

Auxiliary processes and operations include process heaters, compressor engines, sulfur recovery units, blowdown systems, flares, cooling towers, and wastewater treatment facilities.

Finally, all refineries have a feedstock/product storage area (commonly called a "tank farm") with storage tanks whose capacities range from less than 1,000 barrels to more than 500,000 barrels. Also, feedstock/product handling operations (transfer operations) consist of the loading and unloading of transport vehicles (including trucks, rail cars, and marine vessels).



Note: Letters correspond to potential sources of benzene emissions, listed in Table 6-5.

Figure 6-2. Process Flow Diagram for a Model Petroleum Refinery

Source: Reference 139.

For a complete description of the various processes and operations at petroleum refineries refer to References 139, 140, and 141.

6.3.2 Benzene Emissions from Petroleum Refinery Processes and Operations

Benzene emissions, as well as Hazardous Air Pollutant (HAPs) emissions from petroleum refineries can be grouped into five main categories: (1) process vents, (2) storage tanks, (3) equipment leaks, (4) transfer operations, and (5) wastewater collection and treatment. Table 6-5 presents a list of specific processes and operations which are potential sources of benzene emissions at petroleum refineries emitted from one or more of the above categories.[139]

Also, process heaters and boilers located at the different process units across a refinery emit flue gases containing benzene, and other HAPs. The HAPs emitted result either from incomplete combustion of fuel gas or from the combustion products.

According to the Information Collection Request (ICR) and Section 114 survey submitted to EPA by U.S. refiners as part of the Petroleum Refinery NESHAP study, benzene emissions from process vents were reported for the following process units within a refinery: (1) thermal cracking (coking), (2) Methyl Ethyl Ketone (MEK) dewaxing, and (3) miscellaneous vents at crude distillation units, catalytic reforming units, hydrotreating/hydrorefining, asphalt plants, vacuum distillation towers, and full-range distillation units (light ends, naphtha, solvent, etc.). Also, benzene emissions were reported from blowdown and flue gas system vents.

The Section 114 and ICR questionnaire responses also provided estimates of benzene concentrations in refinery processes, and in petroleum refinery products. Table 6-6 summarizes concentrations of benzene for gas, light liquid, and heavy liquid streams at some refinery process units.[142] Table 6-7 summarizes concentrations of benzene in common refinery products.[143,144]

TABLE 6-5. POTENTIAL SOURCES OF BENZENE EMISSIONS AT PETROLEUM REFINERIES

A	Crude Storage
B	Desalting
C	Atmospheric distillation (crude unit)
D	Vacuum distillation
E	Naphtha hydrodesulfurization
F	Catalytic reforming
G	Light hydrocarbon storage and blending
H	Kerosene hydrodesulfurization
I	Gas oil hydrodesulfurization
J	Fluid bed catalytic cracking
K	Moving bed catalytic cracking
L	Catalytic hydrocracking
M	Middle distillate storage and blending
N	Lube oil hydrodesulfurization
O	Deasphalting
P	Residual oil hydrodesulfurization
Q	Visbreaking
R	Coking
S	Lube oil processing
T	Asphalt blowing
U	Heavy hydrocarbon storage and blending
V	Wastewater collection and treatment units

Source: Reference 139.

TABLE 6-6. CONCENTRATION OF BENZENE IN REFINERY PROCESS UNIT STREAMS (WEIGHT PERCENT)

	Stream Type		
Process Unit	Gas	Light Liquid	Heavy Liquid
Crude	1.3	1.21	0.67
Alkylation (sulfuric acid)	0.1	0.23	0.23
Catalytic Reforming	2.93	2.87	1.67
Hydrocracking	0.78	1.09	0.10
Hydrotreating/hydrorefining	1.34	1.38	0.37
Catalytic Cracking	0.39	0.71	0.20
Thermal Cracking (visbreaking)	0.77	1.45	1.45
Thermal Cracking (coking)	0.24	0.85	0.18
Product Blending	1.20	1.43	2.15
Full-Range Distillation	0.83	1.33	1.08
Vacuum Distillation	0.72	0.15	0.22
Isomerization	2.49	2.49	0.62
Polymerization	0.10	0.10	0.10
MEK Dewaxing	0.36	NR	NR
Other Lube Oil Processing	1.20	1.20	0.10

Source: Reference 142.

NR means not reported.

TABLE 6-7. CONCENTRATION OF BENZENE IN REFINERY PRODUCTS

Material	Weight Percent in Liquid
Asphalt	0.03
Aviation Gasoline	0.51
Alkylale	0.12
Crude Oil	0.45
Diesel/Distillate	0.008
Gasoline (all blends)	0.90
Heavy Gas Oil	0.0002
Jet Fuel	1.05
Jet Kerosene	0.004
Naphtha	1.24
Reformates	4.61
Residual Fuel Oil	0.001
Recovered Oil	0.95

Source: References 143, 144 and 158.

Storage tanks at petroleum refineries containing petroleum liquids are potential sources for benzene emissions. VOC emissions from storage tanks, including fixed-roof, external floating-roof, and internal floating-roof types, can be estimated using *Compilation of Air Pollutant Emission Factors (AP-42),* Chapter 7[33] and the TANKS model. Emissions of benzene from storage vessels may be estimated by applying the benzene concentrations in Table 6-7 to the equations in AP-42 which are also used in TANKS.

Equipment leak emissions from refineries occur from process equipment components such as valves, pump seals, compressor seals, pressure relief valves, connectors, open-ended lines, and sampling connections. Non-methane VOC emissions are calculated using emission factors (in lb/hr/component) and emission equations developed by the EPA in the *Protocol for Equipment Leak Emission Estimates*.[54] The number of components at a refinery are specific to a refinery. However, model equipment counts were developed for the petroleum refinery NESHAP for refineries with crude charge capacities less than 50,000 barrels/stream day (bbl/sd) and greater than or equal to 50,000 bbl/sd. These counts are presented in Tables 6-8 and 6-9.[142] Benzene emissions from equipment leaks may be estimated by multiplying the equipment counts, the equipment leak factor, and the benzene concentration in the process from Table 6-6. It is generally assumed that the speciation of compounds inside a process line are equal to the compounds leaking.

The Western States Petroleum Association (WSPA) and the American Petroleum Institute (API) commissioned the development of a 1993 refinery equipment leak study[145] to develop new emission factors and correlation equations.[139] The data from the 1993 study has been combined with data from a 1993 marketing terminal equipment leak study.[146]

For information on emission factors and equations for loading and transport operations, refer to Section 6.4 (Gasoline Marketing) of this document.

TABLE 6-8. MEDIAN COMPONENT COUNTS FOR PROCESS UNITS FROM SMALL REFINERIES[a]

	Valves			Pumps			Pressure Relief Valves			Flanges				
Process Unit	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid	Compressors	Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid	Open-ended Lines	Sampling Connections
Crude Distillation	75	251	216	8	8	2	6	6	5	164	555	454	39	10
Alkylation (sulfuric acid)	278	582	34	18	10	1	12	15	4	705	1296	785	20	16
Alkylation (HF)	102	402	62	13	3	2	12	13	0	300	1200	468	26	8
Catalytic Reforming	138	234	293	8	5	3	5	3	3	345	566	732	27	6
Hydrocracking	300	375	306	12	9	2	9	4	4	1038	892	623	25	10
Hydrotreating/hydrorefining	100	208	218	5	5	2	5	3	5	290	456	538	20	6
Catalytic Cracking	186	375	450	13	14	2	8	8	7	490	943	938	8	8
Thermal Cracking (visbreaking)	206	197	0	7	0	0	4	0	0	515	405	0	0	4
Thermal Cracking (coking)	148	174	277	9	8	2	7	16	13	260	322	459	13	8
Hydrogen Plant	168	41	0	3	0	2	4	2	0	304	78	0	8	4
Asphalt Plant	120	334	250	5	8	2	5	10	9	187	476	900	16	6
Product Blending	67	205	202	6	11	1	10	6	22	230	398	341	33	14
Sulfur Plant	58	96	127	6	6	3	3	88	15	165	240	345	50	3
Vacuum Distillation	54	26	84	6	6	2	2	5	2	105	121	230	16	4
Full-Range Distillation	157	313	118	7	4	2	5	4	6	171	481	210	20	6
Isomerization	270	352	64	9	2	2	7	10	1	432	971	243	7	8
Polymerization	224	563	15	12	0	1	10	5	3	150	450	27	5	7
MEK Dewaxing	145	1208	200	35	39	3	10	14	4	452	1486	2645	19	17
Other Lube Oil Processes	153	242	201	7	5	2	5	5	5	167	307	249	60	6

Source: Reference 142.

[a] Refineries with crude charge capacities less than 50,000 bbl/sd.

TABLE 6-9. MEDIAN COMPONENT COUNTS FOR PROCESS UNITS FROM LARGE REFINERIES[a]

	Valves			Pumps			Pressure Relief Valves			Flanges				
Process Unit	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid	Compressors	Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid	Open-ended Lines	Sampling Connections
Crude Distillation	204	440	498	15	14	2	7	5	12	549	982	1046	75	9
Alkylation (sulfuric acid)	192	597	0	21	0	2	13	4	0	491	1328	600	35	6
Alkylation (HF)	104	624	128	13	8	1	9	11	1	330	1300	180	40	14
Catalytic Reforming	310	383	84	12	2	3	8	11	0	653	842	132	48	9
Hydrocracking	290	651	308	22	12	2	10	12	0	418	1361	507	329	28
Hydrotreating/hydrorefining	224	253	200	7	6	2	9	4	8	439	581	481	49	8
Catalytic Cracking	277	282	445	12	12	2	11	9	13	593	747	890	59	15
Thermal Cracking (visbreaking)	110	246	130	7	6	1	6	3	15	277	563	468	30	7
Thermal Cracking (coking)	190	309	250	12	11	1	8	5	10	627	748	791	100	10
Hydrogen Plant	301	58	0	7	360	3	4	139	0	162	148	0	59	21
Asphalt Plant	76	43	0	4	0	0	3	7	0	90	90	0	24	24
Product Blending	75	419	186	10	10	2	9	16	6	227	664	473	24	8
Sulfur Plant	100	125	110	8	3	1	4	4	4	280	460	179	22	7
Vacuum Distillation	229	108	447	2	12	1	5	1	4	473	136	1072	0	7
Full-Range Distillation	160	561	73	14	2	2	7	8	2	562	1386	288	54	6
Isomerization	164	300	78	9	5	2	15	5	2	300	540	265	36	7
Polymerization	129	351	82	6	2	0	7	12	28	404	575	170	17	9
MEK Dewaxing	419	1075	130	29	10	4	33	6	18	1676	3870	468	0	7
Other Lube Oil Processes	109	188	375	5	16	3	8	6	20	180	187	1260	18	9

Source: Reference 142.

[a] Refineries with crude charge capacities greater than 50,000 bbl/sd.

Air emissions from petroleum refinery wastewater collection and treatment are one of the largest sources of VOC emissions at a refinery and are dependent on variables including wastewater throughput, type of pollutants, pollutant concentrations, and the amount of contact wastewater has with the air.

Table 6-10 presents model process unit characteristics for petroleum refinery wastewater.[147] The table includes average flow factors, average volatile HAP concentrations, and average benzene concentrations by process unit type to estimate uncontrolled emissions from petroleum refinery wastewater streams. Flow factors were derived from Section 114 questionnaire responses compiled for the Refinery NESHAP study. Volatile HAP and benzene concentrations were derived from Section 114 questionnaire responses, 90-day Benzene Waste Operations NESHAP (BWON) reports, and equilibrium calculations.

Uncontrolled wastewater emissions for petroleum refinery process units can be estimated multiplying the average flow factor, the volatile HAP concentrations, and the fraction emitted presented in Table 6-10, for each specific refinery process unit capacity.

Wastewater emission factors for oil/water separators, air flotation systems, and sludge dewatering units are presented in Table 6-11.[148-151]

Another option for estimating emissions of organic compounds from wastewater treatment systems is to use the air emission model presented in the EPA document *Compilation of Air Pollutant Emission Factors (AP-42),* in Section 4.3, entitled “Wastewater Collection, Treatment, and Storage.”[64] This emission model (referred to as SIMS in *AP-42* and now superceded by Water 8) is based on mass transfer correlations and can predict the emissions of individual organic species from a wastewater treatment system.

TABLE 6-10. MODEL PROCESS UNIT CHARACTERISTICS FOR PETROLEUM REFINERY WASTEWATER

Process Unit	Average flow factor[b] (gal/bbl)[c]	Average Benzene Concentration[a] Value (ppmw)[d]	Average Benzene Concentration[a] Origin[e]	Average Volatile HAP Concentration[a] Value (ppmw)[d]	Average Volatile HAP Concentration[a] Origin[e]	Fraction Emitted[f]
Crude distillation	2.9	21	114	140	114	0.85
Alkylation unit	6.0	3	Eq.	6.9	Eq.	0.85
Catalytic reforming	1.5	106	Eq.	238	Eq.	0.85
Hydrocracking unit	2.6	14	114	72	114	0.85
Hydrotreating/ hydrorefining	2.6	6.3	114	32	114	0.85
Catalytic cracking	2.4	13	114	165	114	0.85
Thermal cracking/ coking	5.9	40	Eq.	75	Eq.	0.85
Thermal cracking/ visbreaking	7.1	40	Eq.	75	Eq.	0.85
Hydrogen plant	80[g]	62	90-day	278	Ratio	0.85
Asphalt plant	8.6	40	Eq.	75	Eq.	0.85
Product blending	2.9	24	114	1,810	114	0.85
Sulfur plant	9.7[h]	0.8	90-day	3.4	Ratio	0.85
Vacuum distillation	3.0	12	90-day	53	Ratio	0.85
Full range distillation	4.5	12	114	65	114	0.85
Isomerization	1.5	33	Eq.	117	Eq.	0.85

(continued)

TABLE 6-10. CONTINUED

Process Unit	Average flow factor[b] (gal/bbl)[c]	Average Benzene Concentration[a]		Average Volatile HAP Concentration[a]		Fraction Emitted[f]
		Value (ppmw)[d]	Origin[e]	Value (ppmw)[d]	Origin[e]	
Polymerization	3.5	0.01	90-day	0.04	Ratio	0.85
MEK dewaxing units	0.011	0.1	90-day	27	114	0.49
Lube oil/specialty processing unit	2.5	40	Eq.	75	Eq.	0.85
Tank drawdown	0.02	188	90-day	840	Ratio	0.85

Source: Reference 147.

[a] Average concentration in the wastewater.
[b] All flow factors were derived from Section 114 questionnaire responses.
[c] gal/bbl = gallons of wastewater per barrel of capacity at a given process unit.
[d] ppmw = parts per million by weight.
[e] 114 = Section 114 questionnaire response; 90-day = 90-day BWON report; Eq. = Equilibrium calculation; and Ratio = HAP-to-benzene ratio (4.48).
[f] These factors are given in units of pounds of HAP emitted/pound of HAP mass loading.
[g] This flow factor is given in units of gallons/million cubic feet of gas production.
[h] This flow factor is given in units of gallons/ton of sulfur.

TABLE 6-11. WASTEWATER EMISSION FACTORS FOR PETROLEUM REFINERIES

SCC Number	Description	Emissions Source	Control Device	Emission Factor	Factor Rating	Reference
3-06-005-08	Oil/Water Separators	Oil/water separator	Uncontrolled	1.3 lb of Benzene/10^6 gal of feed water (0.16 kg of Benzene/10^6 l of feed water)	E	148
				923 lb of TOC/10^6 gal of feed water (111 kg of TOC/10^6 l of feed water)	C	149
3-06-005-XX	Air Flotation Systems	Air flotation systems[a]	Uncontrolled	4 lb of Benzene/10^6 gal of feed water (0.48 kg of Benzene/10^6 l of feed water)	E	150
				30 lb of TOC/10^6 gal of feed water (3.60 kg of TOC/10^6 l of feed water)	B	149
3-06-005-XX	Sludge dewatering units	Sludge dewatering unit[b]	Uncontrolled	660 lb of TOC/10^6 lb sludge (660 kg of TOC/10^6 kg sludge)	C	151

[a] Includes dissolved air flotation (DAF) or induced air flotation (IAF) systems.

[b] Based on a 2.2 meter belt filter press dewatering oil/water separator bottoms, DAF float, and biological sludges at an average temperature of 125°F. [151]

6.3.3 Controls and Regulatory Analysis

This section presents information on controls for process vents at petroleum refineries, and identifies other sections in this document that may be consulted to obtain information on control technology for storage tanks, and equipment leaks. Applicable Federal regulations to process vents, storage tanks, equipment leaks, transfer operations, and wastewater emissions are briefly described.

According to the EPA ICR and Section 114 surveys, the most reported types of control for catalyst regeneration process vents at fluid catalytic cracking units were electrostatic precipitators, carbon monoxide (CO) boilers, cyclones, and scrubbers. Some refineries have reported controlling their emissions with scrubbers at catalytic reformer regeneration vents.

For miscellaneous process vents, including miscellaneous equipment in various process units throughout the refinery, the most reported controls were flares, incinerators, and/or boilers. Other controls for miscellaneous process vents reported by refineries include scrubbers, electrostatic precipitators, fabric filters, and cyclones.

The process vent provisions included in the Petroleum Refinery NESHAP promulgated on September 18, 1995 affect organic HAP emissions from miscellaneous process vents throughout a refinery.[49] These vents include but are not limited to vent streams from caustic wash accumulators, distillation condensers/accumulators, flash/knock-out drums, reactor vessels, scrubber overheads, stripper overheads, vacuum (steam) ejectors, wash tower overheads, water wash accumulators, and blowdown condensers/accumulators.

For information about controls for storage tanks refer to Section 4.5.3 - Storage Tank Emissions, Controls, and Regulations.

Storage tanks containing petroleum liquids and benzene are regulated by the following Federal rules:

1. “National Emission Standard for Benzene Emissions from Benzene Vessels;”[61]
2. “Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for which Construction, Reconstruction, or Modification Commenced after July 23, 1984;”[62] and
3. “National Emission Standards for Hazardous Air Pollutants: Petroleum Refineries.”[49]

The Petroleum Refinery NESHAP requires that liquids containing greater than 4 weight percent HAPs at existing storage vessels, and greater than 2 weight percent HAPs at new storage vessels be controlled.

There are two primary control techniques for reducing equipment leak emissions: (1) modification or replacement of existing equipment, and (2) implementation of a Leak Detection and Repair (LDAR) program.

Equipment leak emissions are regulated by the New Source Performance Standards (NSPS) for Equipment Leaks of VOC in Petroleum Refineries promulgated in May 30, 1984.[152] These standards apply to VOC emissions at affected facilities that commenced construction, modification, or reconstruction after January 4, 1983.

The standards regulate compressors, valves, pumps, pressure relief devices, sampling connection systems, open-ended valves or lines, and flanges or other connectors in VOC service.

The Benzene Equipment Leaks National Emission Standard for Hazardous Air Pollutants (NESHAP)[56] and the Equipment Leaks NESHAP[57] for fugitive emission sources regulate equipment leak emissions from pumps, compressors, pressure relief devices, sampling connecting systems, open-ended valves or lines, valves, flanges and other connectors, product accumulator vessels, and specific control devices or systems at petroleum refineries. These NESHAPs were both promulgated in June 6, 1984.

Equipment leak provisions included in the Petroleum Refinery NESHAP require equipment leak emissions to be controlled using the control requirements of the petroleum refinery equipment leaks NSPS or the hazardous organic NESHAP.

Any process unit that has no equipment in benzene service is exempt from the equipment leak requirements of the benzene waste NESHAP. "In benzene service" means that a piece of equipment either contains or contacts a fluid (liquid or gas) that is at least 10 percent benzene by weight (as determined according to respective provisions). Any process unit that has no equipment in organic HAP service is exempt from the equipment leak requirements of the petroleum refinery NESHAP. "In organic HAP service" means that a piece of equipment contains or contacts a fluid that is at least 5 percent benzene by weight.

Refer to Section 6.4 (Gasoline Marketing) of this L&E document for information on control technologies and regulations for loading and transport operations.

For information about controls for wastewater collection and treatment systems, refer to Section 4.5.4 - Wastewater Collection and Treatment System Emissions, Controls, and Regulation.

Petroleum refinery wastewater streams containing benzene are regulated by the following Federal rules:

1. "National Emission Standard for Benzene Waste Operations;"[66]
2. "New Source Performance Standard for Volatile Organic Compound Emissions from Petroleum Refinery Wastewater Systems;"[153] and
3. "National Emission Standards for Hazardous Air Pollutants: Petroleum Refineries."[49]

The wastewater provisions in the Petroleum Refinery NESHAP are the same as the Benzene Waste Operations NESHAP.

6.4 GASOLINE MARKETING

Gasoline storage and distribution activities represent potential sources of benzene emissions. The benzene content of gasoline ranges from less than 1 to almost 5 percent by liquid volume, but typical liquid concentrations are currently around 0.9 percent by weight.[158] Under Title II of the Clean Air Act as amended in 1990, the benzene content of reformulated gasoline (RFG) will be limited to 1 percent volume maximum (or 0.95 percent volume period average) with a 1.3 percent volume absolute maximum. In California, the "Phase 2 Reformulated Gasoline," which will be required starting March 1998, also has a 1 percent volume benzene limit (or 0.8 percent volume average) with an absolute maximum of 1.2 percent volume.[20] For this reason, it is expected that the overall average of benzene content in gasoline will decrease over the next few years. Total hydrocarbon emissions from storage tanks, material transfer, and vehicle fueling do include emissions of benzene. This section describes sources of benzene emissions from gasoline transportation and marketing operations. Because the sources of these emissions are so widespread, individual locations are not identified in this section. Instead, emission factors are presented, along with a general discussion of the sources of these emissions.

The flow of the gasoline marketing system in the United States is presented in Figure 6-3.[153] The gasoline distribution network includes storage tanks, tanker ships and barges, tank trucks and railcars, pipelines, bulk terminals, bulk plants, and service stations. From refineries, gasoline is delivered to bulk terminals by way of pipelines, tanker ships, or barges. Bulk terminals may also receive petroleum products from other terminals. From bulk terminals, petroleum products (including gasoline) are distributed by tank trucks to bulk plants. Both bulk terminals and bulk plants deliver gasoline to private, commercial, and retail customers. Daily product at a terminal averages about 250,000 gallons (950,000 liters), in contrast to about 5,000 gallons (19,000 liters) for an average size bulk plant.[154]

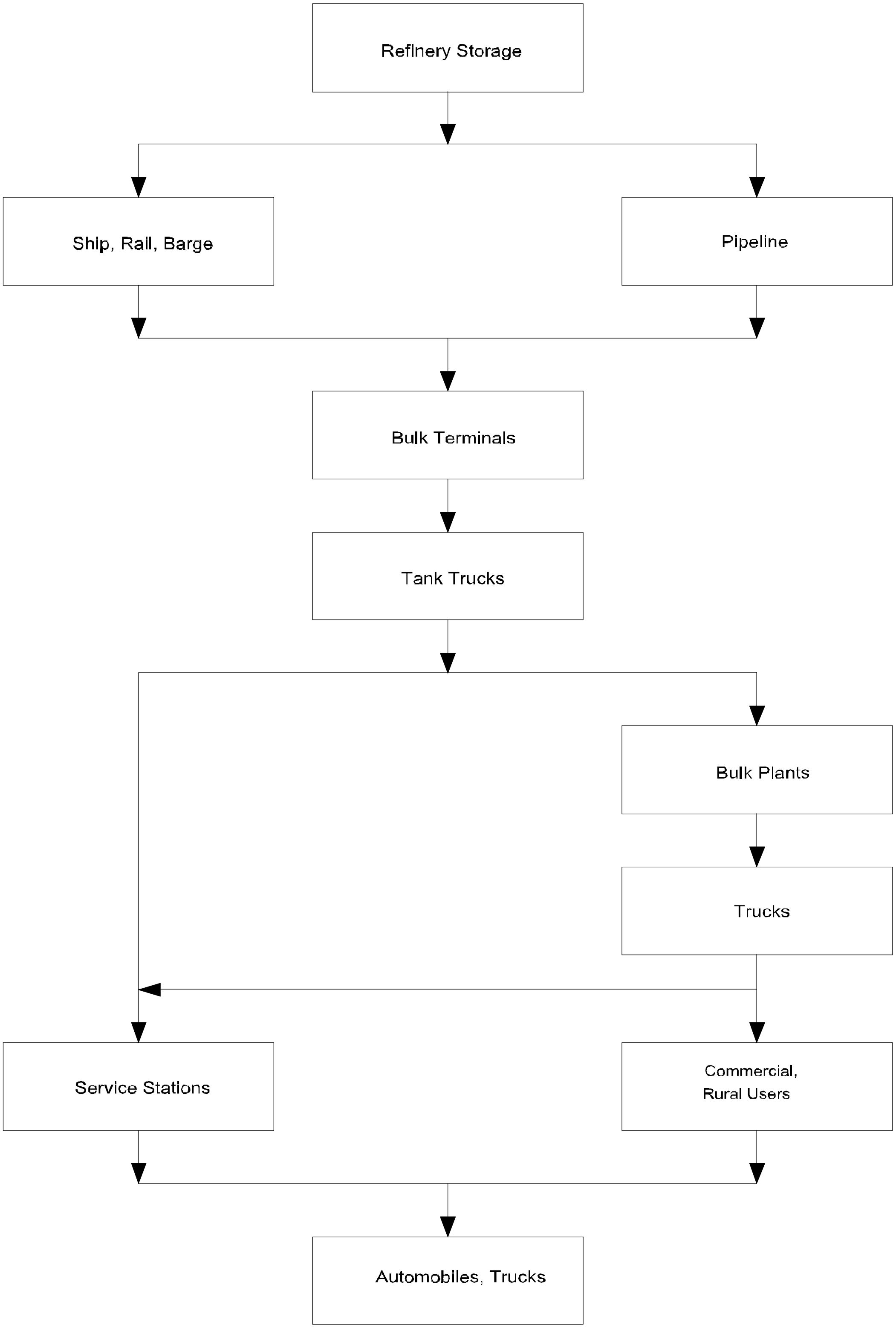


Figure 6-3. The Gasoline Marketing Distribution System in the United States

Source: Reference 153.

Service stations receive gasoline by tank truck from terminals or bulk plants or directly from refineries, and usually store the gasoline in underground storage tanks. Gasoline service stations are establishments primarily selling gasoline and automotive lubricants.

Gasoline is by far the largest volume of petroleum product marketed in the United States, with a nationwide consumption of 115 billion gallons (434 billion liters) in 1993.[155] There are presently an estimated 1,300 bulk terminals storing gasoline in the United States.[156] About half of these terminals receive products from refineries by pipeline (pipeline breakout stations), and half receive products by ship or barge delivery (bulk gas-line terminals). Most of the terminals (66 percent) are located along the east coast and in the Midwest. The remainder are dispersed throughout the country, with locations largely determined by population patterns.

The benzene emission factors presented in the following discussions were derived by multiplying AP-42 VOC emission factors for transportation and marketing[157] times the fraction of benzene in the vapors emitted. The average weight fraction of benzene in gasoline vapors (0.009) was taken from Reference 157. When developing emission estimates, the gasoline vapor emission factors should be modified by specific benzene weight fraction in the vapor, if available. Also a distinction should be made between winter and summer blends of gasoline (a difference in the Reid vapor pressure of the gasoline, which varies from an average of 12.8 psi in the winter to an average of 9.3 in non-winter seasons) to account for the different benzene fractions present in both.[158]

The transport of gasoline with marine vessels, distribution at bulk plants, and distribution at service stations, their associated benzene emissions, and their controls are discussed below.

6.4.1 Benzene Emissions from Loading Marine Vessels

Benzene can be emitted while crude oil and refinery products (gasoline, distillate oil, etc.) are loaded and transported by marine tankers and barges. Loading losses are the primary source of evaporative emissions from marine vessel operations.[159] These emissions occur as vapors in "empty" cargo tanks are expelled into the atmosphere as liquid is added to the cargo tank. The vapors may be composed of residual material left in the "empty" cargo tank and/or the material being added to the tank. Therefore, the exact composition of the vapors emitted during the loading process may be difficult to predict.

Benzene emissions from tanker ballasting also occur as a result of vapor displacement. Ballasting emissions occur as the ballast water enters the cargo tanks and displace vapors remaining in the tank from the previous cargo. In addition to loading and ballasting losses, transit losses occur while the cargo is in transit.[157,160]

Volatile organic compound (VOC) emission factors for petroleum liquids for marine vessel loading are provided in the EPA document *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 5[157] and the EPA document *VOC/HAP Emissions from Marine Vessel Loading Operations - Technical Support Document for Proposed Standards.*[159]

Uncontrolled VOC and benzene emission factors for loading gasoline in marine vessels are presented in Table 6-12. This table also presents emission factors for tanker ballasting losses and transit losses from gasoline marine vessels.

Table 6-13 presents total organic compound emission factors for marine vessels including loading operations, and transit for crude oil, distillate oil, and other fuels. Emissions of benzene associated with loading distillate fuel and other fuels are very low, due primarily to their low VOC emission factor and benzene content. When developing benzene emission estimates, the total organic compound emission factors presented in Table 6-13 should be multiplied by specific benzene weight fraction in the fuel vapor, if available.

TABLE 6-12. UNCONTROLLED VOLATILE ORGANIC COMPOUND AND BENZENE EMISSION FACTORS FOR LOADING, BALLASTING, AND TRANSIT LOSSES FROM MARINE VESSELS

SCC Number	Emission Source	VOC Emission Factor[a] lb/1000 gal Transferred (mg/liter Transferred)	Benzene Emission Factor[b] lb/1000 gal Transferred (mg/liter Transferred)	Emission Factor Rating
4-06-002-36/ 4-06-002-37	Ship/Ocean Barge[c] Loading Operations - Uncleaned, volatile previous cargo	2.6 (315)	0.023 (2.8)	D
4-06-002-034/ 4-06-002-035	Ship/Ocean Barge[c] Loading Operations - Ballasted; volatile previous cargo	1.7 (205)	0.015 (1.8)	D
4-06-002-36	Ship/Ocean Barge[c] Loading Operations - Cleaned; volatile previous cargo	1.5 (180)	0.014 (1.6)	D
4-06-002-31/ 4-06-002-32/ 4-06-002-36	Ship/Ocean Barge[c] Loading Operations - Any condition; nonvolatile previous cargo	0.7 (85)	0.006 (0.77)	D
4-06-002-00/ 4-06-002-40	Ship/Ocean Barge[c] Loading Operations - Typical situation, any cargo	1.8 (215)	0.016 (1.9)	D
4-06-002-38	Barge[c] Loading Operations - Uncleaned; volatile previous cargo	3.9 (465)	0.035 (4.2)	D
4-06-002-33	Barge[c] Loading Operations - Gas-free, any cargo	2.0 (245)	0.018 (2.2)	D
4-06-002-39	Tanker Ballasting	0.8 (100)	0.007 (0.9)	D
4-06-002-42	Transit	2.7 (320)[d]	0.024 (2.8)[d]	D

Source: References 157 and 159.

[a] Factors are for nonmethane-nonethane VOC emissions.

[b] Based on the average weight percent of benzene/VOC ratio of 0.009.[159]

[c] Ocean barge is a vessel with compartment depth of 40 feet; barge is a vessel with compartment depth of 10-12 feet.

[d] Units for this factor are lb/week-1000 gal (mg/week-liter) transported.

TABLE 6-13. UNCONTROLLED TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR PETROLEUM MARINE VESSEL SOURCES[a]

Emission source	Crude Oil[b] lb/10^3 gal (mg/ℓ)	Jet Naphtha[b] lb/10^3 gal (mg/ℓ)	Jet Kerosene lb/10^3 gal (mg/ℓ)	Distillate Oil No. 2 lb/10^3 gal (mg/ℓ)	Residual Oil No. 6 lb/10^3 gal (mg/ℓ)	Emission Factor Rating
Loading operations						
Ships/ocean barge	0.61 (73)	0.50 (60)	0.005 (0.63)	0.005 (0.55)	0.00004 (0.004)	D
Barge	1.0 (120)	1.2 (150)	0.013 (1.60)	0.012 (1.40)	0.00009 (0.011)	D
Transit[c]	1.3 (150)	0.7 (84)	0.005 (0.60)	0.005 (0.54)	$3x10^{-5}$ (0.003)	E

Source: Reference 157.

[a] Emission factors are calculated for a dispensed product temperature of 60°F.

[b] Nonmethane-nonethane VOC emission factors for a typical crude oil are 15 percent lower than the total organic factors shown. The example crude oil has a Reid Vapor Pressure of 5 psia.

[c] Units are mg/week-ℓ transferred or lb/week-10^3 gal transferred.

6.4.2 Benzene Emissions from Bulk Gasoline Plants and Bulk Gasoline Terminals

Each operation in which gasoline is transferred or stored is a potential source of benzene emissions. At bulk terminals and bulk plants, loading, unloading, and storing gasoline are sources of benzene emissions.

Emissions from Gasoline Loading and Unloading

The gasoline that is stored in above ground tanks at bulk terminals and bulk plants is pumped through loading racks that measure the amount of product. The loading racks consist of pumps, meters, and piping to transfer the gasoline or other liquid petroleum products. Loading of gasoline into tank trucks can be accomplished by one of three methods: splash, top submerged, or bottom loading. Bulk plants and terminals use the same three methods for loading gasoline into tank trucks. In splash loading, gasoline is introduced into the tank truck directly through a hatch located on the top of the truck.[160] Top submerged loading is done by attaching a downspout to the fill pipe so that gasoline is added to the tank truck near the bottom of the tank. Bottom loading is the loading of product into the truck tank from the bottom. Emissions occur when the product being loaded displaces vapors in the tank being filled. Top submerged loading and bottom loading reduce the amount of material (including benzene) that is emitted by generating fewer additional vapors during the loading process.[160] A majority of facilities loading tank trucks use bottom loading.

Table 6-14 lists emission factors for gasoline vapor and benzene from gasoline loading racks at bulk terminals and bulk plants.[160] The gasoline vapor emission factors were taken from Reference 157. The benzene factors were obtained by multiplying the gasoline vapor factor by the average benzene content of the vapor (0.009 percent).[158]

TABLE 6-14. BENZENE EMISSION FACTORS FOR GASOLINE LOADING RACKS AT BULK TERMINALS AND BULK PLANTS

SCC Number	Loading Method	Gasoline Vapor Emission Factor[a] lb/1000 gal (mg/liter)	Benzene Emission Factor[b] lb/1000 gal (mg/liter)	Emission Factor Rating
4-04-002-50	Splash loading - normal service	11.9 (1430)	0.11 (12.9)	D
4-04-002-50	Submerged loading[c] - normal service	4.9 (590)	0.044 (5.3)	D
4-04-002-50	Balance service[d]	0.3 (40)	0.004 (0.36)	D

Source: Reference 160.

[a] Gasoline factors represent emissions of nonmethane-nonethane VOC. Factors are expressed as mg gasoline vapor per liter gasoline transferred. [156]

[b] Based on an average benzene/VOC ratio of 0.009. [157]

[c] Submerged loading is either top or bottom submerged.

[d] Splash and submerged loading. Calculated using a Stage I control efficiency of 95 percent.

Emissions from Storage Tanks

Storage emissions of benzene at bulk terminals and bulk plants depend on the type of storage tank used. A typical bulk terminal may have four or five above ground storage tanks with capacities ranging from 400,000 to 4 million gallons (1,500 to 15,000 m^3).[160] Most tanks in gasoline service are of an external floating roof design. Fixed-roof tanks, still used in some areas to store gasoline, use pressure-vacuum vents to operate at a slight internal pressure or vacuum and control breathing losses. Some tanks may use vapor balancing or processing equipment to control working losses.

The major types of emissions from fixed-roof tanks are breathing and working losses. Breathing loss is the expulsion of vapor from a tank vapor space that has expanded or contracted because of daily changes in temperature and barometric pressure. The emissions occur in the absence of any liquid level change in the tank. Combined filling and emptying losses are called “working losses.” Emptying losses occur when the air that is drawn into the tank during liquid removal saturates with hydrocarbon vapor and is expelled when the tank is filled.

A typical external floating-roof tank consists of a cylindrical steel shell equipped with a deck or roof that floats on the surface of the stored liquid, rising and falling with the liquid level. The liquid surface is completely covered by the floating roof except in the small annular space between the roof and the shell. A seal attached to the roof touches the tank wall (except for small gaps in some cases) and covers the remaining area. The seal slides against the tank wall as the roof is raised or lowered. The floating roof and the seal system serve to reduce the evaporative loss of the stored liquid.

An internal floating-roof tank has both a permanently affixed roof and a roof that floats inside the tank on the liquid surface (contact roof), or is supported on pontoons several inches above the liquid surface (noncontact roof). The internal floating-roof rises and falls with the liquid level, and helps to restrict the evaporation of organic liquids.

The four classes of losses that floating roof tanks experience include withdrawal loss, rim seal loss, deck fitting loss, and deck seam loss. Withdrawal losses are caused by the stored liquid clinging to the side of the tank following the lowering of the roof as liquid is withdrawn. Rim seal losses are caused by leaks at the seal between the roof and the sides of the tank. Deck fitting losses are caused by leaks around support columns and deck fittings within internal floating roof tanks. Deck seam losses are caused by leaks at the seams where panels of a bolted internal floating roof are joined.

Table 6-15 shows emission factors during both non-winter and winter for storage tanks at a typical bulk terminal.[158] The emission factors were derived from AP-42 equations and a weight fraction of benzene in the vapor of 0.009.[158] Table 6-16 shows uncontrolled emission factors for gasoline vapor and benzene for a typical bulk plant.[160] Table 6-17 shows emission factors during both non-winter and winter months for storage tanks at pipeline breakout stations.[158] The emission factor equations in AP-42 are based on the same equations contained in the EPA's computer-based program "TANKS." Since TANKS is regularly updated, the reader should refer to the latest version of the TANKS program (version 3.1 at the time this document was finalized) to calculate the latest emission factors for fixed- and floating-roof storage tanks. The factors in Tables 6-15 and 6-17 were calculated with equations from an earlier version of TANKS and do not represent the latest information available. They are presented to show the type of emission factors that can be developed from the TANKS program.

Emissions from Gasoline Tank Trucks

Gasoline tank trucks have been demonstrated to be major sources of vapor leakage. Some vapors may leak uncontrolled to the atmosphere from dome cover assemblies, pressure-vacuum (P-V) vents, and vapor collection piping and vents. Other sources of vapor leakage on tank trucks that occur less frequently include tank shell flaws, liquid and vapor transfer hoses, improperly installed or loosened overfill protection sensors, and vapor couplers. This leakage has been estimated to be as high as 100 percent of the vapors which

TABLE 6-15. BENZENE EMISSION FACTORS FOR STORAGE LOSSES AT A TYPICAL GASOLINE BULK TERMINAL

		Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		
SCC Number	Storage Method	Non-Winter	Winter	Non-Winter	Winter	Emission Factor Rating
4-04-001-07/ 4-04-001-08	Fixed Roof[d] - Working Losses (Uncontrolled)	35.6 (32.3)	46.4 (42.1)	0.320 (0.291)	0.418 (0.379)	E
4-04-001-04/ 4-04-001-05	Fixed Roof[d] - Breathing Losses (Uncontrolled)	9.42 (8.55)	13.2 (12.0)	0.085 (0.077)	0.119 (0.108)	E
4-04-001-XX	External Floating Roof[e] - Working Losses	--[f] (--[g])	--[f] (--[g])	--[f] (--[g])	--[f] (--[g])	E
4-04-001-31/ 4-04-001-32	External Floating Roof[e] - Standing Storage Losses - Primary Metallic Shoe Seal and Uncontrolled Fittings	12.6 (11.4)	17.61 (15.98)	0.113 (0.103)	0.158 (0.144)	E
4-04-001-41/ 4-04-001-42	External Floating Roof[e] - Standing Storage Losses - Secondary Metallic Shoe Seal and Uncontrolled Fittings	5.9 (5.38)	8.31 (7.54)	0.035 (0.031)	0.075 (0.068)	E
4-04-001-XX	External Floating Roof[e] - Primary and Secondary Metallic Shoe Seals and Uncontrolled Fittings	3.85 (3.49)	5.38 (4.88)	0.053 (0.048)	0.048 (0.044)	E
4-04-001-XX	Internal Floating Roof[d] - Vapor-mounted Rim Seal Losses	1.12 (1.02)	1.59 (1.44)	0.0101 (0.0092)	0.0143 (0.0130)	E
4-04-001-XX	Internal Floating Roof[d] - Liquid-Mounted Seal Losses	0.51 (0.46)	0.71 (0.64)	0.0046 (0.0041)	0.0063 (0.0058)	E
4-04-001-XX	Internal Floating Roof[d] - Vapor Primary and Secondary Seal	0.42 (0.38)	0.60 (0.54)	0.0038 (0.0034)	0.0054 (0.0049)	E
4-04-001-XX	Internal Floating Roof[d] - Uncontrolled Fitting Losses[h]	1.11 (1.01)	1.56 (1.42)	0.0100 (0.0091)	0.0141 (0.0128)	E

(continued)

TABLE 6-15. CONTINUED

		Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		
SCC Number	Storage Method	Non-Winter	Winter	Non-Winter	Winter	Emission Factor Rating
4-04-001-XX	Internal Floating Roof[d] - Controlled Fitting Losses[i]	0.76 (0.69)	1.07 (0.97)	0.0068 (0.0062)	0.0096 (0.0087)	E
4-04-001-XX	Internal Floating Roof[d] - Deck Seam Losses	0.57 (0.52)	0.80 (0.73)	0.0052 (0.0047)	0.0072 (0.0066)	E
4-04-001-XX	Internal Floating Roof[d] - Working Losses	--[j] (--[k])	--[j] (--[k])	--[j] (--[k])	--[j] (--[k])	E

Source: Reference 158.

[a] Emission factors calculated with equations from Chapter 4.3 of AP-42 (TANKS program version 1.0), using a non-winter RVP of 9.3 psia, a winter RVP of 12.8 psia, and a temperature of 60°F. The reader should be aware that the TANKS program is regularly updated and that the latest version of the program should be used to calculate emission factors. At the time this document was printed, version 3.1 of the TANKS program was available.

[b] Terminal with 250,000 gallons/day (950,000 liters/day) with four storage tanks for gasoline.

[c] Based on gasoline emission factor and an average benzene/VOC ratio of 0.009.

[d] Typical fixed-roof tank or internal floating roof tank based upon capacity of 2,680 m^3 (16,750 bbls), a diameter of 50 feet (15.2 meters), and a height of 48 feet (14.6 meters).

[e] Typical floating-roof tank based upon capacity of 36,000 bbls (5,760 m^3), a diameter of 78 feet (24.4 meters), and a height of 40 feet (12.5 meters).

[f] Gasoline vapor emission factor = (5.1 x 10^{-8} Q) ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (4.6 x 10^{-10} Q) ton/yr.

[g] Gasoline vapor emission factor = (4.6 x 10^{-8} Q) Mg/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (4.1 x 10^{-10} Q) Mg/yr.

[h] Calculated assuming the "typical" level of control in the "TANKS" program.

[i] Calculated assuming the "controlled" level of control in the "TANKS" program.

[j] Gasoline vapor emission factor = (8.1 x 10^{-8} Q) ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (7.3 x 10^{-10} Q) ton/yr.

[k] Gasoline vapor emission factor = (7.3 x 10^{-8} Q) Mg/yr, where Q is the throughput through the tank in barrels.
Benzene emission factor = (6.6 x 10^{-10} Q) Mg/yr.

"--" means no data available.

TABLE 6-16. GASOLINE VAPOR AND BENZENE EMISSION FACTORS FOR A TYPICAL BULK PLANT

SCC Number	Emission Source	Gasoline Vapor Emission Factor[a] lb/1000 gal (mg/liter)	Benzene Emission Factor[b] lb/1000 gal (mg/liter)	Emission Factor Rating
4-04-002-01	Storage Tanks - Fixed Roof - Breathing Loss	5.0 (600)	0.5 (5.4)	E
4-04-002-04	Storage Tanks - Fixed Roof - Working Loss:			
	Filling	9.6 (1150)	0.086 (10.3)	E
	Emptying	3.8 (460)	0.034 (4.1)	E
4-04-002-50	Gasoline Loading Racks:			
	Splash Loading (normal service)	11.9 (1430)	0.107 (12.9)	E
	Submerged Loading (normal service)	4.9 (590)	0.044 (5.3)	E
	Splash and Submerged Loading (balance service)[c]	0.3 (40)	0.002 (0.4)	E

Source: Reference 160.

[a] Typical bulk plant with gasoline throughput of 19,000 liters/day (5,000 gallons/day).
[b] Based on gasoline emission factor and an average benzene/VOC ratio of 0.009.
[c] Calculated using a Stage I control efficiency of 95 percent.

TABLE 6-17. BENZENE EMISSION FACTORS FOR STORAGE LOSSES AT A TYPICAL PIPELINE BREAKOUT STATION[a,b]

		Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		
SCC Number	Storage Method	Non-Winter	Winter	Non-Winter	Winter	Emission Factor Rating
4-04-00X-XX	Fixed Roof Uncontrolled - Breathing Losses	36.9 (33.5)	52.0 (47.2)	0.332 (0.302)	0.468 (0.425)	E
4-04-00X-XX	Fixed Roof Uncontrolled - Working Losses	477.5 (433.3)	621.5 (564.0)	4.297 (3.9)	5.6 (5.1)	E
4-04-00X-XX	Internal Floating Roof - Vapor-mounted rim seal losses	2.26 (2.05)	3.16 (2.87)	0.020 (0.018)	0.028 (0.026)	E
4-04-00X-XX	Internal Floating Roof - Liquid-mounted rim seal losses	1.01 (0.92)	1.42 (1.29)	0.009 (0.008)	0.013 (0.012)	E
4-04-00X-XX	Internal Floating Roof - Vapor primary and secondary seal	0.84 (0.76)	1.18 (1.07)	0.008 (0.007)	0.011 (0.010)	E
4-04-00X-XX	Internal Floating Roof - Uncontrolled fitting losses[c]	2.60 (2.36)	3.65 (3.31)	0.023 (0.021)	0.033 (0.030)	E
4-04-00X-XX	Internal Floating Roof - Controlled fitting losses[d]	1.77 (1.61)	2.48 (2.25)	0.016 (0.014)	0.022 (0.020)	E
4-04-00X-XX	Internal Floating Roof - Deck seam losses	2.29 (2.08)	3.20 (2.90)	0.021 (0.019)	0.029 (0.026)	E
4-04-00X-XX	Internal Floating Roof - Working losses primary and secondary seal	--[e] (--[f])	--[e] (--[f])	--[e] (--[f])	--[e] (--[f])	E
4-04-00X-XX	External Floating Roof - Standing Storage losses - Primary seal	15.43 (14.00)	21.61 (19.61)	0.139 (0.126)	0.194 (0.176)	E
4-04-00X-XX	External Floating Roof - Standing Storage losses - Secondary seal	6.91 (6.27)	9.69 (8.79)	0.062 (0.056)	0.087 (0.079)	E

(continued)

TABLE 6-17. CONTINUED

		Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		
SCC Number	Storage Method	Non-Winter	Winter	Non-Winter	Winter	Emission Factor Rating
4-04-00X-XX	External Floating Roof - Standing Storage losses - Primary and secondary fittings	5.10 (4.63)	7.03 (6.38)	0.046 (0.042)	0.063 (0.057)	E
4-04-00X-XX	External Floating Roof- Standing Storage losses - Working losses	--[g] (--[h])	--[g] (--[h])	--[g] (--[h])	--[g] (--[h])	E

Source: Reference 158.

[a] Emission factors calculated with equations from Chapter 4.3 of AP-42 (TANKS program version 1.0), using a non-winter RVP of 9.3 psia, a winter RVP of 12.8 psia, and a temperature of 60°F. The reader should be aware that the TANKS program is regularly updated and that the latest version of the program should be used to calculate emission factors. At the time this document was printed, version 3.1 of the TANKS program was available.

[b] Assumes storage vessels at pipeline breakout stations have a capacity of 50,000 bbl (8,000 m^3), a diameter of 100 feet (30 meters), and a height of 40 feet (12 meters).

[c] Calculated assuming the "typical" level of control in the "TANKS" program.

[d] Calculated assuming the "Controlled" level of control in the "TANKS" program.

[e] Gasoline vapor emission factor = (5.1 x 10^{-8}Q) ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (4.6 x 10^{-10} Q) ton/yr.

[f] Gasoline vapor emission factor = (4.6 x 10^{-8}Q) Mg/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (4.1 x 10^{-10} Q) Mg/yr.

[g] Gasoline vapor emission factor = (8.1 x 10^{-8}Q) ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = (7.3 x 10^{-10} Q) ton/yr.

[h] Gasoline vapor emission factor = (7.3 x 10^{-8}Q) Mg/yr, where Q is the throughput through the tank in barrels.
Benzene emission factor = (6.6 x 10^{-10} Q) Mg/yr.

"--" means data not available.

should have been captured and to average 30 percent. Because terminal controls are usually found in areas where trucks are required to collect vapors after delivery of product to bulk plants or service stations (balance service), the gasoline vapor emission factor associated with uncontrolled truck leakage was assumed to be 30 percent of the uncontrolled balance service truck loading factor (980 mg/liter x 0.30 = 294 mg/liter).[160] Thus the emission factor for benzene emissions from uncontrolled truck leakage is 2.6 mg/liter, based on a benzene/vapor ratio of 0.009.

6.4.3 Benzene Emissions from Service Stations

The discussion on service station operations is divided into two areas: the filling of the underground storage tank (Stage I) and automobile refueling (Stage II). Although terminals and bulk plants also have two distinct operations (tank filling and truck loading), the filling of the underground tank at the service station ends the wholesale gasoline marketing chain. The automobile refueling operations interact directly with the public so that control of these operations can be performed by putting control equipment on either the service station or the automobile.

Stage I Emissions at Service Stations

Normally, gasoline is delivered to service stations in large tank trucks from bulk terminals or smaller account trucks from bulk plants. Emissions are generated when hydrocarbon vapors in the underground storage tank are displaced to the atmosphere by the gasoline being loaded into the tank. As with other loading losses, the quantity of the service station tank loading loss depends on several variables, including the quantity of liquid transferred, size and length of the fill pipe, the method of filling, the tank configuration and gasoline temperature, vapor pressure, and composition. A second source of emissions from service station tankage is underground tank breathing. Breathing losses tend to be minimal for underground storage tanks due to nearly constant ground temperatures and are primarily the result of barometric pressure changes.

Stage II Emissions of Service Stations

In addition to service station tank loading losses, vehicle refueling operations are considered to be a major source of emissions. Vehicle refueling emissions are attributable to vapor displaced from the automobile tank by dispensed gasoline and to spillage. The major factors affecting the quantity of emissions are dispensed fuel temperature, differential temperature between the vehicle's tank temperature and the dispensed fuel temperature, and fuel Reid vapor pressure (RVP).[161,162] Several other factors that may have an effect upon refueling emissions are: fill rate, amount of residual fuel in the tank, total amount of fill, position of nozzle in the fill-neck, and ambient temperature. However, the magnitude of these effects is much less than that for any of the major factors mentioned above.[161]

Spillage loss is made up of configurations from prefill and postfill nozzle drip and from spit-back and overflow from the vehicle's fuel tank filler pipe during filling. Table 6-18 lists the uncontrolled emission factors for a typical gasoline service station.[160,163] This table incudes an emission factor for displacement losses from vehicle refueling. However, the following approach is more accurate to estimate vehicle refueling emissions.

Emissions can be calculated using MOBILE 5a, EPA's mobile source emission factor computer model. MOBILE 5a uses the following equation:[163]

$$E_r = 264.2\ [(-5.909) - 0.0949\ (\Delta T) + 0.0884\ (T_D) + 0.485\ (RVP)]$$

where:

E_r = Emission rate, mg VOC/ℓ of liquid loaded

RVP = Reid vapor pressure, psia (see Table 6-19)[163]

ΔT = Difference between the temperature of the fuel in the automobile tank and the temperature of the dispensed fuel, °F (see Table 6-20)[161]

T_D = Dispensed fuel temperature, °F (see Table 6-21)[164]

Using this emission factor equation, vehicle refueling emission factors can be derived for specific geographic locations and for different seasons of the year.

TABLE 6-18. GASOLINE VAPOR AND BENZENE EMISSION FACTORS FOR A TYPICAL SERVICE STATION

SCC Number	Emission Source	Gasoline Vapor Emission Factor[a] lb/1000 gal (mg/liter)	Benzene Emission Factor[b] lb/1000 gal (mg/liter)	Emission Factor Rating
4-06-003-01	Underground Storage Tanks - Tank Filling Losses - Splash Fill	11.5 (1,380)	0.104 (12.4)	E
4-06-003-02	Underground Storage Tanks - Tank Filling Losses - Submerged Fill	7.3 (880)	0.066 (7.9)	E
4-06-003-06	Underground Storage Tanks - Tank Filling Losses - Balanced Submerged Filling[c]	0.3 (40)	0.003 (0.4)	E
4-06-003-07	Underground Storage Tanks - Breathing Losses	1.0 (120)	0.009 (1.1)	E
4-06-004-01	Vehicle Refueling[d] - Displacement Losses			
	- Uncontrolled	11.0 (1,320)	0.099 (11.9)	E
	- Controlled	1.1 (132)	0.0099 (1.2)	E
4-06-004-02	Vehicle Refueling[d] - Spillage	0.7 (84)	0.0063 (0.76)	E

Source: References 160 and 163.

[a] Typical service station has a gasoline throughput of 190,000 liters/month (50,000 gallons/month).

[b] Based on gasoline emission factor and an average benzene/VOC ratio of 0.009.

[c] Calculated using a Stage I control efficiency of 95 percent.

[d] Vehicle refueling emission factors can also be derived for specific geographic locations and for different seasons of the year using the MOBILE 5a, EPA's mobile source emission factor computer model.[161]

In the absence of specific data, Tables 6-19, 6-20, and 6-21 may be used to estimate refueling emissions. Tables 6-19, 6-20, and 6-21 list gasoline RVPs, ΔT, and T_D values respectively for the United States as divided into six regions:

Region 1: Connecticut, Delaware, Illinois, Indiana, Kentucky, Maine, Maryland, Massachusetts, Michigan, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Virginia, West Virginia, and Wisconsin.

Region 2: Alabama, Arkansas, Florida, Georgia, Louisiana, Mississippi, North Carolina, South Carolina, and Tennessee.

Region 3: Arizona, New Mexico, Oklahoma, and Texas.

Region 4: Colorado, Iowa, Kansas, Minnesota, Missouri, Montana, Nebraska, North Dakota, South Dakota, and Wyoming.

Region 5: California, Nevada, and Utah.

Region 6: Idaho, Oregon, and Washington.

6.4.4 Control Technology for Marine Vessel Loading

Marine vapor control systems can be divided into two categories: vapor recovery systems and vapor destruction systems. There are a wide variety of vapor recovery systems that can be used with vapor collection systems. Most of the vapor recovery systems installed to date include refrigeration, carbon adsorption/absorption, or lean oil absorption. Three major types of vapor destruction or combustion systems that can operate over the wide flow rate and heat content ranges of marine applications are: open flame flares, enclosed flame flares, and thermal incinerators.[165]

When selecting a vapor control system for a terminal, the decision on recovering the commodity depends on the nature of the VOC stream (expected variability in flow rate and hydrocarbon content), and locational factors, such as availability of utilities and distance from the tankship or barge to the vapor control system. The primary reason for selecting incineration is that many marine terminals load more than one commodity.[159,164]

TABLE 6-19. RVP LIMITS BY GEOGRAPHIC LOCATION

State	Weighted average Summer (Apr.-Sep.)	Winter (Oct.-Mar.)	Annual
Alabama	8.6	12.8	10.6
Alaska	13.9	15.0	14.3
Arizona	8.4	11.6	10.0
Arkansas	8.5	13.5	10.7
California	8.6	12.6	10.6
Colorado	8.6	13.1	10.7
Connecticut	9.7	14.5	12.0
Delaware	9.7	14.3	11.9
District of Columbia	8.8	14.1	11.4
Florida	8.7	12.9	10.7
Georgia	8.6	12.8	10.7
Hawaii	11.5	11.5	11.5
Idaho	9.5	13.2	11.3
Illinois	9.7	14.2	12.0
Indiana	9.7	14.3	11.9
Iowa	9.6	14.2	11.8
Kansas	8.6	13.1	10.8
Kentucky	9.6	14.0	11.7
Louisiana	8.6	12.8	10.6
Maine	9.6	14.5	11.9
Maryland	9.0	14.3	11.6
Massachusetts	9.7	14.5	12.0
Michigan	9.7	14.5	12.0
Minnesota	9.7	14.3	11.8
Mississippi	8.6	12.8	10.7
Missouri	8.7	13.8	11.1
Montana	9.5	14.3	11.7

(continued)

TABLE 6-19. CONTINUED

State	Weighted average		
	Summer (Apr.-Sep.)	Winter (Oct.-Mar.)	Annual
Nebraska	9.5	13.5	11.4
Nevada	8.5	12.5	10.4
New Hampshire	9.7	14.5	12.0
New Jersey	9.7	14.4	12.1
New Mexico	8.5	12.4	10.3
New York	9.7	14.5	12.0
North Carolina	8.8	13.6	11.1
North Dakota	9.7	14.2	11.7
Ohio	9.7	14.3	11.9
Oklahoma	8.6	12.9	10.7
Oregon	9.0	13.9	11.2
Pennsylvania	9.7	14.5	12.0
Rhode Island	9.7	14.5	12.1
South Carolina	9.0	13.3	11.0
South Dakota	9.5	13.5	11.3
Tennessee	8.8	13.6	11.1
Texas	8.5	12.5	10.4
Utah	8.7	13.3	10.9
Vermont	9.6	14.5	12.0
Virginia	8.8	14.0	11.3
Washington	9.7	14.3	11.9
West Virginia	9.7	14.3	11.9
Wisconsin	9.7	14.3	11.9
Wyoming	9.5	13.6	11.5
Nationwide Annual Average	9.4		11.4
Nonattainment Annual Average	9.2		11.3

Source: Reference 163.

TABLE 6-20. SEASONAL VARIATION FOR TEMPERATURE DIFFERENCE BETWEEN DISPENSED FUEL AND VEHICLE FUEL TANK[a]

	Temperature difference (°F)				
	Average annual	Summer (Apr.-Sep.)	Winter (Oct.-Mar.)	5-Month Ozone Season (May-Sep.)	2-Month Ozone Season (July-Aug.)
National average	4.4	8.8	-0.8	9.4	9.9
Region 1	5.7	10.7	-0.3	11.5	12.5
Region 2	4.0	6.8	0.9	7.5	8.2
Region 3	3.7	7.6	-0.4	7.1	7.0
Region 4	5.5	11.7	-2.4	12.1	13.3
Region 5	0.1	3.9	-4.4	5.1	3.2

Source: Reference 161.

[a] Region 6 was omitted, as well as Alaska and Hawaii.

TABLE 6-21. MONTHLY AVERAGE DISPENSED LIQUID TEMPERATURE (T_D)

	Weighted average		
	Summer (Apr.-Sep.)	Winter (Oct.-Mar.)	(Annual)
National average	74	58	66
Region 1	70	51	61
Region 2	85	76	81
Region 3	79	62	70
Region 4	74	56	65
Region 5	79	63	72
Region 6	64	50	57

Source: Reference 164.

For additional information on emission controls at marine terminals refer to References 159 and 165.

6.4.5 Control Technology for Gasoline Transfer

At many bulk terminals and bulk plants, benzene emissions from gasoline transfer are controlled by CTG, NSPS, and new MACT programs. Control technologies include the use of a vapor processing system in conjunction with a vapor collection system.[160] Vapor balancing systems, consisting of a pipeline between the vapor spaces of the truck and the storage tanks, are closed systems. These systems allow the transfer of displaced vapor into the transfer truck as gasoline is put into the storage tank.[160]

Also, these systems collect and recover gasoline vapors from empty, returning tank trucks as they are filled with gasoline from storage tanks. The control efficiency of the balance system ranges from 93 to 100 percent.[157] Figure 6-4 shows a Stage I control vapor balance system at a bulk plant.[160]

At service stations, vapor balance systems contain the gasoline vapors within the station's underground storage tanks for transfer to empty gasoline tank trucks returning to the bulk terminal or bulk plant. Figure 6-5 shows a diagram of a service station vapor balance system.[160] For more information on Stage II controls refer to Section 6.4.7.

6.4.6 Control Technology for Gasoline Storage

The control technologies for benzene emissions from gasoline storage involve upgrading the type of storage tank used or adding a vapor control system. For fixed-roof tanks, emissions are most readily controlled by installation of internal floating roofs. An internal floating roof reduces the area of exposed liquid surface on the tank and, therefore,

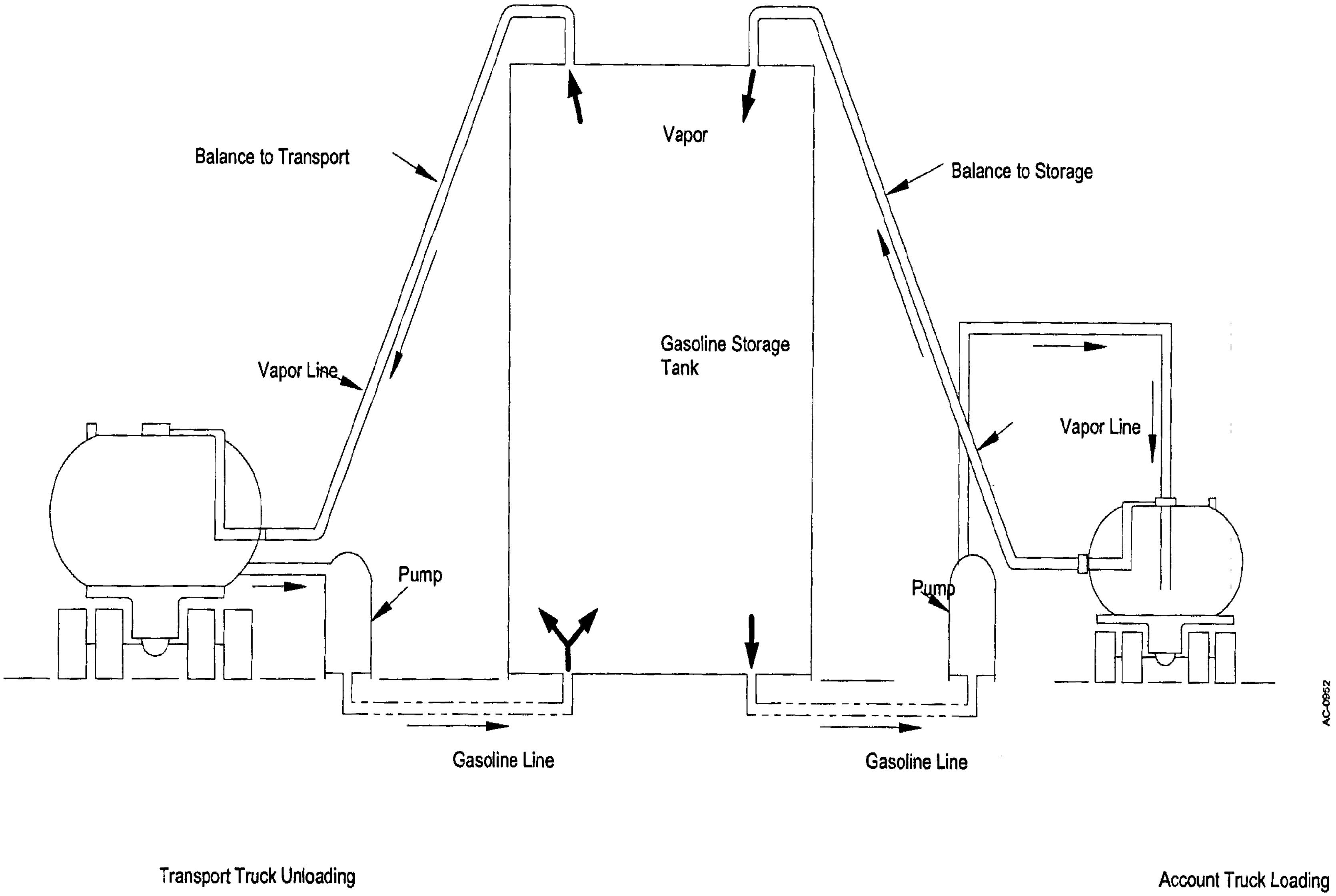


Figure 6-4. Bulk Plant Vapor Balance System (Stage I)

Source: Reference 160.

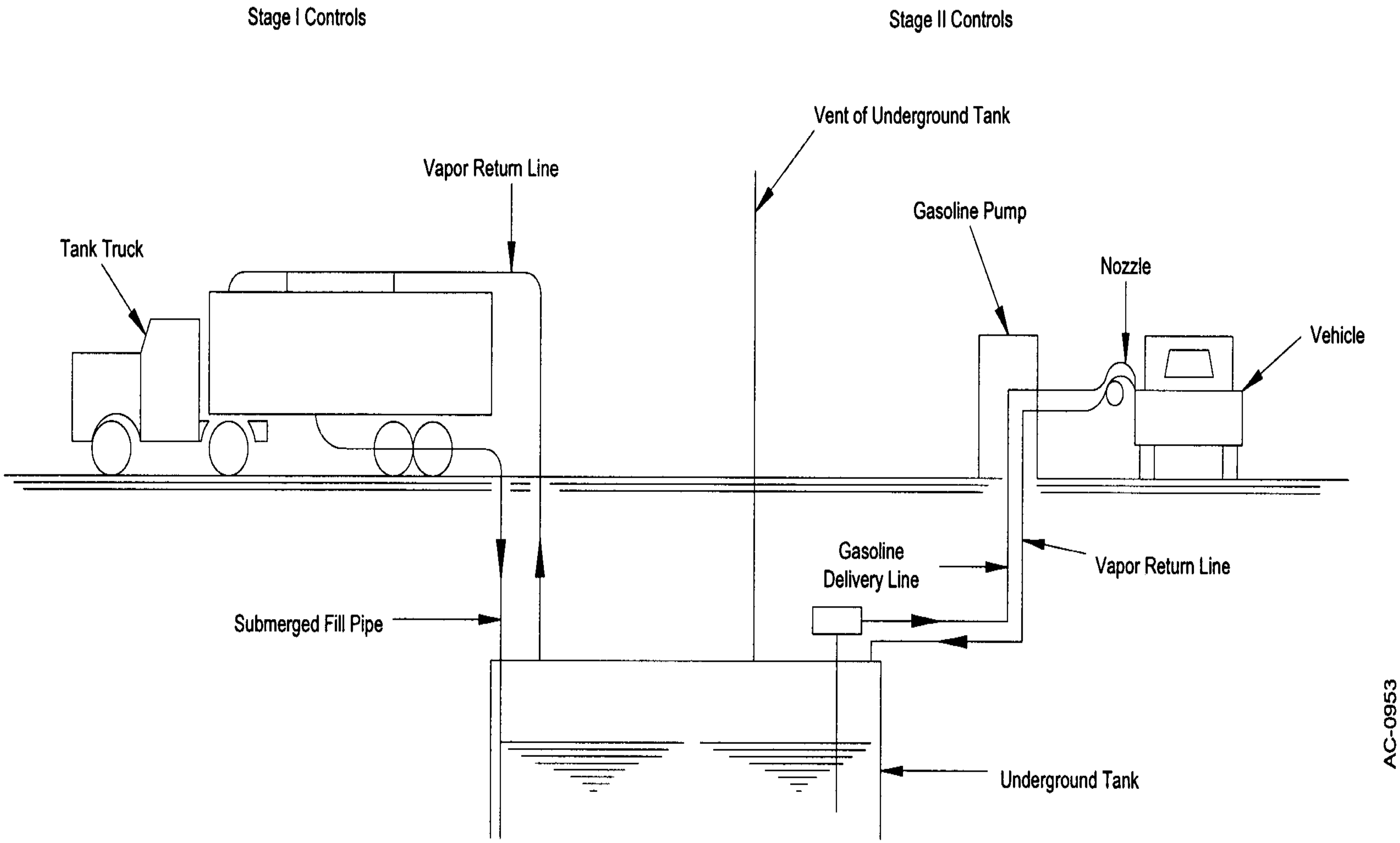


Figure 6-5. Service Station Vapor Balance System

Source: Reference 160.

decreases evaporative loss. Installing an internal floating roof in a fixed-roof tank can reduce total emissions by 68.5 to 97.8 percent.[160]

For external floating-roof tanks, no control measures have been identified for controlling withdrawal losses and emissions.[160] These emissions are functions of the turnover rate of the tank and the characteristics of the tank shell. Rim seal losses in external floating roof tanks depend on the type of seal. Liquid-mounted seals are more effective than vapor-mounted seals in reducing rim seal losses. Metallic shoe seals are more effective than vapor-mounted seals but less effective than liquid-mounted seals.[160]

For additional information on control technology for storage tanks refer to the EPA documents *Compilation of Air Pollutant Emission Factors* (AP-42), Chapter 7[33] and Reference 158.

6.4.7 Control Technology for Vehicle Refueling Emissions

Vehicle refueling emissions are attributable to vapor displaced from the automobile tank by dispensed gasoline and to spillage.

The two basic refueling vapor control alternatives are: control systems on service station equipment (Stage II controls), and control systems on vehicles (onboard controls). Onboard controls are basically limited to the carbon canister.

There are currently three types of Stage II systems in limited use in the United States: the vapor balance, the hybrid, and the vacuum assist systems. In the vapor balance system, gasoline vapor in the automobile fuel tank is displaced by the incoming liquid gasoline and is prevented from escaping to the atmosphere at the fillneck/nozzle interface by a flexible rubber “boot.” This boot is fitted over the standard nozzle and is attached to a hose similar to the liquid hose. The hose is connected to piping which vents to the underground tank. An exchange is made (vapor for liquid) as the liquid displaces vapor to the underground storage tank. The underground storage tank assists this transaction by drawing in a volume of vapor equal to the volume of liquid removed.[160]

The vacuum assist system differs from the balance system in that a "blower" (a vacuum pump) is used to provide an extra pull at the nozzle/fillneck interface. Assist systems can recover vapors effectively without a tight seal at the nozzle/fillpipe interface because only a close fit is necessary. A slight vacuum is maintained at the nozzle/fillneck interface allowing air to be drawn into the system and not allowing the vapors to escape. Because of this assist, the interface "boot" need not be as tight fitting as with balance systems. Further, the vast majority of assist nozzles do not require interlock mechanisms. Assist systems generally have vapor passage valves located in the vapor passage somewhere other than in the nozzles, resulting in a nozzle which is less bulky and cumbersome than nozzles employed by vapor balance systems.[160]

There are four assist systems that are currently available and certified by the California Air Resources Board (CARB): the Hasstech, the Healy, the Hirt, and the Amoco Bellowless Nozzle System.[163]

The hybrid system borrows from the concepts of both the balance and vacuum assist systems. It is designed to enhance vapor recovery at the nozzle/fillneck interface by vacuum, while keeping the vacuum low enough so that a minimum level of excess vapor/air is returned to the underground storage tank.

With the hybrid system, a small amount of the liquid gasoline (less than 10 percent) pumped from the storage tank is routed (before metering) to a restricting nozzle called an aspirator. As the gasoline goes through this restricting nozzle, a small vacuum is generated. This vacuum is used to draw vapors into the rubber boot at the interface. Because the vacuum is so small, very little excess air, if any, is drawn into the boot, hose and underground storage tank, and thus there is no need for a secondary processor, such as the vacuum assist's incinerator.[153]

Results of the California Air Resources Board certification testing program on Stage II vapor recovery systems indicate that all of the Stage II vapor recovery systems discussed above are capable of achieving an emission reduction of 95 percent.[160] However, efficiencies vary depending upon inspection frequency, maintenance, and number of stations exempted. Reference 163 discusses efficiency in more detail.

Onboard vapor control systems consist of carbon canisters installed on the vehicle to control refueling emissions. The carbon canister system adsorbs, on activated carbon, the vapors which are displaced from the vehicle fuel tank by the incoming gasoline. Such a system first absorbs the emissions released during refueling and subsequently purges these vapors from the carbon to the engine carburetor when it is operating. This system is essentially an expansion of the present evaporative emissions control system used in all new cars to minimize breathing losses from the fuel tank and to control carburetor evaporative emissions. However, unlike the present system, a refueling vapor recovery system will require a tight seal at the nozzle/fillneck interface during refueling operations to ensure vapors flow into the carbon canister and are not lost to the atmosphere. An efficiency of 98 percent has been reported for control of automobile refueling losses using onboard control systems.[160]

For additional information on control of vehicle refueling emissions at gasoline dispensing facilities refer to Reference 163.

6.4.8 Regulatory Analysis

Gasoline loading emissions at bulk gasoline terminals are regulated by the New Source Performance Standards promulgated on August 18, 1983.[166] These standards apply to VOC emissions at affected facilities that commenced construction or modification after December 17, 1980. The standards regulate bulk gasoline terminals with a throughput greater than 75,700 liters per day.

Also, the NESHAP for gasoline distribution that was promulgated on December 14, 1994, regulates organic hazardous air pollutant (HAP) emissions (including benzene) from gasoline loading and transport operations. The NESHAP covers HAP emissions from storage vessels, piping and handling, and loading at bulk gasoline terminals, and storage vessels at piping systems that handle the gasoline at pipeline breakout stations.[167]

6.5 PUBLICLY OWNED TREATMENT WORKS

Publicly owned treatment works (POTWs) treat wastewater from residential, institutional, commercial, and industrial facilities. In general, benzene emissions from POTWs originate from the benzene content of industrial wastewater that is introduced into POTWs, and benzene may be emitted by volatilization at the liquid surface of the wastewater.

Industrial wastewater sent to POTWs from industrial facilities may be pre-treated or untreated, depending on State and Federal industrial wastewater quality standards. The following discussion describes the various treatment process units at POTWs from which benzene may be emitted.

6.5.1 Process Description of POTWs

A POTW treats wastewater using physical, chemical, and biological treatment processes. Most POTWs are required by Federal and State laws to treat wastewater using “primary” treatment methods to remove coarse and suspended solids and “secondary” treatment methods to remove biodegradable organics, pathogens, and additional solids. Additionally, some POTWs are required to use “tertiary” treatment methods to remove refractory organics, nutrients (e.g., phosphorus and nitrogen), dissolved inorganic salts, and heavy metals, among other contaminants. As the wastewater is treated, all of the collected solids and sludge undergo additional processing at the POTW to reduce sludge volume, organic content, and bacterial activity prior to disposal.

The following discussion describes the various process units included in a typical POTW facility (shown in Figure 6-6), that uses primary and secondary wastewater treatment methods.[168] As discussed in Section 6.6.2, a testing program for organic emissions from POTWs documented that benzene is emitted from most of these process units.

Comminutors

Comminutors (or shredders) are devices that are used to grind or cut waste solids to about one-quarter-inch (6 mm) particles. In one common type of comminutor, the untreated wastewater enters a slotted cylinder within which another similar cylinder with sharp-edged slots rotates rapidly. As the solids are reduced in size, they pass through the slots of the cylinders and move on with the liquid to the treatment plant. Comminution eliminates the need to use screens, which collect large solid waste material that must be disposed of separately from the sludge.[169]

Aerated Grit Chambers

Grit chambers are used at many POTWs to remove dense solids (both inorganic and organic) present in wastewater (e.g., sand, gravel, glass, coffee grounds). Aerated grit chambers work by imparting a helical flow pattern to the sewage by aerating one side of the chamber. The aeration allows the dense grit to settle while keeping less dense organic material in suspension. Benzene emissions arise from aeration of the wastewater in the grit chamber.[168]

Primary Sedimentation Tanks

The main function of primary sedimentation tanks is to remove suspended material that settles readily from raw sewage. This material includes slower-settling organic matter as well as fast-settling grit if the POTW does not have grit removal upstream. Additionally, the system removes floatable solids, which are composed mostly of fats and grease. The wastewater enters the tank at one end, flows through the tank and under a surface

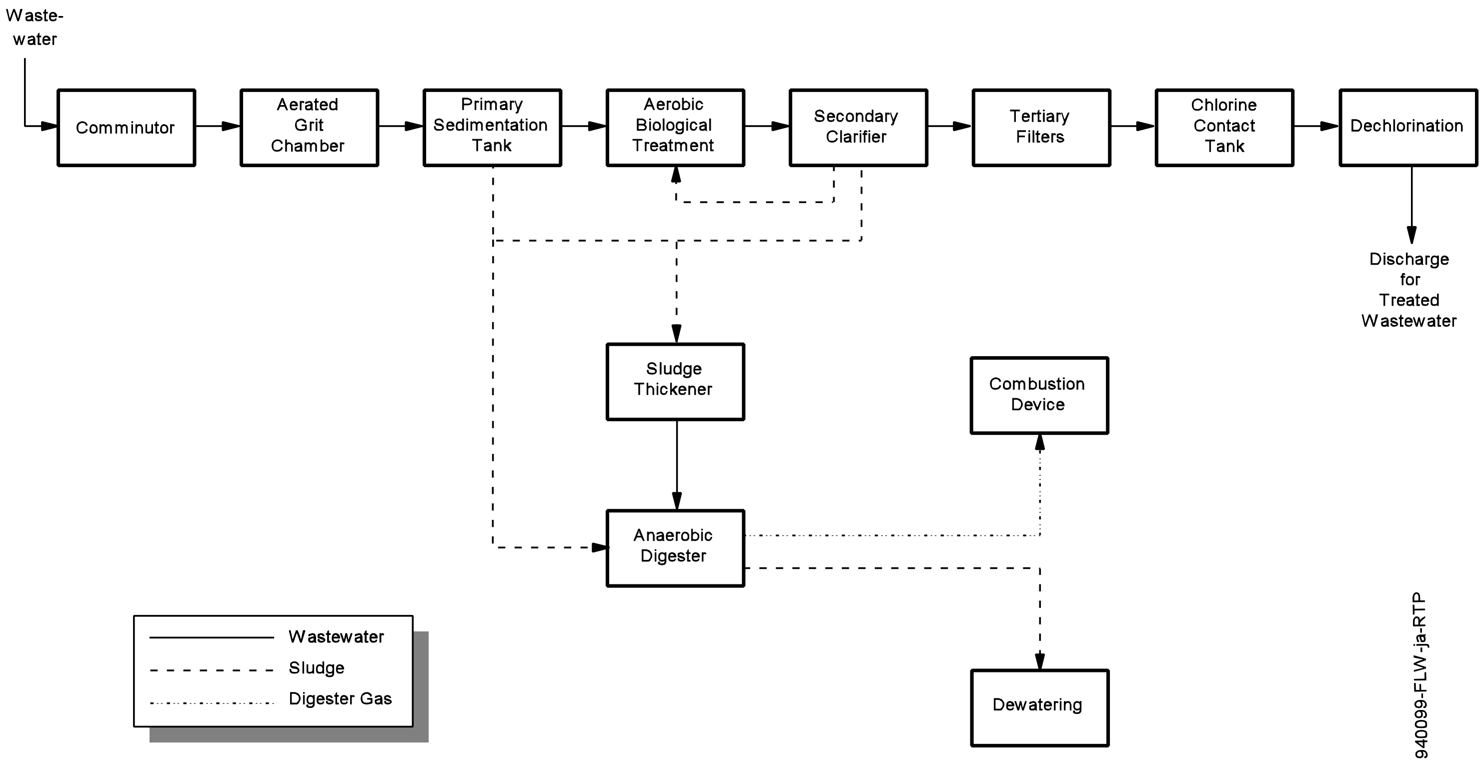


Figure 6-6. Process Flow Diagram for a Typical POTW

Source: Reference 168.

baffle located near the tank's downstream edge, over a weir, and into an effluent channel. Sludge collects on the bottom of the tank. A system of scrapers collects the sludge from the bottom of the tank and pumps it to gravity sludge thickeners for further treatment. The surface baffle skims the surface of the water and collects the floatables for removal and treatment in anaerobic digesters.

Small amounts of benzene are released by volatilization from the quiescent section of the tank prior to the weir. Most of the benzene emissions from the primary sedimentation tank result from the turbulence that the water undergoes dropping over the weir into the outlet conveyance channel. The height of the water drop from the weir is a measure of the energy dissipated and may relate to the release of benzene emissions.[168]

Aerobic Biological Treatments

Aerobic biological treatment involves the use of microorganisms to metabolize dissolved and colloidal organic matter in the wastewater in an aerobic environment. Two types of processes are used: suspended-growth and attached-growth. The most common suspended-growth process used in POTWs is the activated sludge process; the most common attached-growth process is the trickling filter. These two types of processes are described below.[169]

Activated Sludge Process--In the activated sludge process, a high concentration of microorganisms that have settled in the secondary clarifiers (called activated sludge) is added to settled wastewater that enters an aerobic tank. The mixture enters an aeration tank, where the organisms and wastewater undergo further mixing with a large quantity of air or oxygen to maintain an aerobic environment. There are three common types of aeration tanks: diffused air, mechanically mixed air, and pure oxygen (which can be diffused or mechanically mixed). Diffused air systems aerate the water by bubbling air from the atmosphere through the water from the bottom of the tank. Mechanically mixed air systems use mechanical surface mixers that float on the water surface.

In pure oxygen systems (which are more likely to be covered systems), pure oxygen is fed to either submerged diffusers or to the head space over a tank employing mechanical aerators. In diffused air or oxygen systems, the air or oxygen bubbles can strip VOC from the liquid phase depending on the concentrations and partial pressures of the specific substances. In mechanically mixed systems, the area where the wastewater/activated sludge mixture is agitated is a potential source of VOC (benzene) emissions.[168,169]

<u>Trickling Filter</u>--The trickling filter is an aerobic attached-growth treatment process that uses microorganisms growing on a solid media to metabolize organic compounds in the wastewater. Trickling filter media beds are typically 40 to 100 ft in diameter and 15 to 40 ft deep. Influent wastewater from the primary sedimentation tank is sprayed on top of the media bed. The wastewater is biologically treated as it trickles downward through the media. Effluent from the process is collected by the underdrain system and sent to a secondary clarifier. Ambient air is blown upward through the media to provide oxygen to sustain microbial growth. The exhaust air from the process may contain benzene that was stripped from the wastewater during treatment.[168]

Secondary Clarification

Secondary clarification is a gravity sedimentation process used in wastewater treatment to separate out the activated sludge solids from the effluent from the upstream biotreatment process. Effluent from the biological treatment process is introduced into the clarifier through submerged diffusers. As the wastewater flows through the clarifier tank from inlet to outlet weirs, the solids settle to the bottom of the tank while the floatables and scum are skimmed off the top. The tank bottom is sloped slightly to the discharge end of the tank to two hoppers, where sludge is collected by a chain and flight conveyor system and returned to the biological treatment system or to the waste sludge handling system. The quiescent section of the tank may release benzene by volatilization from the water surface. However, most of the benzene emissions from the secondary clarifier result from the turbulence that the water undergoes dropping over the weir into the outlet conveyance channel. In some cases, the weir is notched, such that the water flows through the notches, falling only a few inches onto a support structure. In this latter case, there is much less turbulence in the water, and it is expected that there would be fewer emissions of VOC than in the case where the water free-falls directly into the collection channel.[168]

Tertiary Filters

Tertiary filters remove unsettled particles from the wastewater by using enclosed (pressure) filters or open (gravity) filters. The filtering medium typically consists of sand and anthracite coal, and may consist of one or two grain sizes. To collect activated sludge effluent, the filters typically remove particles in the size ranges of 3 to 5 μm and 80 to 90 μm. Alum or polymer is often added prior to filtration to form a floc and thus increase particulate removal.

Cleaning of tertiary filters (called backwashing) typically occurs by forcing water back through the filter. The backwash water is typically recirculated upstream in the plant. Except for the brief periods during backwash, gravity tertiary filters have quiescent surfaces, and little VOC release would be expected. Pressure filters are totally enclosed, and no air emissions occur during filtration from these units.[168]

Chlorine Contact Tanks

For the purposes of disinfection, chlorine in the form of chlorine gas or calcium or sodium hypochlorite is fed into the wastewater just prior to the chlorine contact tank. The chlorine contact tank is designed to allow the mixture of chlorine and wastewater to remain in contact long enough to adequately kill the target organisms (15 minutes to 2 hours). The typical flow pattern is a serpentine pattern, consisting of interior baffle walls within a rectangular tank. Although water surfaces are generally quiescent, most chlorine contact tanks have weirs at the end of the tank to control water levels in the tank. Depending on the depth of fall and flow rate, the turbulence at the weir overflow may result in benzene emissions.[168]

Dechlorination Chambers

Typically, a dechlorination chamber is located adjacent to the chlorine contact tank to remove chlorine residual in the disinfected wastewater. Chlorinated effluent from the chlorine contact tank flows into the dechlorination chamber through a gate valve. In the dechlorination chamber, an SO_2 solution or sodium bisulfate is introduced into the wastewater through submerged diffusers. The wastewater is hydraulically mixed as the SO_2 is added. The dechlorinated water is discharged from the facility.[168]

Sludge Thickeners

Sludge thickeners collect primary sludge (from the primary sedimentation tank) and waste-activated sludge (from the secondary clarifier) to reduce the volume of the sludge prior to treatment in an anaerobic digester. The two most common types of thickening processes are gravity sludge thickeners and dissolved air floatation thickeners. These two types of thickeners are described below.[168] Additionally, centrifuges are used to thicken sludge both prior to and after aerobic digestion. (Centrifuges are discussed below under dewatering techniques.)

Gravity Sludge Thickener--In this process, sludge is thickened by allowing heavier sludge particles to settle. Sludge is pumped into the center of a circular tank from below. Heavier solid particles sink to the bottom of the tank, are removed as thickened sludge, and are sent to digesters. Lighter sludge particles (e.g., greases) float to the surface of the tank and are removed into a scum trough, where they are directed to a scum conditioner. As sludge is added to the tank, the sludge flows outward radially, and liquid effluent from the process flows outward over weirs and into the effluent trough located on the periphery of the tank. Typically, this liquid returns to the aeration tanks in the activated sludge process for further treatment.[168]

Dissolved Air Flotation Thickener--This process is used to float sludge by forcing the sludge to rise to the water surface. Sludge is pumped into a circular tank with central feed or into a rectangular tank with end feed. As the sludge enters the tank, microbubbles are introduced into the sludge by pressurizing in a retention tank a portion of the effluent liquid from the tank. Pressurization of the liquid causes the air to be dissolved in the liquid phase. After pressurization, the recirculated effluent is mixed with the sludge feed. When the pressurized liquid is released to atmospheric pressure, the dissolved air is released into the solution in the form of microbubbles. As the sludge and pressurized liquid mix, the sludge and air mixture rises to the surface in the form of a sludge blanket. Sludge thickening occurs as a result of the sludge blanket and by drainage of entrained water from the sludge blanket. Surface skimmers are used to remove the sludge blanket from the water surface for further treatment in an anaerobic digester.

Anaerobic Digestion

Anaerobic digestion is a biological process conducted in the absence of free oxygen in which anaerobic and facultative bacteria metabolize organic solids in sludge, releasing methane and CO_2 as a by-product. Anaerobic digesters are most commonly cylindrical, with a diameter of 20 to 125 ft and a depth of 20 to 40 ft. In most digesters, to promote adequate contact between the anaerobic biota and organic matter, the sludge is mixed by either internal gas recirculation or by digested sludge recirculation. Additionally, the sludge is kept heated to about 95°F (35°C) by either direct steam injection into the sludge or by recirculating sludge through an external heat exchanging device. With mixing and heating, sludge undergoes digestion for about 15 to 25 days.[168,169]

Most digesters are closed containers under a slight pressure. Under normal operation, there should be no direct emissions of benzene to the atmosphere. The digester gas produced is typically collected and routed to internal combustion engines to produce steam or generate electricity. (Refer to Section 7.5 for information about benzene emissions from an internal combustion engine fueled with POTW digester gas.) If the digester is not covered or the digester gases are not collected, then benzene may be emitted directly from the digester.[168]

Dewatering Techniques

Sludge dewatering operations involve removal of water from sludges by gravity, compression, and evaporation processes. Common methods of dewatering are using a belt filter press, a sludge centrifuge, and sludge drying beds.

Belt Filter Press--Digested sludge is mixed with flocculating cationic polymers which aid in the separation of the solids from the water. The flocculated sludge is initially spread out horizontally over a moving filter belt that passes under plows that turn the sludge/polymer solution, aiding in the dewatering process. After gravity thickening on the belt, the partially dewatered sludge is conveyed to and falls into a vertical compression zone, where water is squeezed out of the sludge between two filter belts moving concurrently through a series of rollers. The filtrate from dewatering is collected and returned to the head of the treatment plant for processing. Sludge particles enmeshed in the polyester belt fabric are continuously washed off by a highly pressurized spray. The dried sludge (“cake”) product is collected and carried to silos for storage.

Benzene emissions from the belt filter press process may be released from the following locations: (1) the gravity section, where liquid sludge is discharged and tilled by plows, (2) the filtrate pans, where filtrate cascades down from the belts to the filtrate collection channel below, (3) the compression zone, where the sludge is squeezed between the two belts, and (4) the drainage sump into which the filtrate and wash water are discharged.[168]

Sludge Centrifuge--Digested or pre-digested sludge mixed with flocculating cationic polymers is introduced into a spinning cylinder with a conical end bowl that rotates at sufficient velocity to force the solids to the sides of the drum. Inside the bowl, a concentric screw conveyor with helical flights turns at a slightly different speed than the rotating drum, forcing the dewatered solids to a discharge at one end of the centrifuge, while the liquid flows over to a weir into a discharge at the other end. The dewatered sludge is collected and stored.[168] Benzene emissions may be emitted from the point where the separated liquid flows over the weir and is discharged from the centrifuge.

Sludge Drying Bed--A certain volume of sludge is piped into shallow beds, where the sludge is allowed to dry by gravity settling, evaporation, and percolation. Some drying beds are equipped with a system for decanting the liquid from the drying bed or draining the liquid through a sand bed to a collection pipe. Due to factors such as rainfall, ambient temperature, wind speed, relative humidity, amount of sun, and the character of the sludge, the drying time varies from 30 to 60 days.[168] These same factors will likely affect the level of benzene emissions from the sludge drying beds.

6.5.2 Benzene Emissions From POTWs

Under a program called the Pooled Emission Estimation Program (PEEP), 21 POTW facilities in California were tested for emissions of benzene (among other VOC) from 18 types of process units commonly included in POTW wastewater treatment processes. With the exception of one type of process unit (comminutor controlled with wet scrubber), the emissions test data yielded uncontrolled benzene emission factors. On average, three facilities were tested for each type of process unit. The types of process units that were tested are discussed above in section 6.6.1, and include aerated processes (aerated grit chambers, three types of activated sludge units, trickling filters, and dissolved air floatation thickeners), gas handling processes (anaerobic digesters and digester gas combustion devices), quiescent basins (primary sedimentation tanks, secondary clarifiers, tertiary filters, chlorine contact tanks, dechlorination, and gravity thickeners), sludge facilities (belt filter press, sludge centrifuges, and sludge drying beds), and other processes (comminutors).

Based on the data collected by PEEP, emission factors could be developed for most of the above process steps in the form of pounds of benzene emitted per million gallons of wastewater treated at a POTW. One type of process unit tested (mechanically-mixed activated sludge) did not yield air emissions of benzene above the detection limit in the tests performed; however, benzene was detected in the wastewater treated by the tested units. Additionally, a benzene emission factor for the dechlorination process unit could only be calculated in the form of pounds of benzene emitted per pound of benzene in the wastewater influent to the dechlorination chamber. Refer to Table 6-22 for a listing of the emission factors.[3,168]

With one exception, all of the emission factors presented in Table 6-21 represent uncontrolled emissions of benzene. However, many facilities employ measures for odor control that may also reduce benzene emissions to the atmosphere (see discussion in Section 6.6.3). Most of the facilities tested under PEEP did employ odor control methods; however, benzene emissions after control were not measured.

6.5.3 Control Technologies for POTWs

In general, the only types of control devices and techniques found at POTWs are the scrubbers and covers used to improve the odor of the air released from the process units. Using the information provided by PEEP, it could be determined which process units commonly employ covers and scrubbers.

In many cases, aerated grit chambers are covered and vented to a scrubber. Primary sedimentation tanks are sometimes covered and vented to a scrubber; however, many of these units are uncovered. Activated sludge units may sometimes be completely covered and vented to a scrubber or partially covered and vented to the atmosphere. This practice is more common if a pure oxygen system is employed. Trickling filter units are sometimes covered and vented to a scrubber. Secondary clarifiers may be uncovered or partially covered over the weir discharge area with no vents. Tertiary filters are commonly uncovered.

TABLE 6-22. SUMMARY OF BENZENE EMISSION FACTORS FOR POTWs

SCC Number	Emission Source	Control Device	Emission Factor lb/million gal (kg/million liters)[a]	Emission Factor Rating
5-01-007-07	Comminutor	Wet scrubber	6.50×10^{-3} (7.79×10^{-4})	E
5-01-007-15	Aerated grit chamber	Uncontrolled	3.56×10^{-3} (4.27×10^{-4})	C
5-01-007-20	Primary sedimentation tank	Uncontrolled	5.50×10^{-4} (6.59×10^{-5})	C
5-01-007-31	Diffused air activated sludge	Uncontrolled	6.67×10^{-4} (7.99×10^{-5})	B
5-01-007-33	Pure oxygen activated sludge	Uncontrolled	3.80×10^{-6} (4.55×10^{-7})	B
5-01-007-34	Trickling filter	Uncontrolled	1.60×10^{-3} (1.92×10^{-4})	C
5-01-007-40	Secondary clarifier	Uncontrolled	1.40×10^{-4} (1.68×10^{-5})	C
5-01-007-50	Tertiary filter	Uncontrolled	4.00×10^{-6} (4.79×10^{-7})	B
5-01-007-60	Chlorine contact tank	Uncontrolled	1.39×10^{-4} (1.67×10^{-5})	E
5-01-007-61	Dechlorination	Uncontrolled	7.50×10^{-1} lb/lb (7.50×10^{-1} kg/kg)[b]	B
5-01-007-71	Gravity sludge thickener	Uncontrolled	2.09×10^{-4} (2.50×10^{-5})	B

(continued)

TABLE 6-22. CONTINUED

SCC Number	Emission Source	Control Device	Emission Factor lb/million gal (kg/million liters)[a]	Emission Factor Rating
5-01-007-72	Dissolved air floatation thickener	Uncontrolled	3.00×10^{-3} (3.59×10^{-4})	B
5-01-007-81	Anaerobic digester	Uncontrolled	3.08×10^{-1} (3.69×10^{-2})	B
5-01-007-91	Belt filter press	Uncontrolled	5.00×10^{-2} (5.99×10^{-3})	B
5-01-007-92	Sludge centrifuge	Uncontrolled	2.05×10^{-3} (2.46×10^{-4})	B
5-01-007-93	Sludge drying bed	Uncontrolled	2.80×10^{-3} (3.36×10^{-4})	B

Source: References 3 and 168.

[a] Factors are expressed as lb (kg) of benzene emitted per million gal (million liters) of wastewater treated.

[b] Factor is expressed as lb (kg) of benzene emitted per lb (kg) of benzene in the wastewater influent to the process unit (emission source).

Chlorine contact tanks are either uncovered or partially covered. Dechlorination units are often enclosed in a building that vents to a scrubber. Thickeners are commonly covered and sometimes vented to a scrubber. Anaerobic digesters are commonly closed under a slight pressure, and the gas is sent to an internal combustion engine or boiler to produce steam or electricity; however, some digesters may vent to the atmosphere. Belt filter presses are commonly enclosed in a building that vents to a scrubber. Sludge centrifuges are commonly enclosed and vented to a scrubber. Drying beds are most commonly uncovered.[168]

6.5.4 Regulatory Analysis

At the present, there are no Federal regulations that apply directly to benzene air emissions from POTWs. However, two regulations indirectly apply: the HON and the Benzene Waste Operations NESHAP. Both of these apply directly to specific types of industrial facilities that may generate wastewater containing benzene. Both regulations stipulate that these facilities may comply with the treatment requirements by sending their wastewater to an off-site treatment plant. However, the off-site plant must remove or destroy the benzene in the wastewater to the level specified in the regulations. Further information on the regulation can be found in Section 4.5.4 of this document.

6.6 MUNICIPAL SOLID WASTE LANDFILLS

A municipal solid waste (MSW) landfill unit is a discrete area of land or an excavation that receives household waste, but is not a land application unit (i.e. for receiving sewage sludge), surface impoundment, injection well, or waste pile. An MSW landfill unit may also receive other types of wastes, such as commercial solid waste, nonhazardous sludge, and industrial solid waste. Benzene emissions from MSW landfills are expected to originate from the non-household sources of MSW. The types of waste potentially accepted by MSW landfills include:

- MSW;

- Household hazardous waste;
- Municipal sludge;
- Municipal waste combustion ash;
- Infectious waste;
- Waste tires;
- Industrial non-hazardous waste;
- Conditionally exempt small quantity generator hazardous waste;
- Construction and demolition waste;
- Agricultural wastes;
- Oil and gas wastes; and
- Mining wastes.

MSW management in the United States is dominated by disposal in landfills. Approximately 67 percent of solid waste is landfilled, 16 percent is incinerated, and 17 percent is recycled or composted. There were an estimated 5,345 active MSW landfills in the United States in 1992. In 1990, active landfills were receiving an estimated 130 million tons (118 million Mg) of waste annually, with 55 to 60 percent reported as household waste and 35 to 45 percent reported as commercial waste.[170]

6.6.1 Process Description of MSW Landfills[170]

There are three major designs for municipal landfills: the area method, the trench method, and the ramp method. They all utilize a three-step process, which includes spreading the waste, compacting the waste, and covering the waste with soil. The area fill method involves placing waste on the ground surface or landfill liner, spreading it in layers, and compacting it with heavy equipment. A daily soil cover is spread over the compacted waste. The trench method entails excavating trenches designed to receive a day's worth of waste. The soil from the excavation is often used for cover material and wind breaks. The ramp method is typically employed on sloping land, where waste is spread and compacted in a manner similar to the area method; however, the cover material obtained is generally from the front of the working face of the filling operation. The trench and ramp methods are not commonly used, and are not the preferred methods when liners and leachate collection systems are utilized or required by law.

Modern landfill design often incorporates liners constructed of soil (e.g., recompacted clay) or synthetics (e.g., high density polyethylene) or both to provide an impermeable barrier to leachate (i.e., water that has passed through the landfill) and gas migration from the landfill.

6.6.2 Benzene Emissions from MSW Landfills

The rate of benzene emissions from a landfill is governed by gas production and transport mechanisms. Production mechanisms involve the production of the emission constituent in its vapor phase through vaporization, biological decomposition, or chemical reaction. Transport mechanisms involve the transportation of benzene in its vapor phase to the surface of the landfill, through the air boundary layer above the landfill, and into the atmosphere. The three major transport mechanisms that enable transport of benzene in its vapor phase are diffusion, convection, and displacement.[170]

Uncontrolled Benzene Emissions[170]

Uncontrolled benzene emissions from a landfill may be estimated by utilizing the series of equations provided below. The three equations estimate the following three variables: (1) the uncontrolled methane generation rate, (2) the uncontrolled benzene emission rate (calculated based on the uncontrolled methane generation rate), and (3) the uncontrolled benzene mass emission rate (calculated based on the uncontrolled benzene emission rate). As indicated, the second equation utilizes the product of the first equation, and the third equation utilizes the product of the second equation.

The uncontrolled CH_4 volumetric generation rate may be estimated for individual landfills by using a theoretical first-order kinetic model of CH_4 production developed by EPA. This model is known as the Landfill Air Emissions Estimation model, and it can be accessed from the EPA's Control Technology Center bulletin board. The Landfill Air Emissions Estimation model equation is as follows:

$$Q_{CH4} = L_o R (e^{-kc} - e^{-kt})$$

where:

Q_{CH4} = Methane volumetric generation rate at time t, m^3/yr
L_o = Methane generation potential, m^3 CH_4/Mg refuse
R = Average annual acceptance rate of degradable refuse during active life, Mg/yr
e = Base log, unitless
k = Methane generation rate constant, yr^{-1}
c = Time since landfill closure, yrs (c = 0 for active landfills)
t = Time since the initial refuse placement, yrs

Site-specific landfill information is generally available for variables R, c, and t. When refuse acceptance rate information is scant or unknown, R can be determined by dividing the refuse in place by the age of the landfill. Also, nondegradable refuse should be subtracted from the mass of acceptance rate to prevent overestimation of CH_4 generation. The average annual acceptance rate should only be estimated by this method when there is inadequate information on the actual average acceptance rate.

Values for variables L_o and k must be estimated. Estimation of the potential CH_4 generation capacity of refuse (L_o) is generally treated as a function of the moisture and organic content of the refuse. Estimation of the CH_4 generation constant (k) is a function of a variety of factors, including moisture, pH, temperature, and other environmental factors, and landfill operating conditions. Specific CH_4 generation constants can be computed by use of EPA Method 2E.

The Landfill Air Emission Estimation model uses the proposed regulatory (see Section 6.6.4) default values for L_o and k. However, the defaults were developed for regulatory compliance purposes. As a result, the model contains conservative L_o and k default values in order to protect human health, to encompass a wide range of landfills, and to encourage the use of site-specific data. Therefore, different L_o and k values may be appropriate in estimating landfill emissions for particular landfills and for use in an emissions inventory.

A higher k value of 0.05/yr is appropriate for areas with normal or above normal precipitation. An average k value is 0.04/yr. For landfills with drier waste, a k value of 0.02/yr is more appropriate. An L_o value of 125 m^3/Mg (4,005 ft^3/ton) refuse is appropriate for most landfills. It should be emphasized that in order to comply with the proposed regulation (see Section 6.6.4), the model defaults for k and L_o must be applied as specified in the final rule.

Based on the CH_4 volumetric generation rate calculated above, the benzene volumetric emission rate from a landfill can be estimated by the following equation:

$$Q_{BZ} = 2\ Q_{CH4} * C_{BZ}/(1x10^6)$$

where:

Q_{BZ} = Benzene volumetric emission rate, m^3/yr
Q_{CH4} = CH_4 volumetric generation rate, m^3/yr (from the Landfill Air Emission Estimation model)
C_{BZ} = Benzene concentration in landfill gas, ppmv
2 = Multiplication factor (assumes that approximately 50 percent of landfill gas is CH_4)

Uncontrolled emission concentrations of benzene based on a landfill site's history of co-disposal with hazardous wastes are presented in Table 6-23.[3,170] An analysis of

TABLE 6-23. SUMMARY OF UNCONTROLLED EMISSION CONCENTRATIONS OF BENZENE FROM LANDFILLS

SCC Number	Emission Source	Type of Waste Disposed	Emission Concentration (ppmv)	Emission Factor Rating
5-02-006-02	Landfill dump	MSW co-disposed with hazardous waste	24.99	D
		MSW, unknown history of co-disposal with hazardous waste	2.25	B
		MSW only	0.37	D

Source: References 3 and 170.

benzene emissions data based on the co-disposal history of the individual landfills from which the concentration data were derived indicates that benzene emissions do vary with the amount of hazardous waste co-disposed. These benzene concentrations have already been corrected for air infiltration and can be used, when site-specific data are not available, as input parameters (for the variable C_{BZ}) in the above equation for estimating benzene volumetric emission rates from landfills.

Then, based on the benzene volumetric emission rate calculated using the above equation, the uncontrolled mass emission rate of benzene from a landfill can be estimated by the following equation:

$$I_{BZ} = Q_{BZ} * \frac{78.113}{(8.205x10^{-5}\ m^{3}\text{-atm/mol-}^{\circ}K)\ (1000\ g)\ (273 + T)}$$

where:

I_{BZ} = Uncontrolled benzene mass emission rate, kg/yr
Q_{BZ} = Benzene volumetric emission rate, m^3/yr
T = Temperature of landfill gas, °C
78.113 = Molecular weight of benzene

This equation assumes that the operating pressure of the system is approximately 1 atmosphere. If the temperature of the landfill gas is not known, a temperature of 25°C is recommended.

Controlled Benzene Emissions

As discussed in more detail in Section 6.6.3, emissions from landfills are typically controlled by installing a gas collection system and destroying the collected gas through the use of internal combustion engines, flares, or turbines. The control system for landfills consists of two stages, and estimating controlled benzene emissions involves the following two steps: (1) estimating the amount of benzene that is not collected by the gas collection system, and (2) estimating the amount of collected benzene that is not destroyed by the control device.

The amount of benzene that is not collected by the gas collection system may be calculated with the following equation:

$$UC_{BZ} = \left(1 - \frac{\text{Collection Efficiency}}{100}\right) * I_{BZ}$$

where:

UC_{BZ} = Uncollected benzene mass emission rate, kg/yr
Collection Efficiency = Collection efficiency of the gas collection system, %
I_{BZ} = Uncontrolled benzene mass emission rate, kg/yr

If the site-specific collection efficiency cannot be determined, one may assume that a gas collection system collects 75 percent of the benzene emitted by a landfill. Reported collection efficiencies typically range from 60 to 85 percent, with the average of 75 percent being most commonly used for estimation of UC_{BZ}.

The amount of benzene that is not destroyed by the control device may be calculated with the following equation:

$$ND_{BZ} = \left(1 - \frac{\text{Destruction Efficiency}}{100}\right) * (I_{BZ} - UC_{BZ})$$

where:

ND_{BZ} = Non-destroyed benzene mass emission rate, kg/yr
Destruction Efficiency = Destruction efficiency of the control device, %

I_{BZ} = Uncontrolled benzene mass emission rate, kg/yr
UC_{BZ} = Uncollected benzene mass emissions rate, kg/yr

If the site-specific destruction efficiency of a control device cannot be determined, one may assume the destruction efficiencies provided here. Flares have been documented to destroy

89.5 percent of the benzene routed to the flare. Internal combustion engines have been documented to destroy 83.8 percent of the benzene routed to the internal combustion engine. After promulgation of standards proposed in 1991 (see Section 6.6.4), however, all control devices utilized at both new and existing landfills may be required to reduce the non-methanogenic organic compounds (NMOCs) in the collected gas by 98 weight percent.

Alternatively, if the control device utilized is a flare and the heat content of the landfill gas is known, the emission factor provided in Table 6-24 may be used to calculate non-destroyed benzene emissions.[3] Additionally, if the control device is an industrial boiler, refer to Section 7.4 for information regarding controlling benzene emissions from an industrial boiler treating landfill gas.

After UC_{BZ} and ND_{BZ} have been calculated, these two variables may be added together to calculate the total benzene mass emission rate after the control system.

6.6.3 Control Technologies for MSW Landfills[170]

Landfill gas collection systems are either active or passive systems. Active collection systems provide a pressure gradient in order to extract landfill gas by use of mechanical blowers or compressors. Passive systems allow the natural pressure gradient created by the increase in landfill pressure from landfill gas generation to mobilize the gas for collection.

Landfill gas control and treatment options include (1) combustion of the landfill gas, and (2) purification of the landfill gas. Combustion techniques include techniques that do not recover energy (e.g., flares and thermal incinerators) and techniques that recover energy and generate electricity from the combustion of the landfill gas (e.g., gas turbines and internal combustion engines). Boilers can also be employed to recover energy from landfill gas in the form of steam. Flares involve an open combustion process that requires oxygen for combustion; the flares can be open or enclosed. Thermal incinerators heat an organic chemical

TABLE 6-24. CONTROLLED BENZENE EMISSION FACTOR FOR LANDFILLS

SCC Number	Emission Source	Control Device	Emission Factor lb/MMBtu (g/kJ)[a]	Emission Factor Rating
5-02-006-01	Landfill Dump	Flare	7.10×10^{-6} (3.05×10^{-9})[b]	D

Source: Reference 3.

[a] Emission factor is in lb (g) of benzene emitted per MMBtu (kJ) of heat input to the flare.
[b] Based on two tests conducted at two landfill sites.

to a high enough temperature in the presence of sufficient oxygen to oxidize the chemical to CO_2 and water. Purification techniques can also be used to process raw landfill gas to pipeline quality natural gas by using adsorption, absorption, and membranes.

6.6.4 Regulatory Analysis[170]

Proposed NSPS and emission guidelines for air emissions from MSW landfills for certain new and existing landfills were published in the Federal Register on May 30, 1991, and promulgated March 12, 1996. The regulation requires that Best Demonstrated Technology be used to reduce MSW landfill emissions from affected new and existing MSW landfills with a design capacity greater than 2.8 million tons (2.5 million Mg by mass or 2.5 million cubic meters by volume) of MSW and emitting greater than or equal to 55 tons/yr (50 Mg/yr) of NMOCs. The MSW landfills that would be affected by the proposed NSPS would be each new MSW landfill and each existing MSW landfill that has accepted waste since May 30, 1991, or that has capacity available for future use. Control systems would require (1) a well-designed and well-operated gas collection system, and (2) a control device capable of reducing NMOCs in the collected gas by 98 weight percent.

6.7 PULP, PAPER, AND PAPERBOARD INDUSTRY

In the pulp, paper, and paperboard industry, wood pulp is chemically treated by dissolving the lignin that binds the cellulose together and then extracting the cellulose to make paper and paperboard. Four types of chemical wood pulping processes are practiced in the

United States. Kraft pulping is the most prevalent type of process, accounting for about 85 percent of pulp production. Three other pulping processes, semi-chemical, soda-mill, and acid sulfite, account for 4, 5, and 6 percent of domestic pulp production, respectively. Because kraft pulping is the most common type of pulping and the other processes are relatively similar to it, kraft pulping will be the focus of this section. More information on the other three pulping processes can be found in References 171 and 172.

The distribution of kraft pulp mills in the United States in 1993 is shown in Table 6-25.[171] Kraft pulp mills are located primarily in the southeast, whose forests provide over 60 percent of U.S. pulpwood.

The U.S. EPA is developing benzene emission factors for pulp and papermaking processes in conjunction with MACT standards that are under development. Please refer to the CHIEF bulletin board for benzene emission factors that will be forthcoming from the MACT development process. More information on the MACT effort is given in Section 6.7.2.

6.7.1 Process Description for Pulp, Paper, and Paperboard Making Processes

The key unit operations in the kraft pulp and papermaking process include: (1) cooking and evaporation, (2) pressure knotting and screening, (3) brown stock washing, (4) decker washing and screening, (5) oxygen delignification, (6) pulp storage, (7) chemical recovery and causticizing, (8) co-product recovery, (9) bleaching, and (10) paper making. Common potential emission points found in the pulp and papermaking process are listed in Table 6-26.[173] Each of the key steps, along with their associated emission points, are illustrated in the diagram of a typical Kraft pulping and recovery process (Figure 6-7) and these are discussed below in more detail.[171] Bleaching, which is frequently used as a final step, and papermaking are discussed at the end of this section.

TABLE 6-25. DISTRIBUTION OF KRAFT PULP MILLS IN THE UNITED STATES (1993)

State	Kraft Pulp Mills
Alabama	16
Arizona	1
Arkansas	7
California	4
Florida	8
Georgia	12
Idaho	1
Kentucky	2
Louisiana	10
Maine	7
Maryland	1
Michigan	3
Minnesota	2
Mississippi	6
Montana	1
New Hampshire	1
North Carolina	5
Ohio	1
Oklahoma	1
Oregon	7
Pennsylvania	3
South Carolina	6
Tennessee	2
Texas	6
Virginia	4
Washington	7
Wisconsin	4
Total	126

Source: Reference 171.

TABLE 6-26. LIST OF COMMON POTENTIAL EMISSION POINTS WITHIN THE KRAFT PULP AND PAPERMAKING PROCESS

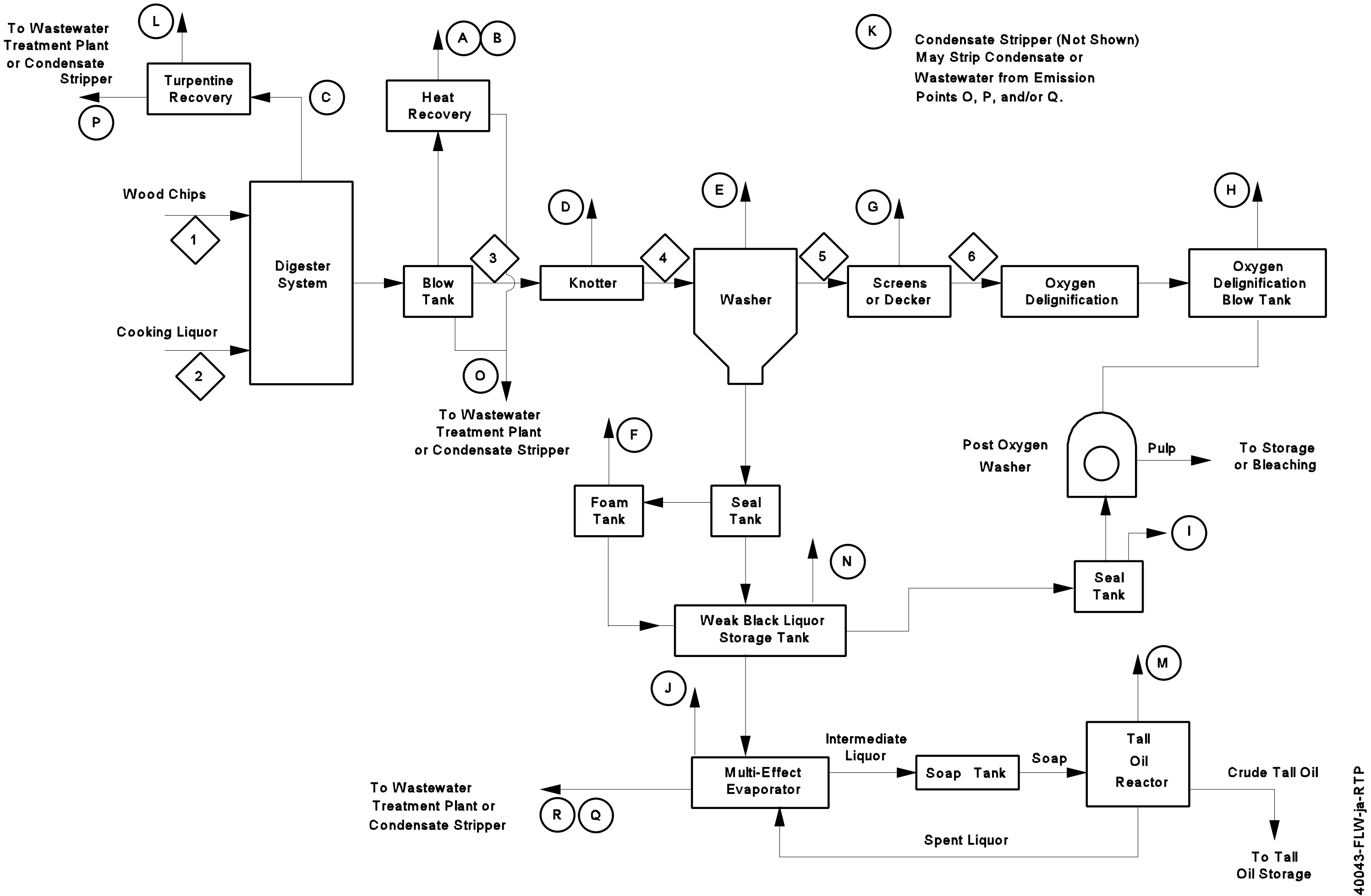
Digester relief vents	Washer filtrate tanks
Turpentine recovery system vents	Decker
Digester blow gas vents	Screen
Noncondensible gas system vents	Weak black liquor storage tank
Evaporator noncondensible gas vent	Recovery furnace stack
Evaporator hotwell gas vent	Slaker/causticizer vents
Knotter	Lime kiln stack
Brownstock or pulp washer	Bleach plant vents
Washer foam tanks	Papermachine vents

Source: Reference 173.

Cooking and Evaporation

The pulping or cooking process begins with the digester, which is a pressure vessel that is used to chemically treat chips and other cellulosic fibrous materials (such as straw, bagasse, rags, etc.) under elevated temperature and pressure to separate fibers from each other. This digestion process frequently takes place in an aqueous chemical solution (frequently a white liquor solution of sodium hydroxide and sodium sulfide). The digestion process may be batch or continuous. After cooking the liquor containing the cooking chemicals and lignin is separated from the pulp and sent to a series of evaporators for concentration.

The entire digester and black liquor evaporator system includes (a) the outlet to the incinerator for the low-volume-high-concentration (LVHC) gases that are commonly collected and routed to such an incineration device, (b) chip bin exhaust vents, and (c) other miscellaneous digester and evaporator system emission points. These systems were combined since all kraft mills collect and incinerate digester relief gases (Vent C), digester blow tank and accumulator gases (Vent A [continuous] and Vent B [batch process]), and evaporator



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 6-7. Typical Kraft Pulp-making Process with Chemical Recovery

Source: Reference 171.

condenser vents (Vent J). The gases at these emission points are assumed to be routed to the combustion device and the benzene reduced by 98 percent.[171]

Deknotting and Prewash Screening

The pulp from the blow tank enters a knotter where knots (pieces of undigested wood) are removed prior to pulp washing in order to produce a higher-quality chemical pulp (Emission Point D).[171] The pressure knotter and pre-washer screening system includes all the equipment following the digester system (i.e., post blow tank) and preceding the first stage of brown stock washing. There are two types of knotters typically used in the industry, open and pressurized. The air flow across the two types varies. Open knotters have a greater flow and, therefore, are expected to have higher emissions than pressurized knotters. Knotter systems typically include equipment such as knot drainer hoods, knot tanks, knot elevators, and screened stock chests. Not every piece of equipment is necessarily vented to the atmosphere (Emission Point D). The emission factor presented is based on the assumption of a pressurized knotter and pre-washing screening system.

Brown Stock Wash

Pulp that has been through the blow tank and knotter is then washed with water in the brownstock washing process. The purpose of washing is to remove black liquor from the pulp so as to recover the cooking chemicals sodium and sulfur and to avoid contamination during subsequent processing steps. The brown stock washing system includes all the brown stock washers, associated filtrate tanks, vacuum pump exhausts, and any interstage storage chests that follow pre-washer screening. In washing, water (fresh or recycled) is used to rinse the pulp and recover the black liquor. There are two basic types of brown stock washing systems, the rotary vacuum drum system and the more advanced pressure or diffusion washers. Emissions from the washing process occur as compounds entrained in the pulp and black liquor slurry volatilize (Emission Point E).

The diluted or “weak” black liquor is recovered in a washer filtrate tank and sent to the evaporator area. A washer foam tank is typically used to capture the foam separated in the filtrate tank. Foam is formed when soap, which is dissolved by the caustic cooking liquors, goes through the washing process. In general, defoaming is completed in the foam tank using centrifugal or mechanical force to break up the foamed mass. This force allows air trapped in the foam mass to vent to the atmosphere from the washer foam tank (Emission Point F). The defoamed weak black liquor is routed to a weak black liquor storage tank (Emission Point N) before it is typically piped to the evaporator area.[171]

Screening and Decking

Screening is performed to remove oversized particles from the pulp slurry after washing the pulp and prior to the papermaking process. The decker is a washing and thickening unit that follows brown stock washing and precedes oxygen delignification (if present), bleaching (if present), or the paper machines. The decker unit is assumed to consist of a drum and a filtrate tank, both of which are assumed to be vented to the atmosphere. The emissions from each part of this decker unit (i.e., both the washer and the filtrate tank) fall within the range of emissions reported for individually tested decker washers and decker filtrate tanks and is therefore assumed to be representative.

Decker vents may be either hooded (an open space above the decker with a hood covering the unit) or well-enclosed (tightly fitted hood around the unit, no open space except through the hood). Hooded deckers are likely to have a much greater air flow across the decker, and therefore are expected to have greater emissions (Emission Point G).

Oxygen Delignification

Following the screening and/or decking, delignification of pulp with oxygen (called oxygen delignification) prior to bleaching is sometimes used. By removing more of the lignin from the pulp, this pretreatment step helps to reduce the amount of chemicals used by the bleach plant.

The oxygen delignification (OD) system begins with the oxygen reactor and associated blow tank (Emission Point H). This system includes a series of two washers and/or presses following the oxygen reactor blow tank, each with a filtrate tank. An interstage storage chest located between the first and second washers and/or presses is also a common configuration.

Pulp Storage Tank

Pulp storage tanks refers to the large bulk storage tanks following OD (if present) or brown stock washers that store the pulp that is to be routed to the bleach plant or to the paper machines. One pulp storage tank is assumed to be present for each pulping line.

Chemical Recovery and Causticizing

The chemical recovery and causticizing area of the mill is where strong black liquor recovered from the evaporators and concentrators is converted into white liquor for reuse in the digesters. This system includes all the equipment associated with chemical recovery, beginning with the recovery furnace, the smelt dissolving tanks and ending with the white liquor clarifier.

The chemical recovery and causticizing area is an example of a mill system where the number of pieces of equipment tested was driving the emissions. In other words, if one mill tested all the components of the recovery loop, that mill would show higher emissions for the causticizing area system. The causticizing area system can be broken down into the following subsystems:

Recovery furnace. Strong black liquor from the multiple effect evaporators is concentrated from 50 to about 70 percent solids either in a concentrator or in a direct contact evaporator before being fired in a recovery furnace. The organics in the liquor provide the energy required to both make steam and to capture the inorganic chemicals as smelt at the bottom of the furnace.

Smelt dissolving tank. Smelt from the recovery furnace is fed into the tank where it is dissolved by weak wash. Smelt dissolving tanks are typically equipped with a venturi scrubber for particulate control. Weak wash from the lime mud washer is often used as the make-up solution in the scrubber, with spent scrubbing solution flowing into the dissolving tank.

Green liquor clarifier. Effluent from the smelt dissolving tank (green liquor) enters a clarifier. Dregs are drained off the bottom of the clarifier, and the clarified green liquor passes on to a slaker.

Slaker and causticizers. Green liquor from the green liquor clarifier is converted into white liquor by adding lime in the slaker and causticizers. Emissions from the causticizers and the slaker are typically routed to a common venturi scrubber with green liquor or fresh mill water as the scrubbing medium.

White liquor clarifier. White liquor is clarified and the clarified white liquor is sent to storage. The bottoms from the white liquor clarifier (lime mud) are sent to a mud washer.

Lime mud washer system. Lime mud from the white liquor clarifier is washed here with fresh mill water. The wash water effluent from the mud washer is termed weak wash which is used in the smelt dissolving tank. The lime mud washer system includes the actual washer plus all associated equipment such as dilution tanks, pressure filters, and mix tanks. If condensates are used as the wash water, the emissions could be much higher, depending on the quality of the condensates.

Lime kiln. The lime kiln accepts washed lime mud and calcines it to produce lime. This lime in turn is fed to the slaker, and the cycle is repeated. The lime kiln is typically equipped with a venturi scrubber using fresh mill water as the scrubbing medium for particulate emission control. Alternatively, particulates may be controlled by an electrostatic precipitator (ESP).

Co-product Recovery

Turpentine and soap (tall oil) are two saleable coproducts that may be byproducts of the pulping process. Turpentine is recovered from digester relief gases when resinous softwoods such as pines are pulped. In general, the digester relief gases are vented to a condenser to reduce the gas moisture content and to a cyclone separator to remove any small wood chips or fines. Emissions are generated as turpentine and water and are separated in a decanter. These emissions are released through the turpentine recovery system vent. Tall oils are recovered in a reactor, but emissions are expected to be low because the weak black liquor has already been stripped of volatiles in the evaporation process (Vent M).[171]

Bleaching

Bleaching is the process of further delignifying and whitening pulp by chemically treating it to alter the coloring matter and to impart a higher brightness.

To enhance the physical and optical qualities (whiteness and brightness) of the pulp, one of two types of chemical bleaching is used. The first type of bleaching, called brightening, uses selective chemicals (such as hydrogen peroxide) that destroy chromatographic groups but do not materially attack the lignin. Brightening produces a product with a temporary brightness (such as newspaper). In the second type (true bleaching), oxidizing chemicals (such as chlorine, chlorine dioxide, and sodium hypochlorite) are used to remove residual lignin, resulting in a high-quality, stable paper pulp.[171]

The most common bleaching and brightening agents are chlorine, chlorine dioxide, hydrogen peroxide, oxygen, caustic (sodium hydroxide) and sodium hypochlorite. Typically, the pulp is treated with each chemical in a separate stage. One example stage which illustrates the use of one bleaching agent is shown in Figure 6-8.[171] Each stage includes a tower where the bleaching occurs (Vent A). The washer (Vent B) removes the bleaching chemicals and dissolved lignins from the pulp prior to entering the next stage. The seal tank (Vent C) collects the washer effluent to be used as wash water in other stages or to be sewered (Vent D).[171]

Paper Machine

Paper machine emissions include all the emissions from the various pieces of equipment following pulp storage and/or bleaching that are used to turn the pulp into a finished paper product. The data show that the factor driving emissions from paper machines is paper type (i.e., unbleached versus bleached).

Wastewater/Condensate Treatment

In addition to process vents, emissions also occur from the treatment of wastewater or condensates generated during the making of pulp and paper (Emission Point O).[171]

6.7.2 Benzene Emissions from Pulp, Paper and Papermaking Processes

EPA published MACT standards for the pulp, paperboard, and papermaking industry on April 15, 1998.[173] While the supporting documentation for these standards does not specifically call out benzene as a major pollutant from pulp and paper mills, it

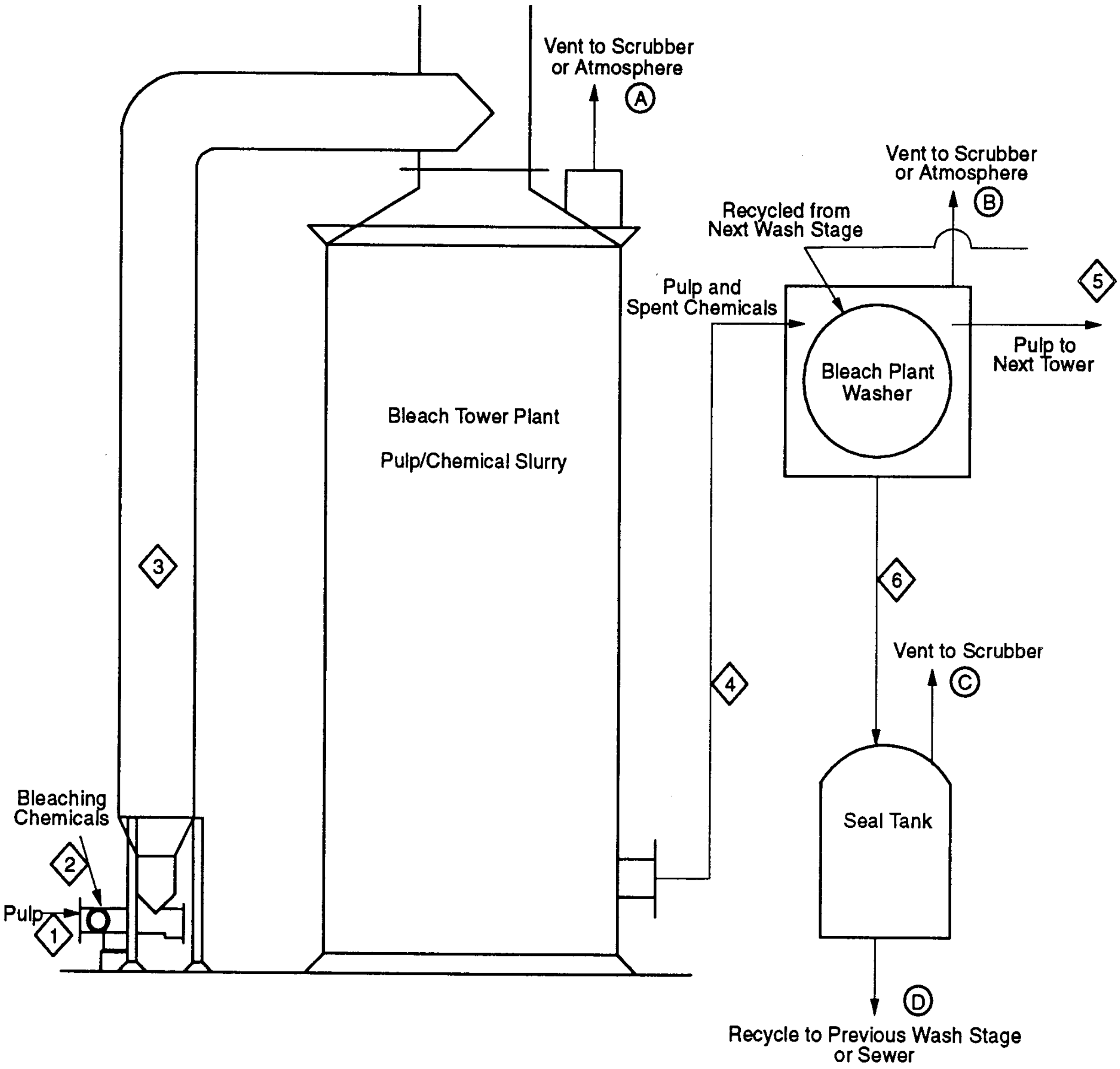


Figure 6-8. Typical Down-flow Bleach Tower and Washer

Source: Reference 171.

does mention benzene as being emitted from this source and as a pollutant that would be affected by VOC reductions achieved by compliance with the standards.

Emission points may include the digester relief vents, digester blow gas vents, brownstock or pulp washer, screen, as well as bleaching and brightening. Once washing has occurred, it is expected that benzene would be found in the wastewater, which is recycled for use throughout the process. Such uses of this recycled water include as a solvent for digesting chemicals, as the pulp digesting medium, as pulp waste water, and as a diluent for screening, cleaning, and subsequent pulp processing. Benzene emissions would then be expected from each step in the pulping process where this recycled wastewater is used. Note that the extent of benzene emissions (as with any HAP) during the pulping process is a function of the level of pulp production, type of digestion (batch or continuous), and the type of wood pulped.

6.8 SYNTHETIC GRAPHITE MANUFACTURING

Synthetic graphite is a composite of coke aggregate (filler particles), petroleum pitch (binder carbon), and pores (generally with a porosity of 20 to 30 percent). Synthetic graphite is a highly refractory material that has been thermally stabilized to as high as 5,400°F (3,000°C). Graphite is a valuable structural material because it has high resistance to thermal shock, does not melt, and possesses structural strength at temperatures well above the melting point of most metals and alloys. Applications for synthetic graphite include the following industries: aerospace (e.g., nose cones, motor cases, and thermal insulation), chemical (e.g., heat exchangers and centrifugal pumps and electrolytic anodes for the production of chlorine and aluminum), electrical (e.g., telephone equipment products, electrodes in fuel cells and batteries, and contacts for circuit breakers and relays), metallurgical (e.g., electric furnace electrodes for the production of iron and steel, furnace linings, ingot molds, and extrusion dies), nuclear (e.g., moderators, thermal columns, and fuel elements), and miscellaneous (e.g., motion picture projector carbons).[174]

The number of facilities manufacturing synthetic graphite in the United States was not identified.

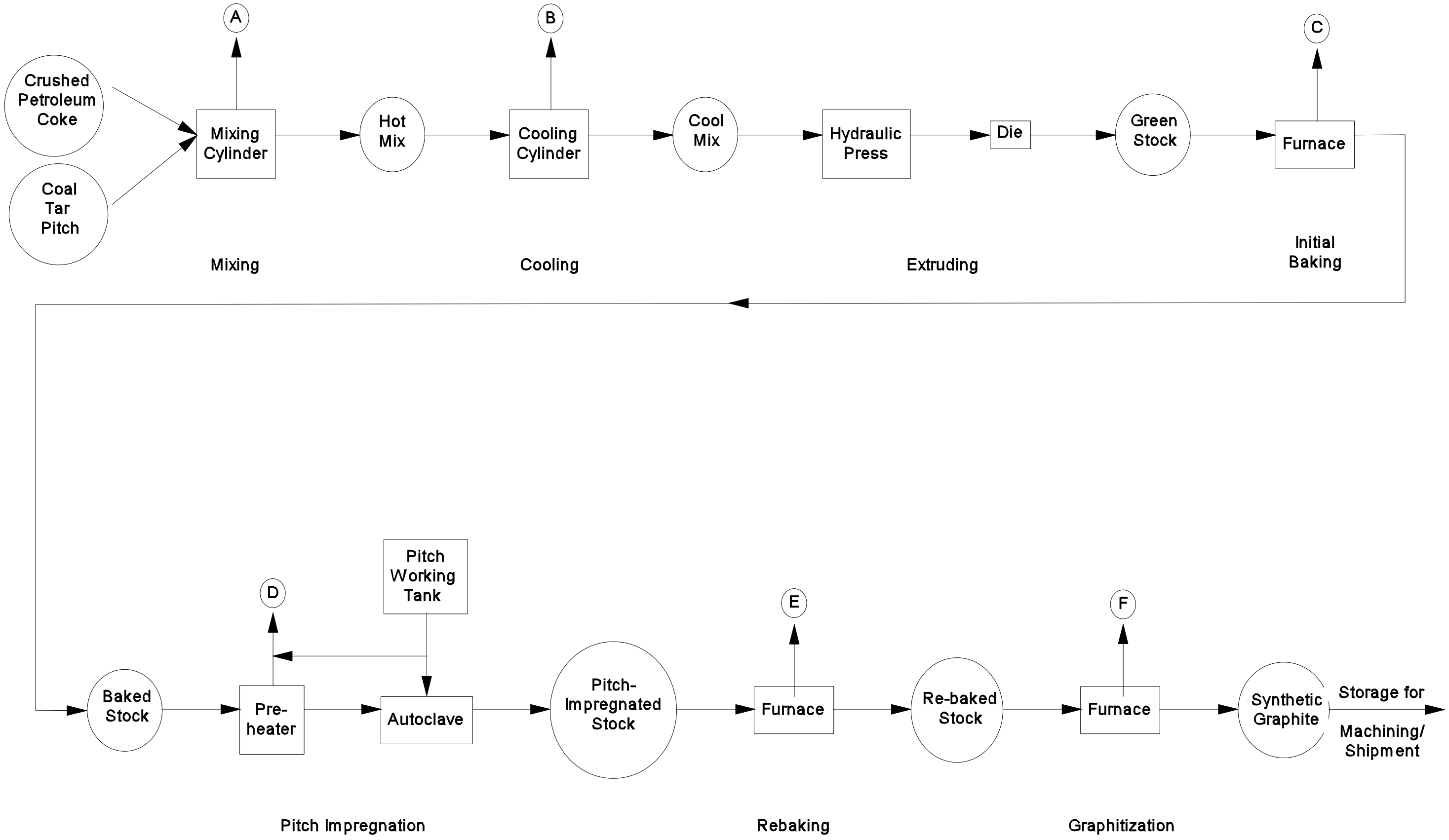
6.8.1 Process Description for Synthetic Graphite Production

Synthetic graphite is produced from calcined petroleum coke and coal tar pitch through a series of processes including crushing, sizing, mixing, cooling, extruding, baking, pitch impregnation, rebaking, and graphitization. Throughout the process of thermal conversion of organic materials to graphite, the natural chemical driving forces cause the growth of larger and larger fused-ring aromatic systems, and ultimately result in the formation of the stable hexagonal carbon network of graphite. A process flow diagram of the synthetic graphite manufacturing process is provided in Figure 6-9.[174,175]

Calcined petroleum coke (i.e., raw coke that has been heated to temperatures above 2,200°F (1,200°C) to remove volatiles and shrink the coke to produce a strong, dense particle) is crushed and screened to obtain uniform-sized fractions for the formulation of dry ingredient. Coal tar pitch is stored in heated storage tanks and is pumped to the mixing process, as needed, as the liquid ingredient. The dry ingredient is weighed and loaded, along with a metered amount of coal tar pitch, into a heated mixing cylinder (heated to at least 320°F [160°C]), where they are mixed until they form a homogeneous mixture. During the mixing process, vapors (Vent A in Figure 6-9) are ducted to a stack where they are discharged to the atmosphere.[174,175]

The heated mixture is sent to a cooling cylinder which rotates, cooling the mixture with the aid of cooling fans to a temperature slightly above the softening point of the binder pitch. Vapors from the cooling process (Vent B in Figure 6-9) are often vented to a PM control device before being vented to the atmosphere.[174,175]

The cooled mixture is charged to a hydraulic press, then pressed through a die to give the mixture the desired shape and size. The extruded mixture is referred to as “green



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

940075-FLW-ja-RTP

Figure 6-9. Process Flow Diagram for Manufacture of Synthetic Graphite

Source: Reference 174.

stock." The green stock is placed in cooling ponds, where it is further cooled and awaits shipping to the baking process.[175]

In general, for producing graphite with high-performance applications, the baking process consists of three stages: initial baking, pitch impregnation, and rebaking. In producing graphite for some lower-performance applications, the pitch impregnation step is excluded. This baking process chemically changes the binder pitch within the green stock by forming a permanent carbon bond between the coke particles. By using a slow heating rate, the baking process removes most of the shrinkage in the product associated with pyrolysis of the pitch binder. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The impregnation step deposits additional coke in the open pores of the baked stock, thereby improving the properties of the subsequent graphite product. The product (later referred to as "rebaked stock") is a solid, rigid body that is much harder and stronger than the green stock.[174,175]

Initial baking is achieved by placing the green stock into a furnace cell (if a recirculating furnace is used) or a can (if a sagger or pit furnace is used) and surrounding the stock with a suitable pack media to support the stock. During the baking process, the furnace temperature is increased incrementally (e.g., starting at 350 to 400°F [175 to 200°C] and ending at 400 to 570°F (200 to 300°C]). The furnace temperature varies according to the stock. During the initial baking process, fumes (Vent C in Figure 6-9) are often vented to an afterburner prior to discharge to the atmosphere.[175]

Baked stock is pre-heated in a pre-heater to a desired temperature prior to impregnation with pitch. Fumes from the pre-heater (Vent D in Figure 6-9) are often vented to an afterburner before release to the atmosphere. The pre-heated, baked stock is loaded into autoclaves where a vacuum is pulled. Heated petroleum pitch (or coal tar) is pumped from storage to the autoclave. Vapors from the storage tank for the heated pitch (Vent D in Figure 6-9) are often vented to an afterburner prior to their release to the atmosphere. The baked stock is impregnated with pitch under increased temperature and pressure. The pitch impregnated stock is then stored prior to the rebaking process. Many high-performance applications of graphite (e.g., nuclear and aerospace applications) require that the baked stock be multiply pitch-treated to achieve the greatest possible assurance of high performance.[174,175]

Rebaking is similar to initial baking. The same types of furnaces are used for both baking and rebaking. The pitch impregnated stock is heated to higher temperatures than the green stock (e.g., from 210°F [100°C] to 900 to 1,800°F [500 to 1,000°C]). During the rebake process, fumes (Vent E in Figure 6-9) are often vented to an afterburner. Off-gases from the afterburner are vented to the atmosphere.[174,175]

The last step in the manufacturing process is graphitization. In this step, electricity is used to create temperatures, by resistance, high enough to cause physical and chemical changes in the rebaked stock (the carbon atoms in the petroleum coke and pitch orient into the graphite lattice configuration). As a result of this step, the hard-baked stock becomes softer and machinable, the stock becomes an electrical conductor, and impurities vaporize.[174,175]

In the graphitization step, rebaked stock is placed in a furnace, either perpendicular or parallel to the direction of the current flow, depending on the type of furnace used. Electricity is used to create temperatures in the stock exceeding 4,350°F (2,400°C), and preferably 5,070 to 5,450°F (2,800 to 3,000°C). After graphitization, the stock (i.e., synthetic graphite) is stored for on-site use or shipment. Fumes from the furnace are vented to the atmosphere (Vent F in Figure 6-9).[174,175]

6.8.2 Benzene Emissions from Synthetic Graphite Production[175]

There is limited information currently available about benzene emissions from synthetic graphite production plants. Emission factors for the mixing and cooling cylinders (Vents A and B in Figure 6-9) are provided in Table 6-27.[175] Additionally, one emission test report indicated that benzene is emitted from the initial baking, rebaking, and

TABLE 6-27. EMISSION FACTORS FOR SYNTHETIC GRAPHITE PRODUCTION

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/lb (g/kg)[a]	Emission Factor Rating
3-XX-XXX-XX	Synthetic Graphite	Mixing Cylinder (Vent A)	Uncontrolled	2.82×10^{-4} (1.41×10^{-4})	D
3-XX-XXX-XX	Synthetic Graphite	Cooling Cylinder (Vent B)	Uncontrolled	3.70×10^{-4} (1.8×10^{-4})	D

Source: Reference 175.

[a] Emission factor is lb (g) of benzene emitted per lb (kg) of synthetic graphite produced.

pitch-impregnation processes (Vents C through E in Figure 6-9); however, emission factors could not be developed.[175]

6.8.3 Control Technologies for Synthetic Graphite Production[175]

As discussed in Section 6.9.1, afterburners may be used to control emissions of unburned hydrocarbons from the initial baking and rebaking furnace (Vents C and E in Figure 6-9), as well as the preheater and heated storage tank used for the pitch impregnation process (Vent D in Figure 6-9). Data regarding the use of afterburners in this application were not available; however, it is likely that the afterburners would reduce benzene emissions. Additionally, an ESP may be used to control particulate emissions from the cooling cylinder; however, it is unlikely that an ESP would reduce benzene emissions.

6.9 CARBON BLACK MANUFACTURE

The chemical carbon black consists of finely divided carbon produced by the thermal decomposition of hydrocarbons in the vapor phase, unlike coke that is produced by the pyrolysis of solids. Carbon black is a major industrial chemical used primarily as a reinforcing agent in rubber compounds, which accounts for over 90 percent of its use. It is used primarily in tires (both original equipment and replacement), which accounts for over 70 percent of its use.[176] Other tire-related applications include inner tubes and retreads. Other uses include automotive hoses and belts, wire and cable, roofing, pigment in inks and coatings and as a plastic stabilizer.[176] As of January 1994, there were 24 carbon black manufacturing facilities in the United States. Over 75 percent of all carbon black production occurs in the States of Texas and Louisiana (36 and 40 percent, respectively). The location of all facilities and their estimated annual production capacities in 1993 are provided in Table 6-28.[177] The manufacture of carbon black is of potential concern for benzene emissions because the predominantly used production process involves the combustion of natural gas and the high-temperature pyrolysis of aromatic liquid hydrocarbons.

TABLE 6-28. LOCATIONS AND ANNUAL CAPACITIES OF CARBON BLACK PRODUCERS IN 1994

Company	Facility Location	Annual Capacity, millions of pounds (millions of kg)
Cabot Corporation	Franklin, LA	260 (118)
	Pampa, TX	60 (27)
	Villa Platte, LA	280 (127)
	Waverly, WV	180 (82)
Chevron Corporation	Cedar Bayou, TX	20 (9)
Columbian Chemicals Company	El Dorado, AR	120 (54)
	Moundsville, WV	170 (77)
	North Bend, LA	220 (100)
	Ulysses, KS	85 (39)
Degussa Corporation	Arkansas Pass, TX	180 (82)
	Belpre, OH[a]	130 (59)
	New Iberia, LA	200 (91)
Ebonex Corporation	Melvindale, MI	8 (3.6)
General Carbon Company	Los Angeles, CA	1 (0.45)
Hoover Color Corporation	Hiwassee, VA	1 (0.45)
J.M. Huber Corporation	Baytown, TX	225 (102)
	Borger, TX	175 (79)
	Orange, TX	135 (61)
Sid Richardson Carbon and Gasoline Company	Addis, LA	145 (66)
	Big Springs, TX	115 (52)
	Borger, TX	275 (125)
Witco Corporation	Phoenix City, AL	60 (27)
	Ponca City, OK	255 (116)
	Sunray, TX	120 (54)
TOTAL		3,420 (1,551)

Source: Reference 177.

[a] Emissions of 81,000 lb/yr (36,741 kg/yr) of benzene reported for 1992.[111]

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

6.9.1 Process Description for Carbon Black Manufacture

Approximately 90 percent of all carbon black produced in the United States is manufactured by the oil-furnace process, a schematic of which is given in Figure 6-10. The process streams identified in Figure 6-10 are defined in Table 6-29.[178,179] Generally, all oil-furnace carbon black plants are similar in overall structure and operation. The most pronounced differences in plants are primarily associated with the details of decomposition furnace design and raw product processing.[178]

In the oil-furnace process, carbon black is produced by the pyrolysis of an atomized liquid hydrocarbon feedstock in a refractory-lined steel furnace. Processing temperatures in the steel furnace range from 2,408 to 2,804°F (1,320 to 1,540°C). The heat needed to accomplish the desired hydrocarbon decomposition reaction is supplied by the combustion of natural gas.[178]

Feed materials used in the oil-furnace process consist of petroleum oil, natural gas, and air. Also, small quantities of alkali metal salts may be added to the oil feed to control the degree of structure of the carbon black.[179] The ideal raw material for the production of modern, high structure carbon blacks is an oil which is highly aromatic; low in sulfur, asphaltenes and high molecular weight resins; and substantially free of suspended ash, carbon, and water. To provide maximum efficiency, the furnace and burner are designed to separate, insofar as possible, the heat generating reaction from the carbon forming reaction. Thus, the natural gas feed (Stream 2 in Figure 6-10) is burned to completion with preheated air (Stream 3) to produce a temperature of 2,408 to 2,804°F (1,320 to 1,540°C). The reactor is designed so that this zone of complete combustion attains a swirling motion, and the oil feed (Stream 1), preheated to 392 to 698°F (200 to 370°C), is sprayed into the center of the zone. Preheating is accomplished by heat exchange with the reactor effluent and/or by means of a gas-fired heater. The oil is cracked to carbon and hydrogen with side reactions producing carbon oxides, water, methane, acetylene and other hydrocarbon products. The heat

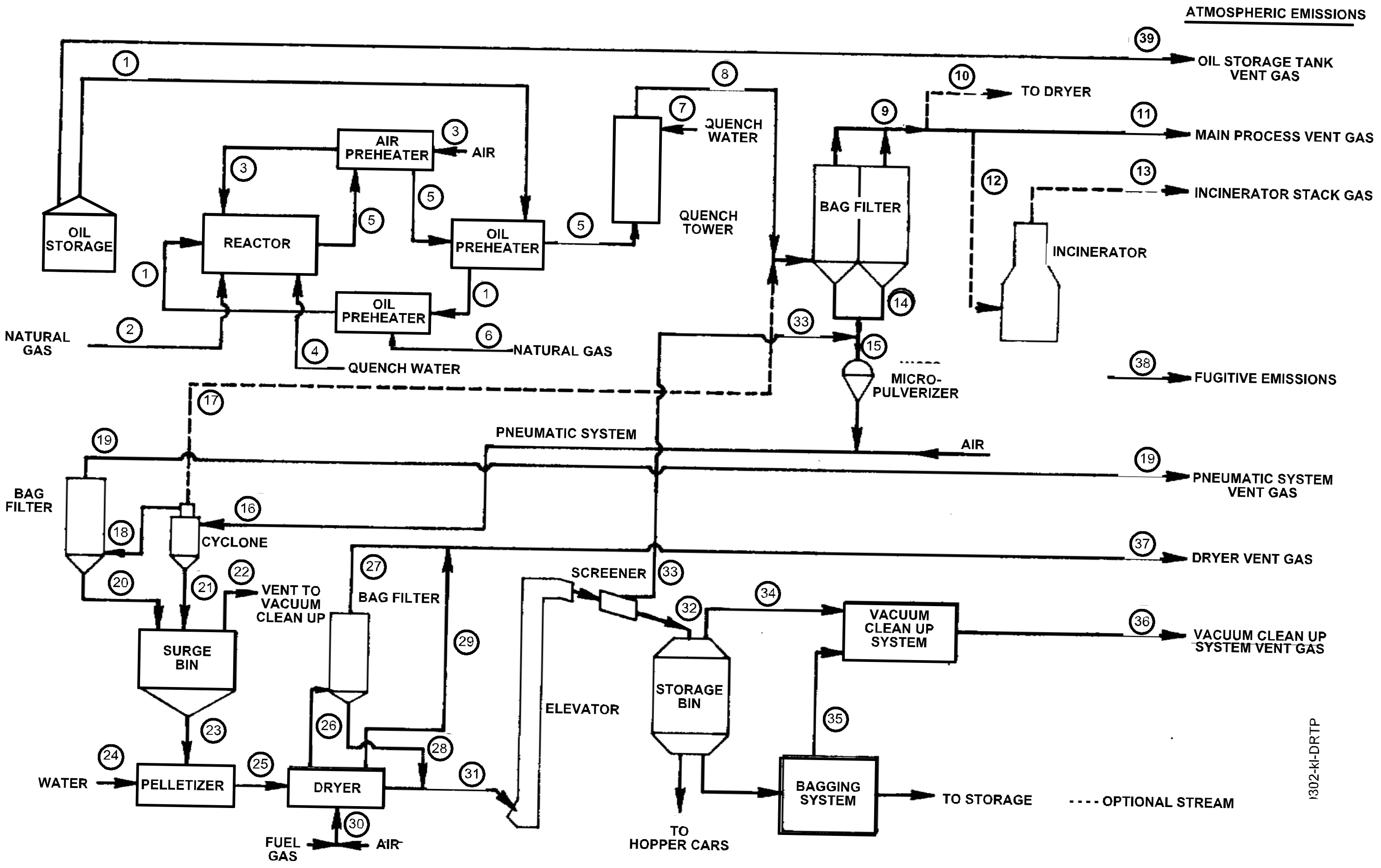


Figure 6-10. Process Diagram for an Oil-Furnace Carbon Black Plant

Source: Reference 179.

TABLE 6-29. STREAM CODES FOR THE OIL-FURNACE PROCESS ILLUSTRATED IN FIGURE 6-10

Stream	Identification	Stream	Identification
1	Oil feed	21	Carbon black from cyclone
2	Natural gas feed	22	Surge bin vent
3	Air to reactor	23	Carbon black to pelletizer
4	Quench water	24	Water to pelletizer
5	Reactor effluent	25	Pelletizer effluent
6	Gas to oil preheater	26	Dryer direct heat source vent
7	Water to quench tower	27	Dryer bag filter vent
8	Quench tower effluent	28	Carbon black from dryer bag filter
9	Bag filter effluent	29	Dryer indirect heat source vent
10	Vent gas purge for dryer fuel	30	Hot gases to dryer
11	Main process vent gas	31	Dried carbon black
12	Vent gas to incinerator	32	Screened carbon black
13	Incinerator stack gas	33	Carbon black recycle
14	Recovered carbon black	34	Storage bin vent gas
15	Carbon black to micropulverizer	35	Bagging system vent gas
16	Pneumatic conveyor system	36	Vacuum cleanup system vent gas
17	Cyclone vent gas recycle	37	Dryer vent gas
18	Cyclone vent gas	38	Fugitive emissions
19	Pneumatic system vent gas	39	Oil storage tank vent gas
20	Carbon black from bag filter		

Source: Reference 178.

transfer from the hot combustion gases to the atomized oil is enhanced by highly turbulent flow in the reactor.[179]

The reactor converts 35 to 65 percent of the feedstock carbon content to carbon black, depending on the feed composition and the grade of black being produced. The yields are lower for the smaller particle size grades of black. Variables that can be adjusted to produce a given grade of black include operating temperature, fuel concentration, space velocity in the reaction zone, and reactor geometry (which influences the degree of turbulence in the reactor). A typical set of reactor operating conditions for high abrasion furnace carbon black is given in Table 6-30.[179]

The hot combustion gases and suspended carbon black are cooled to about 1004°F (540°C) by a direct water spray in the quench area, which is located near the reactor outlet. The reactor effluent (Stream 5 in Figure 6-10) is further cooled by heat exchange in the air and oil preheaters. It is then sent to a quench tower where direct water sprays finally reduce the stream temperature to 446°F (230°C).

Carbon black is recovered from the reactor effluent stream by means of a bag filter unit. The raw carbon black collected in the bag filter unit must be further processed to become a marketable product. After passing through the pulverizer, the black has a bulk density of 1.50 to 3.68 lb/ft^3 (24 to 59 kg/m^3), and it is too fluffy and dusty to be transported. It is therefore converted into pellets or beads with a bulk density of 6.06 to 10.68 lb/ft^3 (97 to 171 kg/m^3). In this form, it is dust-free and sufficiently compacted for shipment.

6.9.2 Benzene Emissions from Carbon Black Manufacture

Although no emission factors are readily available for benzene from carbon black manufacture, one carbon black manufacturer with annual capacity of 130 million pounds (59 million kg) using the oil-furnace process reported benzene emissions of 81,000 lb/yr (36,741 kg/yr) for 1992, which translates to 6.23x10^{-4} lb (2.83x10^{-4} kg) benzene per lb (kg)

TABLE 6-30. TYPICAL OPERATING CONDITIONS FOR CARBON BLACK MANUFACTURE (HIGH ABRASION FURNACE)

Parameter	Value
Rate of oil feed	27 ft^3/hr (0.76 m^3/hr)
Preheat temperature of oil	550°F (288°C)
Rate of air feed	234,944 ft^3/hr (6,653 m^3/hr)
Rate of natural gas feed	22,001 ft^3/hr (623 m^3/hr)
Furnace temperature in reaction zone	2,552°F (1,400°C)
Rate of carbon black production	860 lb/hr (390 kg/hr)
Yield of black (based on carbon in oil feed)	60 percent

Source: Reference 179.

carbon black produced. No regulations applicable to carbon black manufacture were identified that would affect benzene emissions. The emission factor is given in Table 6-31.[111]

TABLE 6-31. EMISSION FACTOR FOR CARBON BLACK MANUFACTURE

SCC Number	Description	Emission Factor (lb benzene/lb carbon black)	Emission Factor Rating
	Oil Furnace Process	6.23×10^{-4}	

Source: Reference 111.

6.10 RAYON-BASED CARBON FIBER MANUFACTURE

Rayon-based carbon fibers are used primarily in cloth for aerospace applications, including phenolic impregnated heat shields and in carbon-carbon composites for missile parts and aircraft brakes.[180] Due to their high carbon content, these fibers remain stable at very high temperatures.

A list of U.S. producers of rayon-based carbon fibers is given in Table 6-32.[177]

TABLE 6-32. RAYON-BASED CARBON FIBER MANUFACTURERS

Manufacturer	Location
Amoco Performance Products, Inc.	Greenville, SC
BP Chemicals (Hitco) Inc. Fibers and Materials Division	Gardena, CA
Polycarbon, Inc.	Valencia, CA

Source: Reference 177.

6.10.1 Process Description for the Rayon-Based Carbon Fiber Manufacturing Industry

There are three steps in the production process of rayon-based carbon cloth:

- Preparation and heat treating;
- Carbonization; and
- High heat treatment (optional).[180]

In the preparation and heat treating step, the rayon-based cloth is heated at 390 to 660°F (200 to 350°C). Water is driven off (50 to 60 percent weight loss) during this step to form a char with thermal stability. In the carbonization step, the cloth is heated to 1,800 to 3,600°F (1,000 to 2,000°C), where additional weight is lost and the beginnings of a carbon layer structure is formed. To produce a high strength rayon-based fiber, a third step is needed. The cloth is stretched and heat treated at temperatures near 5,400°F (3,000°C).[180]

6.10.2 Benzene Emissions from the Rayon-Based Carbon Fiber Manufacturing Industry

Benzene emissions occur from the exhaust stack of the carbon fabric dryer, which is used in carbonization of the heat treated rayon.[180] An emission factor for this source is given in Table 6-33.[181]

6.10.3 Controls and Regulatory Analysis

No controls or regulations were identified for the rayon-based carbon fiber manufacturing industry.

6.11 ALUMINUM CASTING

The aluminum casting industry produces aluminum products, such as aluminum parts for marine outboard motors, from cast molds. Sections 6.11.1 through 6.12.3 describe the aluminum casting process, benzene emissions resulting from this process, and air emission control devices utilized in the process to reduce benzene emissions.

The number of aluminum casting facilities in the United States was not identified.

6.11.1 Process Description for Aluminum Casting Facilities

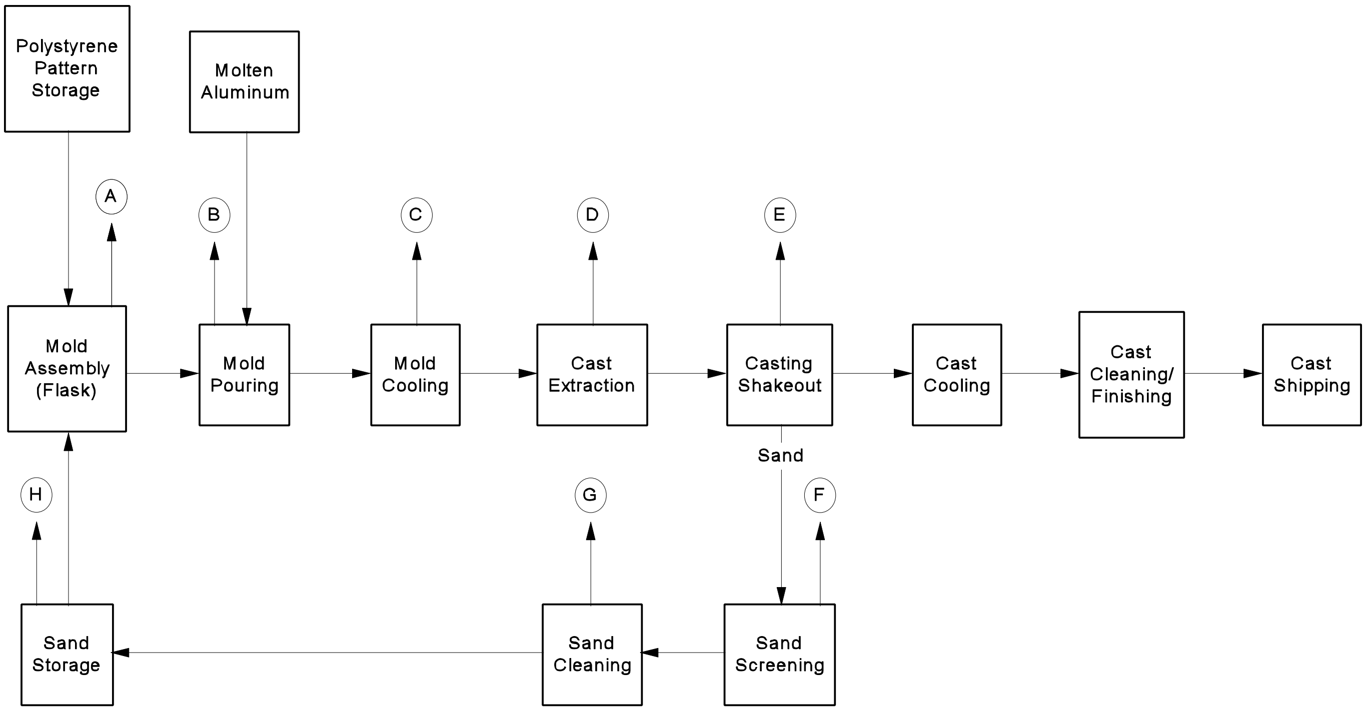
A common method for making the mold for aluminum motor parts is to utilize polystyrene foam patterns or “positives” of the desired metal part. The basic principle of the casting operation involves the replacement of the polystyrene pattern held within a sand mold with molten metal to form the metal casting. Figure 6-11 presents a simplified flow diagram for a typical aluminum casting facility utilizing polystyrene patterns.

TABLE 6-33. EMISSION FACTOR FOR RAYON-BASED CARBON MANUFACTURE

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/lb (g/kg)[a]	Emission Factor Rating
3-64-920-000	Rayon-based Carbon Fibers	Carbon Fabric Dryer	Uncontrolled	7.17×10^{-7} (7.17×10^{-4})	B

Source: Reference 181.

[a] Emission factor is lb (g) of benzene emitted per lb (kg) of rayon-based carbon produced.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 6-11. Flow Diagram of a Typical Aluminum Casting Facility

The aluminum casting process essentially consists of four stages: (1) mold assembly, (2) casting (i.e., mold pouring, mold cooling, and cast extraction), (3) cast cleaning and finishing (i.e., casting shakeout, cast cooling, and cast cleaning and finishing), and (4) sand handling (i.e., sand screening and cleaning). A polystyrene foam pattern is first coated with a thin layer of ceramic material for stability. The polystyrene foam pattern is placed within a metal flask. Sand is poured into the flask, surrounding and covering the pattern. The sand is compacted around the polystyrene pattern to form the mold. Low levels of benzene may be emitted from the sand fill operation, depending on the residue of organic matter remaining on the sand recycled from the casting shakeout process step. These emissions may be collected in a fume hood and vented to the atmosphere (Vent A in Figure 6-11).

The metal flask is moved to the pouring station where molten aluminum is poured into the mold. The foam vaporizes as it is displaced by the molten aluminum, which fills the cavity left within the sand mold. A majority of the foam vapors migrate into the sand and remain trapped in the sand until the casting shakeout process. Some of the vapors are released during the mold pouring event. These vapors are collected in a fume hood and vented to the atmosphere (Vent B in Figure 6-11).

The poured molds are conveyed within the flasks along a cooling conveyor, allowing the aluminum casting to harden. The cooling process may result in benzene emissions (as depicted as Vent C in Figure 6-11).

When the casting has formed and cooled sufficiently, the cast is extracted from the metal flask. Benzene may be emitted from this process step. The emissions are captured and vented to the atmosphere (Vent D in Figure 6-11).

The casting and flask are moved to the casting shake-out area, where sand used in forming the mold is dumped from the flask and removed from the casting by utilizing vibration to loosen the compacted sand. The collected sand (including pieces of molding) are shaken, breaking up the sand mold. The majority of benzene emissions occur during this step. Vapors released by breaking the sand molds are captured and either treated with a catalytic incinerator or released to the atmosphere (Vent E in Figure 6-11).

The shaken sand is sent through a screen, then transported to a cleaning process for removal of remaining residue, such as a fluidized bed. Benzene emissions may be emitted during these process steps (depicted as Vents F and G in Figure 6-11). The cleaned sand is then transported to storage for reuse in the process.

Meanwhile, the casting, which has just undergone shakeout, is sent through a series of cooling, cleaning, and finishing steps to produce a final product. Benzene may be emitted from these process steps. The final products are stored to await shipping off-site.

6.11.2 Benzene Emissions From Aluminum Metal Casting

Benzene emissions from aluminum metal casting are produced by the vaporization of the polystyrene foam patterns used to form the molds, resulting from contact of the foam with molten aluminum. As described in Section 6.11.1, the polystyrene foam vapors migrate into the sand inside the mold, becoming trapped in the sand mold. As a result, most benzene emissions from the process are associated with sand handling activities, such as casting shake-out and sand screening. However, additional benzene is emitted from the casting steps, including mold pouring, mold cooling, and cast extraction.

Two test reports from two aluminum casting facilities were used to develop benzene emission factors.[182,183] Both facilities utilized polystyrene foam patterns in their casting operations. One facility was equipped with a catalytic incinerator on its casting shakeout operation and a fabric filter on its sand cleaning operation (utilizing a fluidized bed for sand cleaning).[183] The other facility was equipped with fabric filters on its mold assembly operation (i.e., filling the flask with sand), cast extraction, casting shakeout, and sand screening operations.[182]

General facility benzene emissions were measured at the two facilities. For one facility, general facility emissions consisted of emissions from the mold assembly, cast extraction, casting shakeout, sand screening, and sand storage operations, all of which were controlled by fabric filters.[182] For the other facility, general facility emissions consisted of emissions from the mold assembly, mold pouring, cast extraction, casting shakeout, and sand cleaning operations, and only the cleaning operation was controlled with a fabric filter.[183] Additionally, benzene emissions from the casting shakeout operation were measured both before and after the catalytic incinerator, yielding a benzene control efficiency of 89 percent.[183] The emission factors associated with these emission data are shown in Table 6-34.[181]

6.11.3 Control Technologies for Aluminum Casting Operations

Fabric filters are most commonly utilized for controlling emissions from aluminum casting operations; however, these control devices are not utilized for controlling benzene emissions, but are rather used to control fugitive dust emissions from sand handling. The only control device identified for controlling benzene emissions is a catalytic incinerator. As specified in Section 6.12.2, it has been demonstrated that catalytic incinerators achieve 89 percent reduction in benzene emissions.

No regulations were identified that control emissions of benzene from aluminum casting operations. However, a MACT standard for control of HAPs from secondary aluminum facilities is currently underway.

6.12 ASPHALT ROOFING MANUFACTURING

The asphaltic material that is obtained toward the end of the process of fractional distillation of crude oil is mainly used as asphalt paving concrete (discussed in Section 7.9) and for asphalt roofing. The asphalt roofing manufacturing process and the emissions associated with its manufacture are described in this section.

TABLE 6-34. EMISSION FACTORS FOR ALUMINUM CASTING

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
3-04-001-99	Secondary Metals- Secondary Aluminum- Not Classified	General Facility (Vents A, D, E, F, and H)	Uncontrolled	7.08×10^{-2} (3.54×10^{-2})	D
		General Facility (Vents A, B, D, E, and G)	Uncontrolled	7.47×10^{-2} (3.73×10^{-2})	D
3-04-001-14	Secondary Metals- Secondary Aluminum- Pouring/Casting	Casting Shakeout Operation	Catalytic Incinerator	6.09×10^{-3} (3.45×10^{-3})	D
			Uncontrolled	5.48×10^{-3} (2.74×10^{-2})	D

Source: Reference 181.

[a] Emission factor is lb (kg) of benzene emitted per ton (Mg) of molten aluminum poured.

In 1992, there were 98 asphalt roofing manufacturing plants operating in the United States. A list of all current facilities, as identified by the Asphalt Roofing Manufacturers Association, is provided in Table 6-35.[184] Total national production in 1993 of asphalt roofing materials (saturated felts) was estimated at 557,487 tons (505,749 Mg).[184] States containing a relatively significant number of roofing plants include California (14), Texas (14), Ohio (6), and Alabama (5). These four states contain approximately 40 percent of the total number of roofing facilities. The majority of all plants nationwide are located in urban as opposed to rural areas.

6.12.1 Process Description

The production of asphalt roofing materials is common owing to the widespread usage of these materials in the United States. The asphalt roofing industry manufactures asphalt-saturated felt rolls, shingles, roll roofing with mineral granules on the surface, and smooth roll roofing, which may contain a small amount of mineral dust or mica on the surface. Most of these products are used in roof construction, but small quantities are used in walls and other building applications.[185]

The asphaltic material derived from crude oil and used to make asphalt roofing products is also called asphalt flux. The handling and storing of asphalt flux is a potential source of benzene emissions. Asphalt is normally delivered to an asphalt roofing plant in bulk by pipeline, tanker truck, or railcar. Bulk asphalt delivered in liquid form may range in temperature from 200 to 400°F (93 to 204°C), depending on the type of asphalt and local practice.[186-188]

With bulk liquid asphalt, the most common method of unloading is to couple a flexible pipe to the tanker and pump the asphalt directly into the appropriate storage tanks. The tanker cover is partially open during the transfer. Because this is a closed system, the

TABLE 6-35. ASPHALT ROOFING MANUFACTURERS

Company	Roofing Plant Location
Allied-Signal Incorporated	Detroit, MI Fairfield, AL Ironton, OH
Bird Incorported	Norwood, MA
The Celotex Corporation	Camden, AR Fremont, CA Birmingham, AL Goldsboro, NC Houston, TX Lockland, OH Perth Amboy, NJ San Antonio, TX Los Angeles, CA Memphis, TN
Certainteed Corporation	Shakopee, MN Oxford, NC Milan, OH
Elk Corportion of America	Ennis, TX Tuscaloosa, AL
Fields Corporation	Kent, WA Tacoma, WA
GAF Building Materials, Inc.	Baltimore, MD Dallas, TX Erie, PA Fontana, CA Millis, MA Minneapolis, MN Mobile, AL Mount Vernon, IN Savannah, GA Tampa, FL
Gate Roofing Manufacturing, Inc.	Green Cove Springs, FL
Georgia-Pacific Corporation	Ardmore, OK Daingerfield, TX Franklin, OH Hampton, GA Quakertown, PA

(continued)

TABLE 6-35. CONTINUED

Company	Roofing Plant Location
Globe Building Materials	Whiting, IN St. Paul, MN Chester, WV
GS Roofing Products Company, Inc.	Charleston, SC Ennis, TX Little Rock, AR Martinez, CA Peachtree City, GA Portland, OR Shreveport, LA Wilmington, CA
Herbert Malarkey Roofing Company	Portland, OR
IKO Chicago Incorporated	Chicago, IL
IKO Production Incorporated	Franklin, OH Wilmington, DE
Koppers Industries, Incorporated	Birmingham, AL Chicago, IL Follensbee, WV Houston, TX
Leatherback Industries	Alburquerque, NM Hollister, CA
Lunday-Thagard Company	South Gate, CA
Manville Sales Corporation	Fort Worth, TX Pittsburg, CA Savannah, GA Waukegan, IL
Neste Oil Services	Belton, TX Calexico, CA Fresno, CA Houston, TX Long Beach, CA Pittsburg, CA Salt Lake City, UT San Diego, CA

(continued)

TABLE 6-35. CONTINUED

Company	Roofing Plant Location
Owens-Corning Fiberglas Corporation	Atlanta, GA Brookville, IN Compton, CA Denver, CO Detroit, MI Houston, TX Irving, TX Jacksonville, FL Jessup, MD Kearny, NJ Medina, OH Memphis, TN Minneapolis, MN Morehead City, NC Oklahoma City, OK Portland, OR
PABCO Roofing Products	Richmond, CA Tacoma, WA
TAMKO Asphalt Products, Incorporated	Dallas, TX Frederick, MD Joplin, MO Phillipsburg, KS Tuscaloosa, AL
TARCO, Incorporated	North Little Rock, AR Belton, TX
U.S. Intec, Incorporated	Corvallis, OR Monroe, GA

Source: Reference 184.

only potential sources of emissions are the tanker and the storage tanks. The magnitude of the emissions from the tanker is at least partially dependent on how far the cover is opened.

Another unloading procedure, of which there are numerous variations, is to pump the hot asphalt into a large open funnel that is connected to a surge tank. From the surge tanks, the asphalt is pumped directly into storage tanks. Emission sources under the surge tank configuration are the tanker, the interface between the tanker and the surge tank, the surge tank, and the storage tanks. The quantity of emissions depends on the asphalt's temperature and characteristics.

After delivery, asphalt flux is usually stored at 124 to 174°F (51 to 79°C), although storage temperatures of up to 450°F (232°C) have been noted. The lower temperatures are usually maintained with steam coils in the tanks. Oil- or gas-fired preheaters are used to maintain the asphalt flux at temperatures above 200°F (93°C).[186-188]

Asphalt is transferred within a roofing plant by closed pipeline. Barring leaks, the only potential emissions sources are at the end-points of the pipes. These end-points are the storage tanks, the asphalt heaters (if not the closed tube type), and the air-blowing stills.

Asphalt flux is used to make two roofing grades of asphalt: saturant and coating. Saturant and coating asphalts are primarily distinguished by the differences in their softening points. The softening point of saturant asphalts is between 104 to 165°F (40 and 74°C); coating asphalts soften at about 230°F (110°C). These softening points are achieved by “blowing” hot asphalt flux, that is, by blowing air through tanks of hot asphalt flux.

The configuration of a typical air-blowing operation is shown in Figure 6-12.[185] This operation consists primarily of a blowing still, which is a tank with a sparger fitted near its base. The purpose of the sparger is to increase contact between the blowing air and the asphalt. Air is forced through holes in the sparger into a tank of hot (400 to 470°F [204 to 243°C]) asphalt flux. The air rises through the asphalt and initiates an exothermic oxidation

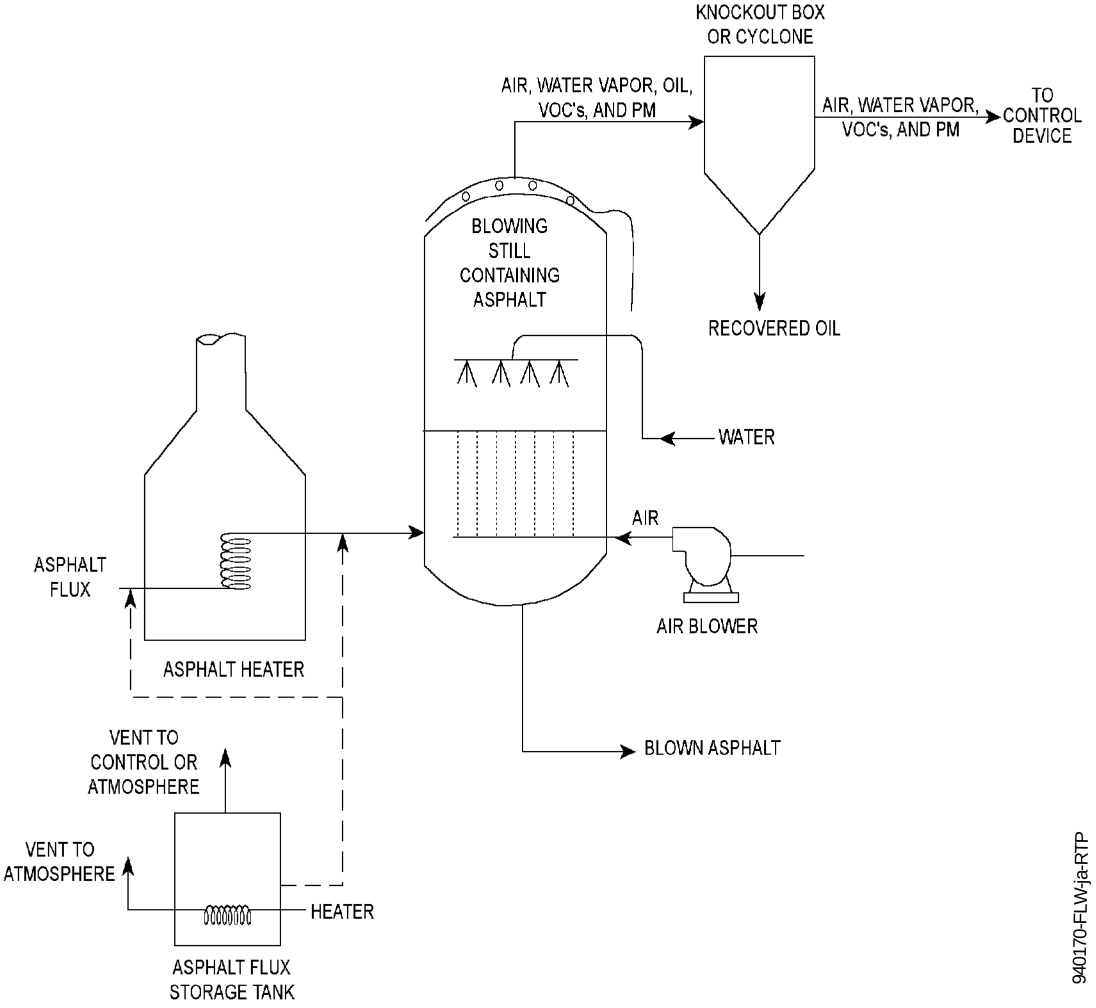


Figure 6-12. Asphalt Blowing Process Flow Diagram

Source: Reference 185.

reaction. Oxidizing the asphalt has the effect of raising its softening temperature, reducing penetration, and modifying other characteristics. Inorganic salts such as ferric chloride ($FeCl_3$) may be used as catalysts added to the asphalt flux during air blowing to better facilitate these transformations.[185]

The time required for air blowing of asphalt depends on a number of factors including the characteristics of the asphalt flux, the characteristics desired for the finished product, the reaction temperature, the type of still used, the air injection rate, and the efficiency with which the air entering the still is dispersed throughout the asphalt. Blowing times may vary in duration from 30 minutes to 12 hours, with typical times from 1 to 4.5 hours.[185,186]

Asphalt blowing is a highly temperature-dependent process because the rate of oxidation increases rapidly with increases in temperature. Asphalt is preheated to 400 to 470°F (204 to 243°C) before blowing is initiated to ensure that the oxidation process will start an acceptable rate. Conversion does take place at lower temperatures but is much slower. Because of the exothermic nature of the reaction, the asphalt temperature rises as blowing proceeds. This, in turn, further increases the reaction rate. Asphalt temperature is normally kept at about 500°F (260°C) during blowing by spraying water onto the surface of the asphalt, although external cooling may also be used to remove the heat of reaction. The allowable upper limit to the reaction temperature is dictated by safety considerations, with the maximum temperature of the asphalt usually kept at least 50°F (28°C) below the flash point of the asphalt being blown.[186]

The design and location of the sparger in the blowing still governs how much of the asphalt surface area is physically contacted by the injected air, and the vertical height of the still determines the time span of this contact. Vertical stills, because of their greater head (asphalt height), require less air flow for the same amount of asphalt-air contact. Both vertical and horizontal stills are used for asphalt blowing, but in new construction, the vertical type is preferred by the industry because of the increased asphalt-air contact and consequent reduction in blowing times.[186] Also, asphalt losses from vertical stills are reported to be less than those from horizontal stills. All recent blowing still installations have been of the vertical type.

Asphalt blowing can be either a batch process or a continuous operation; however, the majority of facilities use a batch process. Asphalt flux is sometimes blown by the oil refiner or asphalt processor to meet the roofing manufacturer's specifications. Many roofing manufacturers, however, purchase the flux and carry out their own blowing.

Blown asphalt (saturant and coating asphalt) is used to produce asphalt felt and coated asphalt roofing and siding products in the processes depicted in Figures 6-13 and 6-14.[185] The processes are identical up to the point where the material is to be coated. A roll of felt is installed on the felt reel and unwound onto a dry floating looper. The dry floating looper provides a reservoir of felt material to match the intermittent operation of the felt roller to the continuous operation of the line. Felt is unwound from the roll at a faster rate than is required by the line, with the excess being stored in the dry looper. The flow of felt to the line and the tension on the material is kept constant by raising the top set of rollers and increasing looper capacity. The opposite action occurs when a new roll is being put on the felt reel and spliced in, and the felt supply ceases temporarily. There are no benzene emissions generated in this processing step.[186]

Following the dry looper, the felt enters the saturator, where moisture is driven out and the felt fibers and intervening spaces are filled with saturant asphalt. (If a fiberglass mat web is used instead of felt, the saturation step and the subsequent drying-in process are bypassed.) The saturator also contains a looper arrangement, which is almost totally submerged in a tank of asphalt maintained at a temperature of 450 to 500°F (232 to 260°C). The absorbed asphalt increases the sheet or web weight by about 150 percent. At some plants, the felt is sprayed on one side with asphalt to drive out the moisture prior to dipping. This approach reportedly results in higher benzene emissions than does use of the dip process alone.[186] The saturator is a significant benzene emissions source within the asphalt roofing process.

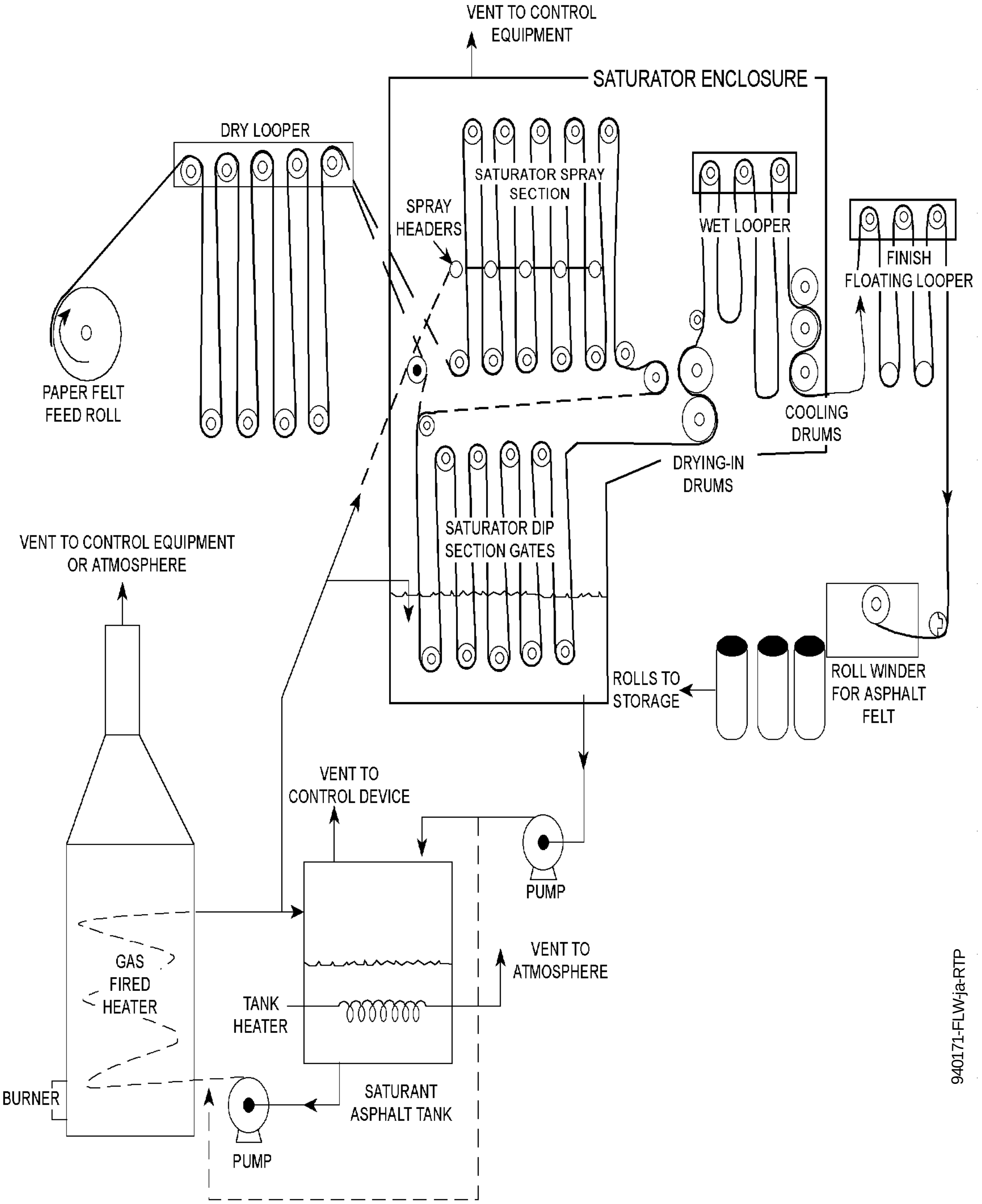


Figure 6-13. Asphalt-Saturated Felt Manufacturing Process

Source: Reference 185.

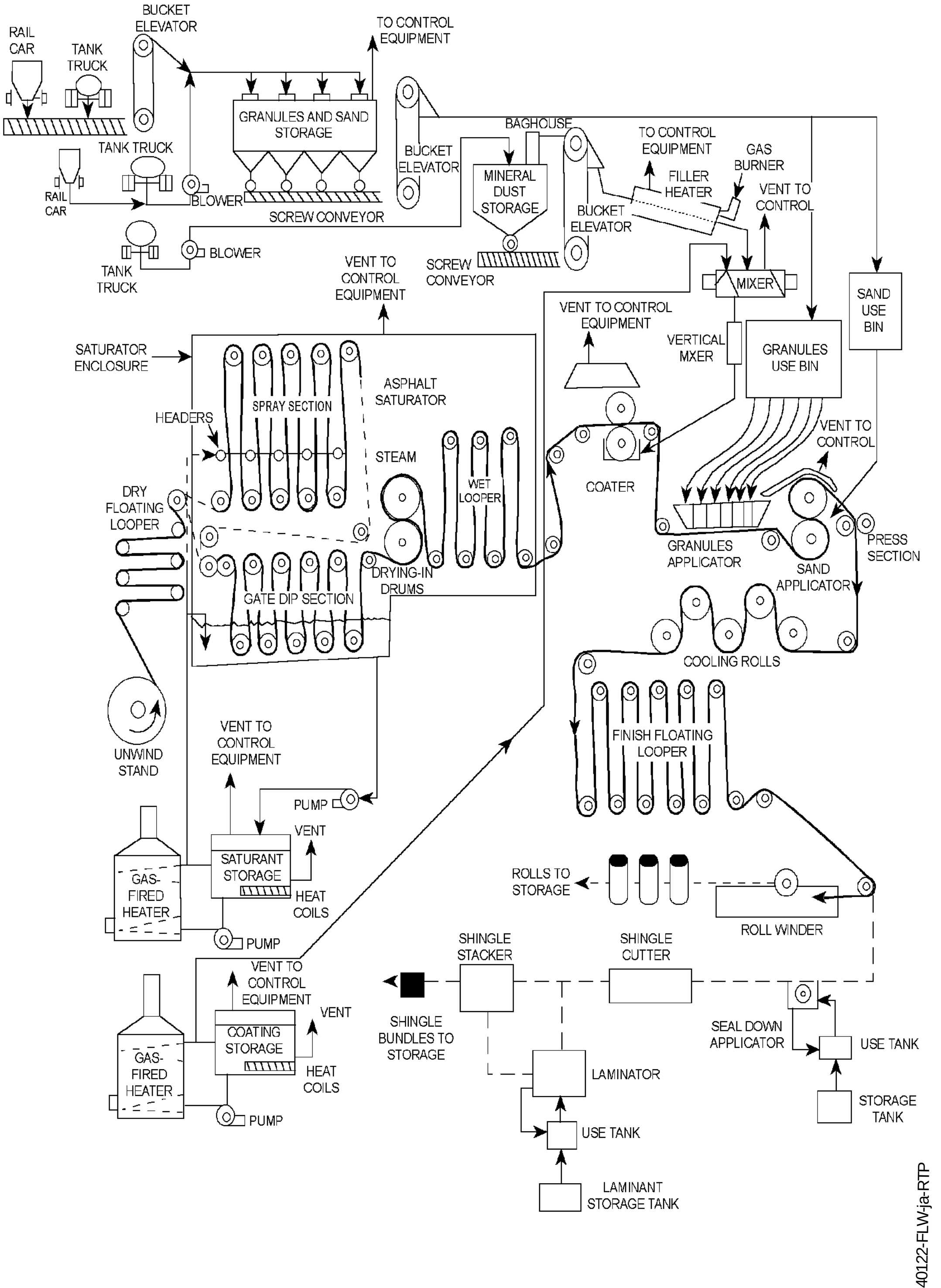


Figure 6-14. Organic Shingle and Roll Manufacturing Process Flow Diagram

Source: Reference 185.

The saturated felt then passes through drying-in drums and onto the wet looper, sometimes called the hot looper. The drying-in drums press surface saturant into the felt. Depending on the required final product, additional saturant may also be added at this point. The amount of absorption depends on the viscosity of the asphalt and the length of time the asphalt remains fluid. The wet looper increases absorption by providing time for the saturant asphalt to penetrate the felt. The wet looper operation has been shown to be a significant source of organic particulate emissions within the asphalt roofing process; however, the portion that is benzene has not been defined.[186,187]

If saturated felt is being produced, the sheet passes directly to the cool-down section. For surfaced roofing products, however, the saturated felt is carried to the coater station, where a stabilized asphalt coating is applied to both the top and bottom surfaces. Stabilized coating contains a mineral stabilizer and a harder, more viscous coating asphalt that has a higher softening point than saturant asphalt. The coating asphalt and mineral stabilizer are mixed in approximately equal proportions. The mineral stabilizer may consist of finely divided lime, silica, slate dust, dolomite, or other mineral materials.

The weight of the finished product is controlled by the amount of coating used. The coater rollers can be moved closer together to reduce the amount of coating applied to the felt, or separated to increase it. Many modern plants are equipped with automatic scales that weigh the sheets in the process of manufacture and warn the coater operator when the product is running under or over specifications. The coater is a significant emissions source within the roofing production process. It releases asphalt fumes containing organics, some of which may be benzene compounds.[186,187]

The function of the coater-mixer is to mix coating asphalt and a mineral stabilizer in approximately equal proportions. The stabilized asphalt is then piped to the coating pan. The asphalt is piped in at about 450 to 500°F (232 to 260°C), and the mineral stabilizer is delivered by screw conveyor. There is often a preheater immediately ahead of the coater-mixer to dry and preheat the material before it is fed into the coater-mixer. This eliminates moisture problems and also helps to maintain the temperature above 320°F (160°C) in the coater-mixer. The coater-mixer is usually covered or enclosed, with an exhaust pipe for the air displaced by (or carried with) the incoming materials. The coater-mixer is viewed as a potential source of benzene emissions, but not a significant one.[186,187]

The next step in the production of coated roofing products is the application of mineral surfacing. The surfacing section of the roofing line usually consists of a multi-compartmented granule hopper, two parting agent hoppers, and two large press rollers. The hoppers are fed through flexible hoses from one or more machine bins above the line. These machine bins provide temporary storage and are sometimes called surge bins. The granule hopper drops colored granules from its various compartments onto the top surface of the moving sheet of coated felt in the sequence necessary to produce the desired color pattern on the roofing. This step is not required for smooth-surfaced products.[186]

Parting agents such as talc and sand (or some combination thereof) are applied to the top and back surfaces of the coated sheet from parting agent hoppers. These hoppers are usually of an open-top, slot-type design, slightly longer than the coated sheet is wide, with a screw arrangement for distributing the parting agent uniformly throughout its length. The first hopper is positioned between the granule hopper and the first large press roller, and 8 to 12 inches (0.2 to 0.3 m) above the sheet. It drops a generous amount of parting agent onto the top surface of the coated sheet and slightly over each edge. Collectors are often placed at the edges of the sheet to pick up this overspray, which is then recycled to the parting agent machine bin by open screw conveyor and bucket elevator. The second parting agent hopper is located between the rollers and dusts the back side of the coated sheet. Because of the steep angle of the sheet at this point, the average fall distance from the hopper to the sheet is usually somewhat greater than on the top side, and more of the material falls off the sheet.[186]

In a second technique used to apply backing agent to the back side of a coated sheet, a hinged trough holds the backing material against the coated sheet and only material that will adhere to the sheet is picked up. When the roofing line is not operating, the trough is tipped back so that no parting agent will escape past its lower lip.

Immediately after application of the surfacing material, the sheet passes through the cool-down section. Here the sheet is cooled rapidly by passing it around water-cooled rollers in an abbreviated looper arrangement. Usually, water is also sprayed on the surfaces of the sheet to speed the cooling process. The cool-down section is not a source of benzene emissions.

Following cooling, self-sealing coated sheets usually have an asphalt seal-down strip applied. The strip is applied by a roller, which is partially submerged in a pan of hot sealant asphalt. The pan is typically covered to minimize fugitive emissions. No seal-down strip is applied to standard shingle or roll-goods products. Some products are also texturized at this point by passing the sheet over an embossing roll that imparts a pattern to the surface of the coated sheet.[186]

The cooling process for both asphalt felt and coated sheets is completed in the next processing station, known as the finish looper. In the finish looper, sheets are allowed to cool and dry gradually. Secondly, the finish looper provides line storage to match the continuous operation of the line to the intermittent operation of the roll winder. It also allows time for quick repairs or adjustments to the shingle cutter and stacker during continuous line operation or, conversely, allows cutting and packaging to continue when the line is down for repair. Usually, this part of the process is enclosed to keep the final cooling process from progressing too rapidly. Sometimes, in cold weather, heated air is also used to retard cooling. The finish looper is not viewed as a source of benzene emissions.[186]

Following finishing, asphalt felt to be used in roll goods is wound on a mandrel, cut to the proper length, and packaged. When shingles are being made, the material from the finish looper is fed into the shingle-cutting machine. After the shingles have been cut, they are moved by roller conveyor to manual or automatic packaging equipment. They are then stacked on pallets and transferred by forklift to storage areas or waiting trucks.[186]

6.12.2 Benzene Emissions from Asphalt Roofing Manufacture

The primary benzene emission sources associated with asphalt roofing are the asphalt air-blowing stills (and associated oil knockout boxes) and the felt saturators.[186] An emission factor for benzene emissions from the blowing stills or saturators is given in Table 6-36.[189] Additional potential benzene emission sources may include the wet looper, the coater-mixer, the felt coater, the seal-down stripper, and air-blown asphalt storage tanks. Minor fugitive emissions are also possible from asphalt flux and blown asphalt handling and transfer operations.[186-188,190]

Process selection and control of process parameters have been promoted to minimize uncontrolled emissions, including benzene, from asphalt air-blowing stills, asphalt saturators, wet loopers, and coaters. Process controls include the use of:[184]

- Dip saturators, rather than spray or spray-dip saturators;
- Vertical stills, rather than horizontal stills;
- Asphalts that inherently produce low emissions;
- Higher-flash-point asphalts;
- Reduced temperatures in the asphalt saturant pan;
- Reduced asphalt storage temperatures; and
- Lower asphalt-blowing temperatures.

Dip saturators have been installed for most new asphalt roofing line installations in recent years, and this trend is expected to continue. Recent asphalt blowing still installations have been almost exclusively of the vertical type because of its higher efficiency and lower emissions. Vertical stills occupy less space and require no heating during oxidizing

TABLE 6-36. EMISSION FACTOR FOR ASPHALT ROOFING MANUFACTURE

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
3-05-001-01	Petroleum Industry - Asphalt Roofing - Asphalt Blowing - Saturant	Blowing Stills or Saturators	Uncontrolled	52 (26)	E

Source: Reference 189.

[a] Emission factor is in lb (kg) of benzene emitted per ton (Mg) of asphalt roofing produced.

(if the temperature of the incoming flux is above 400°F [204°C]). Vertical stills are expected to be used in new installations equipped with stills and in most retrofit situations.[186]

Asphalt fluxes with lower flash points and softening points tend to have higher emissions of organics because these fluxes generally have been less severely cracked and contain more low-boiling fractions. Many of these light ends can be emitted during blowing. Limiting the minimum softening and flash points of asphalt flux should reduce the amount of benzene-containing fumes generated during blowing because less blowing is required to produce a saturant or coating asphalt. Saturant and coating asphalts with high softening points should reduce benzene emissions from felt saturation and coating operations. However, producing the higher softening point asphalt flux requires more blowing, which increases uncontrolled emissions from the blowing operation.[186]

Although these process-oriented emissions control measures are useful, emissions capture equipment and add-on emissions control equipment are also necessary in asphalt roofing material production facilities. The capture of potential benzene emissions from asphalt blowing stills, asphalt storage tanks, asphalt tank truck unloading, and the coater-mixer can and is being achieved in the industry by the use of enclosure systems around the emissions-producing operations. The enclosures are maintained under negative pressure, and the contained emissions are ducted to control devices.[186] Potential emissions from the saturator, wet looper, and coater are generally collected by a single enclosure by a canopy type hood or an enclosure/hood combination.

No regulations were identified to control benzene emissions from hot-mix asphalt plants.

6.13 CONSUMER PRODUCTS/BUILDING SUPPLIES

This section covers benzene emissions from the application and use of consumer products rather than from the manufacture of such products. Because the types of consumer products to which benzene emissions are attributed are so extensive, no list of manufacturers is presented here.

Benzene emissions from the use of consumer products and building supplies have been reported in the literature. One indoor air quality data base for organic compounds, shows that indoor benzene levels have been measured in residences, commercial buildings, hospitals, schools, and office buildings. Substantiated sources of these benzene emissions were attributed to tobacco smoke, adhesives (including epoxy resins and latex caulks), spot cleaners, paint removers, particle board, foam insulation, inks, photo film, auto exhaust, and wood stain.[191,192] Although benzene emissions were detected from these consumer sources, no specific benzene emission factors were identified. In addition to these consumer sources, detergents have been identified as another possible source of benzene emissions.[191]

In another report, aromatic hydrocarbons (most likely including benzene) were listed as a constituent in certain automotive detailing and cleaning products, including body-cleaning compounds and engine cleaners/degreasers/parts cleaners. However, no specific emission levels were given.[192]

Naphtha (CAS number 8030-30-6) is a mixture of a small percentage of benzene, toluene, xylene, and higher homologs derived from coal tar by fractional distillation. Among its applications, naphtha is used as thinner in paints and varnishes and as a solvent in rubber cement.[106] Because naphtha contains a small percentage of benzene, some benzene emissions would be expected from these products. However, no qualifiable benzene emissions from naphtha-containing products were identified.

The main control for reducing benzene emissions from consumer products is reformulation, such as substituting water or lower-VOC-emitting alternatives.[192]

The federal government and several states are currently working on regulations for the benzene (or VOC) content of consumer products. Consumer products is a very diverse category and the products are used in a variety of applications.[193]

SECTION 7.0
EMISSIONS FROM COMBUSTION SOURCES

The following stationary point and area combustion source categories have been identified as sources of benzene emissions: medical waste incinerators (MWIs), sewage sludge incinerators (SSIs), hazardous waste incinerators, external combustion sources (e.g., utility boilers, industrial boilers, and residential stoves and furnaces), internal combustion sources, secondary lead smelters, iron and steel foundries, portland cement kilns, hot-mix asphalt plants, and open burning (of biomass, tires, and agricultural plastic). For each combustion source category, the following information is provided in the sections below: (1) a brief characterization of the U.S. population, (2) the process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed.

7.1 MEDICAL WASTE INCINERATORS

MWIs burn wastes produced by hospitals, veterinary facilities, crematories, and medical research facilities. These wastes include both infectious ("red bag" and pathological) medical wastes and non-infectious, general housekeeping wastes. The primary purposes of MWIs are to (1) render the waste innocuous, (2) reduce the volume and mass of the waste, and (3) provide waste-to-energy conversion. The total number and capacity of MWIs in the United States is unknown; however, it is estimated that 90 percent of the 6,872 hospitals (where the majority of MWIs are located) in the nation have some type of on-site incinerator, if only a small unit for incinerating special or pathological waste.[194] The document entitled *Locating and Estimating Air Toxic Emissions From Sources of Medical Waste Incinerators*, contains a more detailed characterization of the MWI industry, including a partial list of the U.S. MWI population.

Three main types of incinerators are used for medical waste incineration: controlled-air, excess-air, and rotary kiln. Of the incinerators identified, the majority (>95 percent) are controlled-air units. A small percentage (<2 percent) are excess-air. Less than 1 percent were identified as rotary kiln. The rotary kiln units tend to be larger, and typically are equipped with air pollution control devices. Approximately 2 percent of the total population identified were found to be equipped with air pollution control devices.[195]

7.1.1 Process Description: Medical Waste Incinerators[195]

Controlled-Air Incinerators

Controlled-air incineration is the most widely used MWI technology and it now dominates the market for new systems at hospitals and similar medical facilities. This technology is also known as starved-air incineration, two-stage incineration, and modular combustion. Figure 7-1 presents a schematic diagram of a typical controlled-air unit.[195]

Combustion of waste in controlled-air incinerators occurs in two stages. In the first stage, waste is fed into the primary, or lower, combustion chamber, which is operated with less than the stoichiometric amount of air required for combustion. Combustion air enters the primary chamber from beneath the incinerator hearth (below the burning bed of waste). This air is called primary or underfire air. In the primary (starved-air) chamber, the low air-to-fuel ratio dries and facilitates volatilization of the waste, and most of the residual carbon in the ash burns. At these conditions, combustion gas temperatures are relatively low (1,400 to 1,800°F [760 to 980°C]).

In the second stage, excess air is added to the volatile gases formed in the primary chamber to complete combustion. Secondary chamber temperatures are higher than

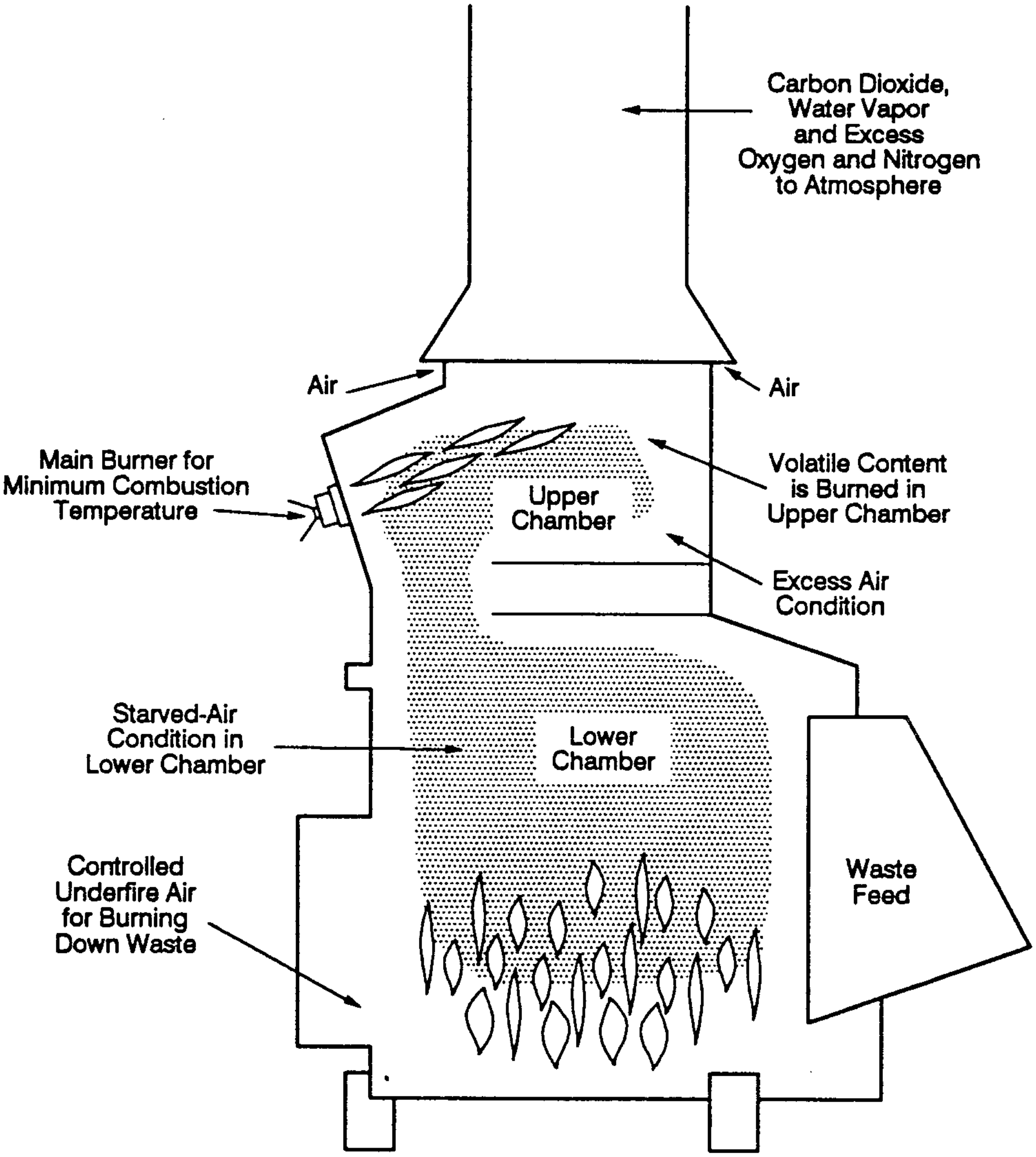


Figure 7-1. Controlled-Air Incinerator

Source: Reference 195.

primary chamber temperatures--typically 1,800 to 2,000°F (980 to 1,095°C). Depending on the heating value and moisture content of the waste, additional heat may be needed. This can be provided by auxiliary burners located at the entrance to the secondary (upper) chamber to maintain desired temperatures.

Waste feed capacities for controlled-air incinerators range from about 75 to 6,500 lb/hour (0.6 to 50 kg/min) (at an assumed fuel heating value of 8,500 Btu/lb [19,700 kJ/kg]). Waste feed and ash removal can be manual or automatic, depending on the unit size and options purchased. Throughput capacities for lower heating value wastes may be higher because feed capacities are limited by primary chamber heat release rates. Heat release rates for controlled-air incinerators typically range from 15,000 to 25,000 Btu/hr-ft^3 (430,000 to 710,000 kJ/hr-m^3).

Because of the low air addition rates in the primary chamber and corresponding low flue gas velocities (and turbulence), the amount of solids entrained in the gases leaving the primary chamber is low. Therefore, the majority of controlled-air incinerators do not have add-on gas cleaning devices.

Excess-Air Incinerators

Excess-air incinerators are typically small modular units. They are also referred to as batch incinerators, multiple-chamber incinerators, and “retort” incinerators. Excess-air incinerators are typically a compact cube with a series of internal chambers and baffles. Although they can be operated continuously, they are usually operated in a batch mode.

Figure 7-2 presents a schematic for an excess-air unit.[195] Typically, waste is manually fed into the combustion chamber. The charging door is then closed and an afterburner is ignited to bring the secondary chamber to a target temperature (typically 1,600 to 1,800°F [870 to 980°C]). When the target temperature is reached, the primary chamber burner ignites. The waste is dried, ignited, and combusted by heat provided by the primary

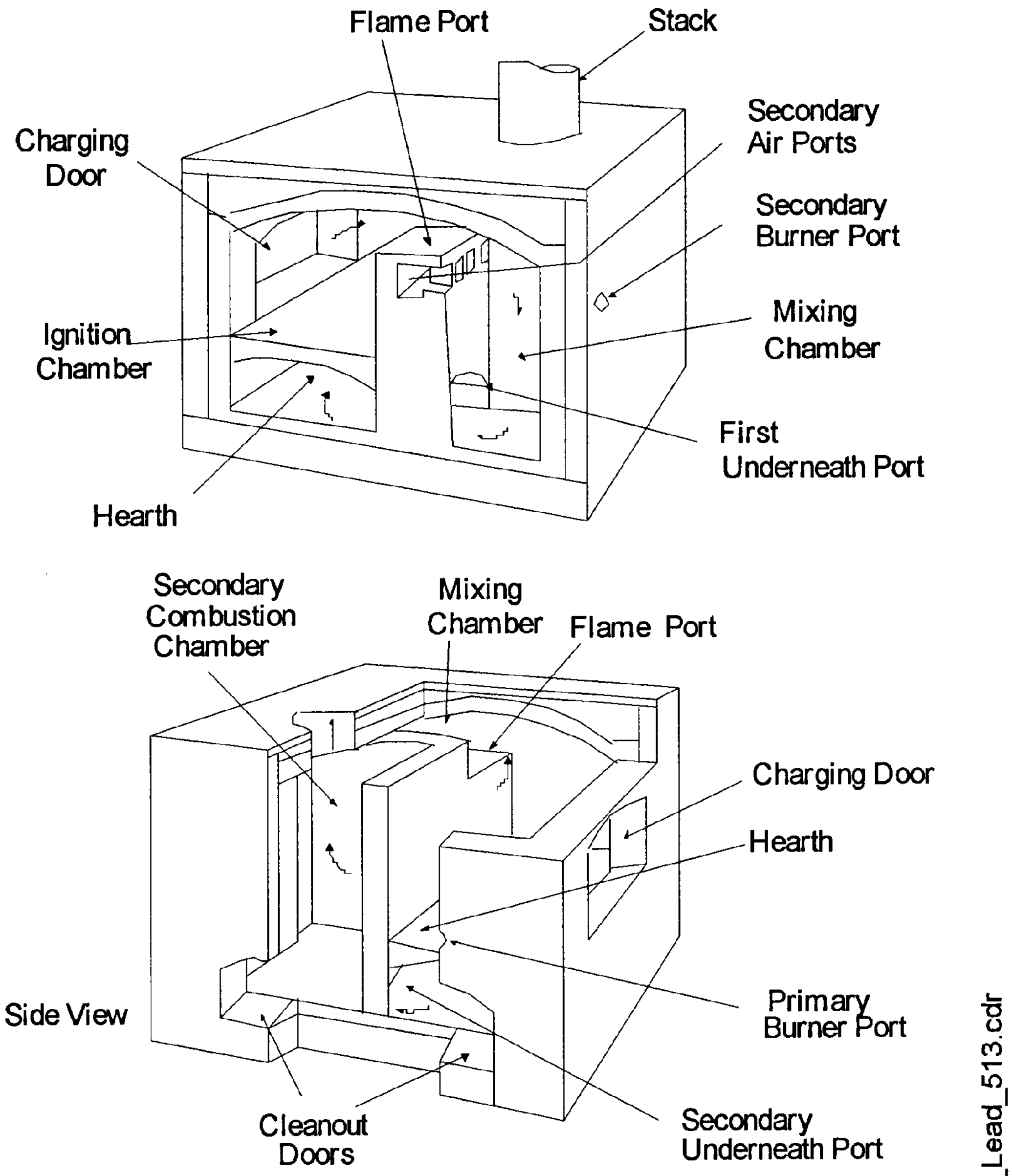


Figure 7-2. Excess-Air Incinerator

Source: Reference 195.

chamber burner, as well as by radiant heat from the chamber walls. Moisture and volatile components in the waste are vaporized and pass (along with combustion gases) out of the primary chamber and through a flame port that connects the primary chamber to the secondary or mixing chamber.

Secondary air is added through the flame port and is mixed with the volatile components in the secondary chamber. Burners are also installed in the secondary chamber to maintain adequate temperatures for combustion of volatile gases. Gases exiting the secondary chamber are directed to the incinerator stack or to a control device. When the waste is consumed, the primary burner shuts off. Typically, the afterburner shuts off after a set time. After the chamber cools, ash is manually removed from the primary chamber floor and a new charge of waste can be added.

Incinerators designed to burn general hospital waste operate at excess air levels of up to 300 percent. If only pathological wastes are combusted, excess air levels near 100 percent are more common. The lower excess air helps maintain higher chamber temperature when burning high-moisture waste. Waste feed capacities for excess-air incinerators are usually 500 lb/hr (3.8 kg/min) or less.

Rotary Kiln Incinerators

Rotary kiln incinerators, like the other types, are designed with a primary chamber where the waste is heated and volatilized and a secondary chamber where combustion of the volatile fraction is completed. The primary chamber consists of a slightly inclined, rotating kiln in which waste materials migrate from the feed end to the ash discharge end. The waste throughput rate is controlled by adjusting the rate of kiln rotation and the angle of inclination. Combustion air enters the primary chamber through a port. An auxiliary burner is generally used to start combustion and maintain desired combustion temperatures. Both the primary and secondary chambers are usually lined with acid-resistant refractory brick. Refer to Figure 7-9 of this chapter for a schematic diagram of a typical rotary kiln incinerator. In

Figure 7-9, the piece of equipment referred to as the "afterburner" is the equivalent of the "secondary chamber" referred to in this section.

Volatiles and combustion gases pass from the primary chamber to the secondary chamber. The secondary chamber operates at excess air. Combustion of the volatiles is completed in the secondary chamber. Because of the turbulent motion of the waste in the primary chamber, solids burnout rates and particulate entrainment in the flue gas are higher for rotary kiln incinerators than for other incinerator designs. As a result, rotary kiln incinerators generally have add-on gas cleaning devices.

7.1.2 Benzene Emissions From Medical Waste Incinerators

There is limited information currently available on benzene emissions from MWIs. One emission factor for benzene emissions is provided in Table 7-1.[196] This factor represents benzene emissions during combustion of both general hospital wastes and pathological wastes.

7.1.3 Control Technologies for Medical Waste Incinerators

Most control of air emissions of organic compounds is achieved by promoting complete combustion by following good combustion practice (GCP). In general, the conditions of GCP are as follows:[194]

- Uniform wastefeed;
- Adequate supply and good air distribution in the incinerator;
- Sufficiently high incinerator gas temperatures (>1,500°F [>815°C]);
- Good mixing of combustion gas and air in all zones;
- Minimization of PM entrainment into the flue gas leaving the incinerator; and

TABLE 7-1. EMISSION FACTOR FOR MEDICAL WASTE INCINERATION

SCC	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Factor Rating
5-02-005-05	Incinerator	Uncontrolled	4.92×10^{-3} (2.46×10^{-3})	D

Source: Reference 196.

[a] Emission factor is in lb (kg) of benzene emitted per ton (Mg) of medical waste incinerated.

- Temperature control of the gas entering the air pollution control device to 450°F (230°C) or less.

Failure to achieve complete combustion of organic materials evolved from the waste can result in emissions of a variety of organic compounds. The products of incomplete combustion (PICs) range from low-molecular-weight hydrocarbons (e.g., methane, ethane, or benzene) to high-molecular-weight organic compounds (e.g., dioxins/furans). In general, adequate oxygen, temperature, residence time, and turbulence will minimize emissions of most organics.

Control of organics may be partially achieved by using acid gas and PM control devices. To date, most MWIs have operated without add-on air pollution control devices. A small percentage (approximately 2 percent) of MWIs do use air pollution control devices, most frequently wet scrubbers and fabric filters. Fabric filters provide mainly PM control. Other PM control technologies include venturi scrubbers and electrostatic precipitators (ESPs). In addition to wet scrubbing, dry sorbent injection and spray dryer absorbers have also been used for acid gas (i.e., hydrogen chloride [HCl] and sulfur dioxide [SO_2]) control. Because it is not documented that acid gas/PM control devices provide reduction in benzene emissions from MWIs, further discussion of these types of control devices is not provided in this section. *Locating and Estimating Air Toxic Emissions From Sources of Medical Waste Incinerators,*[194] contains a more detailed description of the acid gas/PM air pollution control devices utilized for MWIs, including schematic diagrams.

7.1.4 Regulatory Analysis

Air emissions from MWIs are not currently regulated by Federal standards. However, Section 129 of the CAA requires that standards be established for new and existing MWIs. Standards for MWIs were proposed under Section 129 of the CAA on February 27, 1995 (38 FR 10654). Section 129 requires that the standards include emission limits for HCl, SO_2, and CO, among other pollutants. Section 129 also specifies that the standards may require monitoring of surrogate parameters (e.g., flue gas temperature). Thus, the standards may require GCP, which would likely result in benzene emissions reduction. Additionally, the standards may require acid gas/PM control device requirements, which may result in some benzene emissions reduction.

7.2 SEWAGE SLUDGE INCINERATORS

There are approximately 170 sewage sludge incineration (SSI) plants operating in the United States. The three main types of SSIs are: multiple-hearth furnaces (MHF), fluidized-bed combustors (FBC), and electric infrared incinerators. Some sludge is co-fired with municipal solid waste in combustors, based on refuse combustion technology. Refuse co-fired with sludge in combustors based on sludge incinerating technology is limited to MHFs only.[197]

Over 80 percent of the identified operating sludge incinerators are of the multiple-hearth design. About 15 percent are FBCs and 3 percent are electric infrared incinerators. The remaining combustors co-fire refuse with sludge. Most sludge incinerators are located in the Eastern United States, although there are a significant number on the West Coast. New York has the largest number of facilities, with 33. Pennsylvania and Michigan have the next largest number of facilities, with 21 and 19 sites, respectively.[197,198] *Locating and Estimating Air Toxics Emissions for Sewage Sludge Incinerators* contains a diagram showing the geographic distribution of the existing population.[198]

The three main types of sewage sludge incinerators are described in the following sections. Single hearth cyclone, rotary kiln, wet air oxidation, and co-incineration are also briefly discussed.

7.2.1 Process Description: Sewage Sludge Incinerators[197,198]

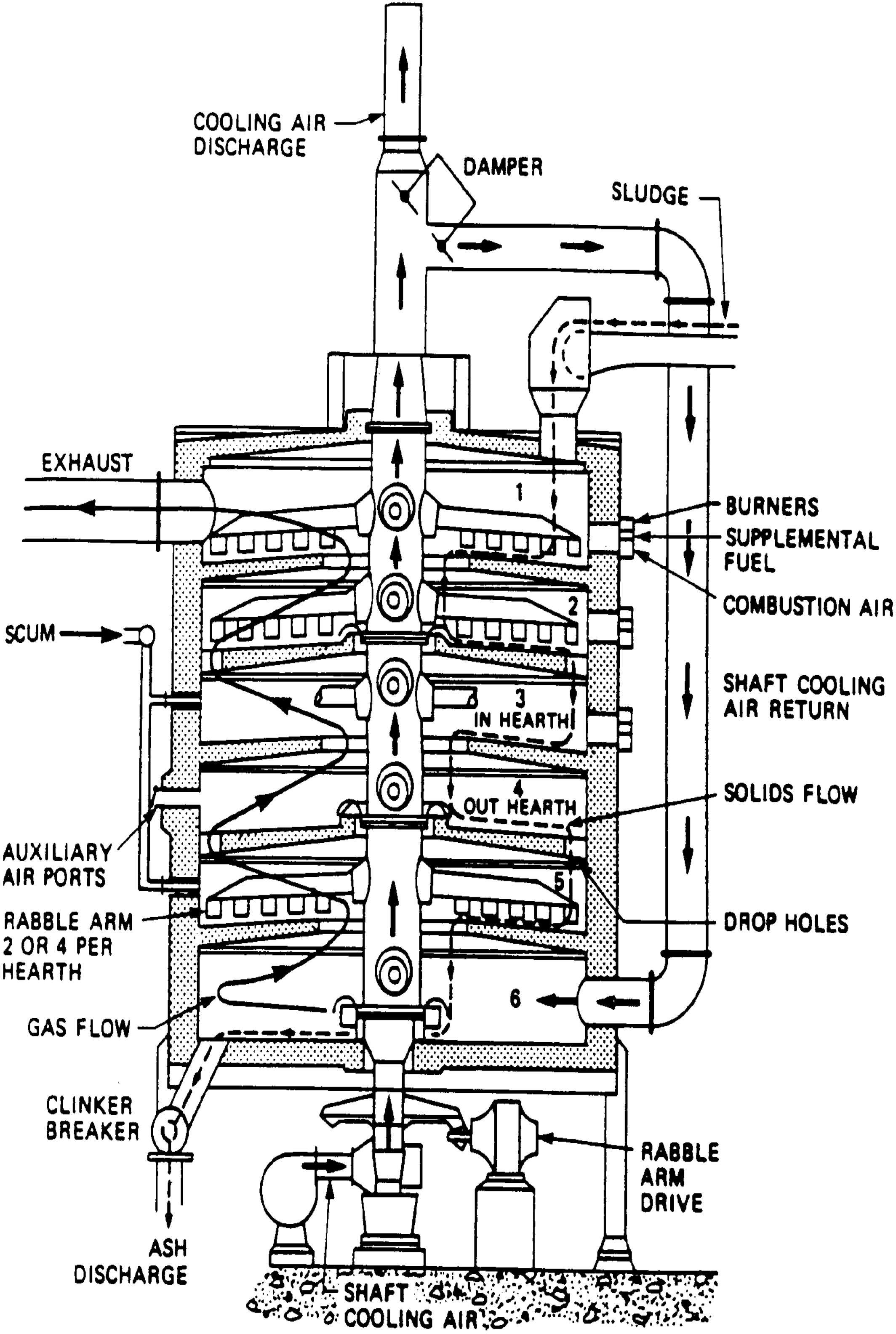
Multiple-Hearth Furnaces

A cross-sectional diagram of a typical MHF is shown in Figure 7-3.[198] The basic MHF is a vertically oriented cylinder. The outer shell is constructed of steel, lined with refractory, and surrounds a series of horizontal refractory hearths. A hollow cast-iron rotating shaft runs through the center of the hearths. Cooling air is introduced into the shaft, which extend above the hearths. Attached to the central shaft are the rabble arms, which extend above the hearths. Each rabble arm is equipped with a number of teeth approximately 6 inches in length and spaced about 10 inches apart. The teeth are shaped to rake the sludge in a spiral motion, alternating in direction from the outside in to the inside out, between hearths. Burners are located in the sidewalls of the hearths to provide auxiliary heat.

In most MHFs, partially dewatered sludge is fed onto the perimeter of the top hearth. The rabble arms move the sludge through the incinerator by raking the sludge toward the center shaft, where it drops through holes located at the center of the hearth. In the next hearth, the sludge is raked in the opposite direction. This process is repeated in all of the subsequent hearths. The effect of the rabble motion is to break up solid material to allow better surface contact with heat and oxygen. A sludge depth of about 1 inch is maintained in each hearth at the design sludge flow rate.

Scum may also be fed to one or more hearths of the incinerator. Scum is the material that floats on wastewater. It is generally composed of vegetable and mineral oils, grease, hair, waxes, fats, and other materials that will float. Scum may be removed from many treatment units, including pre-aeration tanks, skimming tanks, and sedimentation tanks. Quantities of scum are generally small compared to those of other wastewater solids.

Ambient air is first ducted through the central shaft and its associated rabble arms. A portion or all of this air is then taken from the top of the shaft and recirculated into



940300-kl-DRTP

Figure 7-3. Cross Section of a Multiple Hearth Furnace

Source: Reference 198.

the lower-most hearth as preheated combustion air. Shaft cooling air that is not circulated back into the furnace is ducted into the stack downstream of the air pollution control devices. The combustion air flows upward through the drop holes in the hearths, countercurrent to the flow of the sludge, before being exhausted from the top hearth. Air enters the bottom to cool the ash. Provisions are usually made to inject ambient air directly into the middle hearths as well.

Overall, an MHF can be divided into three zones. The upper hearth comprises the drying zone, where most of the moisture in the sludge is evaporated. The temperature in the drying zone is typically between 800 and 1,400°F (425 and 760°C). Sludge combustion occurs in the middle hearth (second zone) as the temperature is increased to 1,100 to 1,700°F (600 to 930°C). The combustion zone can be further subdivided into the upper-middle hearth, where the volatile gases and solids are burned, and the lower-middle hearth, where most of the fixed carbon is combusted. The third zone, made up of the lower-most hearth, is the cooling zone. In this zone, the ash is cooled as its heat is transferred to the incoming combustion air.

Under normal operating conditions, 50 to 100 percent excess air must be added to an MHF in order to ensure complete combustion of the sludge. Besides enhancing contact between fuel and oxygen in the furnace, these relatively high rates of excess air are necessary to compensate for normal variations in both the organic characteristics of the sludge feed and the rate at which it enters the incinerator. When the supply of excess air is inadequate, only partial oxidation of the carbon will occur, with a resultant increase in emissions of CO, soot, and hydrocarbons. Too much excess air, on the other hand, can cause increased entrainment of particulate and unnecessarily high auxiliary fuel consumption.

Fluidized-Bed Combustors

Figure 7-4 shows a cross-sectional diagram of an FBC.[198] FBCs consist of a vertically oriented outer shell constructed of steel and lined with refractory. Tuyeres (nozzles designed to deliver blasts of air) are located at the base of the furnace within a refractory-lined grid. A bed of sand, approximately 2.5 feet (0.75 meters) thick, rests upon the grid. Two

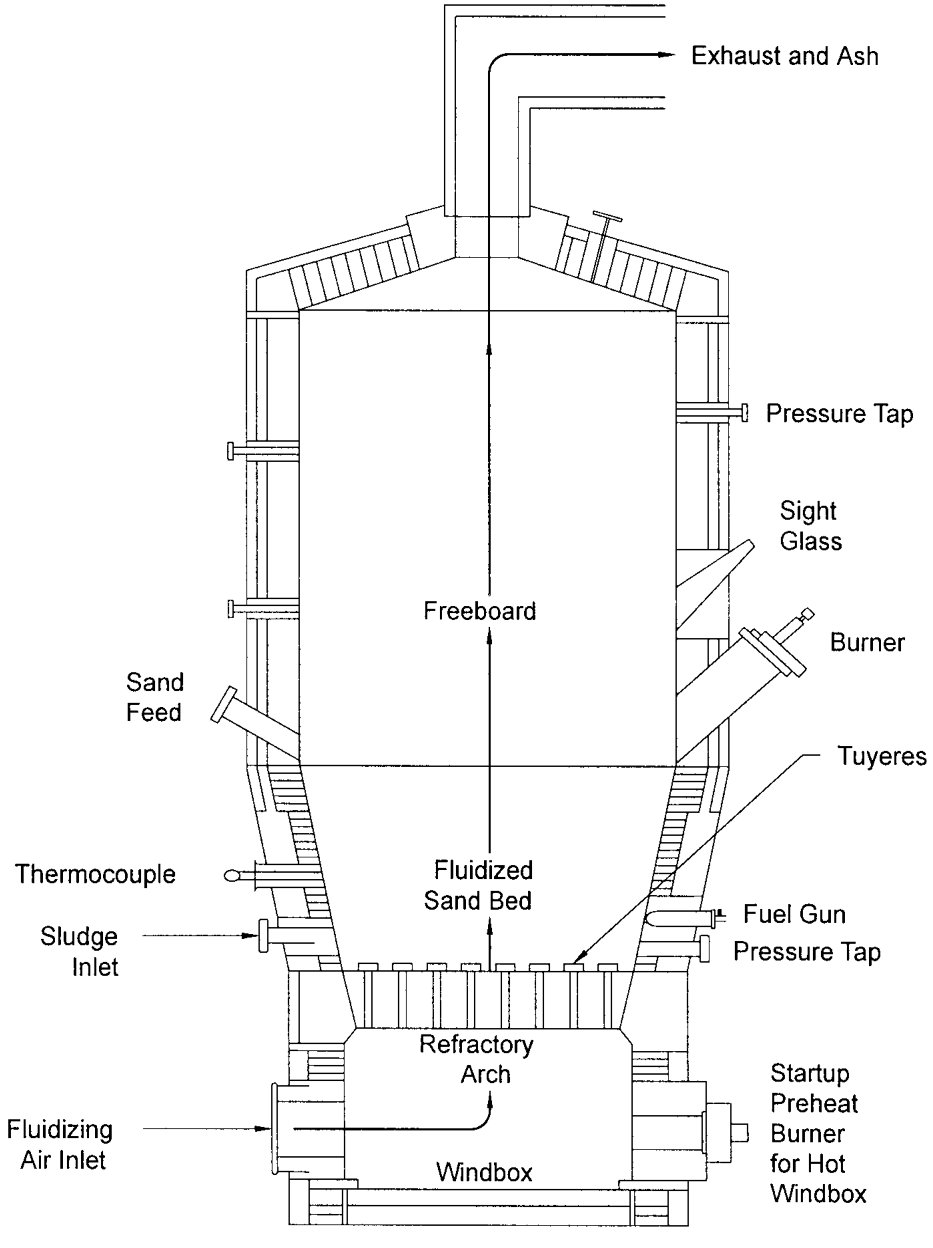


Figure 7-4. Cross Section of a Fluidized Bed Furnace

Source: Reference 198.

general configurations can be distinguished on the basis of how the fluidizing air is injected into the furnace. In the "hot windbox" design, the combustion air is first preheated by passing through a heat exchanger, where heat is recovered from the hot flue gases. Alternatively, ambient air can be injected directly into the furnace from a cold windbox.

Partially dewatered sludge is fed into the lower portion of the furnace. Air injected through the tuyeres at a pressure of 3 to 5 pounds per square inch gauge (20 to 35 kilopascals), simultaneously fluidizes the bed of hot sand and the incoming sludge. Temperatures of 1,400 to 1,700°F (750 to 925°C) are maintained in the bed. As the sludge burns, fine ash particles are carried out the top of the furnace. Some sand is also removed in the air stream and must be replaced at regular intervals.

Combustion of the sludge occurs in two zones. Within the sand bed itself (the first zone), evaporation of the water and pyrolysis of the organic materials occur nearly simultaneously as the temperature of the sludge is rapidly raised. In the freeboard area (the second zone), the remaining free carbon and combustible gases are burned. The second zone functions essentially as an afterburner.

Fluidization achieves nearly ideal mixing between the sludge and the combustion air, and the turbulence facilitates the transfer of heat from the hot sand to the sludge. The most noticeable impact of the better burning atmosphere provided by an FBC is seen in the limited amount of excess air required for complete combustion of the sludge. Typically, FBCs can achieve complete combustion with 20 to 50 percent excess air, about half the excess air required by MHFs. As a consequence, FBCs generally have lower fuel requirements compared to MHFs.

Electric Infrared Incinerators

Electric infrared incinerators consist of a horizontally oriented, insulated furnace. A woven wire belt conveyor extends the length of the furnace and infrared heating elements are located in the roof above the conveyor belt. Combustion air is preheated by the flue gases and is injected into the discharge end of the furnace. Electric infrared incinerators consist of a number of prefabricated modules that can be linked together to provide the necessary furnace length. A cross-section of an electric furnace is shown in Figure 7-5.[198]

The dewatered sludge cake is conveyed into one end of the incinerator. An internal roller mechanism levels the sludge into a continuous layer approximately 1 inch thick across the width of the belt. The sludge is sequentially dried and then burned as it moves beneath the infrared heating elements. Ash is discharged into a hopper at the opposite end of the furnace. The preheated combustion air enters the furnace above the ash hopper and is further heated by the outgoing ash. The direction of air flow is countercurrent to the movement of the sludge along the conveyor. Exhaust gases leave the furnace at the feed end. Excess air rates vary from 20 to 70 percent.

Other Technologies

A number of other technologies have been used for incineration of sewage sludge, including cyclonic reactors, rotary kilns, and wet oxidation reactors. These processes are not in widespread use in the United States and are discussed only briefly.

The cyclonic reactor is designed for small-capacity applications and consists of a vertical cylindrical chamber that is lined with refractory. Preheated combustion air is introduced into the chamber tangentially at high velocities. The sludge is sprayed radially toward the hot refractory walls. Combustion is rapid, such that the residence time of the sludge in the chamber is on the order of 10 seconds. The ash is removed with the flue gases.

Rotary kilns are also generally used for small capacity applications. The kiln is inclined slightly from the horizontal plane, with the upper end receiving both the sludge feed and the combustion air. A burner is located at the lower end of the kiln. The circumference of

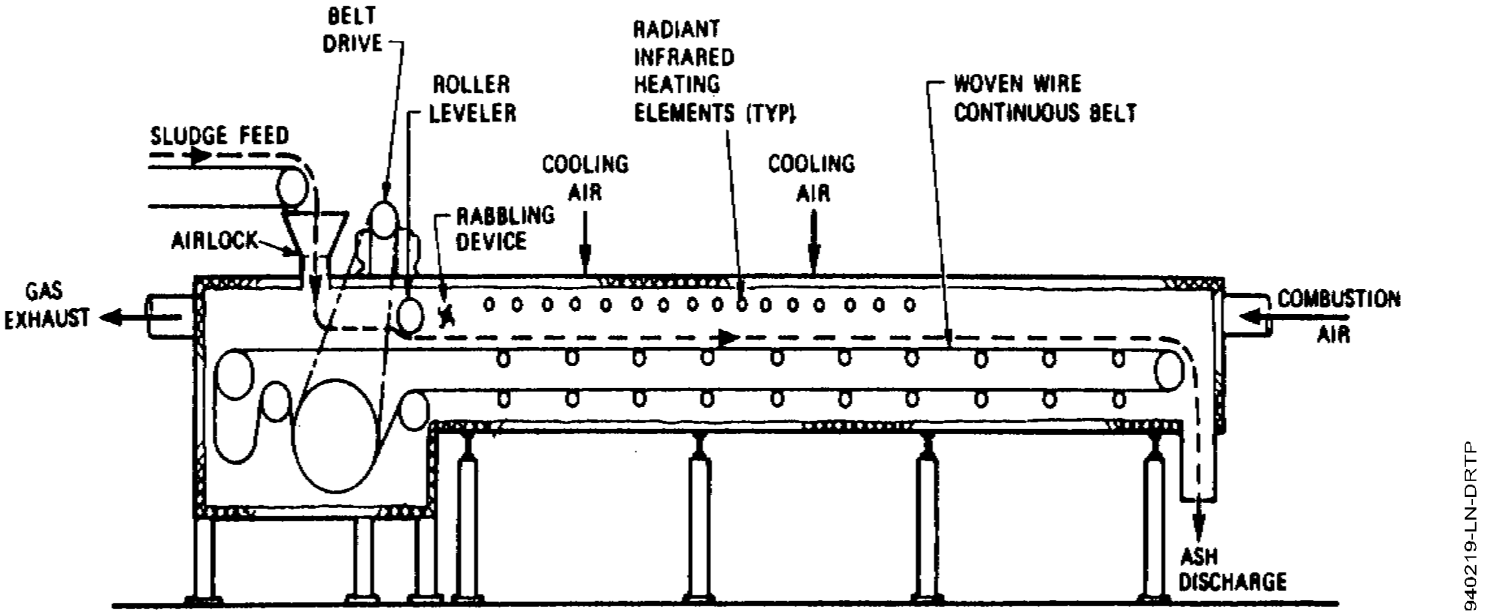


Figure 7-5. Cross Section of an Electric Infrared Furnace

Source: Reference 198.

the kiln rotates at a speed of about 6 inches per second. Ash is deposited into a hopper located below the burner.

The wet oxidation process is not strictly one of incineration; it instead utilizes oxidation at elevated temperature and pressure in the presence of water (flameless combustion). Thickened sludge, at about 6-percent solids, is first ground and mixed with a stoichiometric amount of compressed air. The sludge/air mixture is then circulated through a series of heat exchangers before entering a pressurized reactor. The temperature of the reactor is held between 350 and 600°F (175 and 315°C). The pressure is normally 1,000 to 1,800 pounds per square inch grade (7,000 to 12,500 kilopascals). Steam is usually used for auxiliary heat. The water and resulting ash are circulated out the reactor and are separated in a tank or lagoon. The liquid phase is recycled to the treatment plant. Off-gases must be treated to eliminate odors.

Co-Incineration and Co-Firing

Wastewater treatment plant sludge generally has a high water content and, in some cases, fairly high levels of inert materials. As a result, the net fuel value of sludge is often low. If sludge is combined with other combustible materials in a co-incineration scheme, a furnace feed can be created that has both a low water concentration and a heat value high enough to sustain combustion with little or no supplemental fuel. Virtually any material that can be burned can be combined with sludge in a co-incineration process. Common materials for co-incineration are coal, municipal solid waste (MSW), wood waste, and agricultural waste.

There are two basic approaches to combusting sludge with MSW: (1) use of MSW combustion technology by adding dewatered or dried sludge to the MSW combustion unit, and (2) use of sludge combustion technology by adding processed MSW as a supplemental fuel to the sludge furnace. With the latter, MSW is processed by removing noncombustibles, shredding, air classifying, and screening. Waste that is more finely processed is less likely to cause problems such as severe erosion of the hearths, poor temperature control, and refractory failures.

7.2.2 Benzene Emissions from Sewage Sludge Incineration

Emission factors associated with MHFs and FBCs are provided in Table 7-2.[197] This table provides a comparison of benzene emissions based on no control and control with various PM control devices and an afterburner. However, these emission factors do not reflect the effect of increased operating temperature on reducing benzene emissions. As discussed in Section 7.2.3, increasing the combustion temperature facilitates more complete combustion of organics, resulting in lower benzene emissions. It was not possible in this study to compare the combustor operating conditions of all SSIs for which emissions test data were available to develop the emission factors in Table 7-2.[197] As a result, it was not possible to reflect the effect of combustion temperature on benzene emissions. The emission factors for MHFs presented in Table 7-2 are based on test data of combustors operated at a variety of combustion temperatures in the primary combustion hearths (1,100 to 1,700 °F [600 to 930 °C]).

Using emissions test data for one sewage sludge combustion facility, it was possible to demonstrate the benzene emission reduction achieved with the practice of increasing operating temperature versus utilizing an afterburner or a scrubber. This comparison is provided in Table 7-3.[199] The emissions test data for the one facility used to develop the emission factors presented in Table 7-3 are also averaged into the emission factors presented in Table 7-2.

7.2.3 Control Technologies for Sewage Sludge Incinerators[197,198]

Control of benzene emissions from SSIs is achieved primarily by promoting complete combustion by following GCP. The general conditions of GCP are summarized in Section 7.1.3. As with MWIs, failure to achieve complete combustion of organic materials evolved from the waste can result in emissions of a variety of organic compounds, including

TABLE 7-2. SUMMARY OF EMISSION FACTORS FOR SEWAGE SLUDGE INCINERATION

SCC	Emission Source	Control Device	Emission Factor lb/ton (g/Mg)[a]	Factor Rating
5-01-005-15	MHF	Uncontrolled	1.2×10^{-2} (5.8)	D
		Cyclone/venturi scrubbers	7.0×10^{-4} (3.5×10^{-1})	E
		Venturi scrubber	2.8×10^{-2} (1.4)	E
		Venturi/impingement scrubbers	1.3×10^{-2} (6.3)	D
		Venturi/impingement scrubbers and afterburner	3.4×10^{-4} (1.7×10^{-1})	E
5-01-005-16	FBC	Venturi/impingement scrubbers	4.0×10^{-4} (2.0×10^{-1})	E

Source: Reference 197.

[a] Emission factors are in lb (g) of benzene emitted per ton (Mg) of dry sludge feed.

MHF = multiple hearth furnace.
FBC = fluidized bed combustor.

TABLE 7-3. SUMMARY OF EMISSION FACTORS FOR ONE SEWAGE SLUDGE INCINERATION FACILITY UTILIZING A MULTIPLE HEARTH FURNACE

SCC	Emission Source	Control Device/Method	Emission Factor lb/ton (g/Mg)[a]	Efficiency Percent	Factor Rating
5-01-005-15	Incinerator	Uncontrolled[b]	1.73 x 10^{-2} (8.61)	--	D
		Venturi/Impingement Scrubbers[b]	1.34 x 10^{-2} (6.66)	23	D
		Elevated Operating Temperature[c]	2.65 x 10^{-3} (1.32)	85	D
		Elevated Operating Temperature/Afterburner[c]	1.41 x 10^{-3} (7.02 x 10^{-1})	92	D
		Elevated Operating Temperature/ Afterburner/Venturi and Impingement Scrubbers[c]	3.35 x 10^{-4} (1.67 x 10^{-1})	98	D

Source: Reference 199.

[a] Emission factors are in lb (g) of benzene emitted per ton (Mg) of dry sludge feed.
[b] Furnace operated at "normal" operating temperature of, on average, 1350°F (730°C).
[c] Furnace operated at a higher than "normal" operating temperature of, on average, 1600°F (870°C).

benzene, and adequate oxygen, temperature, residence time, and turbulence will generally minimize emissions of most organics.

Many SSIs have greater variability in their organic emissions than do other waste incinerators because, on average, sewage sludge has a high moisture content and the moisture content can vary widely during operation.[200]

Additional reductions in benzene emissions may be achieved by utilizing PM control devices; however, it is not always the case that a PM control device will reduce benzene emissions. In some cases, the incinerator operating conditions (e.g., combustion temperature and temperature at the air pollution control device) may affect the performance of scrubbers.[199] The types of existing SSI PM controls range from low-pressure-drop spray towers and wet cyclones to higher-pressure-drop venturi scrubbers and venturi/impingement tray scrubber combinations. A few ESPs and baghouses are employed, primarily where sludge is co-fired with MSW.

The most widely used PM control device applied to an MHF is the impingement tray scrubber. Older units use the tray scrubber alone and combination venturi/impingement tray scrubbers are widely applied to newer MHFs and some FBCs. Most electric incinerators and some FBCs use venturi scrubbers only. As indicated in Table 7-3, venturi/impingement tray scrubbers have been demonstrated to reduce benzene emissions from SSIs.

A schematic diagram of a typical combination venturi/impingement tray scrubber is presented in Figure 7-6.[198] Hot gas exits the incinerator and enters the precooling or quench section of the scrubber. Spray nozzles in the quench section cool the incoming gas, and the quenched gas then enters the venturi section of the control device.

Venturi water is usually pumped into an inlet weir above the quencher. The venturi water enters the scrubber above the throat, completely flooding the throat. Turbulence created by high gas velocity in the converging throat section deflects some of the water

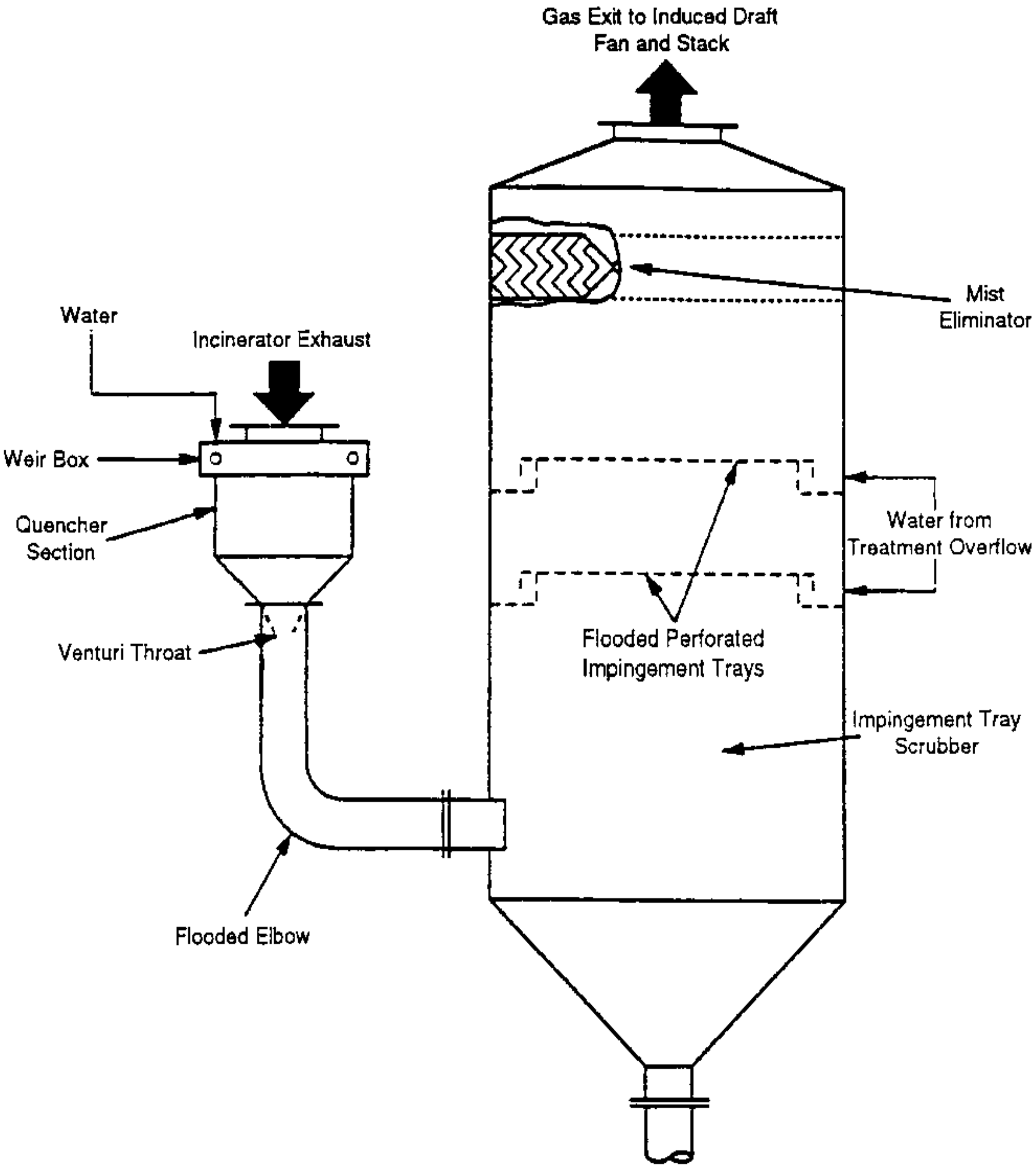


Figure 7-6. Venturi/Impingement Tray Scrubber

Source: Reference 198.

traveling down the throat into the gas stream. PM carried along with the gas stream impacts on these water particles and on the water wall. As the scrubber water and flue gas leave the venturi section, they pass into the flooded elbow, where the stream velocity decreases, allowing the water and gas to separate. By restricting the throat area within the venturi, the linear gas velocity is increased and the pressure drop is subsequently increased, increasing PM removal efficiency.

At the base of the flooded elbow, the gas stream passes through a connecting duct to the base of the impingement tray tower. Gas velocity is further reduced upon entry to the tower as the gas stream passes upward through the perforated impingement trays. Water usually enters the trays from inlet ports on opposite sides and flows across the tray. As gas passes through each perforation in the tray, it creates a jet that bubbles up the water and further entrains solid particles. At the top of the tower is a mist eliminator to reduce the carryover of water droplets in the stack effluent gas. The impingement section can contain from one to four trays.

In the case of MHFs, afterburners may be utilized to achieve additional reduction of organic emissions, including benzene. MHFs produce more benzene emissions because they are designed with countercurrent air flow. Because sludge is usually fed into the top of the furnace, hot air and wet sludge feed are contacted at the top of the furnace, such that any compounds distilled from the solids are immediately vented from the furnace at temperatures too low to completely destroy them.

Utilization of an afterburner provides a second opportunity for these unburned hydrocarbons to be fully combusted. In afterburning, furnace exhaust gases are ducted to a chamber, where they are mixed with supplemental fuel and air and completely combusted. Additionally, some incinerators have the flexibility to allow sludge to be fed to a lower hearth, thus allowing the upper hearth(s) to function essentially as an afterburner.

7.2.4 Regulatory Analysis

Prior to 1993, organic emissions from SSIs were not regulated. On February 19, 1993, Part 503 was added to Subchapter O in Chapter I of Title 40 of the CFR, establishing standards for use or disposal of sewage sludge. Subpart E of Part 503 regulates emissions of total hydrocarbons (THC) from the incineration of SSIs and applies to all SSIs. The THC limit of 100 ppm (measured as a monthly average) is a surrogate for all organic compounds, including benzene. In establishing a standard for organic emissions, EPA had considered establishing a standard for 14 individual organic compounds, including benzene; however, it was concluded that the individual organic pollutants were not significant enough a factor in sewage sludge to warrant requiring individual pollutant limits. Furthermore, based on a long-term demonstration of heated flame ionization detection systems monitoring organic emissions from SSIs, it was concluded that there is an excellent correlation between THC emission levels and organic pollutant emission levels.

The THC limit established in Part 503 is an operational standard that would, in general, not require the addition of control devices to existing incinerators, but would require incinerators to adopt good operating practices on a continuous basis. It is expected that FBCs and MHFs will have no difficulty meeting the standard.[200] To ensure the adoption of GCP, the standard requires continuous THC monitoring using a flame ionization detection system, continuous monitoring of the moisture content in the exit gas, and continuous monitoring of combustion temperature.

7.3 HAZARDOUS WASTE INCINERATION

Hazardous waste is produced in the form of liquids (e.g., waste oils, halogenated and nonhalogenated solvents, other organic liquids, and pesticides/ herbicides) and sludges and solids (e.g., halogenated and nonhalogenated sludges and solids, dye and paint sludges, resins, and latex). Based on a 1986 study, total annual hazardous waste generation in the United States was approximately 292 million tons (265 million metric tons).[201] Only a small fraction of the waste (<1 percent) was incinerated. The major types of hazardous waste streams incinerated were spent nonhalogenated solvents and corrosive and reactive wastes contaminated with organics. Together, these accounted for 44 percent of the waste incinerated. Other prominent wastes included hydrocyanic acid, acrylonitrile bottoms, and nonlisted ignitable wastes.

Hazardous waste can be thermally destroyed through burning under oxidative conditions in incineration systems designed specifically for this purpose and in various types of industrial kilns, boilers, and furnaces. The primary purpose of a hazardous waste incinerator is the destruction of the waste; some systems include energy recovery devices. An estimated 1.9 million tons (1.7 million Mg) of hazardous waste were disposed of in incinerators in 1981.[201] The primary purpose of industrial kilns, boilers, or furnaces is to produce a commercially viable product such as cement, lime, or steam. An estimated 230 million gallons of waste fuel and waste oil were treated at industrial kilns, boilers, and furnaces in 1983.[201] In 1981, it was estimated that industrial kilns, boilers, and furnaces disposed of more than twice the amount of waste that was disposed of via incinerators.[201]

7.3.1 Process Description: Incineration

Incineration is a process that employs thermal decomposition via thermal oxidation at high temperatures (usually 1,650°F [900°C] or greater) to destroy the organic fraction of the waste and reduce volume. A study conducted in 1986 identified 221 hazardous waste incinerators operating under the Resource Conservation and Recovery Act (RCRA) system in the United States. (See Section 7.3.5 for a discussion of this and other regulations applicable to hazardous waste incineration.) These incinerators are located at 189 separate facilities, 171 of which are located at the site of waste generation.[201]

A diagram of the typical process component options in a hazardous waste incineration facility is provided in Figure 7-7.[201] The diagram shows that the major subsystems that may be incorporated into the hazardous waste incineration system are (1) waste

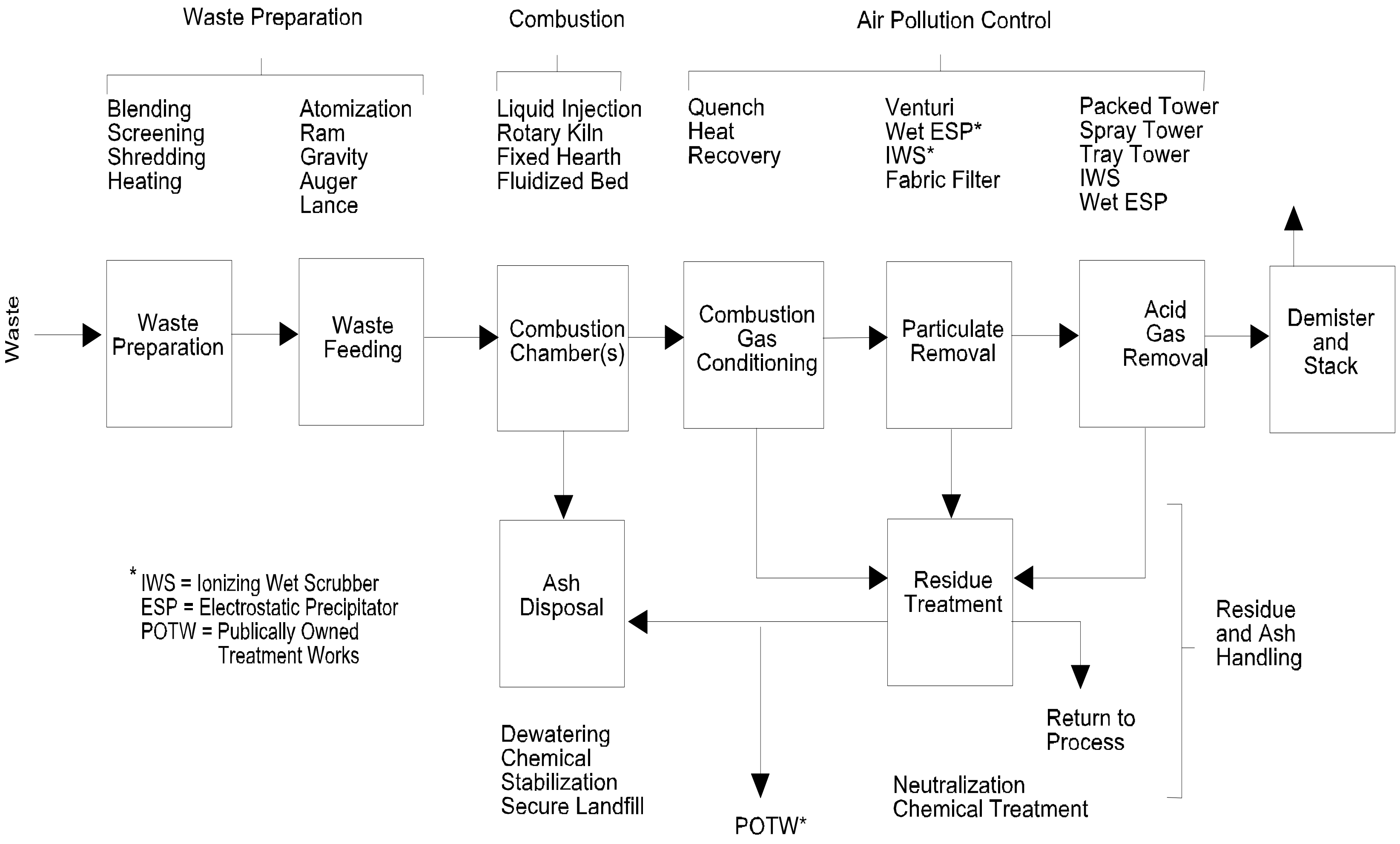


Figure 7-7. General Orientation of Hazardous Waste Incineration Subsystems and Typical Component Options

Source: Reference 201.

preparation and feeding, (2) combustion chamber(s), (3) air pollution control, and (4) residue/ash handling. These subsystems are discussed in this section, except that air pollution control devices are discussed in Section 7.3.4 of this section.

Additionally, energy-recovery equipment may be installed as part of the hazardous waste incineration system, provided that the incinerator is large enough to make energy recovery economically productive (i.e., bigger than about 7 million Btu/hour [7.4 million kJ/hour]) and that corrosive constituents (e.g., HCl) and adhesive particulates are not present at levels that would damage the equipment.[202]

Additionally, a few other technologies have been used for incineration of hazardous waste, including ocean incineration vessels and mobile incinerators. These processes are not in widespread use in the United States and are discussed only briefly.

Waste Preparation and Feeding[201]

The feed method is determined by the physical form of the hazardous waste. Waste liquids are blended and then pumped into the combustion chamber through nozzles or via atomizing burners. Liquid wastes containing suspended particles may need to be screened to avoid clogging of small nozzle or atomizer openings. Liquid wastes may also be blended in order to control the heat content of the liquid to achieve sustained combustion (typically to 8,000 Btu/lb [18,603 kJ/kg]) and to control the chlorine (Cl_2) content of the waste fed to the incinerator (typically to 30 percent or less) to limit the potential for formation of hazardous-free Cl_2 gas in the combustion gas.

Waste sludges are typically fed to the combustion chamber using progressive cavity pumps and water-cooled lances. Bulk solid wastes may be shredded to control particle size and may be fed to the combustion chamber via rams, gravity feed, air lock feeders, vibratory or screw feeders, or belt feeders.

Combustion Chambers[201,202]

The following five types of combustion chambers are available and operating today:[202]

- Liquid injection;
- Rotary kiln;
- Fixed-hearth;
- Fluidized-bed; and
- Fume.

These five types of combustion chambers are discussed below.

Liquid injection--Liquid injection combustion chambers are applicable almost exclusively for pumpable liquid waste, including some low-viscosity sludges and slurries. The typical capacity of liquid injection units is about 8 to 28 million Btu/hour (8.4 to 29.5 million kJ/hr). Figure 7-8 presents a typical schematic diagram of a liquid-injection unit.[201]

Liquid injection units are usually simple, refractory-lined cylinders (either horizontally or vertically aligned) equipped with one or more waste burners. Vertically aligned units are preferred when wastes are high in organic salts and fusable ash content; horizontal units may be used with low-ash waste. Liquid wastes are injected through the burner(s), atomized to fine droplets, and burned in suspension. Burners and separate waste injection nozzles may be oriented for axial, radial, or tangential firing. Good atomization, using gas-fluid nozzles with high-pressure air or steam or with mechanical (hydraulic) means, is necessary to achieve high liquid waste destruction efficiency.

Rotary Kiln--Rotary kiln incinerators are applicable to the destruction of solid wastes, slurries, containerized waste, and liquids. Because of their versatility, they are most

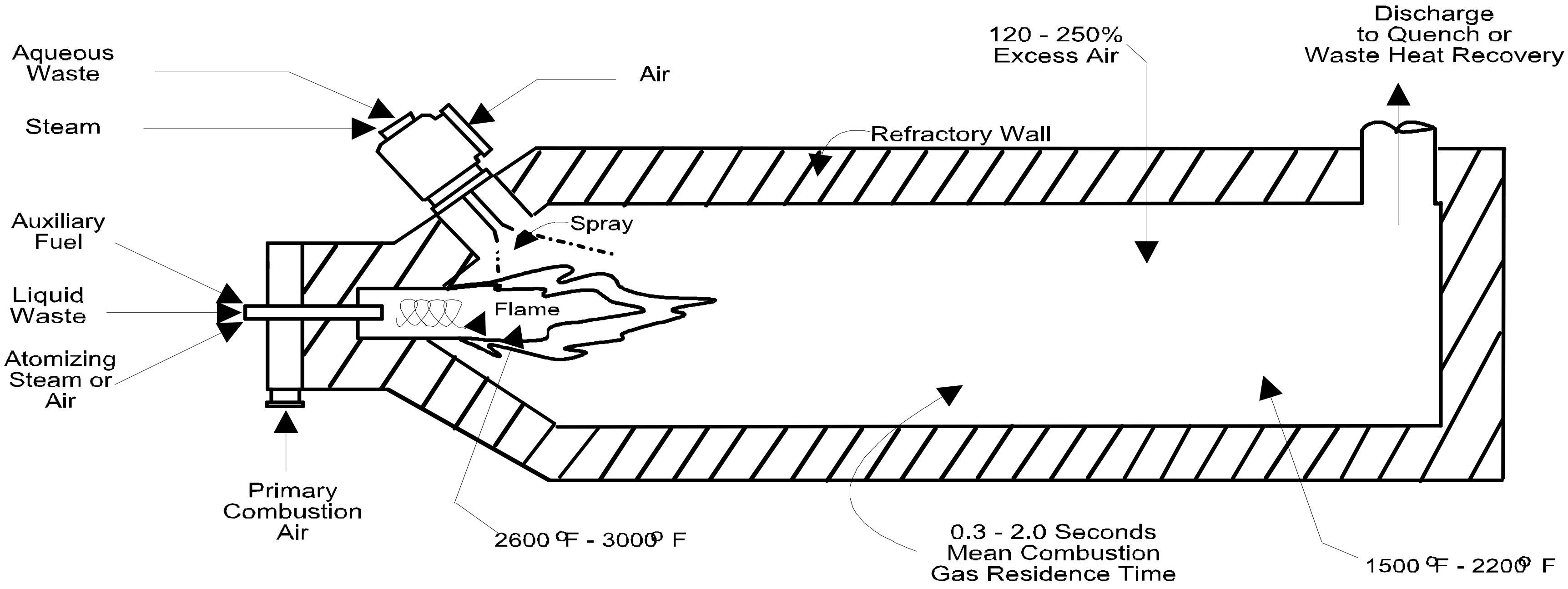


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Figure 7-8. Typical Liquid Injection Combustion Chamber

Source: Reference 201.

frequently used by commercial off-site incineration facilities. The typical capacity of these units is about 10 to 60 million Btu/hour. Figure 7-9 presents a typical schematic diagram of a rotary kiln unit.[201]

Rotary kiln incinerators generally consist of two combustion chambers: a rotating kiln and an afterburner. The rotary kiln is a cylindrical refractory-lined shell that is mounted on a slight incline. The incline facilitates ash and slag removal. Rotation of the shell provides transportation of the waste through the kiln and enhances mixing of the waste with combustion air. The rotational speed of the kiln is used to control waste residence time and mixing. The primary function of the kiln is to convert solid wastes to gases, which occurs through a series of volatilization, destructive distillation, and partial combustion reactions.

An afterburner is connected directly to the discharge end of the kiln. The afterburner is used to ensure complete combustion of flue gases before their treatment for air pollutants. A tertiary combustion chamber may be added if needed. The afterburner itself may be horizontally or vertically aligned, and functions much on the same principles as the liquid injection unit described above. Both the afterburner and the kiln are usually equipped with an auxiliary fuel-firing system to control the operating temperature.

Fixed-Hearth--Fixed-hearth incinerators, also called controlled-air, starved-air, or pyrolytic incinerators, are the third major technology used for hazardous waste incineration. This type of incinerator may be used for the destruction of solid, sludge, and liquid wastes. Fixed-hearth units tend to be of smaller capacity (typically 5 million Btu/hr [5.3 million kJ/hr]) than liquid injection or rotary kiln incinerators because of physical limitations in ram-feeding and transporting large amounts of waste materials through the combustion chamber. Lower relative capital costs and reduced particulate control requirements make fixed-hearth units more attractive than rotary kilns for smaller on-site installations. Figure 7-10 presents a typical schematic diagram of a fixed-hearth unit.[201]

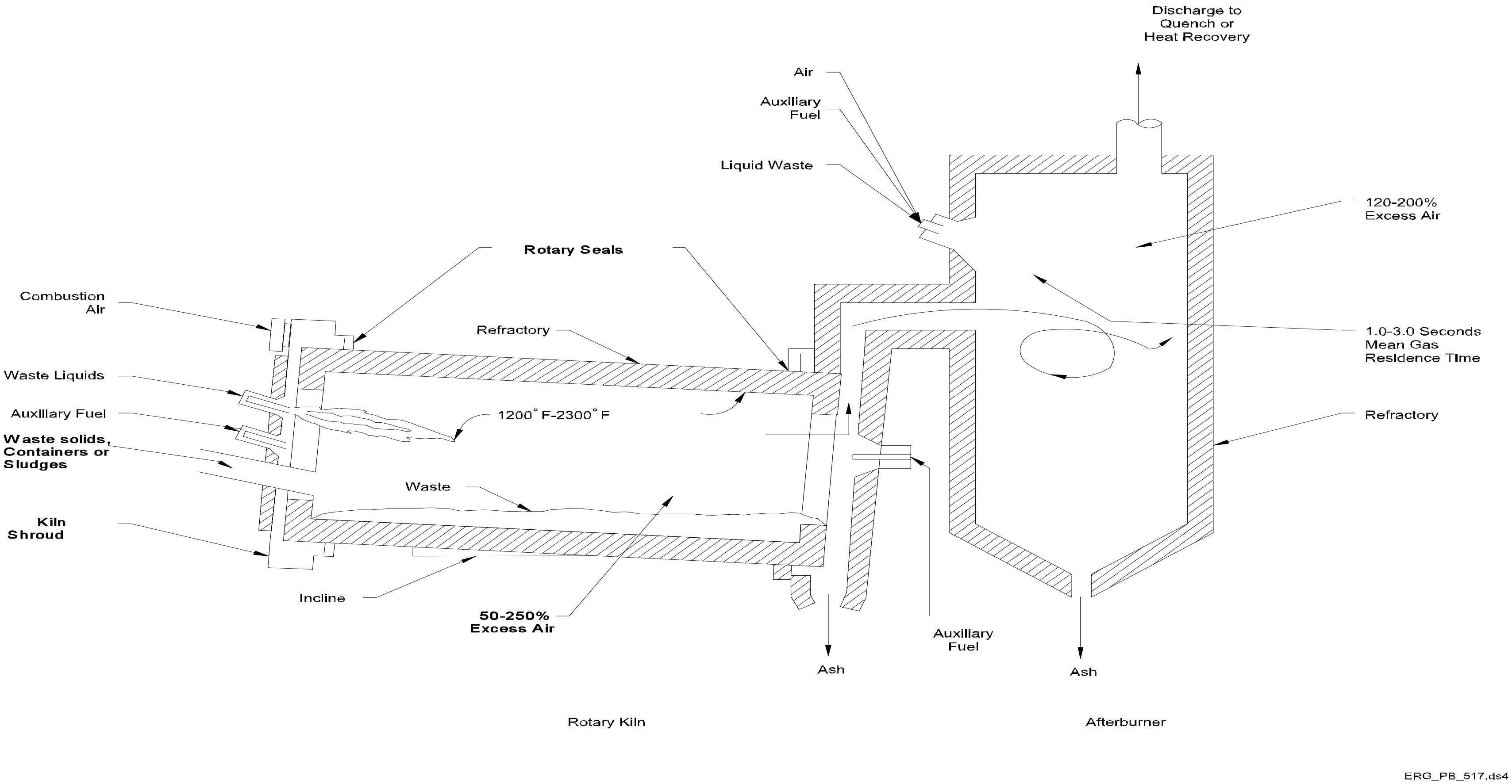

Figure 7-9 Typical Rotary Kiln/Afterburner Combustion Chamber

Source: Reference 201.

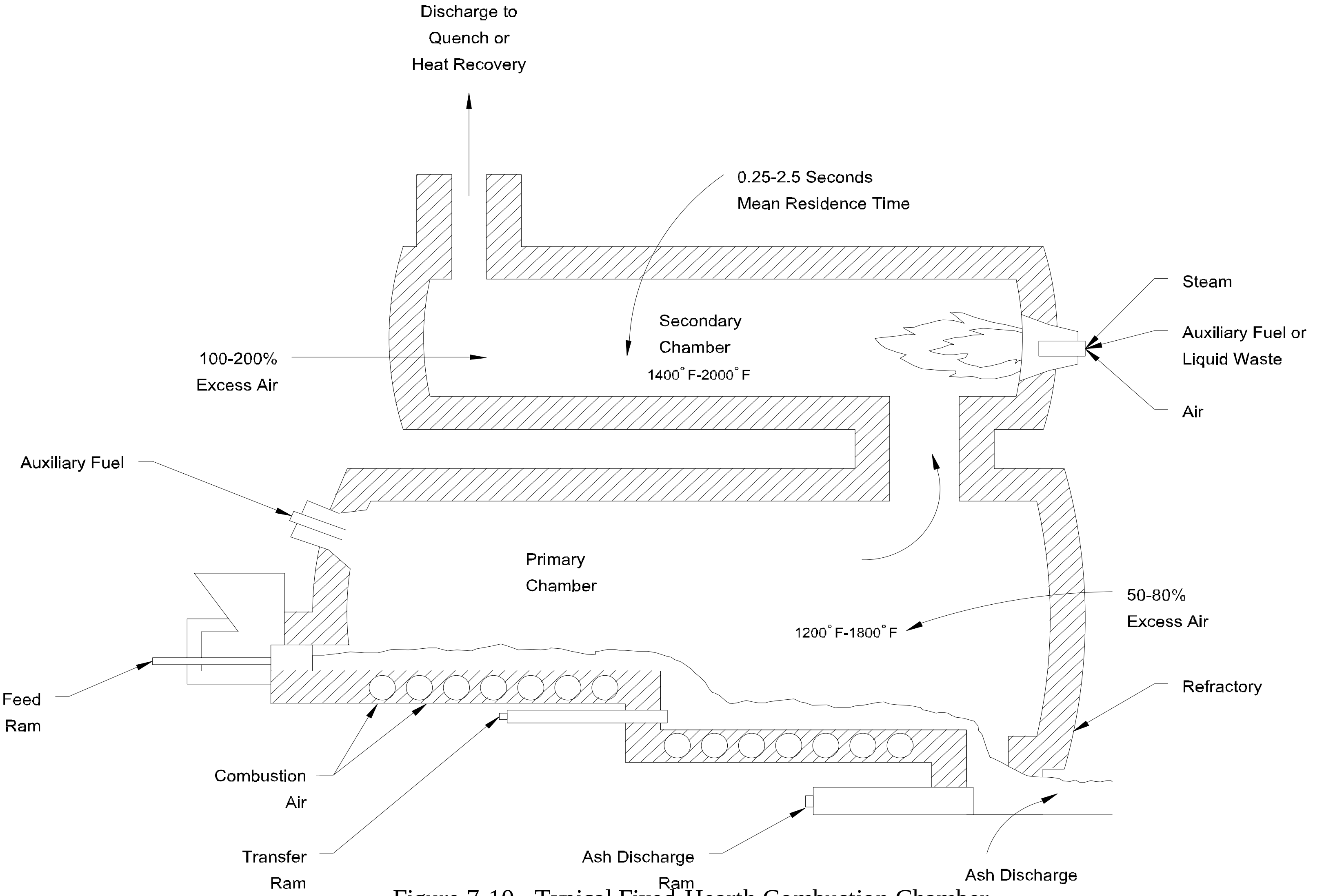

Figure 7-10. Typical Fixed-Hearth Combustion Chamber

Source: Reference 201.

Fixed-hearth units consist of a two-stage combustion process similar to that of rotary kilns. Waste is ram-fed into the primary chamber and burned at about 50 to 80 percent of stoichiometric air requirements. This starved-air condition causes most of the volatile fraction to be destroyed pyrolitically. The resultant smoke and pyrolytic products pass to the secondary chamber, where additional air and, in some cases, supplemental fuel, are injected to complete the combustion.

Fluidized-Bed--FBCs have only more recently been applied to hazardous waste incineration. FBCs may be applied to solids, liquids, and gases; however, this type of incinerator is most effective for processing heavy sludges and slurries. Solids generally require prescreening or crushing to a size less than 2 inches in diameter. The typical capacity of this type of incinerator is 45 million Btu/hr (47.5 million kJ/hr). See Figure 7-4 of this chapter for a typical schematic diagram of an FBC chamber.

FBC chambers consist of a single refractory-lined combustion vessel partially filled with inert granular material (e.g., particles of sand, alumina, and sodium carbonate). Combustion air is supplied through a distributor plate at the base of the combustor at a rate sufficient to fluidize (bubbling bed) or entrain (circulating bed) the bed material. The bed is preheated to startup temperatures by a burner. The bed material is kept at temperatures ranging from 840 to 1,560°F (450 to 850°C). Wastes are injected into the combustion chamber pneumatically, mechanically, or by gravity. Solid wastes are fed into the combustion chamber through an opening above the fluidized bed (similar to the opening for sand feed, represented in Figure 7-4). Liquid wastes are fed into the bottom of the fluidized bed (represented in Figure 7-4 as the opening designated for sludge feed). As the waste is fed to the combustion chamber, heat is transferred from the bed material to the wastes. Upon combustion, the waste returns heat to the bed. The high temperature of the bed also allows for combustion of waste gases above the bed.

Fume--Fume incinerators are used exclusively to destroy gaseous or fume wastes. The combustion chamber is comparable to that of a liquid-injection incinerator

(Figure 7-8) in that it usually has a single chamber, is vertically or horizontally aligned, and uses nozzles to inject the waste into the chamber for combustion. Waste gases are injected by pressure or atomization through the burner nozzles. Wastes may be combusted solely by thermal or catalytic oxidation. If no catalyst is used, the combustion chamber temperature is maintained at 1,200 to 1,800°F (650 to 980°C). If a catalyst is used (e.g., alumina coated with noble metals, such as platinum or palladium, and other metals, such as copper chromate or manganese), the temperature may be maintained at lower temperatures of 500 to 900°F (260 to 480°C).

Residue and Ash Handling[201]

Residue and ash consist of the inorganic components of the hazardous waste that are not destroyed by incineration. Bottom ash is created in the combustion chamber and residue collects in the air pollution control devices. After discharge from the combustion chamber, bottom ash is commonly air-cooled or quenched with water. The ash is then accumulated on site in storage lagoons or in drums prior to disposal to a permitted hazardous waste land disposal facility. The ash may also be dewatered or chemically fixated/stabilized prior to disposal.

Air pollution control residues are typically aqueous streams containing PM, absorbed acid gases, and small amounts of organic material. These streams are collected in sumps or recirculation tanks, where the acids are neutralized with caustic and returned to the process. When the total dissolved solids in the aqueous stream exceeds 3 percent, a portion of the wastes is discharged for treatment and disposal.

Ocean Incinerators

Ocean incineration involves the thermal destruction of liquid hazardous wastes at sea in specially designed tanker vessels outfitted with high-temperature incinerators. Ocean incinerators are identical to land-based liquid injection incinerators, except that current ocean incinerators are not equipped with air pollution control systems. Largely due to public concern over potential environmental effects, ocean incineration of hazardous waste has not been used on a routine basis in the United States.[201]

Mobile Incinerators

Mobile incinerators have been developed for on-site cleanup at uncontrolled hazardous waste sites. Most of these systems are scaled-down, trailer-mounted versions of a conventional rotary kiln or an FBC, with thermal capacities ranging from 10 to 20 million Btu/hr (10.5 to 21.1 million kJ/hr). The performance of these mobile systems has been shown to be comparable to equivalent stationary facilities. Because of their high cost, these types of systems are considered to be cost-effective only at waste sites where large amounts of contaminated material (e.g., soil) would need to be transported off site.[201]

7.3.2 Industrial Kilns, Boilers, and Furnaces

Industrial kilns, boilers, and furnaces burn hazardous wastes as fuel to produce commercially viable products such as cement, lime, iron, asphalt, or steam. These industrial sources require large inputs of fuel to produce the desired product. Hazardous waste, which is considered an economical alternative to fossil fuels for energy and heat, is utilized as a supplemental fuel. In the process of producing energy and heat, the hazardous wastes are subjected to high temperature for a sufficient time to destroy the hazardous content and the bulk of the waste.

Based on a study conducted in 1984, there were over 1,300 facilities using hazardous waste-derived fuels (HWDF) in 1983, accounting for a total of 230 million gallons (871 million liters) of waste fuel and waste oil per year. Although the majority (69 percent) of HWDF is burned by only about 2 percent of the 1,300 facilities (i.e., medium- to large-size industrial boilers, cement and aggregate kilns, and iron-making furnaces), other industries burning significant quantities of HWDF included the paper (SIC 26), petroleum (SIC 29), primary metals (SIC 33), and stone, clay, glass, and concrete (SIC 32) industries.[201] Industrial boilers and furnaces, iron foundries, and cement kilns are described in more detail in Sections 7.4, 7.7, and 7.8, respectively, of this document.

7.3.3 Benzene Emissions From Hazardous Waste Incineration

There are limited data documenting benzene emissions from hazardous waste incinerators. However, as discussed below, benzene is one of the most frequently identified products of incomplete combustion (PICs) in air emissions from hazardous waste incinerators.[203] Two emission factors for benzene emissions are provided in Table 7-4.

7.3.4 Control Technologies for Hazardous Waste Incineration

Most organics control is achieved by promoting complete combustion by following GCP. The general conditions of GCP are summarized in Section 7.1.3. Again, failure to achieve complete combustion of organic materials evolved from the waste can result in emissions of a variety of organic compounds. Benzene is one of the most frequently identified PICs in air emissions from hazardous waste incinerators.[203]

In addition to adequate oxygen, temperature, residence time, and turbulence, control of organics may be partially achieved by using acid gas and PM control devices; however, this has not been documented. The most frequently used control devices for acid gas and PM control are wet scrubbers and fabric filters. Fabric filters provide mainly PM control. Other PM control technologies include venturi scrubbers and ESPs. In addition to wet scrubbing, dry sorbent injection and spray dryer absorbers have also been used for acid gas (HCl and SO_2) control.

TABLE 7-4. SUMMARY OF BENZENE EMISSION FACTORS FOR HAZARDOUS WASTE INCINERATION

SCC	Emission Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Factor Rating
5-03-005-01	Liquid injection incinerator	Uncontrolled[b]	4.66×10^{-5} (2.33×10^{-5})	U
5-03-005-01	Liquid injection incinerator	Various control devices[c]	1.23×10^{-3} (6.16×10^{-4})[d]	U

Source: Reference 3.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of waste incinerated.

[b] The liquid injection incinerator has a built-in afterburner chamber.

[c] The incinerators tested had the following control devices: venturi, packed, and ionized scrubbers; carbon bed filters; and HEPA filters.

[d] The emission factor represents the average of the emission factors for the liquid injection incinerators tested with the various control devices specified in footnote c.

7.3.5 Regulatory Analysis

Organic emissions from hazardous waste incinerators are regulated under 40 CFR 246, Subpart O, promulgated on June 24, 1982.[204] The standards require that in order for a hazardous waste incineration facility to receive a RCRA permit, it must attain a 99.99 percent destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in the waste feed. Each facility must determine which one or more organic compounds, from a list of approximately 400 organic and inorganic hazardous chemicals (including benzene) in Appendix VIII of 40 CFR 261,[205] are POHCs, based on which are the most difficult to incinerate, considering their concentration or mass in the waste feed. Each facility must then conduct trial burns to determine the specific operating conditions under which 99.99 percent DRE is achieved for each POHC.

In order to ensure 99.99 percent DRE, operating limits are established in a permit for each incinerator for the following conditions: (1) CO level in the stack exhaust gas, (2) waste feed rate, (3) combustion temperature, (4) an appropriate indicator of combustion gas velocity, (5) allowable variations in incinerator system design or operating procedures, and (6) other operating requirements considered necessary to ensure 99.99 percent DRE for the POHCs.

Additionally, Subpart O of 40 CFR 246 requires that hazardous waste incineration facilities achieve 99-percent emissions reduction of HCl (if HCl emissions are greater than 1.8 kg/hr [4.0 lb/hr]) and a limit of 180 milligrams per dry standard cubic meter (0.0787 grains per dry standard cublic foot) for PM emissions. These emission limits would require facilities to apply acid gas/PM control devices. As mentioned in Section 7.3.4, acid gas/PM control devices may result in partial control of emissions of organic compounds.

7.4 EXTERNAL COMBUSTION OF SOLID, LIQUID, AND GASEOUS FUELS IN STATIONARY SOURCES FOR HEAT AND POWER GENERATION

The combustion of solid, liquid, and gaseous fuels such as natural gas, oil, coal, and wood waste has been shown to be a minor source of benzene emissions. This section addresses benzene emissions from the external combustion of these types of fuels by stationary sources that generate heat or power in the utility, industrial/commercial, and residential sectors.

7.4.1 Utility Sector[206]

Fossil fuel-fired utility boilers comprise about 72 percent (or 1,696,000 million Btu/hr [497,000 megawatts (MW)]) of the generating capacity of U.S. electric power plants. The primary fossil fuels burned in electric utility boilers are coal, natural gas, and oil. Of these fuels, coal is the most widely used, accounting for 60 percent of the U.S. fossil fuel generating capacity. Natural gas represents about 25 percent and oil represents 15 percent of the U.S. fossil fuel generating capacity.

Most of the coal-firing capability is east of the Mississippi River, with the significant remainder being in the Rocky Mountain region. Natural gas is used primarily in the South Central States and California. Oil is predominantly used in Florida and the Northeast. Fuel economics and environmental regulations affect regional use patterns. For example, coal is not used in California because of stringent air quality limitations. Information on precise utility plant locations can be obtained by contacting utility trade associations such as the Electric Power Research Institute in Palo Alto, California (415-855-2000); the Edison Electric Institute in Washington, D.C. (202-828-7400); or the U.S. Department of Energy (DOE) in Washington, D.C. Publications by EPA/DOE on the utility industry are also useful in determining specific facility locations, sizes, and fuel use.

Process Description of Utility Boilers

A utility boiler consists of several major subassemblies, as shown in Figure 7-11.[206] These subassemblies include the fuel preparation system, the air supply system, burners, the furnace, and the convective heat transfer system. The fuel preparation system, air supply, and burners are primarily involved in converting fuel into thermal energy in the form of hot combustion gases. The last two subassemblies are involved in the transfer of the thermal energy in the combustion gases to the superheated steam required to operate the steam turbine and produce electricity.[206]

Three key thermal processes occur in the furnace and convective sections of the boiler. First, thermal energy is released during controlled mixing and combustion of fuel and oxygen in the burners and furnace. Second, a portion of the thermal energy formed by combustion is adsorbed as radiant energy by the furnace walls. The furnace walls are formed by multiple, closely spaced tubes filled with high-pressure water that carry water from the bottom of the furnace to absorb radiant heat energy to the steam drum located at the top of the boiler. Third, the gases enter the convective pass of the boiler, and the balance of the energy retained by the high-temperature gases is adsorbed as convective energy by the convective heat transfer system (superheater, reheater, economizer, and air preheater).[206]

A number of different furnace configurations are used in utility boilers, including tangentially fired, wall-fired, cyclone-fired, stoker-fired, and FBC boilers. Some of these furnace configurations are designed primarily for coal combustion; others are designed for coal, oil, or natural gas combustion. The types of furnaces most commonly used for firing oil and natural gas are the tangentially fired and wall-fired boiler designs.[207] One of the primary differences between furnaces designed to burn coal versus oil or gas is the furnace size. Coal requires the largest furnace, followed by oil, then gas.[206]

The average size of boilers used in the utility sector varies primarily according to boiler type. Cyclone-fired boilers are generally the largest, averaging about 850 to

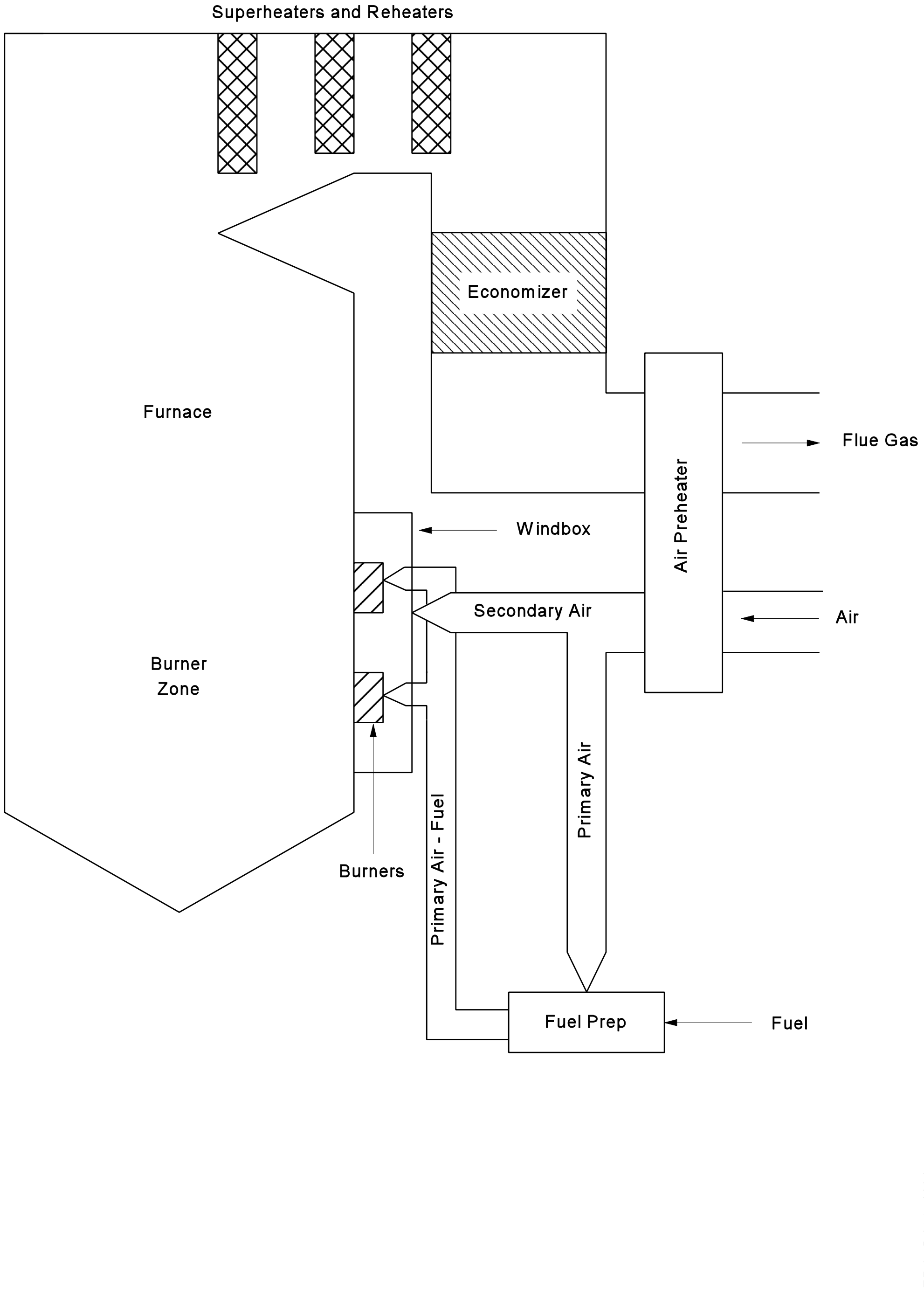

Figure 7-11. Simplified Boiler Schematic

Source: Reference 206.

1,300 million Btu/hr (250 to 380 MW) generating capacity. Tangentially fired and wall-fired boiler designs firing coal average about 410 to 1,470 million Btu/hr (120 to 430 MW); these designs firing oil and natural gas average about 340 to 920 million Btu/hr (100 to 270 MW). Stoker-fired boilers average about 34 to 58 million Btu/hr (10 to 17 MW).[207] Additionally, unit sizes of FBC boilers range from 85 to 1,360 million Btu/hr (25 to 400 MW), with the largest FBC boilers typically closer to 680 million Btu/hr (200 MW).[206]

Tangentially Fired Boiler--The tangentially-fired boiler is based on the concept of a single flame zone within the furnace. The fuel-to-air mixture in a tangentially fired boiler projects from the four corners of the furnace along a line tangential to an imaginary cylinder located along the furnace centerline. When coal is used as the fuel, the coal is pulverized in a mill to the consistency of talcum powder (i.e., at least 70 percent of the particles will pass through a 200-mesh sieve), entrained in primary air, and fired in suspension.[208] As fuel and air are fed to the burners, a rotating “fireball” is formed to control the furnace exit gas temperature and provide steam temperature control during variations in load. The fireball may be moved up and down by tilting the fuel-air nozzle assembly. Tangentially fired boilers commonly burn coal (pulverized). However, oil or gas may also be burned.[206]

Wall-Fired Boiler--Wall-fired boilers are characterized by multiple individual burners located on a single wall or on opposing walls of the furnace. Refer to Figure 7-12 for a diagram of a single wall-fired boiler.[206] As with tangentially fired boilers, when coal is used as the fuel, the coal is pulverized, entrained in primary air, and fired in suspension. In contrast to tangentially fired boilers, which produce a single flame envelope or fireball, each of the burners in a wall-fired boiler has a relatively distinct flame zone. Depending on the design and location of the burners, wall-fired boilers consist of various designs, including single-wall, opposed-wall, cell, vertical, arch, and turbo. Wall-fired boilers may burn (pulverized) coal, oil, or natural gas.[206]

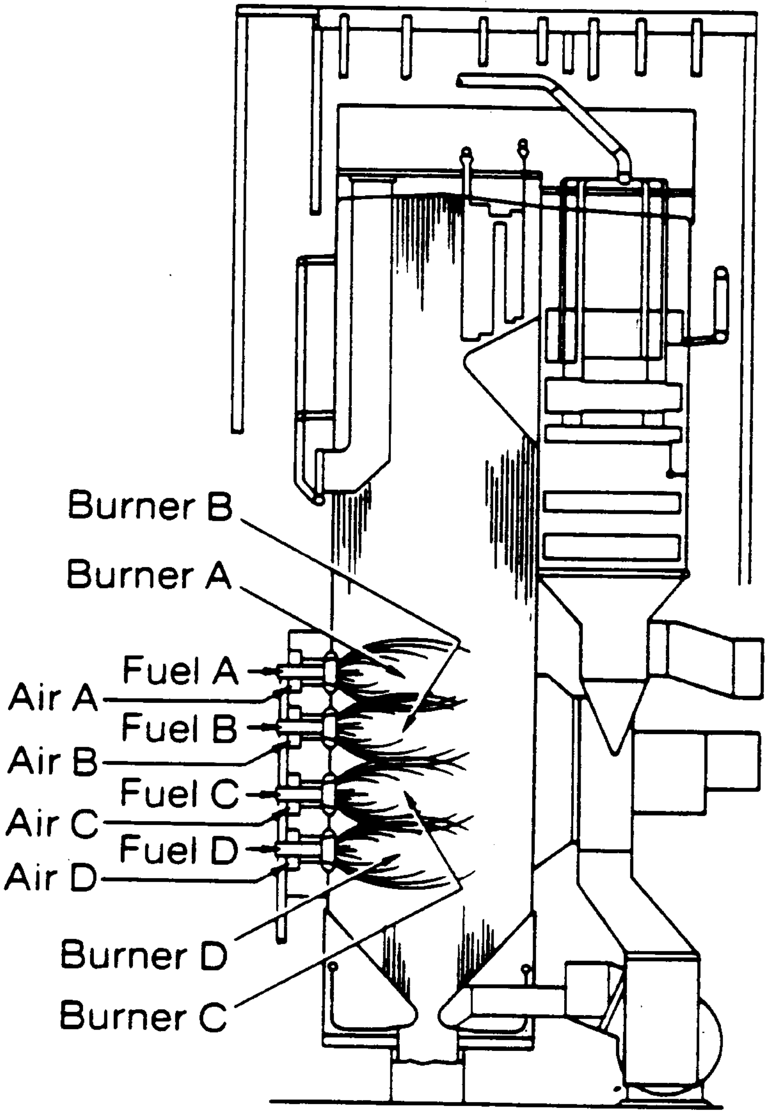

Figure 7-12. Single Wall-fired Boiler

Source: Reference 206.

Cyclone-Fired Boiler--As shown in Figure 7-13, in cyclone-fired boilers, fuel and air are burned in horizontal, cylindrical chambers, producing a spinning, high-temperature flame. When coal is used, the coal is crushed to a 4-mesh size and admitted with the primary air in a tangential fashion. The finer coal particles are burned in suspension and the coarser particles are thrown to the walls by centrifugal force.[207] Cyclone-fired boilers are almost exclusively coal-fired and burn crushed rather than pulverized coal. However, some units are also able to fire oil and natural gas.[206]

Fluidized-Bed Combustion Boiler--Fluidized-bed combustion is a newer boiler technology that is not as widely used as the other, conventional boiler types. In a typical FBC boiler, crushed coal in combination with inert material (sand, silica, alumina, or ash) and/or sorbent (limestone) are maintained in a highly turbulent suspended state by the upward flow of primary air from the windbox located directly below the combustion floor. This fluidized state provides a large amount of surface contact between the air and solid particles, which promotes uniform and efficient combustion at lower furnace temperatures--between 1,575 and 1,650°F (860 and 900°C) compared to 2,500 and 2,800°F (1,370 and 1,540°C) for conventional coal-fired boilers. Fluidized bed combustion boilers have been developed to operate at both atmospheric and pressurized conditions. Refer to Figure 7-14 for a simplified diagram of an atmospheric FBC.[206]

Stoker-Fired Boiler--Rather than firing coal in suspension, mechanical stokers can be used to burn coal in fuel beds. All mechanical stokers are designed to feed coal onto a grate within the furnace. The most common stoker type of boiler used in the utility industry is the spreader-type stoker (refer to Figure 7-15 for a diagram of a spreader type stoker fired-boiler).[206] Other stoker types are overfeed and underfeed stokers.

In spreader stokers, a flipping mechanism throws crushed coal into the furnace and onto a moving fuel bed (grate). Combustion occurs partly in suspension and partly on the grate.[208] In overfeed stokers, crushed coal is fed onto a traveling or vibrating grate from an adjustable gate above and burns on the fuel bed as it progresses through the furnace.

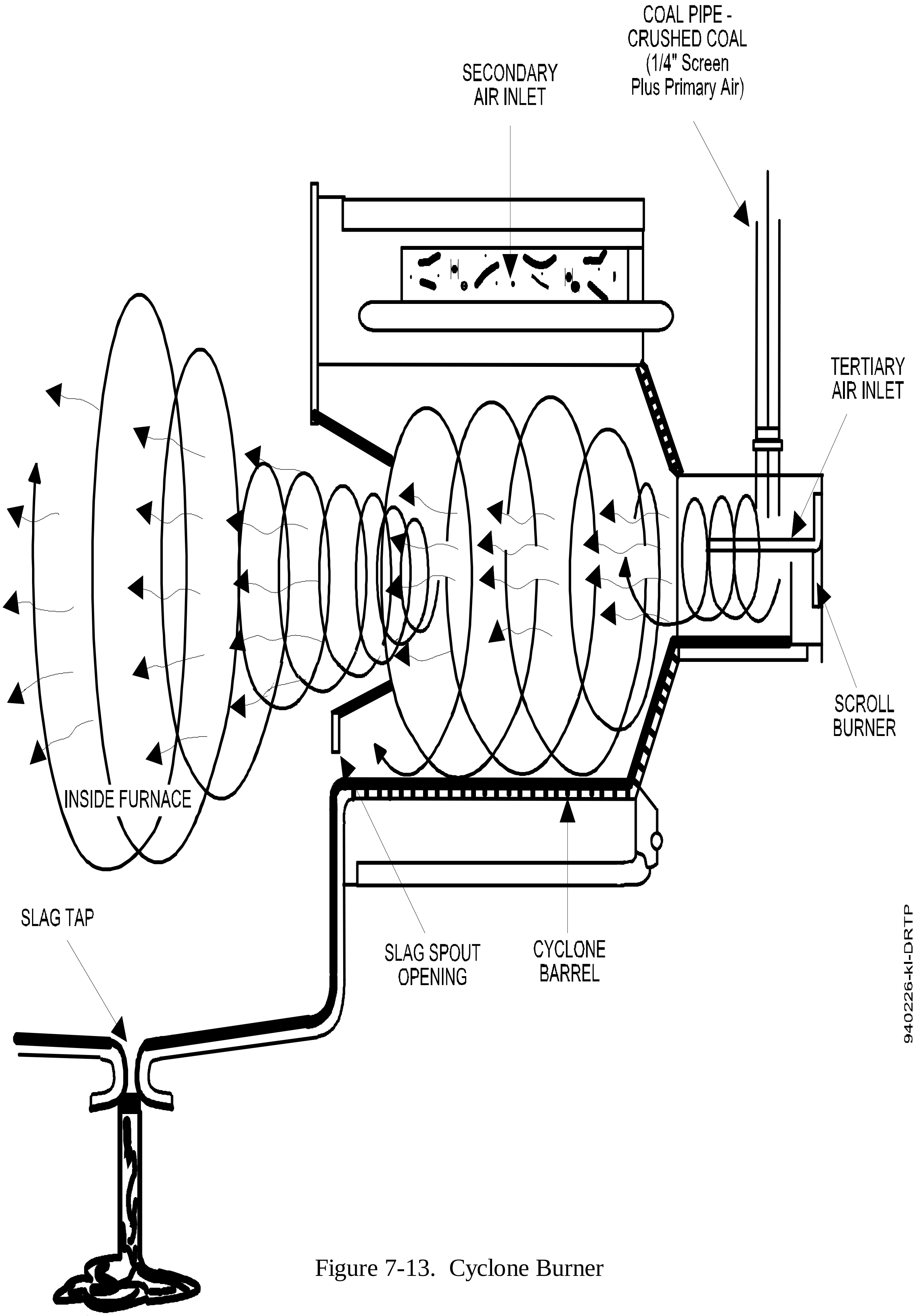

Figure 7-13. Cyclone Burner

Source: Reference 206.

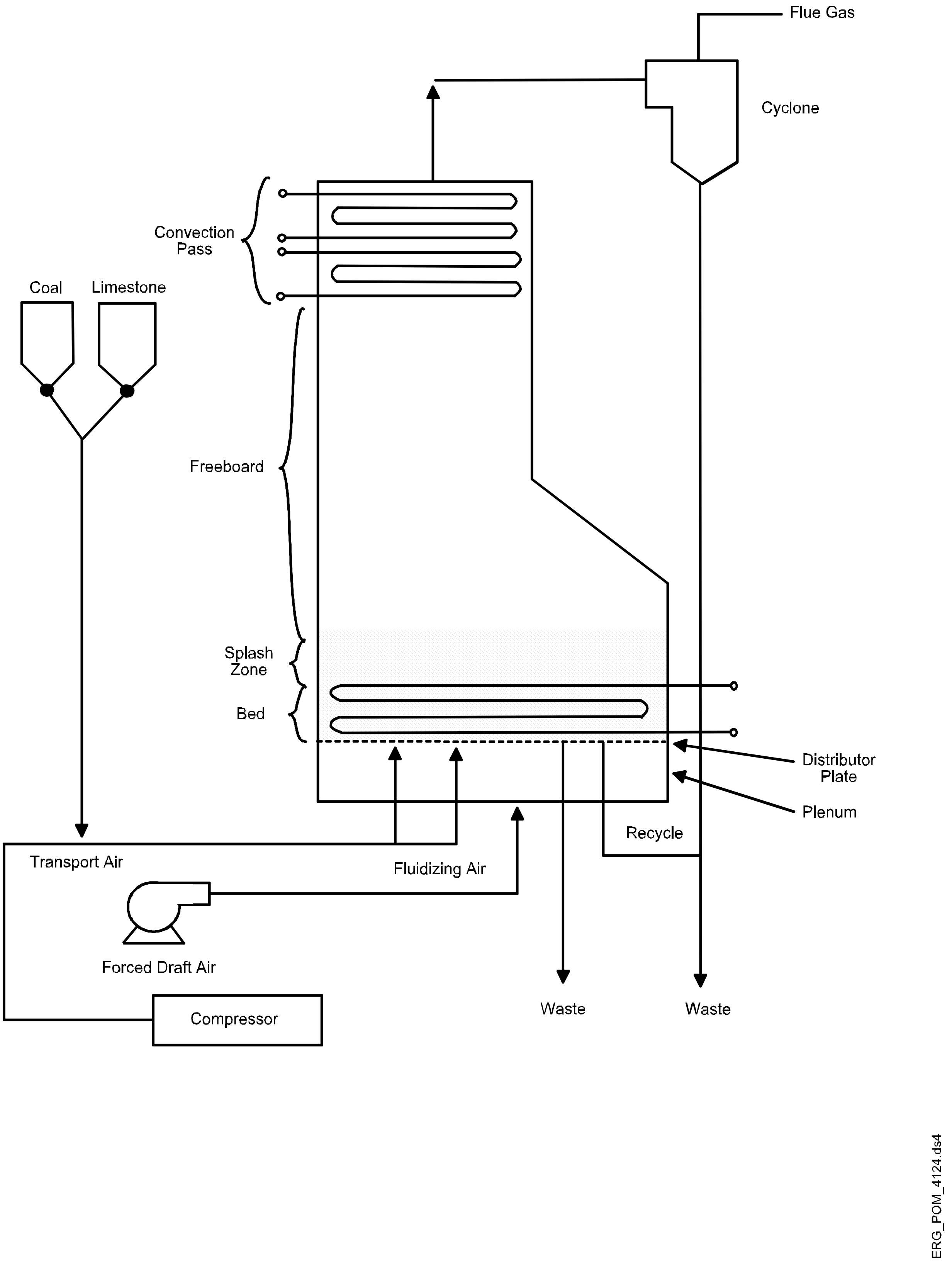

Figure 7-14. Simplified Atmospheric Fluidized Bed Combustor Process Flow Diagram

Source: Reference 206.

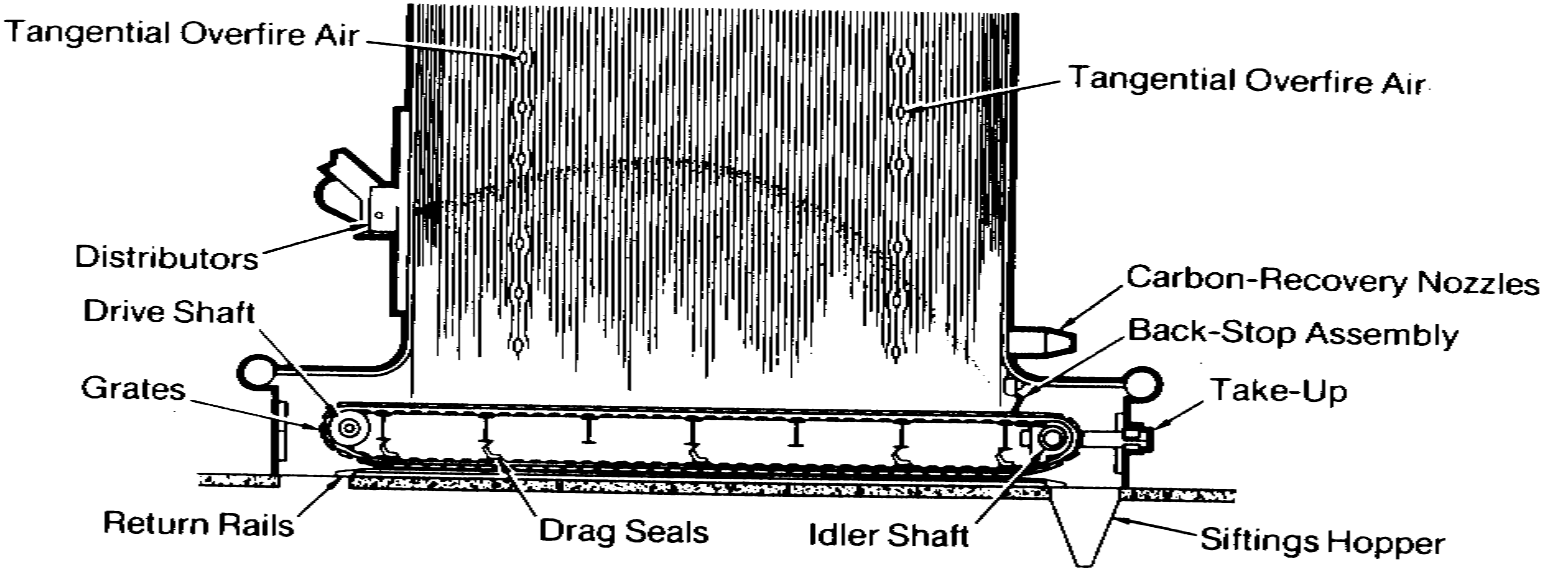

Figure 7-15. Spreader Type Stoker-fired Boiler - Continuous Ash Discharge Grate

Source: Reference 206.

Conversely, in underfeed stokers, crushed coal is forced upward onto the fuel bed from below by mechanical rams or screw conveyors.[206,208]

Benzene Emissions from Utility Boilers

Benzene emissions from utility boilers may depend on various factors, including (1) type of fossil fuel burned, (2) type of boiler used, (3) operating conditions of the boiler, and (4) pollution control device(s) used. As described below, conditions that favor more complete combustion of the fuel generally result in lower organic emissions. Emission factors for benzene emissions from utility boilers are presented in Table 7-5.

Table 7-5 presents three benzene emission factors for two types of coal-fired boilers utilizing three types of PM/SO_2/NO_x air pollution control systems. The data show only slightly higher benzene emissions from a tangentially fired boiler than a cyclone-fired boiler firing coal, and show that there is no significant difference in benzene emissions from the different air pollution control device configurations represented.[209]

Table 7-5 also presents two emission factors for two types of natural gas-fired boilers utilizing flue gas recirculation.[3,209,210] The data show only slightly higher emissions for the opposed-wall boiler than for the tangentially fired boiler. Additionally, the emission tests from which the emission factors were generated demonstrated that changes in unit load and excess air level did not significantly impact benzene emissions from either boiler type.[210]

Control Technologies for Utility Boilers

Utility boilers are highly efficient and generally the best controlled of all combustion sources. Baghouses, ESPs, wet scrubbers, and multicyclones have been applied for PM control in the utility sector. A combination of a wet scrubber and ESP are often used to control both SO_2 and PM emissions.

TABLE 7-5. SUMMARY OF BENZENE EMISSION FACTORS FOR UTILITY BOILERS

SCC	Emission Source	Fuel Type	Control Device	Emission Factor lb/MMBtu (μg/J)[a]	Factor Rating	Reference
1-01-002-03	Cyclone boiler	Coal	Baghouse/SCR/ sulfuric acid condenser[b]	5.58 x 10^{-6} (2.40 x 10^{-6})	D	209
1-01-002-03	Cyclone boiler	Coal	Electrostatic precipitator	7.90 x 10^{-6} (3.40 x 10^{-6})	D	209
1-01-003-02	Tangentially-fired boiler	Lignite[c]	Electrostatic precipitator/ scrubber[d]	3.95 x 10^{-5} (1.70 x 10^{-5})	D	209
1-01-006-01	Opposed-wall boiler[e]	Natural gas	Flue gas recirculation	1.40 x 10^{-6} (6.02 x 10^{-7})	D	210
1-01-006-04	Tangentially-fired boiler[e]	Natural gas	Flue gas recirculation	4.00 x 10^{-7} (1.72 x 10^{-7})	D	210
1-01-009-01	Boiler	Bark[f]	Uncontrolled	3.60 x 10^{-3} lb/ton (1.80 x 10^{-3} kg/Mg)[g]	E	3

[a] Factors are in lb (μg) of benzene emitted per MMBtu (J).

[b] There is an SO_2 reactor prior to the condenser.

[c] The lignite is pulverized and dried.

[d] The scrubber is a spray tower using an alkali slurry.

[e] The furnace has overfire air ports and off-stoichiometric firing.

[f] The bark had a moisture of 50 percent.

[g] Pound (kg) of benzene emitted per ton (Mg) of bark fired.

SCR = selective catalytic reduction.

The above control technologies are not intended to reduce benzene emissions from utility boilers. In general, emissions of organic pollutants, including benzene, are reduced by operating the furnace in such as way as to promote complete combustion of the fossil fuel(s) combusted in the furnace. Therefore, any combustion modification that increases the combustion efficiency will most likely reduce benzene emissions. The following conditions can increase combustion efficiency:[211]

- Adequate supply of oxygen;
- Good air/fuel mixing;
- Sufficiently high combustion temperature;
- Short combustion gas residence time; and
- Uniform fuel load (i.e., consistent combustion intensity).

7.4.2 Industrial/Commercial Sector

Industrial boilers are widely used in manufacturing, processing, mining, and refining primarily to generate process steam, electricity, or space heat at the facility. However, the industrial generation of electricity is limited, with only 10 to 15 percent of industrial boiler coal consumption and 5 to 10 percent of industrial boiler gas and oil consumption used for electricity generation.[212] The use of industrial boilers is concentrated in four major industries: pulp and paper, primary metals, chemicals, and minerals. These industries account for 82 percent of the total firing capacity.[213] Commercial boilers are used by commercial establishments, medical institutions, and educational institutions to provide space heating.

In collecting survey data to support its Industrial Combustion Coordinated Rulemaking (ICCR), the EPA compiled information on a total of 69,494 combustion boiler units in the industrial and commercial sectors.[213] While this number likely underestimates the total population of boilers in the industrial and commercial sectors (due to unreceived survey responses and lack of information on very small units) it provides an indication of the large number of sources included in this category.

Of the units included in the ICCR survey database, approximately 70 percent were classified in the natural gas fuel subcategory, 23 percent in the oil (distillate and residual) subcategory, and 6 percent in the coal burning subcategory. These fuel subcategory assignments are based on the units burning only greater than 90 percent of the specified fuel for that subcategory. All other units (accounting for the other 1 percent of assignments) are assigned to a subcategory of "other fossil fuel."[213]

Other fuels burned in industrial boilers are wood wastes, liquified petroleum gas, asphalt, and kerosene. Of these fuels, wood waste is the only non-fossil fuel discussed here because benzene emissions were not characterized for combustion of the other fuels. The burning of wood waste in boilers is confined to those industries where it is available as a byproduct. It is burned both to obtain heat energy and to alleviate possible solid waste disposal problems. Generally, bark is the major type of waste burned in pulp mills. In the lumber, furniture, and plywood industries, either a mixture of wood and bark waste or wood waste alone is most frequently burned. As of 1980, there were approximately 1,600 wood-fired boilers operating in the United States, with a total capacity of over 102,381 million Btu/hour (30,000 MW).[214]

Industrial and commercial coal combustion sources are located throughout the United States, but tend to follow industry and population trends. Most of the coal-fired industrial boiler sources are located in the Midwest, Appalachian, and Southeast regions. Industrial wood-fired boilers tend to be located almost exclusively at pulp and paper, lumber products, and furniture industry facilities. These industries are concentrated in the Southeast, Gulf Coast, Appalachian, and Pacific Northwest regions. The Pacific Northwest contains many of the boilers firing salt-laden wood bark.

Trade associations such as the American Boiler Manufacturers Association in Arlington, Virginia, (703-522-7350) and the Council of Industrial Boiler Owners in Fairfax Station, Virginia, (703-250-9042) can provide information on industrial boiler locations and trends.[215]

Process Description of Industrial/Commercial Boilers

Some of the same types of boilers used by the utility sector are also used by the industrial/commercial sector; however, the average boiler size used by the industrial/commercial sector is substantially smaller. Additionally, a few types of boiler designs are used only by the industrial sector. For a general description of the major subassemblies of boilers and their key thermal processes, refer to the discussion of utility boilers in Section 7.4.1 and Figure 7-11. The following two sections describe industrial/commercial boilers that fire fossil fuels and wood waste.

Fossil Fuel Combustion--All of the boilers used by the utility industry (described in Section 7.4.1) are "water-tube" boilers, which means that the water being heated flows through tubes and the hot gases circulate outside the tubes. Water-tube boilers represent the majority (57 percent) of industrial and commercial boiler capacity (70 percent of industrial boiler capacity).[212] Water-tube boilers are used in a variety of applications, ranging from supplying large amounts of process steam to providing space heat for industrial and commercial facilities. These boilers have capacities ranging from 10 to 1,500 million Btu/hr (3 to 440 MW), averaging about 410 million Btu/hr (120 MW). The most common types of water-tube boilers used in the industrial/ commercial sector are wall-fired and stoker-fired boilers. Tangentially fired and FBC boilers are less commonly used. Refer to Section 7.4.1 for descriptions of these boiler designs.[213]

The industrial/commercial sector also uses boilers with two other types of heat transfer methods: fire-tube and cast iron boilers. Because their benzene emissions have not been characterized, these types of boilers are only briefly described below.

In fire-tube boilers, the hot gas flows through the tubes and the water being heated circulates outside of the tubes. Fire-tube boilers are not available with capacities as large as those of water-tube boilers, but they are also used to produce process steam and space heat. Most fire-tube boilers have a capacity between 1.4 and 24.9 million Btu/hour (0.4 and7.3 MW thermal). Most installed firetube boilers burn oil or gas.[213]

In cast iron boilers, the hot gas is also contained inside the tubes, which are surrounded by the water being heated, but the units are constructed of cast iron instead of steel. Cast iron boilers are limited in size and are used only to supply space heat. Cast iron boilers range in size from less than 0.3 to 9.9 million Btu/hour (0.1 to 2.9 MW thermal).[213]

<u>Wood Combustion</u>--The burning of wood waste in boilers is mostly confined to those industries where it is available as a byproduct. It is burned both to obtain heat energy and to alleviate solid waste disposal problems. Wood waste may include large pieces such as slabs, logs, and bark strips, as well as cuttings, shavings, pellets, and sawdust.[214]

Various boiler firing configurations are used in burning wood waste. One common type in smaller operations is the dutch oven or extension type of furnace with a flat grate. This unit is widely used because it can burn fuels with very high moisture. Fuel is fed into the oven through apertures in a firebox and is fired in a cone-shaped pile on a flat grate. The burning is done in two stages: (1) drying and gasification, and (2) combustion of gaseous products. The first stage takes place in a cell separated from the boiler section by a bridge wall. The combustion stage takes place in the main boiler section.[214]

In another type of boiler, the fuel-cell oven, fuel is dropped onto suspended fixed grates and fired in a pile. The fuel cell uses combustion air preheating and positioning of secondary and tertiary air injection ports to improve boiler efficiency.[214]

In many large operations, more conventional boilers have been modified to burn wood waste. The units may include spreader stokers with traveling grates or vibrating grate stokers, as well as tangentially fired or cyclone-fired boilers (see Section 7.4.1 for descriptions of these types of boilers). The most widely used of these configurations is the spreader stoker, which can burn dry or wet wood. Fuel is dropped in front of an air jet that casts the fuel out over a moving grate. The burning is done in three stages: (1) drying, (2) distillation and burning of volatile matter, and (3) burning of fixed carbon. Natural gas or oil is often fired as auxiliary fuel. This is done to maintain constant steam when the wood supply fluctuates or to provide more steam than can be generated from the wood supply alone.[214]

Sander dust is often burned in various boiler types at plywood, particle board, and furniture plants. Sander dust contains fine wood particles with low moisture content (less than 20 percent by weight). It is fired in a flaming horizontal torch, usually with natural gas as an ignition aid or supplementary fuel.[214]

A recent development in wood firing is the FBC boiler. Refer to Section 7.4.1 for a description of this boiler type. Because of the large thermal mass represented by the hot inert bed particles, FBCs can handle fuels with high moisture content (up to 70 percent, total basis). Fluidized beds can also handle dirty fuels (up to 30 percent inert material). Wood material is pyrolyzed more quickly in a fluidized bed than on a grate because of its immediate contact with hot bed material. Combustion is rapid and results in nearly complete combustion of organic matter, minimizing emissions of unburned organic compounds.[214]

Benzene Emissions from Industrial/Commercial Boilers

Benzene emissions from industrial/commercial boilers may depend on various factors, including (1) type of fuel burned, (2) type of boiler used, (3) operating conditions of the boiler, and (4) pollution control device(s) used. Conditions that favor more complete combustion of the fuel generally result in lower organic emissions. Additionally, the organic emissions potential of wood combustion is generally thought to be greater than that of fossil fuel combustion because wood waste has a lower heating value, which may decrease combustion efficiency. Emission factors for benzene emissions from industrial and commercial/institutional boilers are presented in Table 7-6.[3,216-220]

Table 7-6 presents emission factors primarily for wood waste combustion. Additionally a few emission factors are presented for fossil fuel (residual oil and coke/coal) and process gas (landfill gas and POTW digester gas) combustion. Most of the emission factors represent emissions from a non-specified type of boiler. Only two boiler types are specified (FBC and spreader-stoker). Additionally, the benzene emission factors presented are emissions following various types of PM and SO_2 emission control systems.

In most cases, Table 7-6 specifies the type of wood waste associated with the emission factors for wood combustion boilers. The composition of wood waste may have an impact on benzene emissions. The composition of wood waste depends largely on the industry from which it originates. Pulping operations, for example, produce great quantities of bark that may contain more than 70 percent by weight moisture, along with sand and other noncombustibles. Because of this, bark boilers in pulp mills may emit considerable amounts of organic compounds to the atmosphere unless they are well controlled. On the other hand, some operations, such as furniture manufacturing, produce a clean, dry wood waste, 5 to 50 percent by weight moisture, with relatively low organic emissions when properly burned. Still other operations, such as sawmills, burn a varying mixture of bark and wood waste that results in particulate emissions somewhere between those of pulp mills and furniture manufacturing. Additionally, when fossil fuels are co-fired with wood waste, the combustion efficiency is typically improved; therefore, organic emissions may decrease.[215]

The type of boiler, as well as its operation, affect combustion efficiency and emissions. Wood-fired boilers require a sufficiently large refractory surface to ensure proper drying of high-moisture-content wood waste prior to combustion. Adequately dried fuel is necessary to avoid a decrease in combustion temperatures, which may increase organic emissions because of incomplete combustion.[215]

TABLE 7-6. SUMMARY OF BENZENE EMISSION FACTORS FOR INDUSTRIAL AND COMMERCIAL/INSTITUTIONAL BOILERS

SCC	Emission Source	Fuel Type	Control Device	Emission Factor lb/MMBtu (μg/J)[a]	Factor Rating	Reference
1-02-004-01	Boiler	No. 6 fuel oil	Uncontrolled	9.38×10^{-5} (4.04×10^{-5})	D	216
1-02-007-99	Boiler	Landfill gas	Uncontrolled	3.78×10^{-4} (1.63×10^{-4})	D	3
1-02-008-04	Boiler	Coke and coal	Baghouse	2.68×10^{-5} (1.15×10^{-5})	D	217
1-02-009-01	Boiler	Bark[b]	ESP	6.90×10^{-4} (2.97×10^{-4})	E	3
1-02-009-03	Boiler	Wood[b]	Wet Scrubber	4.20×10^{-3} (1.81×10^{-3})	E	3
1-02-009-03	Boiler	Wood[c]	Multiple cyclone[d]/ESP	5.12×10^{-4} (2.20×10^{-4})	E	3
1-02-009-03	Boiler	Wood[e]	Multiple cyclone[d]	1.04×10^{-3} (4.46×10^{-4})	E	3
1-02-009-03	FBC Boiler	Wood[f]	Multiple cyclone[d]/ESP	2.70×10^{-5}[g] (1.16×10^{-5})	E	3
1-02-009-05	Boiler	Wood and bark[h]	Multiple cyclone[d]/wet scrubber	1.01×10^{-3} (4.35×10^{-4})	E	3
1-02-009-06	Spreader-stoker boiler	Wood[i]	Multiple cyclone[j]	2.43×10^{-4} (1.05×10^{-4})	D	218

(continued)

TABLE 7-6. CONTINUED

SCC	Emission Source	Fuel Type	Control Device	Emission Factor lb/MMBtu (μg/J)[a]	Factor Rating	Reference
1-02-009-06	Spreader-stoker boiler	Wood	Mechanical dust collector	1.67×10^{-4} (7.18×10^{-5})	D	219
1-02-012-01	Boiler	Almond and wood	Baghouse	5.29×10^{-3} (2.28×10^{-3})	D	220
1-03-007-01	Boiler	POTW digester gas	Uncontrolled	3.50×10^{-3} (1.50×10^{-3})	C	3

[a] Factors are in lb (μg) of benzene emitted per MMBtu (J).
[b] Redwood and fir.
[c] Fir, pine, and cedar hog-fuel and chips.
[d] Without flyash reinjection.
[e] Based on boilers firing sander dust fuel, hog-wood fir, and pine/fir chips.
[f] Pine and fir chips.
[g] Based on detection limit.
[h] Sugar pine sawdust with moisture content of 60 percent.
[i] Hog-wood red oak and aspen, 34 percent moisture.
[j] With flash reinjection.

POTW = publically owned treatment works.
ESP = electrostatic precipitator.

Control Technologies for Industrial/Commercial Boilers

Control techniques for reducing benzene emissions from industrial and commercial boilers are similar to those used for utility boilers. Refer to Section 7.4.1 for a discussion of control techniques also applicable to commercial and industrial boilers.

In Section 7.4.1, various operating conditions are listed that contribute to the combustion efficiency of a boiler (e.g., oxygen supply, good air/fuel mixing, and temperature). It has been demonstrated for a spreader-stoker boiler firing wood that benzene emissions are an order of magnitude lower under good firing conditions than under poor firing conditions (when the boiler was in an unsteady or upset condition). It has also been shown that the ratio of overfire to underfire air plays an important role in benzene emissions. Based on recent test results, the speculation is that if the balance of combustion air heavily favors underfire air, there is insufficient combustion air in the upper furnace to complete the combustion of PICs (including benzene). Conversely, with excess overfire air, the flame-quenching effect of too much combustion air in the upper furnace appears to suppress the combustion of PICs at that stage of the combustion process.[218]

7.4.3 Residential Sector

The residential sector includes furnaces and boilers burning coal, oil, and natural gas, stoves and fireplaces burning wood, and kerosene heaters. All of these units are designed to heat individual homes. Locations of residential combustion sources are tied directly to population trends. Coal consumption for residential combustion purposes occurs mainly in the Northeast, Appalachian, and Midwest regions. Residential oil consumption is greatest in the Northeast and Mid-Atlantic regions. Wood-fired residential units are generally concentrated in heavily forested areas of the United States, which reflects fuel selection based on availability and price.[215]

Process Description for Residential Furnaces, Boilers, Stoves, and Fireplaces

The following sections describe the types of residential furnaces, boilers, stoves, and fireplaces that fire wood, coal, oil, natural gas, kerosene.

Wood Combustion--Residential wood combustion generally occurs in either a wood-fired stove or fireplace unit located inside the house. The following discussion describes the specific characterization of woodstoves, followed by a discussion on fireplaces.

Woodstoves are commonly used in residences as space heaters. They are used both as the primary source of residential heat and to supplement conventional heating systems. Wood stoves have varying designs based on the use or non-use of baffles and catalysts, the extent of combustion chamber sealing, and differences in air intake and exhaust systems.

The EPA has identified five different categories of wood-burning stoves based on differences in both the magnitude and the composition of the emissions:[221]

- Conventional woodstoves;
- Noncatalytic woodstoves;
- Catalytic woodstoves;
- Pellet stoves; and
- Masonry heaters.

Within these categories, there are many variations in device design and operation.

The conventional stove category comprises all stoves that do not have catalytic combustors and are not included in the other noncatalytic categories (i.e., noncatalytic and pellet). Conventional stoves do not have any emissions reduction technology or design features and, in most cases, were manufactured before July 1, 1986. Stoves of many different airflow designs may be included in this category, such as updraft, downdraft, crossdraft and S-flow.[221]

Noncatalytic woodstoves are those units that do not employ catalysts but do have emissions-reducing technology or features. Typical noncatalytic design includes baffles and secondary combustion chambers.[221]

Catalytic stoves are equipped with a ceramic or metal honeycomb device, called a combustor or converter, that is coated with a noble metal such as platinum or palladium. The catalyst material reduces the ignition temperature of the unburned VOC and CO in the exhaust gases, thus augmenting their ignition and combustion at normal stove operating temperatures. As these components burn, the temperature inside the catalyst increases to a point at which the ignition of the gases is essentially self-sustaining.[221]

Pellet stoves are those fueled with pellets of sawdust, wood products, and other biomass materials pressed into manageable shapes and sizes. These stoves have active air flow systems and unique grate design to accommodate this type of fuel. Some pellet stove models are subject to the 1988 NSPS; others are exempt because of their high air-to-fuel ratio (greater than 35-to-1).[221]

Masonry heaters are large, enclosed chambers made of masonry products or a combination of masonry products and ceramic materials. These devices are exempt from the 1988 NSPS because of their weight (greater than 800 kg). Masonry heaters are gaining popularity as a cleaner-burning and heat-efficient form of primary and supplemental heat, relative to some other types of wood heaters. In a masonry heater, a complete charge of wood is burned in a relatively short period of time. The use of masonry materials promotes heat transfer. Thus, radiant heat from the heater warms the surrounding area for many hours after the fire has burned out.[221]

Fireplaces are used primarily for aesthetic effects and secondarily as a supplemental heating source in houses and other dwellings. Wood is the most common fuel for fireplaces, but coal and densified wood "logs" may also be burned.[222] The user intermittently adds fuel to the fire by hand.

Fireplaces can be divided into two broad categories: (1) masonry (generally brick and/or stone, assembled on site, and integral to a structure) and (2) prefabricated (usually metal, installed on site as a package with appropriate duct work). Masonry fireplaces typically have large, fixed openings to the fire bed and dampers above the combustion area in the chimney to limit room air and heat losses when the fireplace is not being used. Some masonry fireplaces are designed or retrofitted with doors and louvers to reduce the intake of combustion air during use.[222]

Prefabricated fireplaces are commonly equipped with louvers and glass doors to reduce the intake of combustion air, and some are surrounded by ducts through which floor-level air is drawn by natural convection, heated, and returned to the room. Many varieties of prefabricated fireplaces are now on the market. One general class is the freestanding fireplace, the most common of which consists of an inverted sheet metal funnel and stovepipe directly above the fire bed. Another class is the "zero clearance" fireplace, an iron or heavy-gauge steel firebox lined inside with firebrick and surrounded by multiple steel walls with spaces for air circulation. Some zero clearance fireplaces can be inserted into existing masonry fireplace openings, and thus are sometimes called "inserts." Some of these units are equipped with close-fitting doors and have operating and combustion characteristics similar to those of woodstoves.[222]

Masonry fireplaces usually heat a room by radiation, with a significant fraction of the combustion heat lost in the exhaust gases and through fireplace walls. Moreover, some of the radiant heat entering the room goes toward warming the air that is pulled into the residence to make up for that drawn up the chimney. The net effect is that masonry fireplaces are usually inefficient heating devices. Indeed, in cases where combustion is poor, where the outside air is cold, or where the fire is allowed to smolder (thus drawing air into a residence without producing appreciable radiant heat energy), a net heat loss may occur in a residence using a fireplace.

Fireplace heating efficiency may be improved by a number of measures that either reduce the excess air rate or transfer back into the residence some of the heat that would normally be lost in the exhaust gases or through fireplace walls. As noted above, such measures are commonly incorporated into prefabricated units. As a result, the energy efficiencies of prefabricated fireplaces are slightly higher than those of masonry fireplaces.[222]

Coal Combustion--Coal is not a widely used source of fuel for residential heating purposes in the United States. Only 0.3 percent of the total coal consumption in 1990 was for residential use.[223] However, combustion units burning coal may be sources of benzene emissions and may be important local sources in areas that have a large number of residential houses that rely on this fuel for heating.

There are a wide variety of coal-burning devices in use, including boilers, furnaces, coal-burning stoves, and wood-burning stoves that burn coal. These units may be hand fed or automatic feed. Boilers and warm-air furnaces are usually stoker-fed and are automatically controlled by a thermostat. The stove units are less sophisticated, generally hand fed, and less energy-efficient than boilers and furnaces. Coal-fired heating units are operated at low temperatures and do not efficiently combust fuel.[215] Therefore, the potential for emissions of benzene exists.

Distillate Oil Combustion--The most frequently used home heating oil in the United States is No. 2 fuel oil, otherwise referred to as distillate oil. Distillate oil is the second most important home heating fuel behind natural gas.[224] The use of distillate oil-fired heating units is concentrated in the Northeast portion of the United States. Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont, Delaware, District of

Columbia, Maryland, New Jersey, New York, and Pennsylvania accounted for approximately 72 percent of the residential share of distillate oil sales.[225]

Residential oil-fired heating units exist in a number of design and operating variations related to burner and combustion chamber design, excess air, heating medium, etc. Residential systems typically operate only in an “on” or “off” mode, with a constant fuel firing rate, as opposed to commercial and industrial applications, where load modulation is used.[226] In distillate oil-fired heating units, pressure or vaporization is used to atomize fuel oil in an effort to produce finer droplets for combustion. Finer droplets generally mean more complete combustion and less organic emissions.

When properly tuned, residential oil furnaces are relatively clean burning, especially as compared to woodstoves.[224] However, another study has shown that in practice not all of the fuel oil is burned and tiny droplets escape the flame and are carried out in the exhaust.[227] This study also concluded that most of the organic emissions from an oil furnace are due to the unburned oil (as opposed to soot from the combustion process), especially in the more modern burners that use a retention head burner, where over 90 percent of the carbon in the emissions was from unburned fuel.[227]

<u>Natural Gas Combustion</u>--Natural gas is the fuel most widely used for home heating purposes, with more than half of all the homes being heated through natural gas combustion. Gas-fired residential heating systems are generally less complex and easier to maintain than oil-burning units because the fuel burns more cleanly and no atomization is required. Most residential gas burners are typically of the same basic design. They use natural aspiration, where the primary air is mixed with the gas as it passes through the distribution pipes. Secondary air enters the furnace around the burners. Flue gases then pass through a heat exchanger and a stack. As with oil-fired systems, there are usually no pollution control equipment installed on gas systems, and excess air, residence time, flame retention devices, and maintenance are the key factors in the control of emissions from these units.

Kerosene Combustion--The sale and use of kerosene space heaters increased dramatically during the 1980s and they continue to be sold and used throughout the United States as supplementary and, in some cases, as primary home heating sources.[228] These units are usually unvented and release emissions inside the home. There are two basic types of kerosene space heaters: convective and radiant.

Emission Factors for Residential Furnaces, Boilers, Stoves, and Fireplaces

The combustion of fossil fuels or wood in residential units is a relatively slow and low-temperature process. Studies do not indicate the cause(s) for benzene formation in the residential sector; however, the mechanism may be similar to that in industrial boilers and utility boilers. Benzene may be formed through incomplete combustion. Because combustion in the residential sector tends to be less efficient than in other sectors, the potential to form benzene may be greater.

Table 7-7 presents emission factors for uncontrolled benzene emissions from both catalytic and non-catalytic woodstoves.[3] Benzene emission factors for other types of residential wood combustion sources are not presented because of limited data.

In general, emissions of benzene can vary widely depending on how the units are operated and the how emissions are measured. The following factors may affect benzene emissions measured from residential wood combustion sources:

- Unit design and degree of excess air;
- Wood type, moisture content, and other wood characteristics;
- Burn rate and stage of burn; and
- Firebox and chimney temperatures.

TABLE 7-7. SUMMARY OF BENZENE EMISSION FACTORS FOR RESIDENTIAL WOODSTOVES

AMS Code	Emission Source	Fuel Type	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Factor Rating
21-04-008-030	Catalytic Woodstove	Wood	Uncontrolled	1.46 (7.30×10^{-1})	E
21-04-008-051	Non-Catalytic Woodstove	Wood	Uncontrolled	1.94 (9.70×10^{-1})	E

Source: Reference 3.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of wood fired.

AMS = area and mobile sources.

Control Techniques for Residential Furnaces, Boilers, Stoves, and Fireplaces

Residential combustion sources are generally not equipped with PM or gaseous pollutant control devices. In coal- and wood-fired sources, stove design and operating practice changes have been made to lower PM, hydrocarbon, and CO emissions. Changes include modified combustion air flow control, better thermal control and heat storage, and the use of combustion catalysts. Such changes may lead to reduced benzene emissions.

Woodstove emissions reduction features include baffles, secondary combustion chambers, and catalytic combustors. Catalytic combustors or convertors are similar to those used in automobiles. Woodstove control devices may lose efficiency over time. Control degradation for any stoves, including noncatalytic woodstoves, may occur as a result of deteriorated seals and gaskets, misaligned baffles and bypass mechanisms, broken refractories, or other damaged functional components.[221] In addition, combustion efficiencies may be affected by differences in the sealing of the chamber and control of the intake and exhaust systems.[215]

7.5 STATIONARY INTERNAL COMBUSTION

Stationary internal combustion (IC) sources are grouped into two categories: reciprocating engines and gas turbines. Stationary IC engines and turbines are principally used for electricity generation and industrial applications such as natural gas processing, and oil and gas exploration, production and transmission.[229]

7.5.1 Reciprocating Engines

Process Description for Reciprocating Engines

Reciprocating engines may be classified into two types: spark and compression ignition (diesel). However, all reciprocating IC engines operate by the same basic process depicted in Figure 7-16.[230] A combustible mixture is first compressed in a small volume between the head of a piston and its surrounding cylinder. The mixture is then ignited and the resulting high-pressure products of combustion push the piston through the cylinder. This movement is converted from linear to rotary motion by a crankshaft. The piston returns, pushing out exhaust gases, and the cycle is repeated.[231]

All diesel-fueled engines are compression-ignited and all gasoline and natural gas fueled engines are spark-ignited; however, natural gas can be used in a compression ignition engine, as discussed below. The two types of reciprocating IC engines, spark ignition and compression ignition, are discussed below, according to the following types of fuel: distillate oil (diesel), gasoline, and natural gas.

<u>Distillate Oil (Diesel)</u>--In compression ignition engines, more commonly known as diesel engines, combustion air is first compression-heated in the cylinder, and fuel is then injected into the hot air. Ignition is spontaneous because the air is above the auto-ignition temperature of the fuel. All distillate oil reciprocating engines are compression-ignited.

Diesel engines usually operate at a higher compression ratio (ratio of cylinder volume when the piston is at the bottom of its stroke to the volume when it is at the top) than spark-ignited engines because fuel is not present during compression; hence, there is no danger of premature auto-ignition. Because engine thermal efficiency rises with increasing pressure ratio (and pressure ratio varies directly with compression ratio), diesel engines are more efficient than spark-ignited engines. This increased efficiency is gained at the expense of poorer response to load changes and a heavier structure to withstand the higher pressures.[232]

The primary domestic use of large stationary diesel engines (greater than 600 hp [447 kW]) is in oil and gas exploration and production. These engines, in groups of three to five, supply mechanical power to operate drilling (rotary table), mud pumping, and hoisting equipment, and may also operate pumps or auxiliary power generators. Another frequent application of large stationary diesel engines is electricity generation for both base and standby

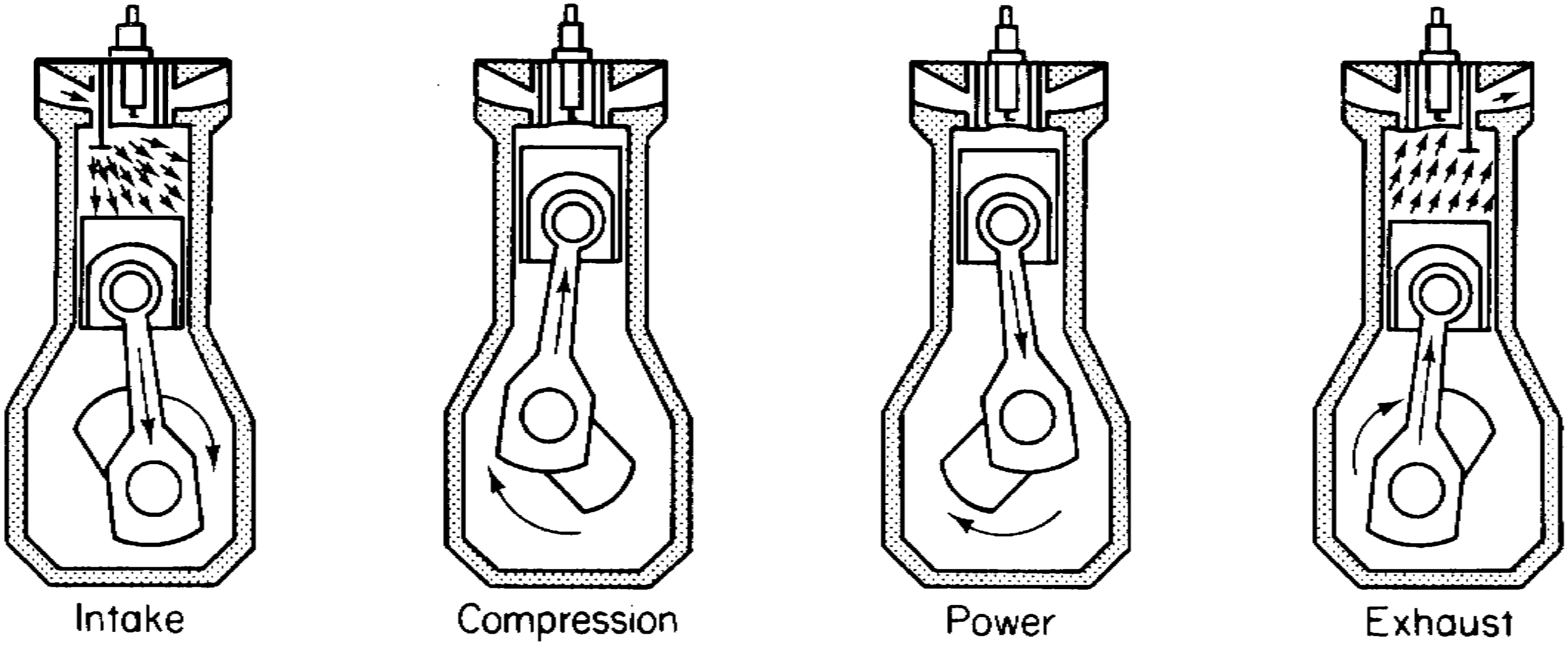

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Figure 7-16. Basic Operation of Reciprocating Internal Combustion Engines

Source: Reference 230.

service. Smaller uses of large diesel engines include irrigation, hoisting, and nuclear power plant emergency cooling water pump operation. The category of smaller diesel engines (up to 600 hp [447 kW]) covers a wide variety of industrial applications such as aerial lifts, fork lifts, mobile refrigeration units, generators, pumps, industrial sweepers/scrubbers, material handling equipment (such as conveyors), and portable well-drilling equipment. The rated power of these engines can be up to 250 hp (186 kW), and substantial differences in engine duty cycles exist.[232]

Gasoline--Spark ignition initiates combustion by the spark of an electrical discharge. Usually, fuel is mixed with the air in a carburetor, but occasionally fuel is injected into the compressed air in the cylinder. All gasoline reciprocating engines are spark-ignited. Gasoline engines up to 600 hp (447 kW) can be used interchangeably with diesel IC engines in the same industrial applications described previously. As with diesel engines, substantial differences in gasoline engine duty cycles exist.[231]

Natural Gas--Most reciprocating IC engines that use natural gas are of the spark-ignited type. As with gasoline engines, the gas is first mixed with the combustion air at an intake valve, but occasionally the fuel is injected into the compressed air in the cylinder. Natural gas can be used in a compression ignition engine, but only if a small amount of diesel fuel is injected into the compressed air/gas mixture to initiate combustion; hence the name dual-fuel engine. Dual-fuel engines were developed to obtain compression ignition performance and the economy of natural gas, using a minimum of 5 to 6 percent diesel fuel to ignite the natural gas. Large dual-fuel engines have been used almost exclusively for prime electric power generation.[231]

Natural gas-fired stationary IC engines are also used in the natural gas industry, primarily to power compressors used for pipeline transportation, field gathering (collecting gas from wells), underground storage, and gas processing plant applications (i.e., prime movers). Pipeline engines are concentrated in the major gas-producing states (such as those along the Gulf Coast) and along the major gas pipelines.[233]

Reciprocating IC engines used in the natural gas industry are separated into three design classes: two-stroke lean burn, four-stroke lean burn, and four-stroke rich burn. Each of these have design differences that affect both baseline emissions as well as the potential for emissions control. Two-stroke engines complete the power cycle in a single engine revolution compared to two revolutions for four-stroke engines. With the two-stroke engine, the fuel/air charge is injected with the piston near the bottom of the power stroke. The valves are all covered or closed and the piston moves to the top of the cylinder compressing the charge. Following ignition and combustion, the power stroke starts with the downward movement of the piston. Exhaust ports or valves are then uncovered to remove the combustion products, and a new fuel/air charge is ingested. Two-stroke engines may be turbocharged using an exhaust-powered turbine to pressurize the charge for injection into the cylinder. Non-turbocharged engines may be either blower-scavenged or piston-scavenged to improve removal of combustion products.[233]

Four-stroke engines use a separate engine revolution for the intake/compression stroke and the power/exhaust stroke. These engines may be either naturally aspirated, using the suction from the piston to entrain the air charge, or turbocharged, using a turbine to pressurize the charge. Turbocharged units produce a higher power output for a given engine displacement, whereas naturally aspirated units have lower initial cost and maintenance. Rich-burn engines operate near the fuel/air stoichiometric limit, with exhaust excess oxygen levels less than 4 percent. Lean-burn engines may operate up to the lean flame extinction limit, with exhaust oxygen levels of 12 percent or greater.[233]

Pipeline population statistics show a nearly equal installed capacity of reciprocating IC engines and turbines. Gas turbines emit considerably smaller amounts of pollutants than do reciprocating engines; however, reciprocating engines are generally more efficient in their use of fuel. For reciprocating engines, two-stroke designs contribute approximately two-thirds of installed capacity in this industry.[233]

Benzene Emissions From Reciprocating IC Engines

Most of the pollutants from IC engines are emitted through the exhaust. However, some hydrocarbons escape from the crankcase as a result of blowby (gases that are vented from the oil pan after they have escaped from the cylinder past the piston rings) and from the fuel tank and carburetor because of evaporation. Nearly all of the hydrocarbons from diesel engines enter the atmosphere from the exhaust. Crankcase blowby is minor because hydrocarbons are not present during compression of the charge. Evaporative losses are insignificant in diesel engines because of the low volatility of diesel fuels. In general, evaporative losses are also negligible in engines using gaseous fuels because these engines receive their fuel continuously from a pipe rather than via a fuel storage tank and fuel pump.

Emission factors for uncontrolled benzene emissions from the following reciprocating engine types and fuel combinations are provided in Table 7-8:
(1) reciprocating/distillate oil and publically owned treatment works (POTW) digester gas, (2) cogeneration/distillate oil, (3) 2-cycle lean burn/natural gas, (4) large bore engine/distillate oil, and (5) large bore engine/distillate oil and gas (dual fuel). Additionally, an emission factor for benzene emissions after a non-selective catalytic reduction control device is provided for a natural gas-fired, 4-cycle, lean-burn reciprocating engine.[3,231-233]

Control Technologies for Reciprocating Engines

Control measures for large stationary diesel engines to date have been directed mainly at limiting NO_x emissions, the primary pollutant from this group of IC engines. All of these controls are engine control techniques except for the selective catalytic reduction (SCR) technique, which is a post-combustion control. As such, all of these controls usually affect the emissions profile for other pollutants as well, and not always positively. The effectiveness of controls on a particular engine will depend on the specific design of each engine, and the effectiveness of each technique can vary considerably.

TABLE 7-8. SUMMARY OF BENZENE EMISSION FACTORS FOR RECIPROCATING ENGINES

SCC	Emission Source	Control Device(s)	Emission Factor lb/MMBtu (ng/J)[a]	Emission Factor Rating	Reference
2-02-001-02	Reciprocating distillate oil-fueled engine	Uncontrolled	9.33×10^{-4} (4.01×10^{-1})	E	3, 232
2-02-001-04	Cogeneration distillate oil-fueled engine	Uncontrolled	5.36×10^{-4} (2.30×10^{-1})	D	3
2-02-002-02	2-cycle lean burn natural gas-fueled engine	Uncontrolled	2.20×10^{-3} (9.46×10^{-1})	E	3, 233
	4-cycle lean burn natural gas-fueled engine	NSCR	7.1×10^{-4} (3.05×10^{-1})	E	233
2-02-004-01	Large bore diesel-fueled engine	Uncontrolled	7.76×10^{-4} (3.34×10^{-1})	E	3, 231
2-02-004-02	Large bore oil- and natural gas-fueled engine (dual fuel)	Uncontrolled	4.45×10^{-3} (1.91)	E	3
2-03-007-02	Reciprocating POTW digester gas-fueled engine	Uncontrolled	6.90×10^{-4} (2.97×10^{-1})	C	3

[a] Factors are in lb (ng) of benzene emitted per MMBtu (J).

NSCR = nonselective catalytic reduction.
POTW = publically owned treatment works.

Other NO_x control techniques include internal/external exhaust gas recirculation (EGR), combustion chamber modification, manifold air cooling, and turbocharging. Various other emissions reduction technologies may be applicable to the smaller diesel and gasoline engines. These technologies are categorized into fuel modifications, engine modifications, and exhaust treatments.

7.5.2 Gas Turbines

Stationary gas turbines are applied in electric power generators, in gas pipeline pump and compressor drives, and in various process industries. Gas turbines (greater than 3 MW(e)] are used in electrical generation for continuous, peaking, or standby power.[79] In 1990, the actual gas-fired combustion turbine generating capacity for electric utilities was 8,524 MW. [234] The current average size of electricity generation gas turbines is approximately 31 MW. Turbines are also used in industrial applications, but information was not available to estimate their installed capacity.

The same fuels used in reciprocating engines are combusted to drive gas turbines. The primary fuels used are natural gas and distillate (No. 2) fuel oil, although residual fuel oil is used in a few applications.[235] The liquid fuel used must be similar in volatility to diesel fuel to produce droplets that penetrate sufficiently far into the combustion chamber to ensure efficient combustion even when a pressure atomizer is used.[230]

Process Description for Gas Turbines

Gas turbines are so named not because they are gas-fired, but because combustion exhaust gas drives the turbine. Unlike reciprocating engines, gas turbines operate in steady flow. As shown in Figure 7-17, a basic gas turbine consists of a compressor, a combustor, and a turbine.[230] Combustion air enters the turbine through a centrifugal

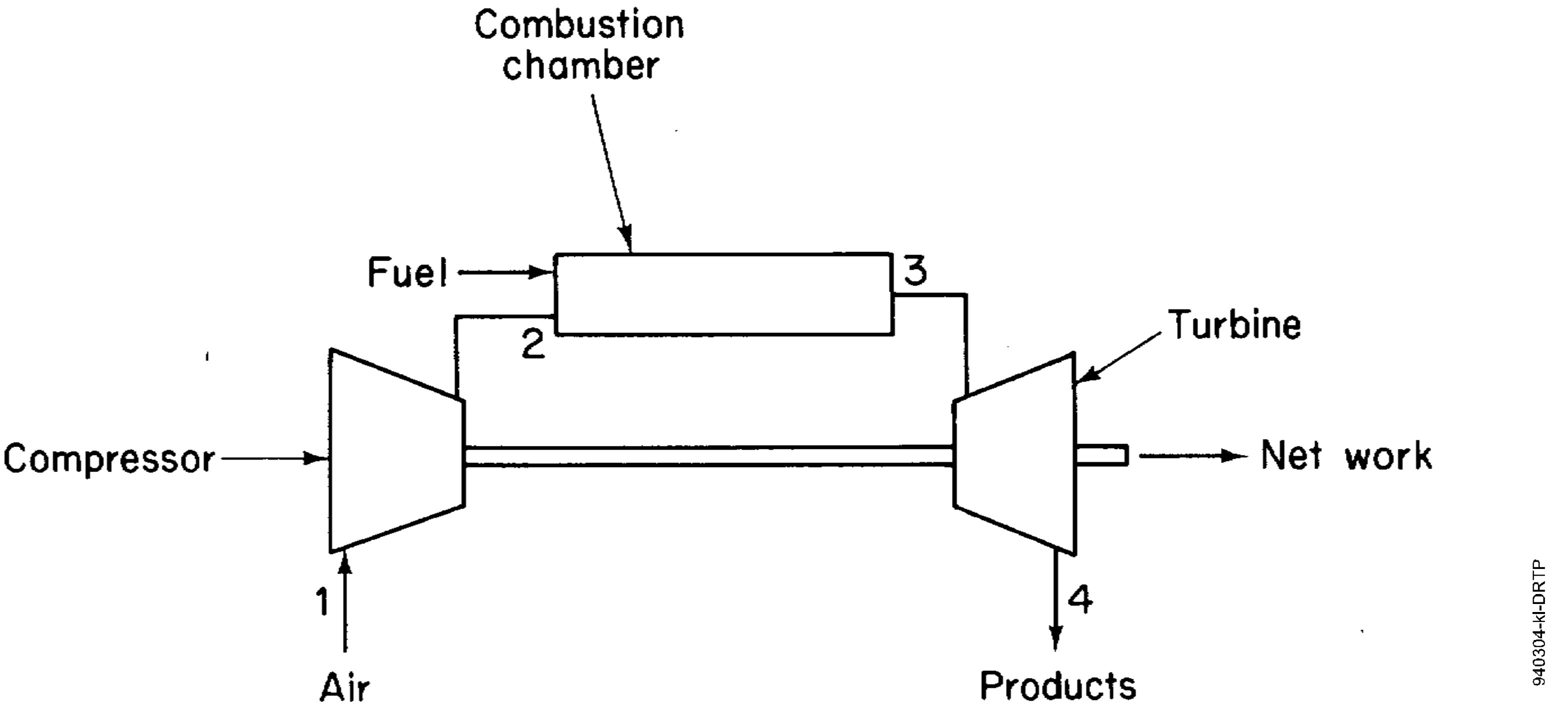


Figure 7-17. Gas Turbine Engine Configuration

Source: Reference 230.

compressor, where the pressure is raised to 5 to 30 atmospheres, depending on load and the design of the engine. Part of the air is then introduced into the primary combustion zone, into which fuel is sprayed. The fuel burns in an intense flame. Gas volume increases with combustion, so as the gases pass at high velocity through the turbine, they generate more work than is required to drive the compressor. This additional work is delivered by the turbine to a shaft to drive an electric power generator or other machinery.[230]

Gas turbines may be classified into three general types: simple-open-cycle, regenerative-open-cycle, and combined-cycle. In the simple-open-cycle, the hot gas discharged from the turbine is exhausted to the atmosphere. In the regenerative-open-cycle, the gas discharged from the turbine is passed through a heat exchanger to preheat the combustion air. Preheating the air increases the efficiency of the turbine. In the combined-cycle, the gas discharged from the turbine is used as auxiliary heat for a steam cycle. Regenerative-type gas turbines constitute only a very small fraction of the total gas turbine population. Identical gas turbines used in the combined-cycle and in the simple-cycle tend to exhibit the same emissions profiles. Therefore, usually only emissions from simple-cycles are evaluated.[229]

Benzene Emissions From Gas Turbines

Table 7-9 presents emission factors for controlled benzene emissions from two gas turbines utilized for electricity generation.[3]

Control Technologies for Gas Turbines

As with reciprocating engines, NO_x is the primary pollutant from gas turbines that controls have been directed at, and techniques for its control still have ramifications for the emissions profiles of other pollutants such as hydrocarbons (including benzene).

TABLE 7-9. SUMMARY OF BENZENE EMISSION FACTORS FOR GAS TURBINES

SCC	Emission Source	Control Device	Emission Factor lb/MMBtu (ng/J)[a]	Emission Factor Rating	Reference
2-01-001-01	Gas turbine fueled with distillate oil	Afterburner	9.13×10^{-5} (3.92×10^{-2})	D	3
2-01-002-01	Gas turbine fueled with natural gas	Catalytic reduction	1.10×10^{-4} (4.73×10^{-2})	E	3

[a] Factors are in lb (ng) of benzene emitted per MMBtu (J).

Water/steam injection is the most prevalent NO_x control for cogeneration/combined-cycle gas turbines. Water or steam is injected with air and fuel into the turbine combustor in order to lower the peak temperatures, which in turn decreases the NO_x produced. The lower average temperature within the combustor may produce higher levels of CO and hydrocarbons as a result of incomplete combustion.[235]

As described in the previous section, SCR is a post-combustion control that selectively reduces NO_x by reaction of ammonia and NO on a catalytic surface to form N_2 and H_2O. Although SCR systems can be used alone, all existing applications of SCR have been used in conjunction with water/steam injection controls. For optimum SCR operation, the flue gas must be within a temperature range of 600 to 800°F (315 to 427°C), with the precise limits dependent on the catalyst. Some SCR systems also utilize a CO catalyst to give simultaneous catalytic CO/NO_x control.[235]

Advanced combustor designs are currently being phased into production turbines. These dry techniques decrease turbine emissions by modifying the combustion mixing, air staging, and flame stabilization to allow operation at a much leaner air/fuel ratio relative to normal operation. Operating at leaner conditions will lower peak temperatures within the primary flame zone of the combustor. The lower temperatures may also increase CO and hydrocarbon emissions.[235]

With the advancement of NO_x control technologies for gas turbines, the emission factors for the installed gas turbine population are quite different than for uncontrolled turbines. However, uncontrolled turbine emissions have not changed significantly. A careful review of specific turbine details should be performed before applying uncontrolled emission factors. Today, most gas turbines are controlled to meet local, State, and Federal regulations.[235]

7.6 SECONDARY LEAD SMELTING

In 1990, primary and secondary smelters in the United States produced 1,380,000 tons (1,255,000 Mg) of lead. Secondary lead smelters produced 946,000 tons (860,000 Mg) or about 69 percent of the total refined lead produced in 1990; primary smelters produced 434,000 tons (395,000 Mg). Table 7-10 lists U.S. secondary lead smelters according to their annual lead production capacity.[236]

7.6.1 Process Description

The secondary lead smelting industry produces elemental lead and lead alloys by reclaiming lead, mainly from scrap automobile batteries. Blast, reverberatory, rotary, and electric furnaces are used for smelting scrap lead and producing secondary lead. Smelting is the reduction of lead compounds to elemental lead in a high-temperature furnace. It requires higher temperatures (2,200 to 2,300°F [1,200 to 1,260°C]) than those required for melting elemental lead (621°F [327°C]). Secondary lead may be refined to produce soft lead (which is nearly pure lead) or alloyed to produce hard lead alloys. Most of the lead produced by secondary lead smelters is hard lead, which is used in the production of lead-acid batteries.[236]

Lead-acid batteries represent about 90 percent of the raw materials at a typical secondary lead smelter, although this percentage may vary from one plant to the next. These batteries contain approximately 18 lb (8.2 kg) of lead per battery consisting of 40 percent lead alloys and 60 percent lead oxide. Other types of lead-bearing raw materials recycled by secondary lead smelters include drosses (lead-containing byproducts of lead refining), which may be purchased from companies that perform lead alloying or refining but not smelting; battery plant scrap, such as defective grids or paste; and scrap lead, such as old pipes or roof flashing. Other scrap lead sources include cable sheathing, solder, and babbitt metal.[236]

As illustrated in Figure 7-18, the normal sequence of operations in a secondary lead smelter is scrap receiving, charge preparation, furnace smelting, and lead refining and

TABLE 7-10. U.S. SECONDARY LEAD SMELTERS

Smelter	Location
Small-Capacity: less than 22,000 tons (20,000 Mg)	
Delatte Metals	Ponchatoula, LA
General Smelting and Refining Company	College Grove, TN
Master Metals, Inc.	Cleveland, OH
Metals Control of Kansas	Hillsboro, KS
Metals Control of Oklahoma	Muskogee, OK
Medium-Capacity: 22,000 to 82,000 tons (20,000 to 75,000 Mg)	
Doe Run Company	Boss, MO
East Penn Manufacturing Company	Lyon Station, PA
Exide Corporation	Muncie, IN
Exide Corporation	Reading, PA
GNB, Inc.	Columbus, GA
GNB, Inc.	Frisco, TX
Gulf Coast Recycling, Inc.	Tampa, FL
Refined Metals Corporation	Beech Grove, IN
Refined Metals Corporation	Memphis, TN
RSR Corporation	City of Industry, CA
RSR Corporation	Middletown, NY
Schuylkill Metals Corporation	Forest City, MO
Tejas Resources, Inc.	Terrell, TX
Large-Capacity: greater than 82,000 tons (75,000 Mg)	
Gopher Smelting and Refining, Inc.	Eagan, MN
GNB, Inc.	Vernon, CA
RSR Corporation	Indianapolis, IN
Sanders Lead Company	Troy, AL
Schuylkill Metals Corporation	Baton Rouge, LA

Source: Reference 236.

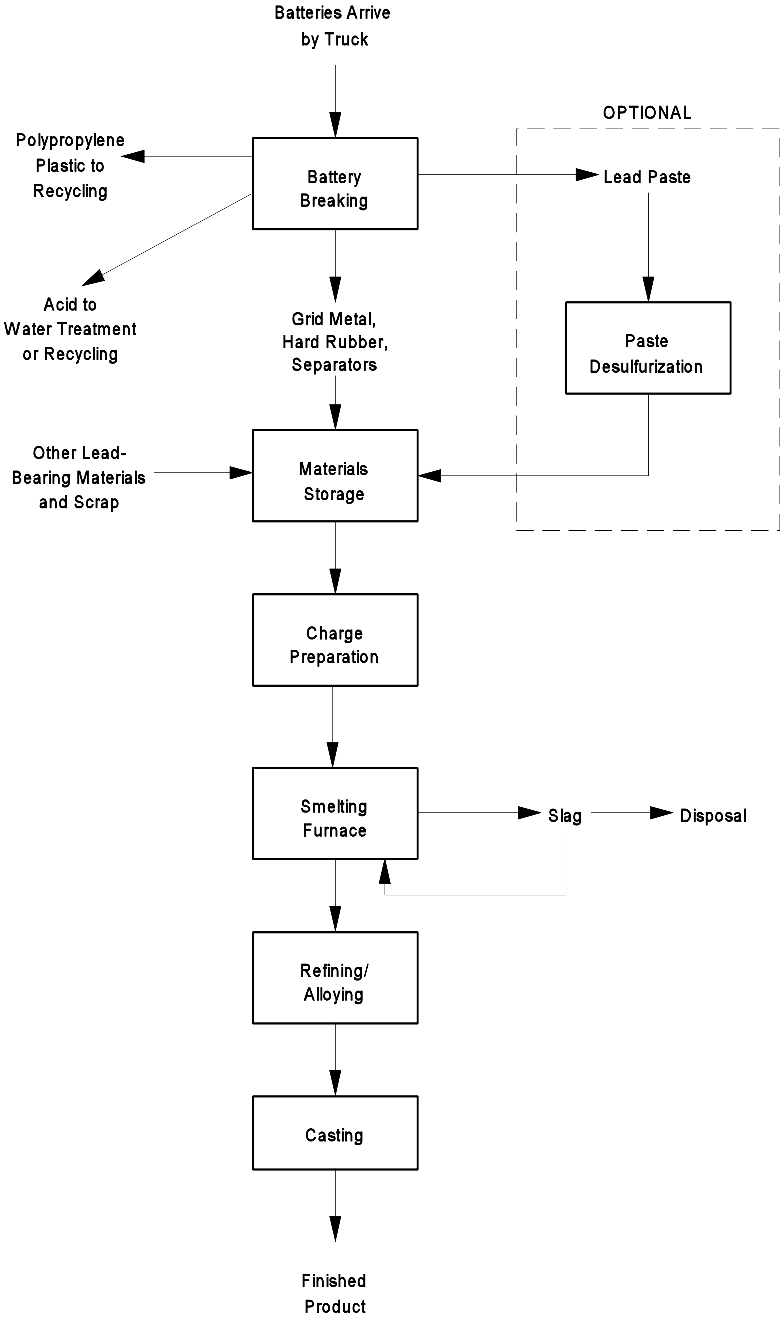


Figure 7-18. Simplified Process Flow Diagram for Secondary Lead Smelting

Source: Reference 236

alloying.[236] In the majority of plants, scrap batteries are first sawed or broken open to remove the lead alloy plates and lead oxide paste material. The removal of battery covers is typically accomplished using an automatic battery feed conveyor system and a slow-speed saw. Hammermills or other crushing/shredding devices are then used to break open the battery cases. Float/sink separation systems are typically used to separate plastic battery parts, lead terminals, lead oxide paste, and rubber parts. The majority of lead smelters recover the crushed plastic materials for recycling. Rubber casings are usually landfilled.

Paste desulfurization, an optional lead recovery step used by secondary lead smelters, requires the separation of lead sulfate and lead oxide paste from the lead grid metal, polypropylene plastic cases, separators, and hard rubber battery cases. Paste desulfurization involves the chemical removal of sulfur from the lead battery paste. The process improves furnace efficiency by reducing the need for fluxing agents to reduce lead-sulfur compounds to lead metal. The process also reduces SO_2 furnace emissions. However, SO_2 emissions reduction is usually a less important consideration because many plants that perform paste desulfurization are also equipped with SO_2 scrubbers. About half of all smelters perform paste desulfurization.

After removing the lead components from the charge batteries, the lead scrap is combined with other charge materials such as refining drosses, flue dust, furnace slag, coke, limestone, sand, and scrap iron and fed to either a reverberatory, blast, rotary or electric smelting furnace. Smelting furnaces are used to produce crude lead bullion, which is refined and/or alloyed into final lead products.

Refining, the final step in secondary lead production, consists of removing impurities and adding alloying metals to the molten lead obtained from the smelting furnaces to meet a customer's specifications. Refining kettles are used for the purifying and alloying of molten lead.

Blast and reverberatory furnaces are currently the most common types of smelting furnaces in the industry, although some new plants are using rotary furnaces. There are currently about 15 reverberatory furnaces, 24 blast furnaces, 5 rotary furnaces, and 1 electric furnace in the secondary lead industry.[236] The following discussion provides process descriptions of these four types of secondary lead smelters.

Reverberatory Furnaces

A reverberatory furnace (Figure 7-19) is a rectangular refractory-lined furnace.[236] Reverberatory furnaces are operated on a continuous basis. Natural gas- or fuel oil-fired jets located at one end or at the sides of the furnace are used to heat the furnace and charge material to an operating temperature of about 2,000°F (1,100°C). Oxygen enrichment may be used to decrease the combustion air requirements. Reverberatory furnaces are maintained at negative pressure by an induced draft fan.

Reverberatory furnace charge materials include battery grids and paste, battery plant scrap, rerun reverberatory furnace slag, flue dust, drosses, iron, silica, and coke. A typical charge over one hour may include 9.3 tons (8.4 Mg) of grids and paste to produce 6.2 tons (5.6 Mg) of lead.[236]

Charge materials are often fed to a natural gas- or oil-fired rotary drying kiln, which dries the material before it reaches the furnace. The temperature of the drying kiln is about 400°F (200°C), and the drying kiln exhaust is drawn directly into the reverberatory furnace or ventilated to a control device. From the rotary drying kiln, the feed is either dropped into the top of the furnace through a charging chute, or fed into the furnace at fixed intervals with a hydraulic ram. In furnaces that use a feed chute, a hydraulic ram is often used as a stoker to move the material down the furnace.

Reverberatory furnaces are used to produce a soft (nearly pure) lead product and a lead-bearing slag. This is done by controlling the reducing conditions in the furnace so that

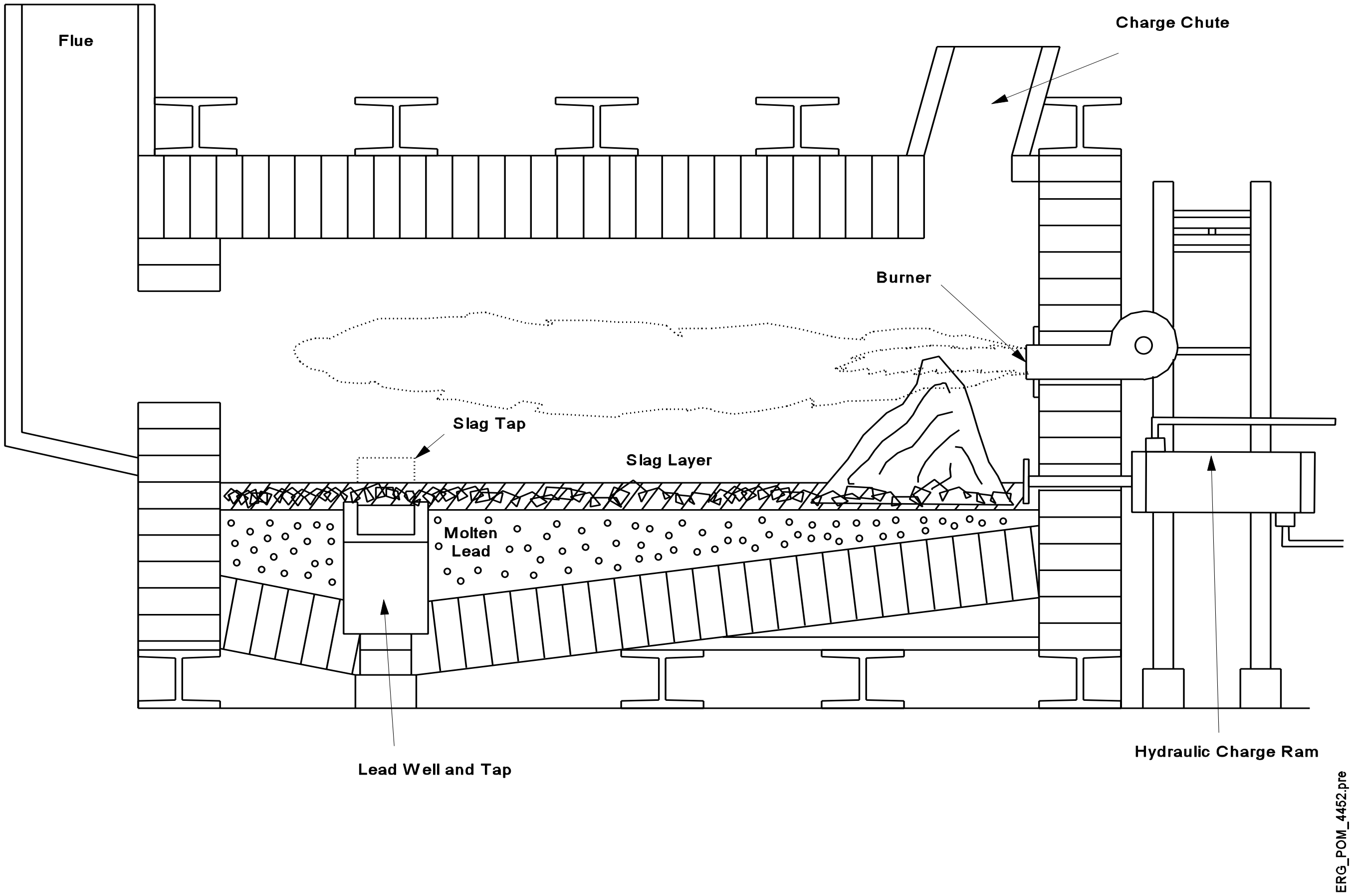


Figure 7-19. Cross-sectional View of a Typical Stationary Reverberatory Furnace

Source: Reference 236.

lead components are reduced to metallic lead bullion and the alloying elements (antimony, tin, arsenic) in the battery grids, posts, straps, and connectors are oxidized and removed in the slag. The reduction of $PbSO_4$ and PbO is promoted by the carbon-containing coke added to the charge material:

$$PbSO_4 + C \rightarrow Pb + CO_2 + SO_2$$

$$2PbO + C \rightarrow 2Pb + CO_2$$

The $PbSO_4$ and PbO also react with the alloying elements to form lead bullion and oxides of the alloying elements, which are removed in the slag.

The molten lead collects in a pool at the lowest part of the hearth. Slag collects in a layer on top of this pool and retards further oxidation of the lead. The slag is made up of molten fluxing agents such as iron, silica, and lime, and typically has significant quantities of lead. Slag is usually tapped continuously and lead is tapped intermittently. The slag is tapped into a crucible. The slag tap and crucible are hooded and vented to a control device. Reverberatory furnace slag usually has a high lead content (as much as 70 percent by weight) and is used as feed material in a blast or electric furnace to recover the lead content. Reverberatory furnace slag may also be rerun through the reverberatory furnace during special slag campaigns before being sent to a blast or electric furnace. Lead may be tapped into a crucible or directly into a holding kettle. The lead tap is usually hooded and vented to a control device.[236]

Blast Furnaces

A blast furnace (Figure 7-20) is a vertical furnace that consists of a crucible with a vertical cylinder affixed to the top. The crucible is refractory-lined and the vertical cylinder consists of a steel water jacket. Oxygen-enriched combustion air is introduced into the furnace through tuyeres located around the base of the cylinder.

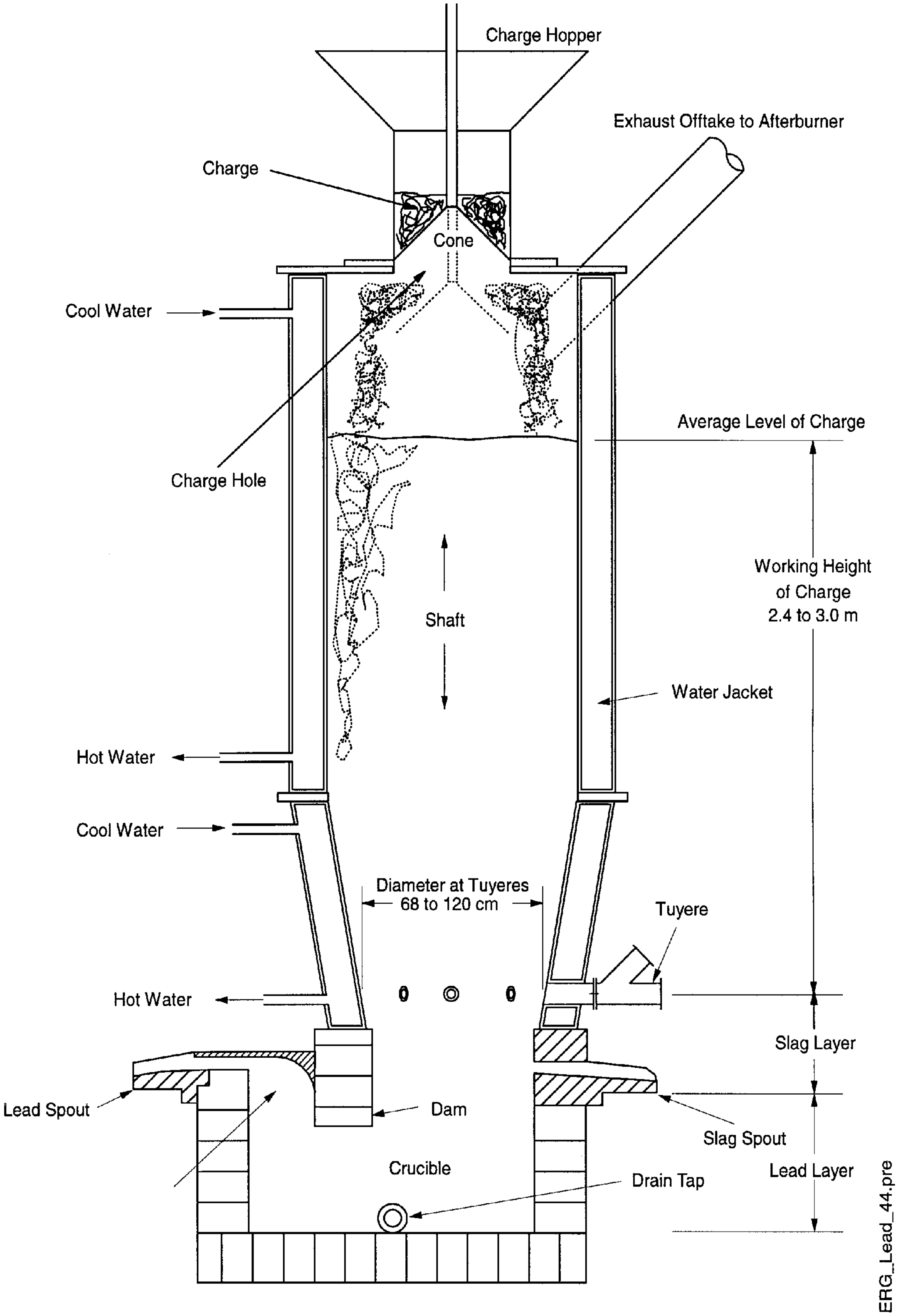


Figure 7-20. Cross Section of a Typical Blast Furnace

Charge materials are pre-weighed to ensure the proper mixture and then introduced into the top of the cylinder using a skip hoist, a conveyor, or a front-end loader. The charge fills nearly the entire cylinder. Charge material is added periodically to keep the level of the charge at a consistent working height while lead and slag are tapped from the crucible. Coke is added to the charge as the primary fuel, although natural gas jets may be used to start the combustion process. Combustion is self-sustaining as long as there is sufficient coke in the charge material. Combustion occurs in the layer of the charge nearest the tuyeres.

At plants that operate only blast furnaces, the lead-bearing charge materials may include broken battery components, drosses from the refining kettles, agglomerated flue dust, and lead-bearing slag. A typical charge over one hour may include 4.8 tons (4.4 Mg) of grids and paste, 0.3 tons (0.3 Mg) of coke, 0.1 tons (0.1 Mg) of calcium carbonate, 0.07 tons (0.06 Mg) of silica, 0.5 tons (0.4 Mg) of cast iron, and 0.2 tons (0.2 Mg) of rerun blast furnace slag, to produce 3.7 tons (3.3 Mg) of lead. At plants that also have a reverberatory furnace, the charge materials will also include lead-bearing reverberatory furnace slag.[236]

Blast furnaces are designed and operated to produce a hard (high alloy content) lead product by achieving more reducing furnace conditions than those typically found in a reverberatory furnace. Fluxing agents include iron, soda ash, limestone, and silica (sand). The oxidation of the iron, limestone, and silica promotes the reduction of lead compounds and prevents oxidation of the lead and other metals. The soda ash enhances the reaction of $PbSO_4$ and PbO with carbon from the coke to reduce these compounds to lead metal.

Lead tapped from a blast furnace has a higher content of alloying metals (up to 25 percent) than lead produced by a reverberatory furnace. In addition, much less of the lead and alloying metals are oxidized and removed in the slag, so the slag has a low metal content (e.g., 1 to 3 percent) and frequently qualifies as a nonhazardous solid waste.

Because air is introduced into the blast furnace at the tuyeres, blast furnaces are operated at positive pressure. The operating temperature at the combustion layer of the charge is between 2,200 and 2,600°F (1,200 and 1,400°C), but the temperature of the gases exiting the top of the charge material is only between 750 and 950°F (400 and 500°C).

Molten lead collects in the crucible beneath a layer of molten slag. As in a reverberatory furnace, the slag inhibits the further oxidation of the molten metal. Lead is tapped continuously and slag is tapped intermittently, slightly before it reaches the level of the tuyeres. If the tuyeres become blocked with slag, they are manually or automatically "punched" to clear the slag. A sight glass on the tuyeres allows the furnace operator to monitor the slag level and ensure that they are clear of slag. At most facilities, the slag tap is temporarily sealed with a clay plug, which is driven out to begin the flow of slag from the tap into a crucible. The slag tap and crucible are enclosed in a hood, which is vented to a control device.

A weir dam and siphon in the furnace are used to remove the lead from beneath the slag layer. Lead is tapped from a blast furnace into either a crucible or directly to a refining kettle designated as a holding kettle. The lead in the holding kettle is kept molten before being pumped to a refining kettle for refining and alloying. The lead tap on a blast furnace is hooded and vented to a control device.

Rotary Furnaces

As noted above, rotary furnaces (sometimes referred to as rotary reverberatory furnaces) (Figure 7-21) are used at only a few recently constructed secondary lead smelters in the United States.[236] Rotary furnaces have two advantages over other furnace types: it is easier to adjust the relative amount of fluxing agents because the furnaces are operated on a batch rather than a continuous basis, and they achieve better mixing of the charge materials than do blast or reverberatory furnaces.

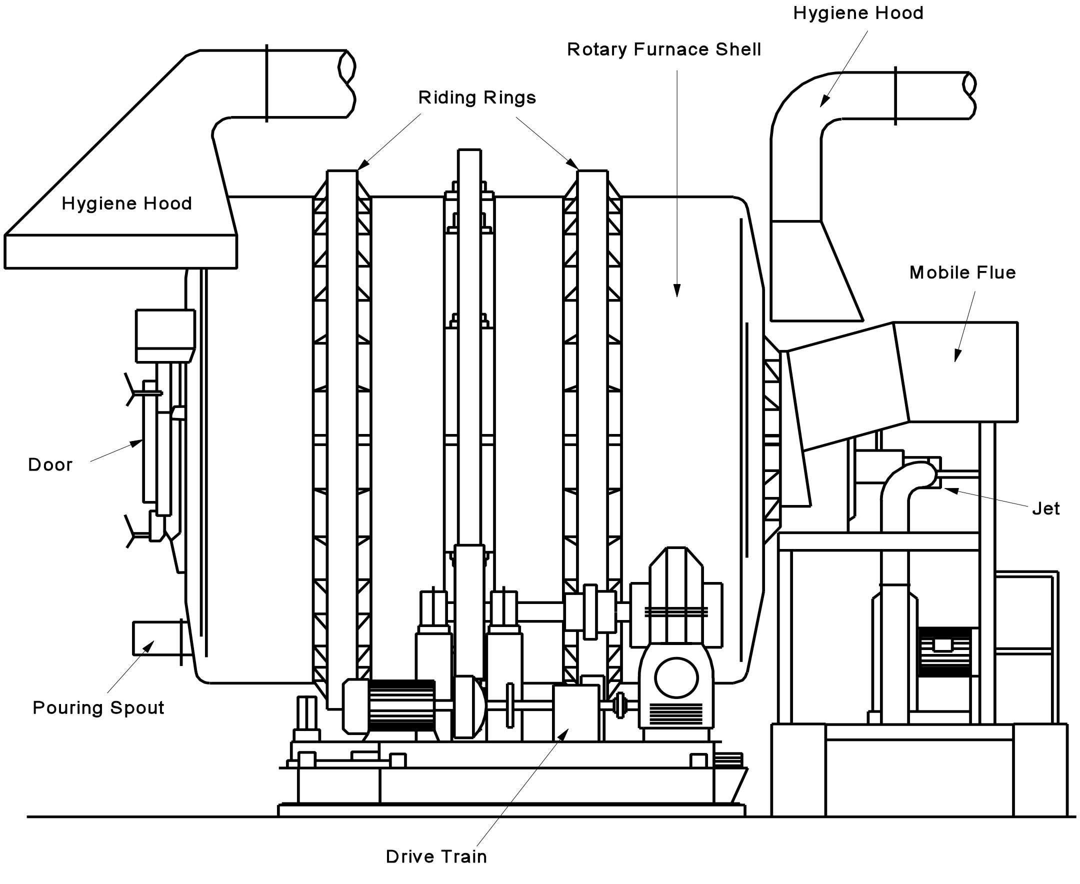


Figure 7-21. Side-view of a Typical Rotary Reverbertory Furnace

Source: Reference 236.

A rotary furnace consists of a refractory-lined steel drum mounted on rollers. Variable-speed motors are used to rotate the drum. An oxygen-enriched natural gas or fuel oil jet at one end of the furnace heats the charge material and the refractory lining of the drum. The connection to the flue is located at the same end as the jet. A sliding door at the end of the furnace opposite from the jet allows charging of material to the furnace. Charge materials are typically placed in the furnace using a retractable conveyor or charge bucket, although other methods are possible.

Lead-bearing raw materials charged to rotary furnaces include broken battery components, flue dust, and drosses. Rotary furnaces can use the same lead-bearing raw materials as reverberatory furnaces, but they produce slag that is relatively free of lead, less than 2 percent. As a result, a blast furnace is not needed for recovering lead from the slag, which can be disposed of as a nonhazardous waste.

Fluxing agents for rotary furnaces may include iron, silica, soda ash, limestone, and coke. The fluxing agents are added to promote the conversion of lead compounds to lead metal. Coke is used as a reducing agent rather than as a primary fuel. A typical charge may consist of 12 tons (11 Mg) of wet battery scrap, 0.8 tons (0.7 Mg) of soda ash, 0.6 tons (0.5 Mg) of coke, and 0.6 tons (0.5 Mg) of iron. This charge will yield approximately 9 tons (8 Mg) of lead product.[236]

The lead produced by rotary furnaces is a semi-soft lead with an antimony content somewhere between that of lead from reverberatory and blast furnaces. Lead and slag are tapped from the furnace at the conclusion of the smelting cycle. Each batch takes 5 to 12 hours to process, depending on the size of the furnace. Like reverberatory furnaces, rotary furnaces are operated at a slight negative pressure.

Electric Furnaces

An electric furnace consists of a large, steel, kettle-shaped container that is refractory-lined (Figure 7-22).[236] A cathode extends downward into the container and an anode is located in the bottom of the container. Second-run reverberatory furnace slag is charged into the top of the furnace. Lead and slag are tapped from the bottom and side of the furnace, respectively. A fume hood covering the top of the furnace is vented to a control device.

In an electric furnace, electric current flows from the cathode to the anode through the scrap charge. The electrical resistance of the charge causes the charge to heat up and become molten. There is no combustion process involved in an electric furnace.

There is only one electric furnace in operation in the U.S. secondary lead industry. It is used to process second-run reverberatory furnace slag, and it fulfills the same role as a blast furnace used in conjunction with a reverberatory furnace. However, the electric furnace has two advantages over a blast furnace. First, because there are no combustion gases, ventilation requirements are much lower than for blast or reverberatory furnaces, and the potential for formation of organics is greatly reduced. Second, the electric furnace is extremely reducing, and produces a glass-like, nearly lead-free slag that is nonhazardous.

7.6.2 Benzene Emissions From Secondary Lead Smelters

Process emissions (i.e., those emitted from the smelting furnace's main exhaust) contain metals, organics (including benzene), HCl, and Cl_2. Process emissions also contain other pollutants, including PM, VOC, CO, and SO_2.

Blast furnaces are substantially greater sources of benzene emissions than reverberatory or rotary furnaces. Low exhaust temperatures from the charge column (about 800°F [430°C]) result in the formation of PICs from the organic material in the feed material.

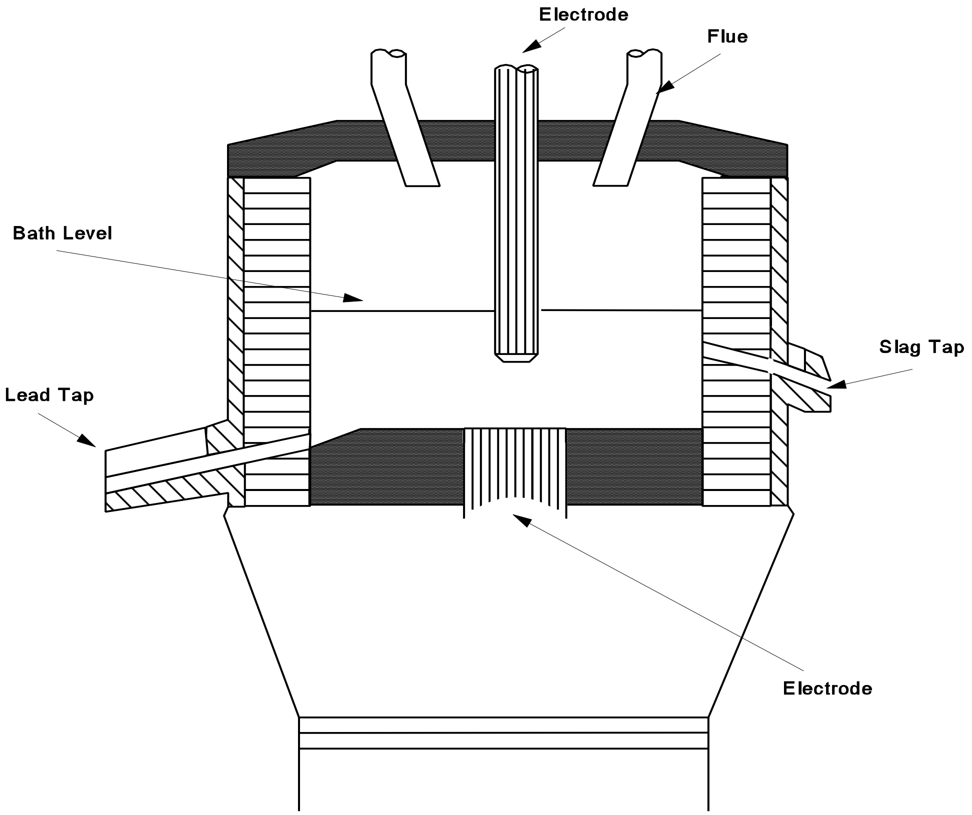


Figure 7-22. Cross-sectional View of an Electric Furnace for Processing Slag

Source: Reference 236.

Uncontrolled THC emissions (which correlate closely with organic pollutant emissions) from a typical 55,000-tons/yr (50,000 Mg/yr) blast furnace are about 309 tons/yr (280 Mg/yr).[236]

Controlled blast furnace benzene emissions are dependent on the add-on controls that are used, which may be anywhere from 80 to 99 percent effective at reducing THC emissions. Rotary and reverberatory furnaces have much higher exhaust temperatures than blast furnaces, about 1,800 to 2,200°F (980 to 1,200°C), and much lower THC emissions because of more complete combustion. Total hydrocarbon emissions from a typical rotary furnace (16,500 tons/yr [15,000 Mg/yr] capacity) are about 38 tons/yr (34 Mg/yr). The majority of these emissions occur during furnace charging, when the furnace's burner is cut back and the temperature is reduced. Emissions drop off sharply when charging is completed and the furnace is brought to normal operating temperature.[236] Benzene emissions from reverberatory furnaces are even lower than those from rotary furnaces because reverberatory furnaces are operated continuously rather than on a batch basis.

Three test reports from three secondary lead smelters were used to develop benzene emission factors.[237-240] All testing was conducted in support of the EPA's Secondary Lead National Emission Standards for Hazardous Air Pollutants (NESHAP) program. The three facilities tested represent the following process configurations: a rotary smelting furnace equipped with a baghouse and SO_2 scrubber; a blast furnace equipped with an afterburner, baghouse, and SO_2 scrubber; and a reverberatory and blast furnace with exhaust from each furnace combined prior to a single afterburner, baghouse, and SO_2 scrubber.

Uncontrolled VOC emissions were measured at all three facilities using VOST.[241] Nineteen VOC, including benzene, were detected by the VOST. Benzene emissions were measured at the blast furnace outlet (before the afterburner) at two facilities, and at the rotary furnace outlet at one facility. Total hydrocarbon emissions were measured at both the blast furnace and rotary furnace outlets and at the afterburner outlets following the blast furnaces. Emission factors for benzene are shown in Table 7-11.[237-240] Although benzene emissions were not measured after the control device, controlled emission factors were

TABLE 7-11. SUMMARY OF BENZENE EMISSION FACTORS FOR SECONDARY LEAD SMELTING

SCC	Emission Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating	Reference
3-04-004-03	Blast furnace	Uncontrolled	4.08×10^{-1} (2.04×10^{-1})	D	237, 238, 240
		Afterburner	2.47×10^{-2} [b] (1.23×10^{-2})	D	237, 238, 240
3-04-004-04	Rotary Furnace[c]	Uncontrolled	1.66×10^{-1} (8.30×10^{-2})	D	239

[a] Emission factors are in lb (kg) of benzene emitted per ton (Mg) of lead smelted.

[b] Average emission factor from two facility test reports.

[c] Batch-operated furnace with two charging episodes per batch and an average of 18 hours per batch (during the emissions test).

estimated using the THC control efficiency for the given process configuration. These estimates assume that the control efficiency for benzene was equal to the control efficiency for THC.

7.6.3 Control Technologies for Secondary Lead Smelters

Controls used to reduce organic emissions from smelting furnaces in the secondary lead smelting industry include afterburners on blast furnaces and combined blast and reverberatory exhausts. Reverberatory and rotary furnaces have minimal benzene emissions because of high exhaust temperatures and turbulence, which promote complete combustion of organics. No controls for THC are necessary for these process configurations.[236]

Benzene emissions from blast furnaces are dependent on the type of add-on control used. An afterburner operated at 1,300°F (700°C) achieves about 84 percent destruction efficiency of THC.[236] Facilities with blast and reverberatory furnaces usually combine the exhaust streams and vent the combined stream to an afterburner. The higher operating temperature of the reverberatory furnace reduces the fuel needs of the afterburner so that the afterburner is essentially “idling.” Any temperature increase measured across the afterburner is due to the heating value of organic compounds in the blast furnace exhaust. A combined reverberatory and blast furnace exhaust stream ducted to an afterburner with an exit temperature of 1,700°F (930°C) can achieve 99-percent destruction efficiency for THC.[236]

Additional controls used by secondary lead smelters include baghouses for particulate and metal control, hooding and ventilation to a baghouse for process fugitives, and scrubbers for HCl and SO_2 control.[236]

7.7 IRON AND STEEL FOUNDRIES

Iron and steel foundries can be defined as those that produce gray, white, ductile, or malleable iron and steel castings. Cast iron and steels are both solid solutions of iron, carbon, and various alloying materials. Although there are many types of each, the iron and steel families can be distinguished by their carbon content. Cast irons typically contain 2 percent carbon or greater; cast steels usually contain less than 2 percent carbon.[242]

Iron castings are used in almost all types of equipment, including motor vehicles, farm machinery, construction machinery, petroleum industry equipment, electrical motors, and iron and steel industry equipment. Steel castings are classified on the basis of their composition and heat treatment, which determine their end use. Steel casting classifications include carbon, low-alloy, general-purpose-structural, heat-resistant, corrosion-resistant, and wear-resistant. They are used in motor vehicles, railroad equipment, construction machinery, aircraft, agricultural equipment, ore refining machinery, and chemical manufacturing equipment.[242]

Based on a survey conducted by EPA in support of the iron and steel foundry MACT standard development, there were 756 iron and steel foundries in the United States in 1992.[243] Foundry locations can be correlated with areas of heavy industry and manufacturing and, in general, with the iron and steel production industry (Ohio, Pennsylvania, and Indiana).

Additional information on iron and steel foundries and their locations may be obtained from the following trade associations:

- American Foundrymen's Society, Des Plaines, Illinois;
- National Foundry Association, Des Plaines, Illinois;
- Ductile Iron Society, Mountainside, New Jersey;
- Iron Casting Society, Warrendale, Pennsylvania; and
- Steel Founders' Society of America, Des Plaines, Illinois.

7.7.1 Process Description for Iron and Steel Foundries

The following four basic operations are performed in all iron and steel foundries:

- Storage and handling of raw materials;
- Melting of the raw materials;
- Transfer of the hot molten metal into molds; and
- Preparation of the molds to hold the molten metal.

Other processes present in most, but not all, foundries include:

- Sand preparation and handling;
- Mold cooling and shakeout;
- Casting cleaning, heat treating, and finishing;
- Coremaking; and
- Pattern making.

A generic process flow diagram for iron and steel foundries is given in Figure 7-23.[242] Figure 7-24 depicts the emission points in a typical iron foundry.[244]

Iron and steel castings are produced in a foundry by injecting or pouring molten metal into cavities of a mold made of sand, metal, or ceramic material. Input metal is melted by the use of a cupola, an electric arc furnace, or an induction furnace. About 70 percent of all iron castings are produced using cupolas, with lesser amounts produced in electric arc and induction furnaces. However, the use of electric arc furnaces in iron foundries is increasing. Steel foundries rely almost exclusively on electric arc or induction furnaces for melting purposes. With either type of foundry, when the poured metal has solidified, the molds are separated and the castings removed from the mold flasks on a casting shakeout unit. Abrasive

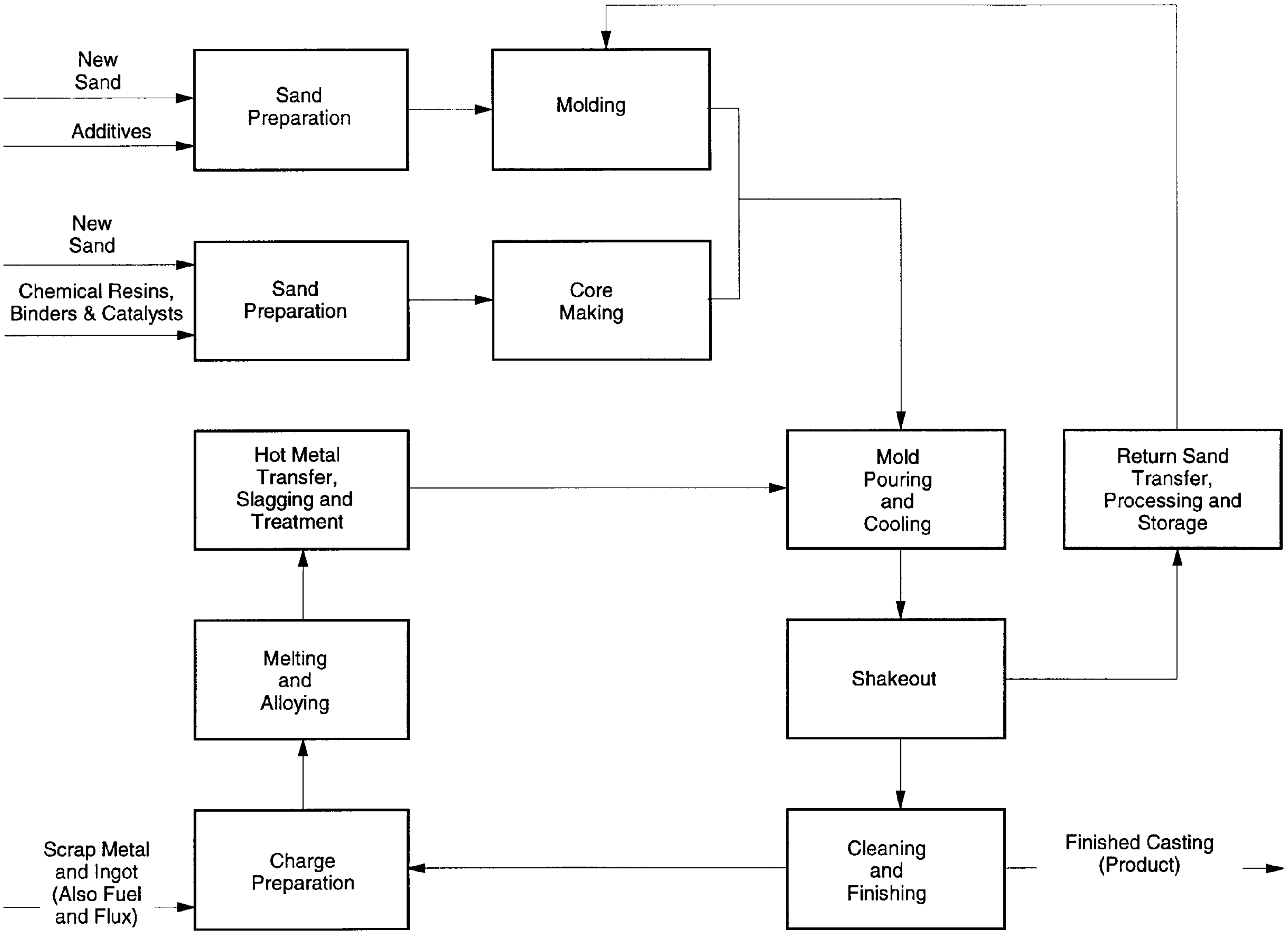


Figure 7-23. Process Flow Diagram for a Typical Sand-Cast Iron and Steel Foundry

Source: Reference 242.

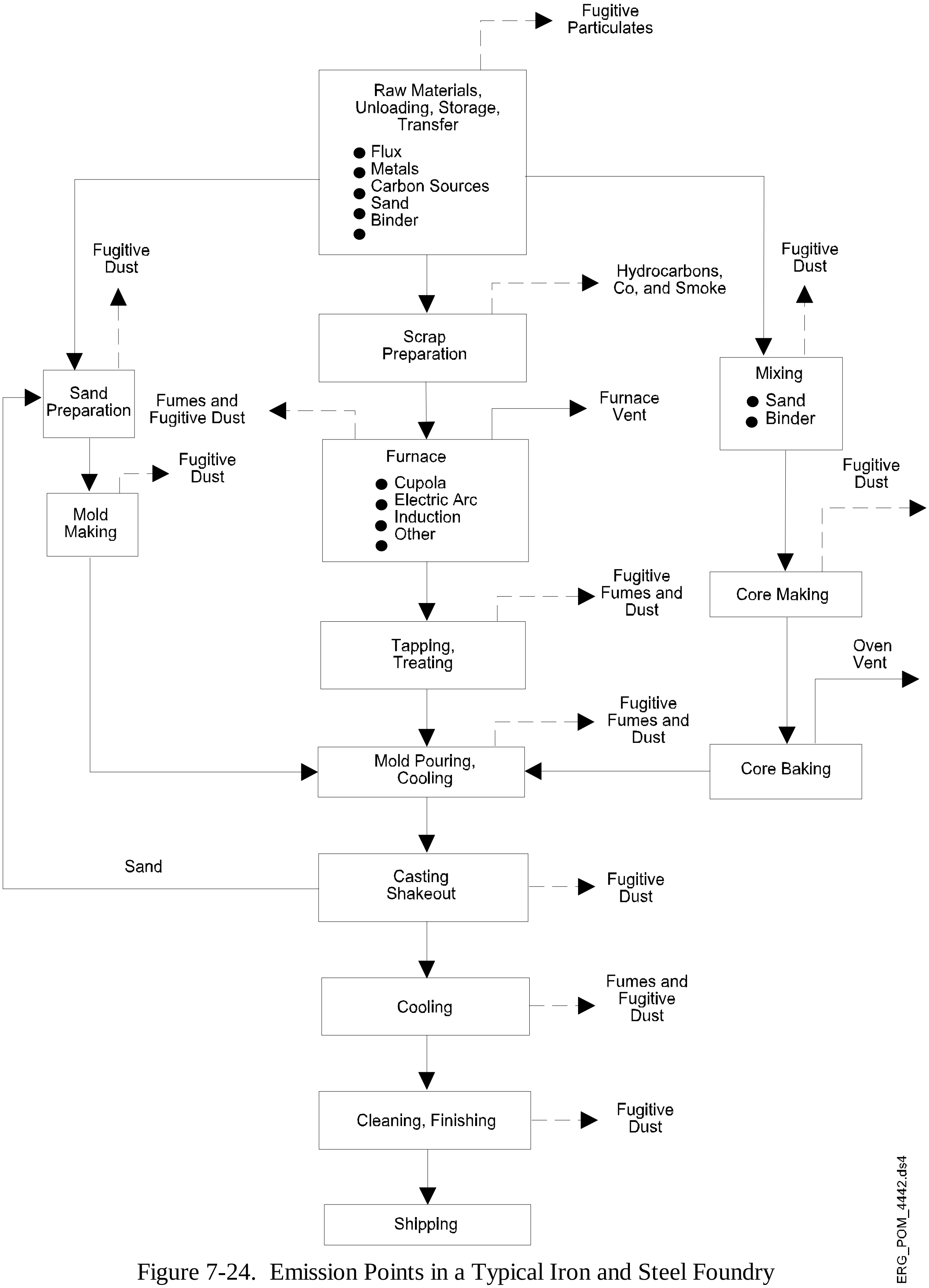


Figure 7-24. Emission Points in a Typical Iron and Steel Foundry

Source: Reference 244.

(shotblasting) cleaning, grinding, and heat treating are performed as necessary. The castings are then inspected and shipped to another industry for machining and/or assembly into a final product.[242]

In a typical foundry operation, charges to the melting unit are sorted by size and density and cleaned (as required) prior to being put in the melter. Charges consist of scrap metal, ingot, carbon (coke), and flux. Prepared charge materials are placed in crane buckets, weighed, and transferred into the melting furnace or cupola. The charge in a furnace or cupola is heated until it reaches a certain temperature and the desired chemistry of the melt has been attained. After the desired product is obtained, the molten metal is either poured out of the furnace into various sized teeming ladles and then into the molds or it is transferred to holding furnaces for later use.

7.7.2 Benzene Emissions From Iron and Steel Foundries

Organic compounds are emitted from various process steps in an iron and steel foundry, including scrap preparation, the furnace, tapping and treating, mold pouring and cooling, casting shakeout, sand cooling, and mold and core production. Benzene may be included among other organic compounds emitted from these process steps. Sources of organic emissions during these process steps include solvent degreasers used during scrap iron charge, coke, and organic binders and organic polymer networks that hold molds and cores together to form the castings.

Data from one testing program at a single gray iron foundry were averaged to develop a benzene emission factor (Table 7-12). The emission sources tested were sand cooler and belts, casting shakeouts and mixers, and pouring and cooling. Vapors from the sand cooler and belts and casting shakeouts and mixers were collected in hoods and ducted to a baghouse. Sampling for benzene was performed in accordance with EPA Method 18. All sampling was performed at the stack, after the control devices. Benzene emissions from the three emission sources were detected; however, because of limited process data availability, a

TABLE 7-12. BENZENE EMISSION FACTOR FOR IRON FOUNDRIES

SCC	Emission Source	Control Device(s)	Emission Factor lb/ton (kg/Mg)	Emission Factor Rating
3-04-003-98	Sand cooling and belts	Baghouse	6.99×10^{-4} (3.50×10^{-4})[a]	D

Source: References 245 and 246.

[a] Factor is in lb (kg) of benzene emitted per ton (Mg) of sand cooled.

benzene emission factor could only be calculated for the sand cooler and belts, as reflected in Table 7-12.[245-246]

Benzene from sand coolers and belts and casting shakeouts and mixers may be emitted as a result of the heating during mold pouring of the organic binders used to form the casting. During mold pouring, the binder materials in the mold are exposed to temperatures near 2,550°F (1,400°C). At these temperatures, pyrolysis of the chemical binder may release organic chemicals, which become trapped in the sand inside the casting. During shakeout and sand cooling, the sand is exposed to the atmosphere and these organic chemicals may be released.

7.7.3 Control Technologies for Iron and Steel Foundries[244]

Scrap preparation with heat or solvent degreasers will emit organic compounds. Catalytic incinerators and afterburners can control about 95 percent of organic emissions.

Emissions released from melting furnaces include organic compounds. The highest concentrations of furnace emissions occur when furnace doors are open during charging, backcharging, alloying, slag removal, and tapping operations. These emissions can escape into the furnace building or can be collected and vented through roof openings. Emission controls for melting and refining operations involve venting furnace gases and fumes directly to a control device. Canopy hoods or special hoods near furnace doors and tapping points capture emissions and route them to emission control systems.

A cupola furnace typically has an afterburner, which achieves up to 95 percent efficiency. The afterburner is located in the furnace stack to oxidize CO and burn organic fumes, tars, and oils. Reducing these contaminants protects the particulate control device from possible plugging and explosion. Toxic emissions from cupolas include both organic and inorganic materials. Cupolas produce the most toxic emissions compared to other melting equipment. During melting in an electric arc furnace, hydrocarbons are emitted from vaporization and incomplete combustion of any oil remaining on the scrap iron charge. Electric induction furnaces emit negligible amounts of hydrocarbon emissions, and are typically uncontrolled except during charging and pouring operations.

Organic emissions are generated during the refining of molten iron before pouring and from the mold and core materials during pouring. Toxic emissions of halogenated and aromatic hydrocarbons are released in the refining process. Emissions from pouring normally are captured by a collection system and vented, either controlled or uncontrolled, to the atmosphere. Emissions continue as the molds cool.

Organics are emitted in mold and core production operations from core baking and mold drying. Afterburners and catalytic incinerators can be used to control organics emissions.

In addition to organic binders, molds and cores may be held together in the desired shape by means of a cross-linked organic polymer network. This network of polymers undergoes thermal decomposition when exposed to the very high temperatures of casting, typically 2,550°F (1,400°C). At these temperatures it is likely that pyrolysis of the chemical binder will produce a complex of free radicals that will recombine to form a wide range of chemical compounds having widely differing concentrations.

There are many different types of resins currently in use, with diverse and toxic compositions. No data are available for determining the toxic compounds in a particular resin that are emitted to the atmosphere and to what extent these emissions occur.

7.8 PORTLAND CEMENT PRODUCTION

Most of the hydraulic cement produced in the United States is Portland cement--a cementitious, crystalline compound composed of metallic oxides. The end-product cement, in its fused state, is referred to as “clinker.” Raw materials used in the process can be calcium carbonate- and aluminum-containing limestone, iron, silicon oxides, shale, clay, and sand.[247] As of December 1990, there were 112 Portland cement plants in the United States operating 213 kilns with a total annual clinker capacity of 80 million tons (73.7 million Mg). The kiln population included 80 wet process kilns and 133 dry process kilns.[247] U.S. Portland cement plants are listed in Table 7-13 .

7.8.1 Process Description for the Portland Cement Industry

In Portland cement production, most raw materials typically are quarried on site and transferred by conveyor to crushers and raw mills. After the raw materials are reduced to the desired particle size, they are blended and fed to a large rotary kiln. The feed enters the kiln at the elevated end, and the burner is located at the opposite end. The raw materials are then changed into cementitious oxides of metal by a countercurrent heat exchange process. The materials are continuously and slowly moved to the low end by the rotation of the kiln while being heated to high temperatures (2,700°F [1,482°C]) by direct firing (Stream 3 in Figure 7-25). In this stage, chemical reactions occur, and a rock-like substance called "clinker" is formed. This clinker is then cooled, crushed, and blended with gypsum to produce Portland cement.[247] The cement is then either bagged or bulk-loaded and transported out.[248]

Cement may be made via a wet or a dry process. Many older kilns use the wet process. In the past, wet grinding and mixing technologies provided more uniform and consistent material mixing, resulting in a higher quality clinker. Dry process technologies have improved, however, to the point that all of the new kilns since 1975 use the dry process.[249] In the wet process, water is added to the mill while the raw materials are being ground. The resulting slurry is fed to the kiln. In the dry process, raw materials are also ground finely in a mill, but no water is added and the feed enters the kiln in a dry state.

More fuel is required for the wet process than the dry process to evaporate the water from the feed. However, for either the wet or dry process, Portland cement production is fuel-intensive. The fuel burned in the kiln may be natural gas, oil, or coal. Many cement

TABLE 7-13. SUMMARY OF PORTLAND CEMENT PLANT CAPACITY INFORMATION

Location	Number of Plants (kilns)	Capacity 10^3 tons/yr (10^3 Mg/yr)
Alabama	5 (6)	4,260 (3,873)
Alaska	1 (0)[a]	0 (0)
Arizona	2 (7)	1,770 (1,609)
Arkansas	2 (5)	1,314 (1,195)
California	12 (20)	10,392 (9,447)
Colorado	3 (5)	1,804 (1,640)
Florida	6 (8)	3,363 (3,057)
Georgia	2 (4)	1,378 (1,253)
Hawaii	1 (1)	263 (239)
Idaho	1 (2)	210 (191)
Illinois	4 (8)	2,585 (2,350)
Indiana	4 (8)	2,830 (2,573)
Iowa	4 (7)	2,806 (2,551)
Kansas	4 (11)	1,888 (1,716)
Kentucky	1 (1)	724 (658)
Maine	1 (1)	455 (414)
Maryland	3 (7)	1,860 (1,691)
Michigan	5 (9)	4,898 (4,453)
Mississippi	1 (1)	504 (458)
Missouri	5 (7)	4,677 (4,252)
Montana	2 (2)	592 (538)
Nebraska	1 (2)	961 (874)
Nevada	1 (2)	415 (377)
New Mexico	1 (2)	494 (449)
New York	4 (5)	3,097 (2,815)
Ohio	4 (5)	1,703 (1,548)

(continued)

TABLE 7-13. CONTINUED

Location	Number of Plants (kilns)	Capacity 10^3 tons/yr (10^3 Mg/yr)
Oklahoma	3 (7)	1,887 (1,715)
Oregon	1 (1)	480 (436)
Pennsylvania	11 (24)	6,643 (6,039)
South Carolina	3 (7)	2,579 (2,345)
South Dakota	1 (3)	766 (696)
Tennessee	2 (3)	1,050 (955)
Texas	12 (20)	8,587 (7,806)
Utah	2 (3)	928 (844)
Virginia	1 (5)	1,117 (1,015)
Washington	1 (1)	473 (430)
West Virginia	1 (3)	822 (747)
Wyoming	1 (1)	461 (419)

Source: Reference 247.

[a] Grinding plant only.

plants burn coal, but supplemental fuels such as waste solvents, chipped rubber, shredded municipal garbage, and coke have been used in recent years.[247] A major trend in the industry is the increased use of waste fuels. In 1989, 33 plants in the United States and Canada reported using waste fuels; the number increased to 55 plants in 1990.[247]

The increased use of hazardous waste-derived fuels (HWDFs) for the kilns is attributed to lower cost and increased availability. As waste generators reduce or eliminate solvents from their waste steams, the streams contain more sludge and solids. As a result, two new hazardous waste fueling methods have emerged at cement kilns. The first method pumps solids (either slurried with liquids or dried and ground) into the hot end of the kiln. The second method (patented by cement kiln processor and fuel blender Cadence, Inc.) introduces containers of solid waste into the calcining zone of the kiln.[250]

The kiln system for the manufacture of Portland cement by dry process with preheater is shown in Figure 7-25. The raw material enters a four-stage suspension preheater, where hot gases from the kiln heat the raw feed and provide about 40-percent calcination (Stream 1) before the feed enters the kiln. Some installations include a precalcining furnace (Stream 2), which provides about 85 percent calcination before the feed enters the kiln.[247]

7.8.2 Benzene Emissions from the Portland Cement Industry and Regulatory Analysis

The raw materials used by some facilities may contain organic compounds, which become a source of benzene emissions during the heating step. However, fuel combustion to heat the kiln is believed to be the greater source of benzene emissions. As shown in Table 7-14, benzene is emitted when either fossil fuels or HWDFs are combusted in the kiln.[247,249,251]

Facilities that burn HWDF are subject to the Boilers and Industrial Furnaces (BIF) rule promulgated February 21, 1991, under the Resource Conservation and Recovery Act (RCRA). The BIF rule requires that a facility that burns hazardous waste demonstrate a

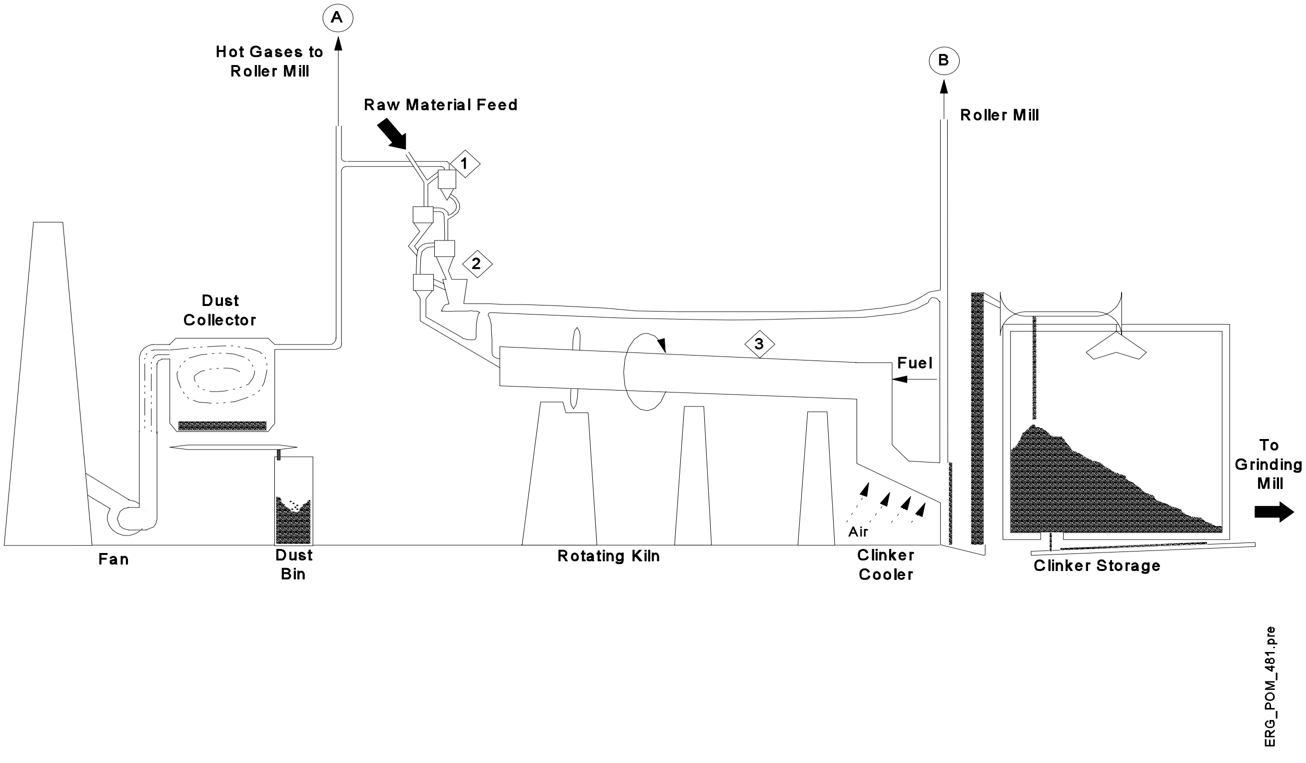


Figure 7-25. Process Diagram of Portland Cement Manufacture by Dry Process With Preheater

Source: Reference 247.

TABLE 7-14. SUMMARY OF EMISSION FACTORS FOR THE PORTLAND CEMENT INDUSTRY

SCC and Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Factor Rating	Reference
3-05-007-06 Cement Manufacturing - Wet Process - Kilns	Kiln--Burning Hazardous Waste Exclusively, or with Coal or Coke	EP	3.7 x 10^{-3} (1.8 x 10^{-3})	B	247, 251
	Kiln--Burning Hazardous Waste and Natural Gas as Fuel	EP	7.5 x 10^{-3} (3.7 x 10^{-3})	D	251
	Kiln--Burning Hazardous Waste and Coal at High Combustion Temperature	EP	3.9 x 10^{-6} (1.9 x 10^{-6})	D	251
3-05-006-06 Cement Manufacturing - Dry Process	Kiln--Burning Coal in Precalciner Process	FF	1.6 x 10^{-2} (8 x 10^{-3})	E	249
	Kiln--Burning Coal and 20 percent TDF[b]	FF	0.17 g/MMBtu	E	249

[a] Expressed as lb (kg) of benzene emitted per Mg (ton) of clinker produced.

[b] Facility burns 65 tons (59 Mg) TDF per day (6,000 tires); MMBtu/ton of clinker produced not reported for this facility.

EP = Electrostatic Precipitator.
FF = Fabric Filter.
TDF = Tire-derived fuel.

99.99 percent destruction efficiency for principal organic hazardous constituents in the waste stream. To guard against products of incomplete combustion, the BIF rule limits CO levels in the kiln and or total hydrocarbon levels in stack gases.[250,251] In addition, a NESHAP for control of HAPs from Portland Cement Kilns is under development.

Table 7-14 presents a summary of benzene emission factors for wet process cement kilns controlled with electrostatic precipitators burning HWDF in conjunction with other fuels.

7.9 HOT-MIX ASPHALT PRODUCTION

In 1994, there were approximately 3,600 asphalt hot-mix plants.[252] Approximately 40 percent of companies that operate hot-mix plants operate a single plant. Because plants must be located near the job site, plants are concentrated in areas where the highway and road network is concentrated.[253] Additional information on the locations of individual hot-mix asphalt facilities can be obtained by contacting the National Asphalt Pavement Association in College Park, Maryland.

7.9.1 Process Description

There are three types of hot-mix asphalt plants operating in the United States: batch-mix, continuous-mix, and drum-mix. At batch-mix and continuous-mix plants, the aggregate drying process is performed separately from the mixing of aggregate with asphalt cement. Drum-mix plants combine these two processes. Production capacities for all three types of plants range from 40 to 600 tons (36 to 544 Mg) of hot mix per hour. Almost all plants in use are of either the batch-mix or the drum-mix types. Less than half a percent of operating hot-mix asphalt plants are of the continuous-mix variety.[79] Over 80 percent of all hot-mix asphalt production plants are mobile.[245]

In the production of hot-mix asphalt (also referred to as asphalt concrete), aggregate is heated to eliminate moisture and then mixed with hot asphalt cement. The resulting hot mixture is pliable and able to be compacted and smoothed. When the hot-mix asphalt cools and hardens, it provides a waterproof and durable pavement for roads, driveways, parking lots, and runways.

Aggregate, the basic raw material of hot-mix asphalt, consists of any hard, inert mineral material, usually gravel, sand, and mineral filler. Aggregate typically comprises between 90 and 95 percent by weight of the asphalt mixture. Because aggregate provides most of the load-bearing properties of a pavement, the performance of the pavement depends on selection of the proper aggregate.

Asphalt cement is used as the binding agent for aggregate. It prevents moisture from penetrating the aggregate, and it acts as a cushioning agent. Typically, asphalt cement constitutes 4 to 6 percent by weight of a hot-mix asphalt mixture.[253]

As with the asphalt flux used to produce asphalt roofing products, asphalt cement is obtained from the distillation of crude oil. It is classified into grades under one of several classification schemes. The most commonly used scheme classifies asphalt cement based on its viscosity at 140°F (60°C). The more viscous the asphalt cement, the higher its numerical rating. An asphalt cement of grade AC-40 is considered a hard asphalt (i.e., a viscosity of 4,000 grams per centimeter per second [g/cm-s or poises]), whereas an asphalt cement of grade AC-2.5 is considered a soft asphalt (i.e., a viscosity of 250 g/cm-s [poises]).

Several western States use a second classification scheme that measures viscosity of the asphalt cement after a standard simulated aging period. This simulated aging period consists of exposure to a temperature of 325°F (163°C) for 5 hours. Viscosity is measured at 140°F (60°C), with grades ranging from AR-1000 for a soft asphalt cement (1000 g/cm-s [poises]) to AR-16000 for a hard asphalt cement (16,000 g/cm-s [poises]).

A third classification scheme is based on the penetration allowed by the asphalt cement. Grade designation 40 to 50 means that a needle with a weight attached will penetrate the asphalt cement between 40 and 50 tenths of a millimeter under standard test conditions. The hard asphalt cements have penetration ratings of 40 to 50, whereas the soft grades have penetration ratings of 200 to 300.[253]

The asphalt cement grade selected for different hot-mix asphalts depends on the type of pavement, climate, and type and amount of traffic expected. Generally, asphalt pavement bearing heavy traffic in warm climates would require a harder asphalt cement than pavement subject to either light traffic or cold climate conditions.

Another material that is used to a greater extent in the production of new or virgin hot-mix asphalt is recycled asphalt pavement (RAP), which is pavement material that has been removed from existing roadways. This RAP material is now used by virtually all companies in their hot-mix asphalt mixtures. The Surface Transportation Assistance Act of 1982 encourages recycling by providing a 5-percent increase in Federal funds to State agencies that recycle asphalt pavement. Rarely does the RAP comprise more than 60 percent by weight of the new asphalt mixture. Twenty-five percent RAP is typical in batch plants, whereas 40 to 50 percent RAP mixtures are typical in drum-mix plants.[253]

Rejuvenating agents are sometimes added to hot-mix asphalts where they are blended with RAP, which brings the weathered and aged asphalt cement in the recycled mixture up to the specifications of a new asphalt mixture. Usually, a soft asphalt cement, a specially prepared high-viscosity oil, or a hard asphalt cement blended with a low-viscosity oil are used as rejuvenating agents. The amount of rejuvenating agent added depends on the properties of the RAP and on the specifications for the hot-mix asphalt product.

The primary processes of a typical batch-mix hot-mix asphalt facility are illustrated in Figure 7-26.[252] Aggregate of various sizes is stockpiled at the plant for easy access. The moisture content of the stockpiled aggregate usually ranges from 3 to 5 percent.

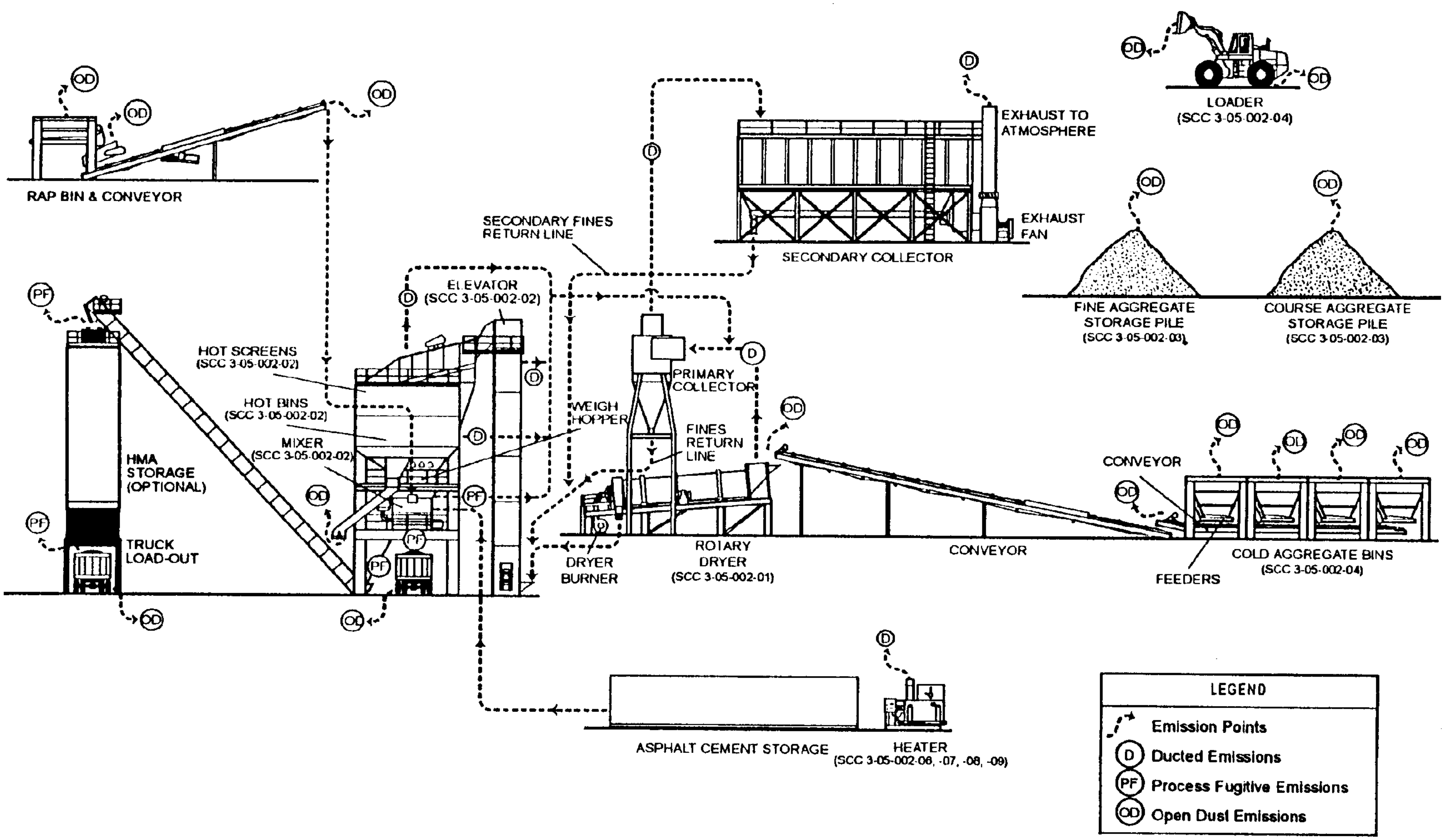


Figure 7-26. General Process Flow Diagram for Batch Mix Asphalt Paving Plants

Source: Reference 252.

The moisture content of recycled hot-mix asphalt typically ranges from 2 to 3 percent. The different sizes of aggregate are typically transported by front-end loader to separate cold feed bins and metered onto a feeder conveyor belt through gates at the bottom of the bins. The aggregate is screened before it is fed to the dryer to keep oversize material out of the mix.

The screened aggregate is then fed to a rotating dryer with a burner at its lower (discharge) end that is fired with fuel oil, natural gas, or propane. The dryer removes moisture from the aggregate and heats the aggregate to the proper mix temperature. Inside the dryer are longitudinal flights (metal slats) that lift and tumble the aggregate, causing a curtain of material to be exposed to the heated gas stream. This curtain of material provides greater heat transfer to the aggregate than would occur if the aggregate tumbled along the bottom of the drum towards the discharge end. Aggregate temperature at the discharge end of the dryer is about 300°F (149°C). The amount of aggregate that a dryer can heat depends on the size of the drum, the size of the burner, and the moisture content of the aggregate. As the amount of moisture to be removed from the aggregate increases, the effective production capacity of the dryer decreases.

Vibrating screens segregate the heated aggregate into bins according to size. A weigh hopper meters the desired amount of the various sizes of aggregate into a pugmill mixer. The pugmill typically mixes the aggregate for approximately 15 seconds before hot asphalt cement from a heated tank is sprayed into the pugmill. The pugmill thoroughly mixes the aggregate and hot asphalt cement for 25 to 60 seconds. The finished hot-mix asphalt is either directly loaded into trucks or held in insulated and/or heated storage silos. Depending on the production specifications, the temperature of the hot-mix asphalt product mix can range from 225 to 350°F (107 to 177°C) at the end of the production process.

When a hot mix containing RAP is produced, the aggregate is superheated (compared to totally virgin hot-mix asphalt production) to about 600°F (315°C) to ensure sufficient heat transfer to the RAP when it is mixed with the virgin materials. The RAP material may be added either to the pugmill mixer or at the discharge end of the dryer. Rarely is more than 30 percent RAP used in batch plants for the production of hot-mix asphalt.

Continuous-mix plants are very similar in configuration to batch plants. Continuous-mix plants have smaller hot bins (for holding the heated aggregate) than do batch plants. Little surge capacity is required of these bins because the aggregate is continuously metered and transported to the mixer inlet by a conveyor belt. Asphalt cement is continuously added to the aggregate at the inlet of the mixer. The aggregate and asphalt cement are mixed by the action of rotating paddles as they are conveyed through the mixer. An adjustable dam at the outlet end of the mixer regulates the mixing time and also provides some surge capacity. The finished mix is transported by a conveyor belt to either a storage silo or surge bin.[253]

Drum-mix plants dry the aggregate and mix it with the asphalt cement in the same drum, eliminating the need for the extra conveyor belt, hot bins and screens, weigh hopper, and pugmill of batch-mix plants. The drum of a drum-mix plant is much like the dryer of a batch plant, but it typically has more flights than do batch dryers to increase veiling of the aggregate and to improve overall heat transfer. The burner in a drum-mix plant emits a much bushier flame than does the burner in a batch plant. The bushier flame is designed to provide earlier and greater exposure of the virgin aggregate to the heat of the flame. This design also protects the asphalt cement, which is injected away from the direct heat of the flame.[253]

Initially, drum-mix plants were designed to be parallel flow as depicted in Figure 7-27.[252] Recently, the counterflow drum-mix plant design shown in Figure 7-28 has become popular.[79] The parallel flow drum-mix process is a continuous mixing type process using proportioning cold-feed controls for the process materials. Aggregate, which has been proportioned by gradations, is introduced to the drum at the burner end. As the drum rotates, the aggregate as well as the combustion products move toward the other end of the drum in parallel. Liquid asphalt cement flow is controlled by a variable flow pump that is electronically linked to the virgin aggregate and RAP weigh scales. The asphalt cement is

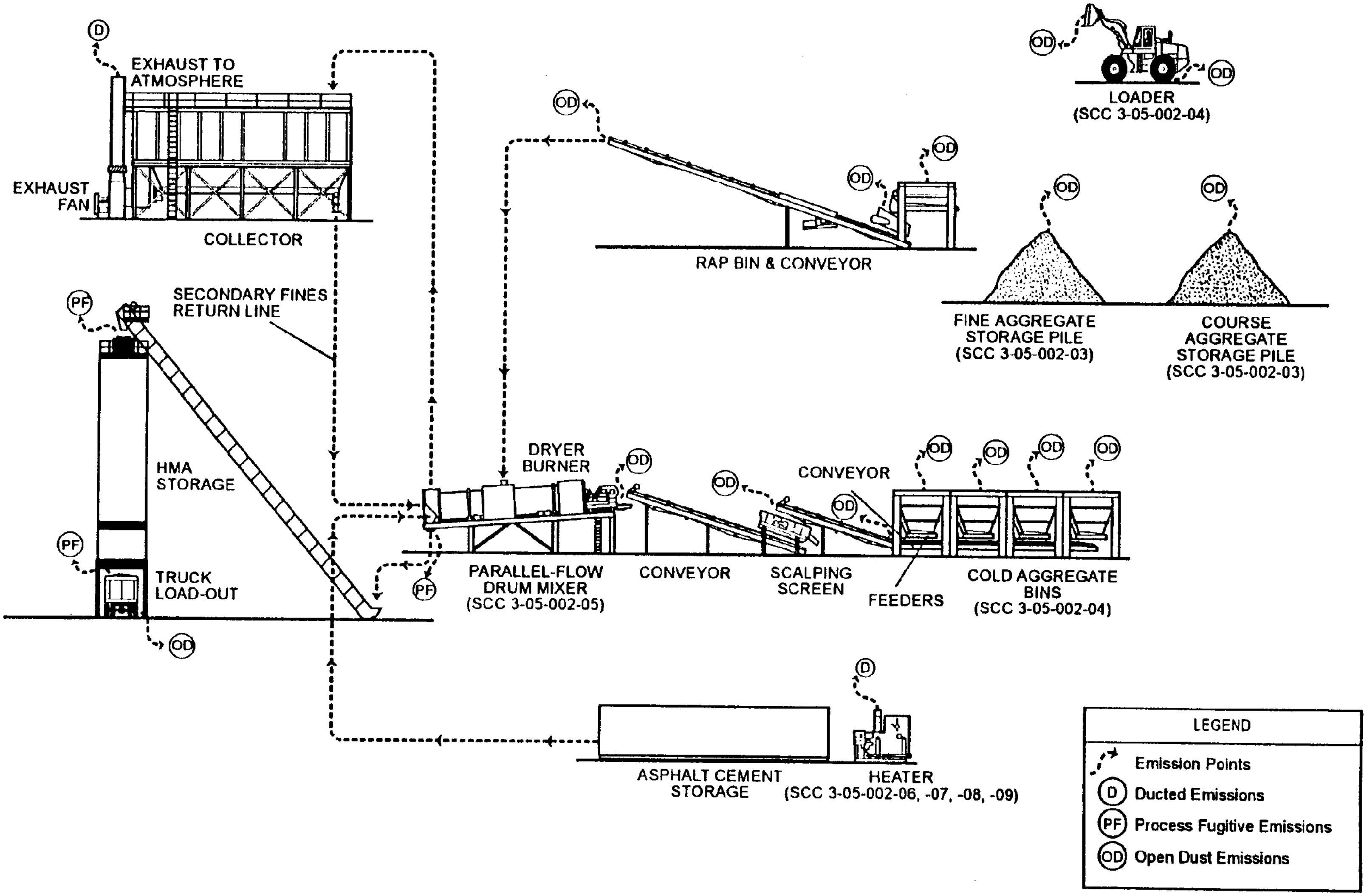


Figure 7-27. General Process Flow Diagram for Drum Mix Asphalt Paving Plants

Source: Reference 252.

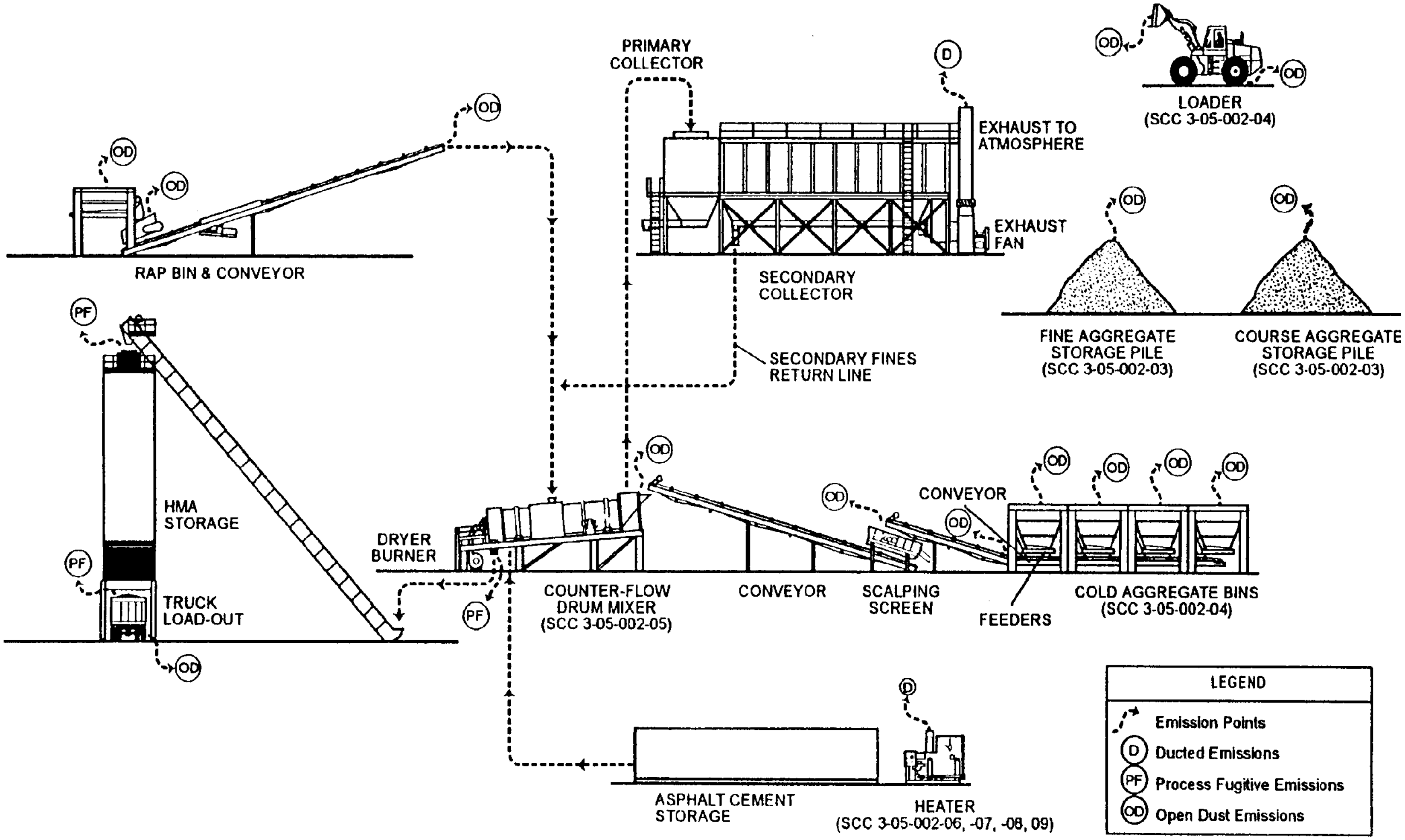


Figure 7-28. General Process Flow Diagram for Counter Flow Drum Mix Asphalt Paving Plants

Source: Reference 252.

introduced in the mixing zone midway down the drum in a lower temperature zone, along with any RAP and PM from the collectors. The mixture is discharged at the end of the drum and conveyed to a surge bin or storage silos. The exhaust gases also exit the end of the drum and pass on to the collection system.[79]

In the counterflow drum-mix type plant, the material flow in the drum is opposite or counterflow to the direction of exhaust gases. In addition, the liquid asphalt cement mixing zone is located behind the burner flame zone so as to keep the materials from direct contact with hot exhaust gases. Liquid asphalt cement flow is still controlled by a variable flow pump and is injected into the mixing zone along with any RAP and PM from primary and secondary collectors.[79]

Parallel-flow drum mixers have an advantage in that mixing in the discharge end of the drum captures a substantial portion of the aggregate dust, thereby lowering the load on the downstream collection equipment. For this reason, most parallel flow drum mixers are followed only by primary collection equipment (usually a baghouse or venturi scrubber). However, because the mixing of aggregate and liquid asphalt cement occurs in the hot combustion product flow, organic emissions (gaseous and liquid aerosol) from parallel-flow drum mixers may be greater than in other processes.[79]

On the other hand, because the liquid asphalt cement, virgin aggregate, and RAP are mixed in a zone removed from the exhaust gas stream, counterflow drum-mix plants will likely have organic emissions (gaseous and liquid aerosol) that are lower than those from parallel-flow drum-mix plants. A counterflow drum-mix plant can normally process RAP at ratios up to 50 percent with little or no observed effect on emissions. Today's counterflow drum-mix plants are designed for improved thermal efficiencies.[79]

Of the 3,600 active hot-mix asphalt plants in the United States, approximately 2,300 are batch-mix plants, 1,000 are parallel-flow drum-mix plants, and 300 are counterflow drum-mix plants. About 85 percent of plants being built today are of the counterflow drum-mix design; batch-mix plants and parallel-flow drum-mix plants account for 10 and 5 percent, respectively.[79]

One major advantage of both types of drum-mix plants is that they can produce material containing higher percentages of RAP than batch-mix plants can produce. The use of RAP significantly reduces the amount of new (virgin) rock and asphalt cement needed to produce hot-mix asphalt. With the greater veiling of aggregate, drum-mix plants are more efficient than batch-mix plants at transferring heat and achieving proper mixing of recycled asphalt and virgin materials.[253]

7.9.2 Benzene Emissions from the Hot-Mix Asphalt Production

Emissions of benzene from hot-mix asphalt plants occur from the aggregate rotary dryers and the asphalt heaters (due to fuel combustion). In Figure 7-26, the emission point for the rotary dryer is indicated by SCC 3-05-002-01, and the emission point for the heater is indicated by SCC 3-05-002-06, -07, -08, and -09. Note that most of the emission points in Figures 7-26 and 7-27 are sources of particulate matter. Most plants employ some form of mechanical collection, typically cyclones, to collect aggregate particle emissions from the rotary dryers. However, these cyclones would have a minimal collection efficiency for benzene.

Other types of controls installed at asphalt hot-mix plants, primarily to control PM emissions, include wet scrubbers or baghouses.[253] These controls are expected to have some effect on reducing benzene emissions; however, the control efficiencies are not known.

Table 7-15 presents four emission factors for the rotary dryer at a hot-mix asphalt plant.[3,254-263] The factors range from 1.41×10^{-4} lb/ton (7.04×10^{-5} kg/Mg) to 1.95×10^{-5} lb/ton (9.75×10^{-6} kg/Mg) and differ in the type of fuel burned to heat the dryer (LPG, oil, natural gas, or diesel) and the type of control device used (cyclone, baghouse, wet scrubber, or uncontrolled). Table 7-15 also presents one emission factor for an

TABLE 7-15. EMISSION FACTORS FOR HOT-MIX ASPHALT MANUFACTURE

SCC and Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Factor Rating	Reference
3-05-002-01 Petroleum Industry- Asphalt Concrete- Rotary Dryer	Rotary Dryer, LPG-fired	Uncontrolled	$5.35\text{x}10^{-4}$ ($2.68\text{x}10^{-4}$)	C	254-256
	Rotary Dryer, oil-fired	Multiple cyclone	$7.70\text{x}10^{-5}$ ($3.85\text{x}10^{-5}$)	C	3, 257
	Rotary Dryer, natural gas- or oil-fired	Baghouse with single cyclone, knock-out box, or multiple cyclone	$2.08\text{x}10^{-4}$ ($1.04\text{x}10^{-4}$)	B	258-261
	Rotary Dryer, natural gas- or diesel-fired	Wet scrubber	$1.95\text{x}10^{-5}$ ($9.75\text{x}10^{-6}$)	C	262, 263
3-05-002-08 Petroleum Industry- Asphalt Concrete- Asphalt heater-Distillate oil	Asphalt Heater, diesel-fired	Uncontrolled	$1.50\text{x}10^{-4}$ ($7.50\text{x}10^{-5}$)	D	254

[a] Emission factors are in lb (kg) of benzene emitted per ton (Mg) of hot-mix asphalt produced.

uncontrolled asphalt heater fired with diesel fuel. The source tests from which these emission factors were derived all use CARB Method 401 for sampling.

No regulations were identified that require control of benzene emissions at hot mix asphalt plants.

7.10 OPEN BURNING OF BIOMASS, SCRAP TIRES, AND AGRICULTURAL PLASTIC FILM

Open burning involves the burning of various materials in open drums or baskets, in fields or yards, and in large open drums or pits. Materials commonly disposed of in this manner include municipal waste, auto body components, landscape refuse, agricultural field refuse, wood refuse, bulky industrial refuse, and leaves. This section describes the open burning of biomass, scrap tires, and agricultural plastic film, and their associated benzene emissions.

7.10.1 Biomass Burning

Fires are known to produce respirable PM and toxic substances. Concern has even been voiced regarding the effect of emissions from biomass burning on climate change.[264] Burning wood, leaves, and vegetation can be a source of benzene emissions. In this document, the burning of any wood, leaves, and vegetation is categorized as biomass burning, and includes yard waste burning, land clearing/burning and slash burning, and forest fires/prescribed burning.[265]

Part of the complexity of fires as a source of emissions results from the complex chemical composition of the fuel source. Different woods and vegetation are composed of varying amounts of cellulose, lignin, and extractives such as tannins, and other polyphenolics, oils, fats, resins, waxes, and starches.[266] General fuel type categories in the National Fire-Danger Rating (NFDR) System include grasses, brush, timber, and slash (residue that remains on a site after timber harvesting).[266] The flammability of these fuel types depends upon plant species, moisture content, whether the plant is alive or dead at the time of burning, weather, and seasonal variations.

Pollutants from the combustion of biomass include CO, NO_x, sulfur oxides (SO_x), oxidants, polycyclic organic matter (POM), hydrocarbons, and PM. The large number of combustion products is due, in part, to the diversity of combustion processes occurring simultaneously within a fire-flaming, smoldering, and glowing combustion. These processes are distinct combustion processes that involve different chemical reactions that affect when and what pollutants will be emitted during burning.[266]

Emission factor models (based on field and laboratory data) have been developed by the U.S. Forest Service. These models incorporate variables such as fuel type and combustion types (flaming or smoldering). Because ratios of toxic air substances are correlated with the release of other primary PICs (such as CO), the models correlate benzene with CO emissions.[266] These emission factor models were used to develop emission factors for the biomass burning sub-categories described in the following sections.[265]

Because of the potential variety in the fuel source and the limited availability of emission factors to match all possible fuel sources, emissions estimates may not necessarily represent the combustion practices occurring at every location in the United States. Therefore, localized practices of such parameters as type of wood being burned and control strategies should be carefully compared.[265]

Yard Waste Burning

Yard waste burning is the open burning of such materials as landscape refuse, wood refuse, and leaves in urban, suburban, and residential areas.[265] Yard waste is often burned in open drums, piles, or baskets located in yards or fields. Ground-level open burning emissions are affected by many variables, including wind, ambient temperature, composition and moisture content of the material burned, and compactness of the pile. It should be noted that this type of outdoor burning has been banned in certain areas of the United States, thereby reducing emissions from this subcategory.[265,267] An emission factor for yard waste is shown in Table 7-16.[265,266]

Land Clearing and Slash Burning

This subcategory includes the burning of organic refuse (field crops, wood, and leaves) in fields (agricultural burning) and wooded areas (slash burning) in order to clear the land. Burning as part of commercial land clearing often requires a permit.[265] Emissions from organic agricultural refuse burning are dependent primarily on the moisture content of the refuse and, in the case of field crops, on whether the refuse is burned in a headfire or a backfire.[267] Other variables, such as fuel loading (how much refuse material is burned per unit of land area) and how the refuse is arranged (piles, rows, or spread out), are also important in certain instances.[267] Emission factors for land clearing/burning and slash burning are shown in Table 7-16.[265,266]

Forest Fires/Prescribed Burning

A forest fire (or wildfire) is a large-scale natural combustion process that consumes various ages, sizes, and types of outdoor vegetation.[268] The size, intensity, and even occurrence of a forest fire depend on such variables as meteorological conditions, the species and moisture content of vegetation involved, and the weight of consumable fuel per acre (fuel loading).[268]

Prescribed or broadcast burning is the intentional burning of forest acres as part of forest management practices to achieve specific wildland management objectives. Controlled burning can be used to reduce fire hazard, encourage wildlife habitat, control insects, and enhance the vigor of the ecosystem.[266] Prescribed burning occurs thousands of times annually in the United States, and individual fires vary in size from a fraction of an acre

TABLE 7-16. SUMMARY OF BENZENE EMISSION FACTORS FOR BIOMASS BURNING

AMS Code	Emission Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
26-10-030-000	Yard Waste Burning	Uncontrolled	1.10 (5.51×10^{-1})	U
28-01-500-000	Land Clearing/Burning	Uncontrolled	9.06×10^{-1} (4.53×10^{-1})	U
28-10-005-000	Slash (Pile) Burning	Uncontrolled	9.06×10^{-1} (4.53×10^{-1})	U

Source: References 265 and 266.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of biomass burned.

AMS = Area and mobile source.

to several thousand acres. Prescribed fire use is often seasonal, which can greatly affect the quantity of emissions produced.[266]

HAP emission factors for forest fires and prescribed burning were developed using the same basic approach for yard waste and land clearing burning, with an additional step to further classify fuel types into woody fuels (branches, logs, stumps, and limbs), live vegetation, and duff (layers of partially decomposed organic matter).[265] In addition to the fuel type, the methodology was altered to account for different phases of burning, namely, flaming and smoldering.[265] The resulting emission factors are shown in Table 7-17.

7.10.2 Tire Burning

Approximately 240 million vehicle tires are discarded annually.[269] Although viable methods for recycling exist, less than 25 percent of discarded tires are recycled; the remaining 175 million are discarded in landfills, stockpiles, or illegal dumps.[269] Although it is illegal in many states to dispose of tires using open burning, fires often occur at tire stockpiles and through illegal burning activities.[267] These fires generate a huge amount of heat and are difficult to extinguish (some tire fires continue for months).

Table 7-18 contains benzene emission factors for chunk tires and shredded tires.[267] When estimating emissions from an accidental tire fire, it should be kept in mind that emissions from burning tires are generally dependent on the burn rate of the tire. A greater potential for emissions exists at lower burn rates, such as when a tire is smoldering rather than burning out of control.[267] The fact that the shredded tires have a lower burn rate indicates that the gaps between tire materials provide the major avenue of oxygen transport. Oxygen transport appears to be a major, if not the controlling mechanism for sustaining the combustion process.

TABLE 7-17. SUMMARY OF BENZENE EMISSION FACTORS FOR BIOMASS BURNING BY FUEL TYPE

AMS Code	Emission Source	Fuel Type	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
28-10-001-000	Forest Fires	Fire wood	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Small wood	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Large wood (flaming)	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Large wood (smoldering)	Uncontrolled	2.52 (1.26)	U
		Live vegetation	Uncontrolled	1.48 (7.4×10^{-1})	U
		Duff (flaming)	Uncontrolled	2.52 (1.26)	U
28-10-015-000	Prescribed Burning (Broadcast)	Fire wood	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Small wood	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Large wood (flaming)	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Large wood (smoldering)	Uncontrolled	2.52 (1.26)	U
		Live vegetation	Uncontrolled	1.48 (7.4×10^{-1})	

(continued)

TABLE 7-17. CONTINUED

AMS Code	Emission Source	Fuel Type	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
		Duff (flaming)	Uncontrolled	6.6×10^{-1} (3.3×10^{-1})	U
		Duff (smoldering)	Uncontrolled	2.52 (1.26)	U

Source: References 265 and 266.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of biomass burned.

AMS = Area and mobile source.

TABLE 7-18. SUMMARY OF BENZENE EMISSION FACTORS FOR OPEN BURNING OF TIRES

SCC	Emission Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
5-03-002-03	Chunk Tires	Uncontrolled	3.05[b,c] (1.53)	C
	Shredded Tires	Uncontrolled	3.86[b,c] (1.93)	C

Source: Reference 267.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of tires burned.

[b] Values are weighted averages because of different burn rates.

[c] The data used to develop the emission factor are averaged over six sets of VOST tubes per day taken over two days.

7.10.3 Agricultural Plastic Film Burning

Agricultural plastic film is plastic film that has been used for ground moisture and weed control. The open burning of large quantities of plastic film commonly coincides with the burning of field crops. The plastic film may also be gathered into large piles and burned, with or without forced air (an air curtain).[267]

Emissions from burning agricultural plastic film are dependent on whether the film is new or has been exposed to vegetation and possibly pesticides. Table 7-19 presents emission factors for benzene emissions from burning new and used plastic film in piles with and without forced air (i.e., air is forced through the pile to simulate an air curtain).[267]

TABLE 7-19. SUMMARY OF BENZENE EMISSION FACTORS FOR OPEN BURNING OF AGRICULTURAL PLASTIC FILM

SCC	Emission Source	Control Device	Emission Factor lb/ton (kg/Mg)[a]	Emission Factor Rating
5-03-002-02	Unused Plastic	Uncontrolled[b]	9.55×10^{-5} (4.77×10^{-5})	C
		Forced Air[c]	5.75×10^{-5} (2.87×10^{-5})	C
	Used Plastic	Uncontrolled[b]	2.47×10^{-5} (1.23×10^{-5})	C
		Forced Air[c]	4.88×10^{-5} (2.44×10^{-5})	C

Source: Reference 267.

[a] Factors are in lb (kg) of benzene emitted per ton (Mg) of agricultural plastic film burned.
[b] Emission factors are for agricultural plastic film gathered in a pile and burned.
[c] Emission factors for agricultural plastic film burned in a pile with a forced air air current.

SECTION 8.0

BENZENE EMISSIONS FROM MOBILE SOURCES

This section quantifies benzene as one component of mobile source hydrocarbon emissions. These emissions occur from mobile sources as evaporative emissions from carburetors, fuel tanks, and crankcases, and as a result of combustion.

Benzene is not added to vehicle fuels such as gasoline or diesel, but is formed during their manufacture, either through catalytic reforming or steam cracking. Most vehicle fuel is processed using catalytic reforming. In catalytic reforming, benzene is produced during the reaction that increases the octane rating of the naphtha fraction of the crude oil used as feedstock. Gasoline produced using this process is approximately 0.90 percent benzene (by weight).[158] (See Section 4.1 for an expanded discussion of catalytic reforming.)

The other vehicle fuel manufacturing process, the use of steam cracking of naphtha feedstock to obtain ethylene, yields gasoline with a higher benzene content--20 to 50 percent. This fuel is blended with other fuels, before it is sold, in order to comply with the limited maximum concentration of 1.3 percent (by volume). However, steam cracking is considered a minor source of vehicle fuel. (Refer to Section 4.3 for an expanded discussion of pyrolysis gasoline and ethylene plants.)

Diesel fuel, on the other hand, is produced by hydrocracking of the gas oil fraction of crude, and contains relatively insignificant amounts of benzene.

Benzene is emitted in vehicle exhaust as unburned fuel and as a product of combustion. Higher-molecular-weight aromatics in the fuel, such as ethylbenzene and toluene, can be converted to benzene as products of combustion, accounting for approximately 70 to 80 percent of the benzene in vehicle exhaust.

The fraction of benzene in the exhaust varies depending on vehicle type, fuel type, and control technology, but is generally between 3 to 5 percent by weight of the exhaust. The fraction of benzene in the evaporative emissions also depends on control technology and fuel composition, and is generally 1 percent of a vehicle's evaporative emissions.

8.1 ON-ROAD MOBILE SOURCES

Results of recent work by the Office of Mobile Sources (OMS) on toxic emissions from on-road motor vehicles are presented in the 1993 report *Motor Vehicle-Related Air Toxics Study* (MVATS).[20] This report was prepared in response to Section 202(l)(1) of the 1990 amended CAA, which directs EPA to complete a study of the need for, and feasibility of, controlling emissions of toxic air pollutants that are unregulated under the Act and are associated with motor vehicles and motor vehicle fuels. The report presents composite emission factors for several toxic air pollutants, including benzene.

The emission factors presented in the MVATS were developed using currently available emissions data in a modified version of the OMS's MOBILE4.1 emissions model (designated MOBTOX) to estimate toxic emissions as a fraction of total organic gas (TOG) emissions. TOG includes all hydrocarbons as well as aldehydes, alcohols, and other oxygenated compounds. All exhaust mass fractions were calculated on a vehicle-by-vehicle basis for six vehicle types: light-duty gasoline vehicles, light-duty gasoline trucks, heavy-duty gasoline trucks, light-duty diesel vehicles, light-duty diesel trucks, and heavy-duty diesel trucks.

OMS assumed that light-duty gas and diesel trucks have the same mass fractions as light-duty gas and diesel vehicles, respectively. In developing mass fractions for light-duty gas vehicles and trucks, four different catalytic controls and two different fuel systems (carbureted or fuel injection) were considered. Mass fractions for heavy-duty gas vehicles were developed for carbureted fuel systems with either no emission controls or a three-way catalyst. These mass fractions were applied to TOG emission factors developed to calculate in-use benzene emission factors. These in-use factors take into consideration evaporative and exhaust emissions as well as the effects of vehicle age.

A number of important assumptions were made in the development of these on-road benzene emission factors, namely:

1. The increase in emissions due to vehicle deterioration with increased mileage is proportional to the increase in TOG;
2. Toxics fractions remain constant with ambient temperature changes; and
3. The fractions are adequate to use for the excess hydrocarbons that come from malfunction and tampering/misfueling.

It should be noted that, in specific situations, EPA mobile methods may over or underestimate actual emissions.

The benzene emission factors by vehicle class in grams of benzene emitted per mile driven are shown in Table 8-1.[270] The OMS also performed multiple runs of the MOBTOX program to derive a pollutant-specific, composite emission factor that represented all vehicle classes, based on the percent of total vehicle miles traveled (VMT) attributable to each vehicle class.[20]

For traditional gasoline, benzene is typically responsible for 70 to 75 percent of the aggregated toxic emissions. Most of this is associated with engine combustion exhaust.

TABLE 8-1. BENZENE EMISSION FACTORS FOR 1990 TAKING INTO CONSIDERATION VEHICLE AGING (g/mi)

	LDGV	LDGT1	LDGT2	LDGT	HDGV	LDDV	LDDT	HDDV	MC	Weighted VMT Mix
Exhaust										
Areas with no I/M	0.088	0.128	0.191	0.144	0.365	0.017	0.024	0.035	0.111	0.108
Areas with basic I/M	0.068	0.128	0.191	0.144	0.365	0.017	0.024	0.035	0.111	0.095
Evaporative	0.011	0.014	0.011	0.013	0.041	--	--	--	0.037	0.012
Refueling Loss	0.002	0.003	0.003	0.003	0.005	--	--	--	0.002	0.002
Running Loss	0.005	0.005	0.008	0.006	0.013	--	--	--	0.005	0.005
Resting Loss	0.001	0.001	0.001	0.001	0.001	--	--	--	0.004	0.001

LDGV = Light-Duty Gasoline Vehicle
LDGT1 = Light-Duty Gasoline Truck [pick-ups and vans with gross vehicle weight of 0 to 600 lb (0 to 272 kg)]
LDGT2 = Light-Duty Gasoline Truck [pick-ups and vans with gross vehicle weight of 601 to 8500 lb (273 to 3,856 kg)]
LDGT = Light-Duty Gasoline Truck (combined category of LDGT1 and LDGT2)
HDGV = Heavy-Duty Gasoline Vehicle
LDDV = Light-Duty Diesel Vehicle
LDDT = Light-Duty Diesel Truck
HDDV = Heavy-Duty Diesel Vehicle
MC = Motorcycle
-- = Not applicable

Oxygenated fuels emit less benzene than traditional gasoline mixes but more than diesel fuel. With the introduction of alternative fuels such as methanol blends, compressed natural gas (CNG), and liquified petroleum gas (LPG), formaldehyde is the dominant toxic emission, accounting for 80 to 90 percent of aggregated toxic emissions.[272] Reductions in benzene emissions associated with the use of methanol fuels is dependent upon the methanol content of the fuel. For instance, benzene emissions for M10 (10 percent methanol and 90 percent unleaded gasoline) are reduced by 20 percent compared with traditional fuel, and for M85 (85 percent methanol and 15 percent unleaded gasoline) the reduction is 84 percent (SAE1992). M100 (100 percent methanol), ethanol, LPG, and CNG emit minimal amounts of benzene.[273] Furthermore, because both LPG and CNG require closed delivery systems, evaporative emissions are assumed to be zero.

8.2 OFF-ROAD MOBILE SOURCES

For off-road mobile sources, EPA prepared the 1991 report *Nonroad Engine Vehicle Emission Study* (NEVES),[274] which presents emission factors for 79 equipment types, ranging from small equipment such as lawn mowers and chain saws to large agricultural, industrial, and construction machinery (see Table 8-2). The equipment types were evaluated based on three engine designs: two-stroke gasoline, four-stroke gasoline, and diesel. Sources for the data include earlier EPA studies and testing and new information on tailpipe exhaust and crankcase emissions supplied by the engine manufacturers. For test data on new engines, OMS made adjustments to better represent in-use equipment emissions taking into consideration evaporative emissions and increases in emissions due to engine deterioration associated with increased equipment age; therefore, new engine data underestimate in-use emissions.[274]

Although these emission factors were intended for calculating criteria pollutant (VOC, NO_2, CO) emissions for SIP emissions inventories, OMS derived emission factors for several HAPs, including benzene, so that national air toxics emissions could be estimated. To estimate benzene emissions, OMS expressed benzene emissions as a weight percent of exhaust

TABLE 8-2. OFF-ROAD EQUIPMENT TYPES AND HYDROCARBON EMISSION FACTORS INCLUDED IN THE NEVES (g/hp-hr)
(FACTOR QUALITY RATING E)

Equipment Type, Area and Mobile Source Code (2-stroke gas/4-stroke gas/diesel)	2-Stroke Gasoline Engines		4-Stroke Gasoline Engines		Diesel Engines	
	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Lawn and Garden, 22-60/65/70-004-						
025 Trimmers/Edgers/Brush Cutters	471.58[a]	--	50.78[a]	7.98[a]	--	--
010 Lawn Mowers	436.80[a]	--	79.17[a]	12.44[a]	--	--
030 Leaf Blowers/Vacuums	452.11[a]	--	40.74[a]	6.40[a]	--	--
040 Rear-Engine Riding Mowers	--	--	19.53[a]	3.07[a]	1.20	0.02
045 Front Mowers	--	--	19.53[a]	3.07[a]	--	--
020 Chain Saws <4 hp	625.80[a]	--	--	--	--	--
050 Shredders <5 hp	436.80[a]	--	79.17[a]	12.44[a]	--	--
015 Tillers <5 hp	436.80[a]	--	79.17[a]	12.44[a]	--	--
055 Lawn and Garden Tractors	--	--	19.74[a]	3.10[a]	1.20	0.02
060 Wood Splitters	--	--	79.17[a]	12.44[a]	1.20	0.02
035 Snow Blowers	436.80[a]	--	79.17[a]	12.44[a]	--	--
065 Chippers/Stump Grinders	--	--	56.55[b]	12.44[b]	1.20	0.02
070 Commercial Turf Equipment	436.80[a]	--	19.74[a]	3.10[a]	--	--
075 Other Lawn and Garden Equipment	436.80[a]	--	79.17[a]	12.44[a]	1.20	0.02
Airport Service, 22-60/65/70-008-						
005 Aircraft Support Equipment	--	--	10.02[b]	2.20[b]	1.57[c]	0.03[c]
010 Terminal Tractors	4.50[b,d]	0.99[b,d]	10.02[b]	2.20[b]	1.57[c]	0.03[c]
Recreational, 22-60/65/70-001-						
030 All-Terrain Vehicles (ATVs)	1260.00[a,e]	--	210.00[a,e]	33.00[a,e]	--	--
040 Minibikes	--	--	210.00[a,e]	33.00[a,e]	--	--
010 Off-Road Motorcycles	1260.00[a,e]	--	150.00[b,e]	33.00[b,e]	--	--
050 Golf Carts	1260.00[a,e]	--	210.00[a,e]	33.00[a,e]	--	--
020 Snowmobiles	228.90[a]	--	--	--	--	--
060 Specialty Vehicles Carts	1260.00[a,e]	--	210.00[a,e]	33.00[a,e]	1.20[e]	0.02[e]

(continued)

TABLE 8-2. CONTINUED

Equipment Type, Area and Mobile Source Code (2-stroke gas/4-stroke gas/diesel)	2-Stroke Gasoline Engines		4-Stroke Gasoline Engines		Diesel Engines	
	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Recreational Marine Vessels, 22-82-005/010/020-						
005 Vessels w/Inboard Engines	873.67[b,f]	--	108.69[b,f]	--	24.39[f]	--
010 Vessels w/Outboard Engines	873.67[b,f]	--	131.57[b,f]	28.94[b,f]	24.39[f]	0.49[f]
015 Vessels w/Sterndrive Engines	873.67[b,f]	--	108.69[b,f]	--	24.39[f]	--
020 Sailboat Auxiliary Inboard Engines	--	--	108.69[b,f]	--	122.45[f]	--
025 Sailboat Auxiliary Outboard Engines	873.67[b,f]	--	131.57[b,f]	28.94[b,f]	122.45[f]	2.45[f]
Light Commercial, less than 50 HP, 22-60/65/70-006-						
005 Generator Sets	436.80[a]	--	19.95[a]	3.14[a]	1.20	0.02
010 Pumps	8.99[a,d]	1.41[a,d]	19.95[a]	3.14[a]	1.20	0.02
015 Air Compressors	--	--	19.95[a]	3.14[a]	1.20	0.02
020 Gas Compressors	6.42[b,d]	1.41[b,d]	--	--	--	--
025 Welders	--	--	19.95[a]	3.14[a]	1.20	0.02
030 Pressure Washers	--	--	19.95[a]	3.14[a]	1.20	0.02
Industrial, 22-60/65/70-003-						
010 Aerial Lifts	4.50[b,d]	1.49[b,d]	10.02[b]	2.20[b]	1.57[c]	0.03[c]
102 Forklifts	4.50[b,d]	1.49[b,d]	10.02[b]	2.20[b]	1.57[c]	0.03[c]
030 Sweepers/Scrubbers	4.50[b,d]	1.49[b,d]	10.02[b]	2.20[b]	1.57[c]	0.03[c]
040 Other General Industrial Equipment	312.00[b]	--	10.02[b]	2.20[b]	1.57[c]	0.03[c]
050 Other Material Handling Equipment	--	--	10.02[b]	2.20[b]	1.57[c]	0.03[c]
Construction, 22-60/65/70-002-						
003 Asphalt Pavers	--	--	9.74[b]	2.14[b]	0.60	0.01
006 Tampers/Rammers	436.80[a]	--	13.63[a]	2.14[a]	0.00	0.00
009 Plate Compactors	436.80[a]	--	13.63[a]	2.14[a]	0.80	0.02
012 Concrete Pavers	--	--	--	--	1.10	0.02

(continued)

TABLE 8-2. CONTINUED

Equipment Type, Area and Mobile Source Code (2-stroke gas/4-stroke gas/diesel)	2-Stroke Gasoline Engines		4-Stroke Gasoline Engines		Diesel Engines	
	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Construction, 22-60/65/70-002- (con't)						
015 Rollers	--	--	19.43[a]	3.05[a]	0.80	0.02
018 Scrapers	--	--	--	--	0.70[c]	0.01[c]
021 Paving Equipment	436.80[a]	--	13.63[a]	2.14[a]	1.01	0.02
024 Surfacing Equipment	--	--	13.63[a]	2.14[a]	0.00	0.00
027 Signal Boards	--	--	13.63[a]	2.14[a]	1.20	0.02
030 Trenchers	--	--	9.74[b]	2.14[b]	1.54[c]	0.03[c]
033 Bore/Drill Rigs	436.80[a]	--	9.74[b]	2.14[b]	1.41[c]	0.03[c]
036 Excavators	--	--	9.74[b]	2.14[b]	0.70[c]	0.01[c]
039 Concrete/Industrial Saws	--	--	13.63[a]	2.14[a]	1.41[c]	0.03[c]
042 Cement and Mortar Mixers	--	--	13.63[a]	2.14[a]	1.01	0.02
045 Cranes	--	--	9.74[b]	2.14[b]	1.26[c]	0.03[c]
048 Graders	--	--	--	--	1.54[c]	0.03[c]
051 Off-Highway Trucks	--	--	--	--	0.84[c]	0.02[c]
054 Crushing/Proc. Equipment	--	--	9.74[b]	2.14[b]	1.41[c]	0.03[c]
057 Rough Terrain Forklifts	--	--	9.74[b]	2.14[b]	1.68[c]	0.03[c]
060 Rubber Tire Loaders	--	--	8.34[b]	1.83[b]	0.84[c]	0.02[c]
063 Rubber Tire Dozers	--	--	--	--	0.84[c]	0.02[c]
066 Tractors/Loaders/Backhoes	--	--	9.74[b]	2.14[b]	1.40[c]	0.03[c]
069 Crawler Tractors	--	--	--	--	1.26[c]	0.03[c]
072 Skid Steer Loaders	--	--	9.74[b]	2.14[b]	2.10[c]	0.04[c]
075 Off-Highway Tractors	--	--	--	--	2.46[c]	0.05[c]
078 Dumpers/Tenders	--	--	13.63[a]	2.14[a]	0.84[c]	0.02[c]
081 Other Construction Equipment	--	--	9.74[b]	2.14[b]	1.41[c]	0.03[c]
Agricultural, 22-60/65/70-005-						
010 2-Wheel Tractors	--	--	11.53[a]	1.81[a]	--	--
015 Agricultural Tractors	--	--	8.24[b]	1.81[b]	2.23[c]	0.04[c]
030 Agricultural Mowers	--	--	15.06[a]	2.37[a]	--	--
020 Combines	--	--	10.77[b]	2.37[b]	1.26[c]	0.03[c]
035 Sprayers	--	--	10.77[b]	2.37[b]	2.23	0.04

(continued)

TABLE 8-2. CONTINUED

Equipment Type, Area and Mobile Source Code (2-stroke gas/4-stroke gas/diesel)	2-Stroke Gasoline Engines		4-Stroke Gasoline Engines		Diesel Engines	
	Exhaust	Crank Case	Exhaust	Crank Case	Exhaust	Crank Case
Agricultural, 22-60/65/70-005- (con't)						
025 Balers	--	--	--	--	2.23	0.04
040 Tillers >5 hp	--	--	79.17[a]	12.44[a]	1.20	0.02
045 Swathers	--	--	10.77[b]	2.37[b]	0.90	0.02
050 Hydro Power Units	--	--	15.08[a]	2.37[a]	2.23	0.04
055 Other Agricultural Equipment	--	--	10.77[b]	2.37[b]	1.82	0.04
Logging, 22-60/65/70-007-						
005 Chain Saws >4 hp	319.20[a]	--	--	--	--	--
010 Shredders >5 hp	--	--	19.53[a]	3.07[a]	--	--
015 Skidders	--	--	--	--	0.84[c]	0.02[c]
020 Fellers/Bunchers	--	--	--	--	0.84[c]	0.02[c]

[a] Adjusted for in-use effects using small utility engine data.
[b] Adjusted for in-use effects using heavy-duty engine data.
[c] Exhaust HC adjusted for transient speed and/or transient load operation.
[d] Emission factors for 4-stroke propane-fueled equipment.
[e] g/hr.
[f] g/gallon.

"--" = Not applicable.

hydrocarbons plus crank case hydrocarbons. In OMS's analysis, it was assumed that the weight percent of benzene for all off-road sources was 3 percent of exhaust hydrocarbons.[275] A range of OMS-recommended weight percent benzene factors for general categories of off-road equipment are presented in Table 8-3.[274] Note that development of equipment-specific emission factors is underway, and when available, those emission factors should be considered instead. To obtain benzene emission estimates from equipment in these general categories of off-road equipment, the benzene weight percent factors noted in Table 8-3 can be applied to hydrocarbon estimates from the different NEVES equipment types.

The NEVES equipment emission factors can be used directly to estimate emissions from specific equipment types if local activity data is available. If general nonroad emission estimates are required, States may choose one of the 33 nonattainment areas, studied in the NEVES report, that is similar in terms of climate and economic activity; the NEVES nonattainment area can be adjusted to estimate emissions in another state by applying a population ratio of the two areas to the NEVES estimate. The NEVES report also has estimates for individual counties of the 33 nonattainment areas such that States or local governments may also produce regional or county inventories by adjusting the NEVES county estimates relative to the population of the different counties. Counties can be chosen from several of the 33 NEVES nonattainment areas if appropriate. For further details on how to calculate emissions from specific equipment types refer to NEVES, for details on calculating emissions of nonroad sources in general see Reference 271.

8.3 MARINE VESSELS

For commercial marine vessels, the NEVES report includes VOC emissions for six nonattainment areas taken from a 1991 EPA study *Commercial Marine Vessel Contribution to Emission Inventories*.[276] This study provided hydrocarbon emission factors for ocean-going commercial vessels and harbor and fishing vessels. The emission factors are shown in Table 8-4.

TABLE 8-3. WEIGHT PERCENT FACTORS FOR BENZENE

As Tested Use	Recommended Off-Road Category	Benzene % by Weight of FID HC[a]
Diesel Forklift Engine	Large Utility Equipment	2.4-3.0
Direct Injection Diesel Automobile	Large Utility Equipment (Cyclic) Construction Equipment	3.1-6.5
Indirect Injection Diesel Automobile	Large Utility Equipment (Cyclic) Marine, Agricultural Large Utility Construction Equipment	1.5-2.1
Leaded Gasoline Automobiles	Large Utility Equipment (Cyclic) Marine, Agricultural, Large Utility	3.0-3.4
Leaded Gasoline Automobiles (12% Misfire)	Large Utility Equipment (Cyclic) Marine, Agricultural, Large Utility	1.1-1.3
1973 Highway Traffic		3.0

Source: Reference 274.

[a] FID HC=Hydrocarbons measured by Flame Ionization Detection.

Ocean-going marine vessels fall into one of two categories--those with steam propulsion and those with motor propulsion. Furthermore, they emit pollution under two modes of operation: underway and at dockside (hotelling). Most steamships use boilers rather than auxiliary diesel engines while hotelling. Currently, there are no benzene toxic emission fractions for steamship boiler burner emissions. The emission factors for motor propulsion systems are based on emission fractions for heavy-duty diesel vehicle engines. For auxiliary diesel generators, emission factors are available only for 500 KW engines, since the 1991 Booz-Allen and Hamilton report indicated that almost all generators were rated at 500 KW or more.

For harbor and fishing vessels, benzene emission factors for diesel engines are provided for the following horsepower categories -- less than 500 hp, 500 to 1,000 hp, 1,000 to 1,500 hp, 1,500 to 2,000 hp, and greater than 2,000 hp. In each of these categories, emission factors are developed for full, cruise, and slow operating modes. Toxic emission

TABLE 8-4. BENZENE EMISSION FACTORS FOR COMMERCIAL MARINE VESSELS

Operating Plant (operating mode/rated output)	Benzene Emission Factor (lb/1000 gal fuel)[a]
Ocean-Going Commercial	
Motor Propulsion	
All underway modes	0.25
Auxiliary Diesel Generators	
500 KW (50% load)	0.87
Harbor and Fishing	
Diesel Engines	
<500 hp	
Full	0.22
Cruise	0.54
Slow	0.60
500-1000 hp	
Full	0.25
Cruise	0.18
Slow	0.18
1000-1500 hp	
Full	0.25
Cruise	0.25
Slow	0.25
1500-2000 hp	
Full	0.18
Cruise	0.25
Slow	0.25
2000+ hp	
Full	0.23
Cruise	0.18
Slow	0.24
Gasoline Engines - all hp ratings	
Exhaust (g/bhp-hr)	0.35
Evaporative (g/hr)	0.64

[a] Benzene exhaust emission factors were estimated by multiplying HC emission factors by benzene TOG fractions. Benzene exhaust emission fractions of HC for all marine diesel engines were assumed to be the same as the TOG emission fraction for heavy-duty diesel vehicles -- 0.0106. The benzene exhaust emission fraction for marine gasoline engines was assumed to be the same as the exhaust TOG emission fraction for heavy duty gasoline vehicles -- 0.0527. The benzene evaporative emission fraction was also assumed to be the same as the evaporative emission HC fraction for heavy duty gasoline vehicles -- 0.0104.

factors are also provided for gasoline engines in this category. These emission factors are not broken down by horsepower rating, and are expressed in grams per brake horsepower hour rather than pounds per thousand gallons of fuel consumed.

8.4 LOCOMOTIVES

As noted in the U.S. EPA's *Procedures for Emission Inventory Preparation,* Volume IV: Mobile Sources,[271] locomotive activity can be defined as either line haul or yard activities. Line haul locomotives, which perform line haul operation, generally travel between distant locations, such as from one city to another. Yard locomotives, which perform yard operations, are primarily responsible for moving railcars within a particular railway yard.

The OMS has included locomotive emissions in its *Motor Vehicle-Related Air Toxic Study*.[20] The emission factors used for locomotives in this report are derived from the heavy-duty diesel on-road vehicles as there are no emission factors specifically for locomotives. To derive toxic emission factors for heavy diesel on-road vehicles, hydrocarbon emission factors were speciated. The emission factors provided in this study (shown in Table 8-5) are based on g/mile traveled.[20]

TABLE 8-5. BENZENE EMISSION FACTORS FOR LOCOMOTIVES

Source	Toxic Emission Fraction	Emission Factor (lb/gal)
Line Haul Locomotive	0.0106[a]	0.00022
Yard Locomotive	0.0106[a]	0.00054

Source: Reference 20.

[a] These fractions are found in Appendix B6 of EPA, 1993, and represent toxic emission fractions for heavy-duty diesel vehicles. Toxic fractions for locomotives are assumed to be the same, since no fractions specific for locomotives are available. It should be noted that these fractions are based on g/mile emissions data, whereas emission factors for locomotives are estimated in lb/gal. The toxic emission fractions were multiplied by the HC emission factors to obtain the toxic emission factors.

8.5 AIRCRAFT

There are two main types of aircraft engines in use: turbojet and piston. A kerosene-like jet fuel is used in the jet engines, whereas aviation gasoline with a lower vapor pressure than automotive gasoline is used for piston engines. The aircraft fleet in the United States numbers about 198,000, including civilian and military aircraft.[277] Most of the fleet is of the single- and twin-engine piston type and is used for general aviation. However, most of the fuel is consumed by commercial jets and military aircraft; thus, these types of aircraft contribute more to combustion emissions than does general aviation. Most commercial jets have two, three, or four engines. Military aircraft range from single or dual jet engines, as in fighters, to multi-engine transport aircraft with turbojet or turboprop engines.[278]

Despite the great diversity of aircraft types and engines, there are considerable data available to aid in calculating aircraft- and engine-specific hydrocarbon emissions, such as the database maintained by the Federal Aviation Administration (FAA) Office of Environment and Energy, FAA Aircraft Engine Emissions Database (FAEED). These hydrocarbon emission factors may be used with weight percent factors of benzene in hydrocarbon emissions to estimate benzene emissions from this source. Benzene weight percent factors in aircraft hydrocarbon emissions are reported in an EPA memorandum [280] concerning toxic emission fractions for aircraft, and are presented in Table 8-6.

TABLE 8-6. BENZENE CONTENT IN AIRCRAFT LANDING AND TAKEOFF EMISSIONS

Description	AMS Code	Weight Percent Benzene	Factor Quality
Military Aircraft	22-75-001-000	2.02	B
Commercial Aircraft	22-75-020-000	1.94	B
Air Taxi Aircraft	22-75-060-000	3.44	C
General Aviation	22-75-050-000	3.91	C

Source: Reference 279 and 280.

Current guidance from EPA for estimating hydrocarbon emissions from aircraft appears in *Procedures for Emission Inventory Preparation*, Volume IV: Mobile Sources.[271] The landing/takeoff (LTO) cycle is the basis for calculating aircraft emissions. The operating modes in an LTO cycle are (1) approach, (2) taxi/idle in, (3) taxi/idle out, (4) takeoff, and (5) climbout. Emission rates by engine type and operating mode are given in the FAEED. To use this procedure, the aircraft fleet must be characterized and the duration of each operating mode determined. From this information, hydrocarbon emissions can be calculated for one LTO for each aircraft type in the fleet. To determine total hydrocarbon emissions from the fleet, the emissions from a single LTO for the aircraft type would be multiplied by the number of LTOs for each aircraft type.

The emission estimation method noted above is the preferred approach as it takes into consideration differences between new and old aircraft. If detailed aircraft information is unavailable, hydrocarbon emission indices for representative fleet mixes are provided in the emissions inventory guidance document *Procedures for Emissions Inventory Preparation*; Volume IV: Mobile Sources.[271] The hydrocarbon emission indices are 0.394 pounds per LTO (0.179 kg per LTO) for general aviation and 1.234 pounds per LTO (0.560 kg per LTO) for air taxis.

The benzene fraction of the hydrocarbon total (in terms of total organic gas) can be estimated by using the percent weight factors from Table 8-6. Because air taxis have larger engines and more of the fleet is equipped with turboprop and turbojet engines than is the general aviation fleet, the percent weight factor is somewhat different from the general aviation emission factor.

8.6 ROCKET ENGINES

Benzene has also been detected from rocket engines tested or used for space travel. Two types of rocket engines are currently in use: sustainer rocket engines, which provide the main continual propulsion, and booster rocket engines, which provide additional force at critical stages of the lift off, such as during the separation of sections of the rocket fuselage.

Source testing of booster rocket engines using RP-1 (kerosene) and liquid oxygen have been completed at an engine test site. Tests for benzene were taken for eight test runs sampling at four locations within the plume envelope below the test stand. Results from these tests yielded a range of benzene emission factors--0.31 to 0.561 lb/ton (0.155 to 0.280 kg/Mg) of fuel combusted--providing an average emission factor of 0.431 lb/ton (0.215 kg/Mg) of fuel combusted, as presented in Table 8-7.[282] It should be noted that booster fuel consumption is approximately five times that of sustainer rocket engines.

TABLE 8-7. EMISSION FACTORS FOR ROCKET ENGINES

AMS Code	Emissions Source	Emission Factor lb/ton (kg/Mg)	Factor Rating
28-10-040-000	Booster rocket engines using RP-1 (kerosene) and liquid oxygen as fuel	0.431 (0.215)[a]	C

Source: Reference 282.

[a] Emission factors are in lb (kg) of benzene emitted per ton (Mg) of fuel combusted.

SECTION 9.0

SOURCE TEST PROCEDURES

Benzene emissions from ambient air, mobile sources, and stationary sources can be measured utilizing the following test methods:[283]

- EPA Method 0030: Volatile Organic Sampling Train (VOST) with EPA Method 5040/5041: Analysis of Sorbent Cartridges from VOST;
- EPA Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography;
- EPA method TO-1: Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS);
- EPA method TO-2: Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry;
- EPA Method TO-14: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canister Sampling and Gas Chromatographic (GC) Analysis;
- EPA Exhaust Gas Sampling System, Federal Test Procedure (FTP); and
- Auto/Oil Air Quality Improvement Research (AQIRP) Speciation Methodology.

If applied to stack sampling, the ambient air monitoring methods may require adaptation or modification. To ensure that results will be quantitative, appropriate precautions must be taken to prevent exceeding the capacity of the methodology. Ambient methods that require the use of sorbents are susceptible to sorbent saturation if high concentration levels exist. If this happens, breakthrough will occur and quantitative analysis will not be possible.

9.1 EPA METHOD 0030[284]

The VOST from SW-846 (third edition) is designed to collect VOCs from the stack gas effluents of hazardous waste incinerators, but it may be used for a variety of stationary sources. The VOST method was designed to collect volatile organics with boiling points in the range of 30°C to 100°C. Many compounds with boiling points above 100°C may also be effectively collected using this method. Because benzene's boiling point is about 80.1°C, benzene concentrations can be measured using this method. Method 0030 is applicable to benzene concentrations of 10 to 100 or 200 parts per billion by volume (ppbv). If the sample is somewhat above 100 ppbv, saturation of the instrument will occur. In those cases, another method, such as Method 18, should be used. Method 0030 is often used in conjunction with analytical Method 5040/5041.

Figure 9-1 presents a schematic of the principal components of the VOST.[241] In most cases, 20 L of effluent stack gas are sampled at an approximate flow rate of 1 L/min, using a glass-lined heated probe. The gas stream is cooled to 20°C by passage through a water-cooled condenser and the volatile organics are collected on a pair of sorbent resin traps. Liquid condensate is collected in the impinger located between the two resin traps. The first resin trap (front trap) contains about 1.6 g Tenax® and the second trap (back trap) contains about 1 g each of Tenax® and petroleum-based charcoal (SKC lot 104 or equivalent), 3:1 by volume.

The Tenax® cartridges are then thermally desorbed and analyzed by purge-and-trap GC/MS along with the condensate catch as specified in EPA Methods 5040/5041. Analysis should be conducted within 14 days of sample collection.

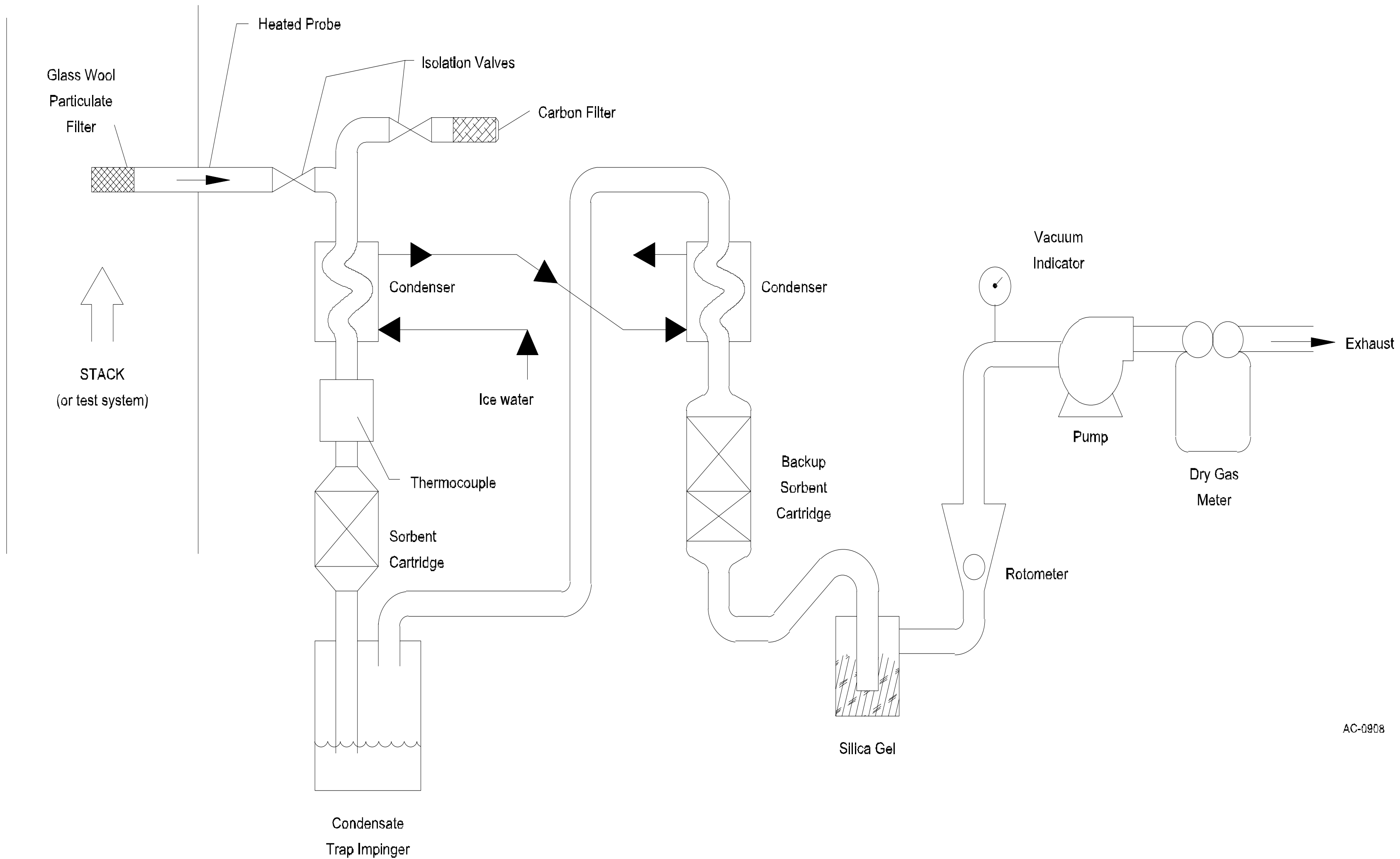


Figure 9-1. Volatile Organic Sampling Train (VOST)

Source: Reference 241.

The sensitivity of Method 0030 depends on the level of interferences in the sample and the presence of detectable levels of benzene in the blanks. Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many interferences are due to exposure to significant concentrations of benzene in the ambient air at the stationary source site and exposure of the sorbent materials to solvent vapors prior to assembly.

To alleviate these problems, the level of the lab blank should be determined in advance. Calculations should be made based on feed concentration to determine if blank level will be a significant problem. Benzene should not be chosen as a target compound at very low feed levels because it is likely there will be significant blank problems.[283]

One of the disadvantages of the VOST method is that because the entire sample is analyzed, duplicate analyses cannot be performed. On the other hand, when the entire sample is analyzed, the sensitivity is increased. Another advantage is that breakthrough volume is not greatly affected by humidity.

9.2 EPA METHODS 5040/5041[283,284]

The contents of the sorbent cartridges (collected using EPA Method 0030) are spiked with an internal standard and thermally desorbed for 10 minutes at 80°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free water, and trapped on an analytical adsorbent trap. After the 10-minute desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile organics are separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of the volatile compounds are calculated using the internal standard technique. EPA Methods 5030 and 8420 may be referenced for specific requirements for the thermal desorption unit, purge-and-trap unit, and GC/MS system.

A diagram of the analytical system is presented in Figure 9-2. The Tenax® cartridges should be analyzed within 14 days of collection. The detection limits for low-resolution MS using this method are usually about 10 to 20 ng or 1 ng/L (3 ppbv).

The primary difference between EPA Methods 5040 and 5041 is the fact that Method 5041 utilizes the wide-bore capillary column (such as 30 m DB-624), whereas Method 5040 calls for a stainless steel or glass-packed column (1.8 x 0.25 cm I.D., 1 percent SP-1000 on 60/80 mesh Carbopack B).

9.3 EPA METHOD 18[285]

EPA Method 18 is the preferred method for measuring higher levels of benzene from a source (approximately 1 part per million by volume [ppmv] to the saturation point of benzene in air). In Method 18, a sample of the exhaust gas to be analyzed is drawn into a stainless steel or glass sampling bulb or a Tedlar® or aluminized Mylar® bag as shown in Figure 9-3.[285] The Tedlar® bag has been used for some time in the sampling and analysis of source emissions for pollutants. The cost of the Tedlar® bag is relatively low, and analysis by gas chromatography is easier than with a stainless steel cylinder sampler because pressurization is not required to extract the air sample in the gas chromatographic analysis process.[286] The bag is placed inside a rigid, leak-proof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. The sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography coupled with flame ionization detection. Based on field and laboratory validation studies, the recommended time limit for analysis is within 30 days of sample collection.[287] One recommended column is the 8-ft x 1/8 in. O.D. stainless steel column packed with 1 percent SP-1000 in 60/80 carbopack B. However, the GC operator should select the column and GC conditions

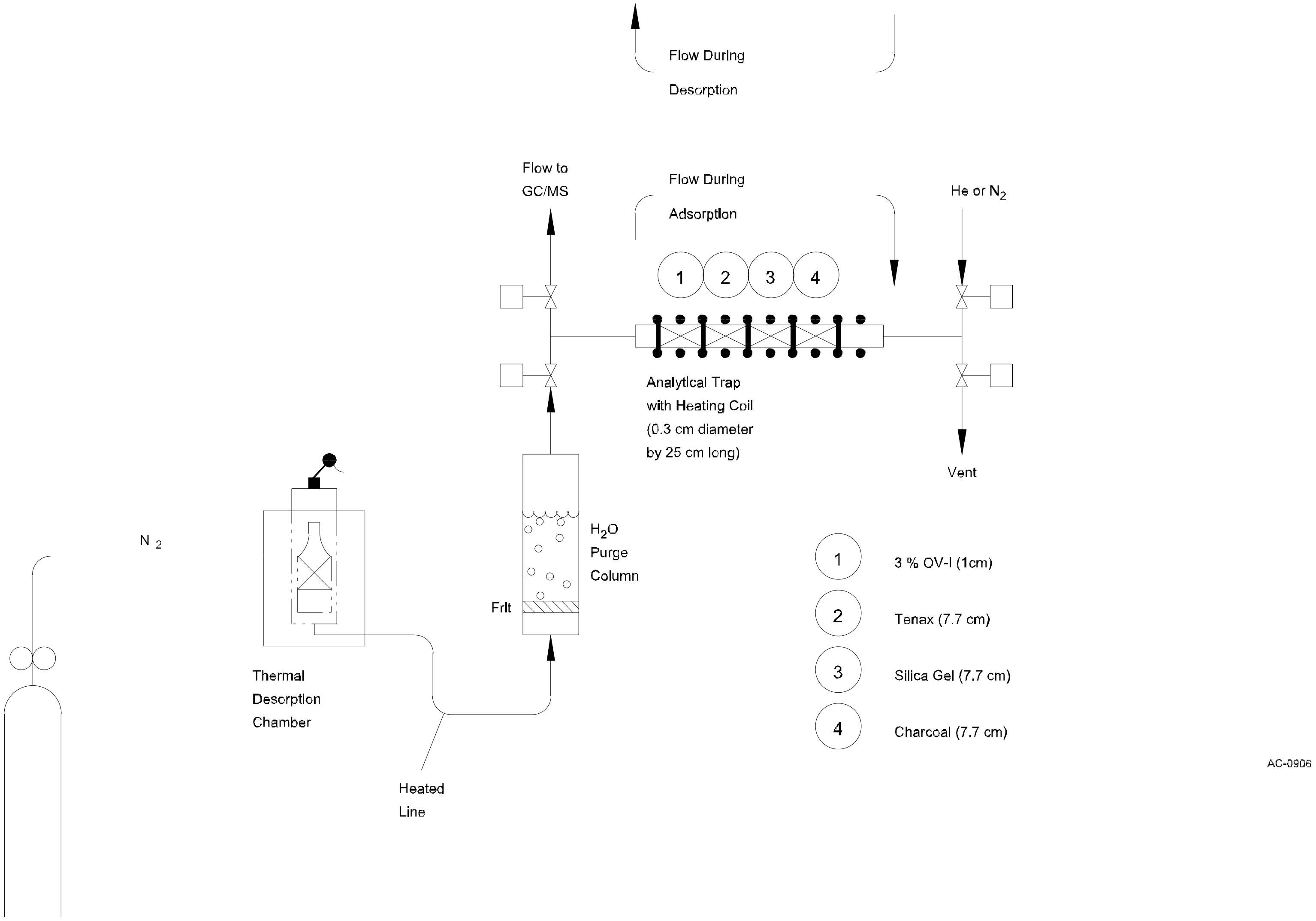


Figure 9-2. Trap Desorption/Analysis Using EPA Methods 5040/5041

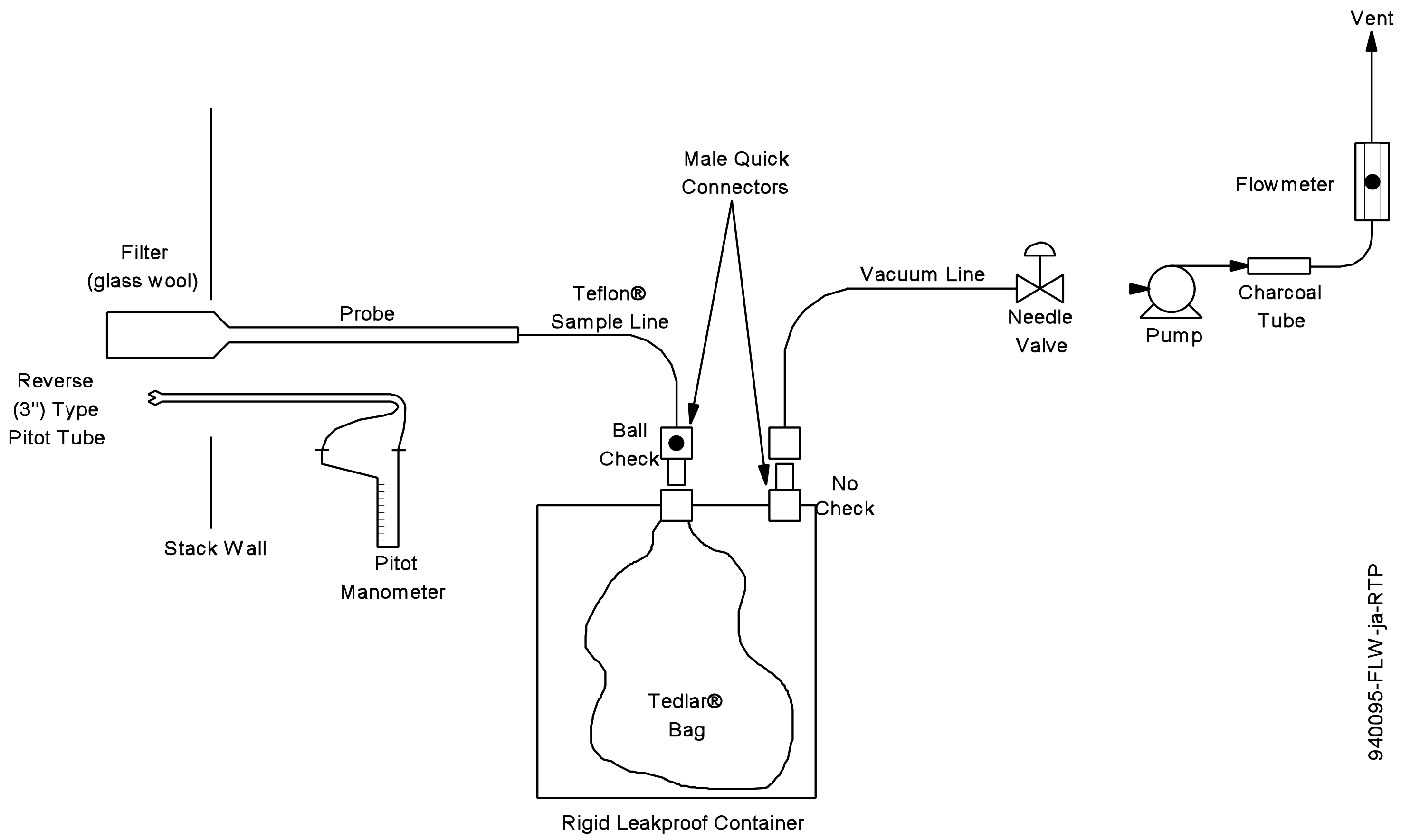


Figure 9-3. Integrated Bag Sampling Train

Source: Reference 285.

that provide good resolution and minimum analysis time for benzene. Zero helium or nitrogen should be used as the carrier gas at a flow rate that optimizes the resolution.

The peak areas corresponding to the retention times of benzene are measured and compared to peak areas for a set of standard gas mixtures to determine the benzene concentrations. The detection limit of this method ranges from about 1 ppm to an upper limit governed by the FID saturation or column overloading. However, the upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

The EPA's Atmospheric Research and Exposure Assessment Laboratory has produced a modified version of Method 18 for stationary source sampling.[286,288] One difference from the original method is in the sampling rate, which is reduced to allow collection of more manageable gas volumes. By reducing the gas volumes, smaller Tedlar® bags can be used instead of the traditional 25-L or larger bags, which are not very practical in the field, especially when a large number of samples is required.[286] A second difference is the introduction of a filtering medium to remove entrained liquids, which improves benzene quantitation precision.

The advantage of EPA Method 18 is that it is rapid and relatively inexpensive. However, it does require a fully equipped chromatography lab and a skilled analyst.

9.4 EPA METHOD TO-1 (COMPENDIUM)

Ambient air concentrations of benzene can be measured using EPA Method TO-1 from *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*.[289] This method is used to collect and determine nonpolar, volatile organics (aromatic hydrocarbons, chlorinated hydrocarbons) that can be captured on Tenax® and determined by thermal desorption techniques. The compounds determined by this method have boiling points in the range of 80 to 200°C.

Method TO-1 can measure benzene concentrations from about 3 to 150 ppbv. The advantages and disadvantages are about the same as for the VOST method, and costs are comparable.

Figure 9-4 presents a block diagram of the TO-1 system. Figure 9-5 presents a diagram of a typical Tenax® cartridge.[289] Ambient air is drawn through the cartridge, which contains approximately 1 to 2 grams of Tenax®. The benzene is trapped on the Tenax® cartridge, which is then capped and sent to the laboratory for analysis utilizing GC/MS according to the procedures specified in EPA Method 5040.

The exact run time, flow rate, and volume sampled varies from source to source depending on the expected concentrations and the required detection limit. Typically, 10 to 20 L of ambient air are sampled. Estimated breakthrough volume of Tenax® (for benzene) is 19 L/g at 38°C. Analysis should be conducted within 14 days of collection. A capillary column (fused silica SE-30 or OV-1) having an internal diameter of 0.3 mm and a length of 50 m is recommended. The MS identifies and quantifies the compounds by mass fragmentation or ion characteristic patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics.

9.5 EPA METHOD TO-2[283,289]

Method TO-2 is used to collect and determine highly volatile, non-polar organics (vinyl chloride, vinylidene chloride, benzene, toluene) that can be captured on a carbon molecular sieve (CMS) trap and determined by thermal desorption techniques. The compounds to be determined by this technique have boiling points in the range of 15 to 120°C. Method TO-2 has the same advantages and disadvantages as the VOST method.

Figure 9-6 presents a diagram of a CMS trap construction and Figure 9-7 shows the GC/MS system used in analyzing the CMS cartridges.[289] Air is drawn through a cartridge

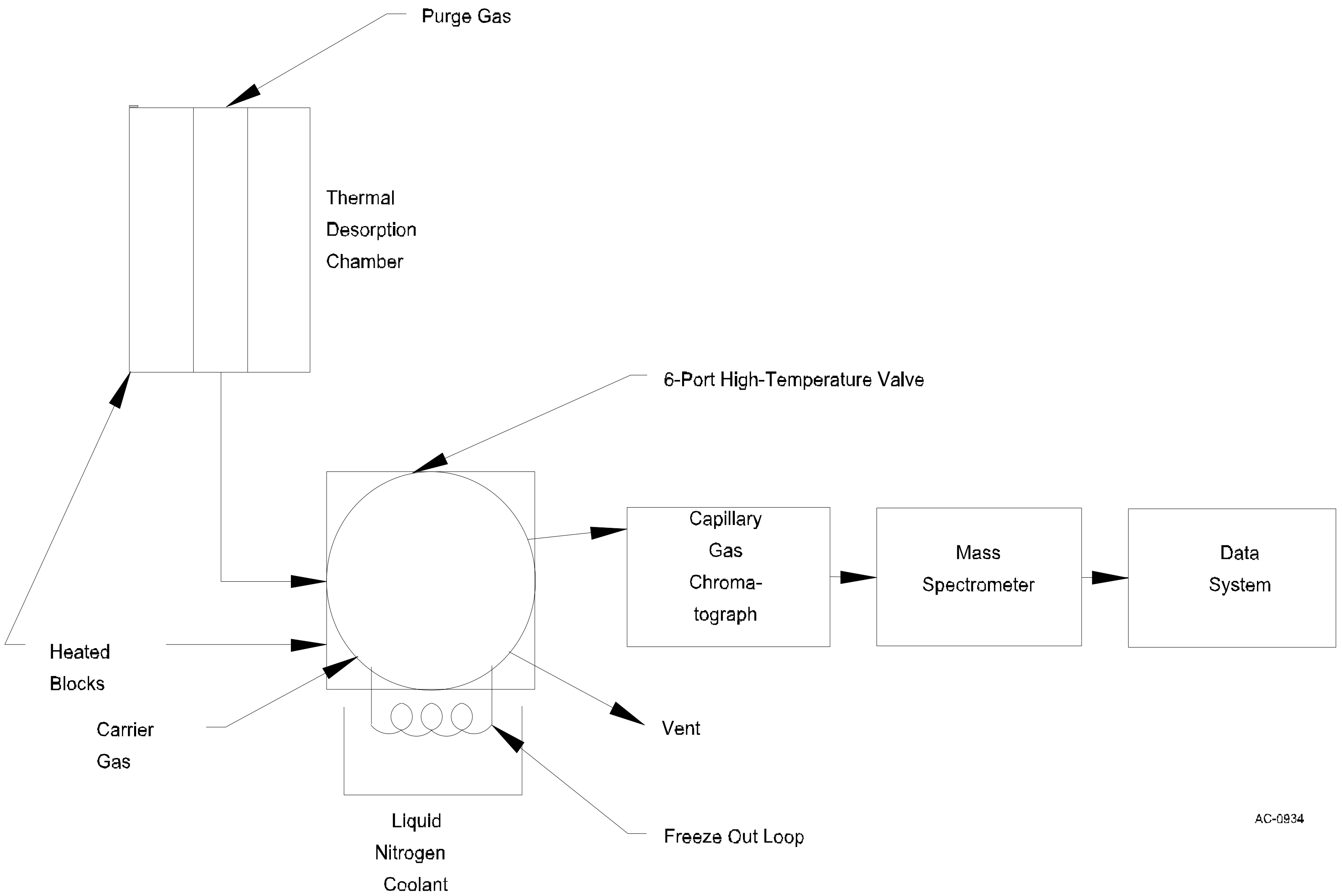
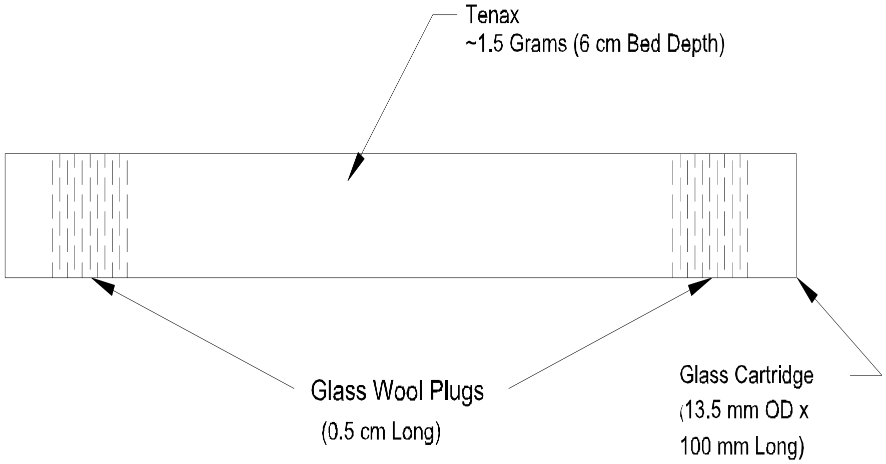
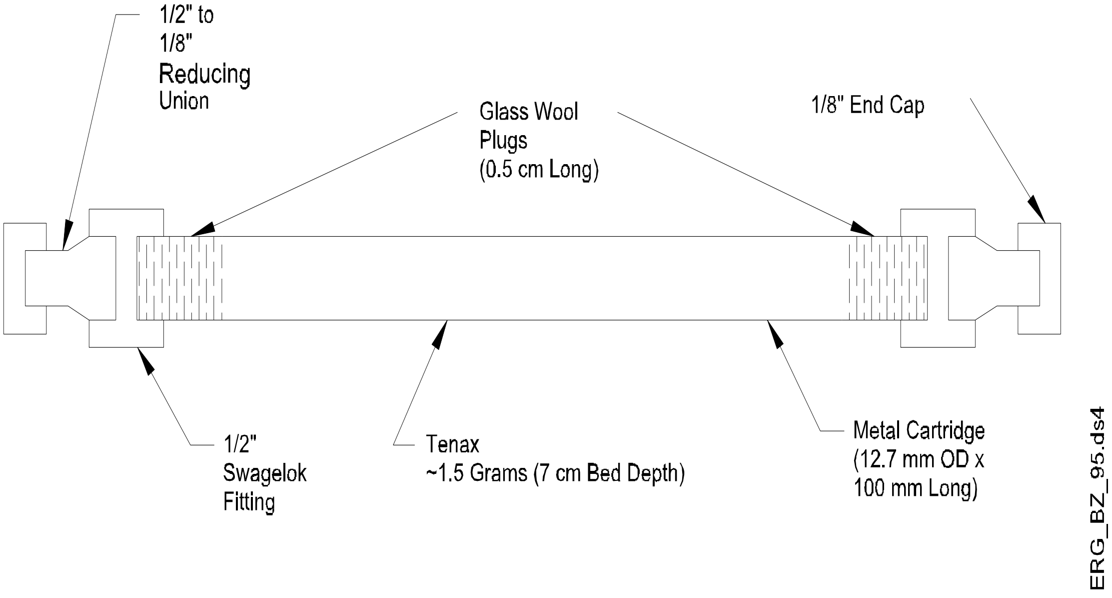


Figure 9-4. Block Diagram of Analytical System for EPA Method TO-1

Source: Reference 289.



(a) Glass Cartridge



(b) Metal Cartridge

Figure 9-5. Typical Tenax® Cartridge

Source: Reference 289.

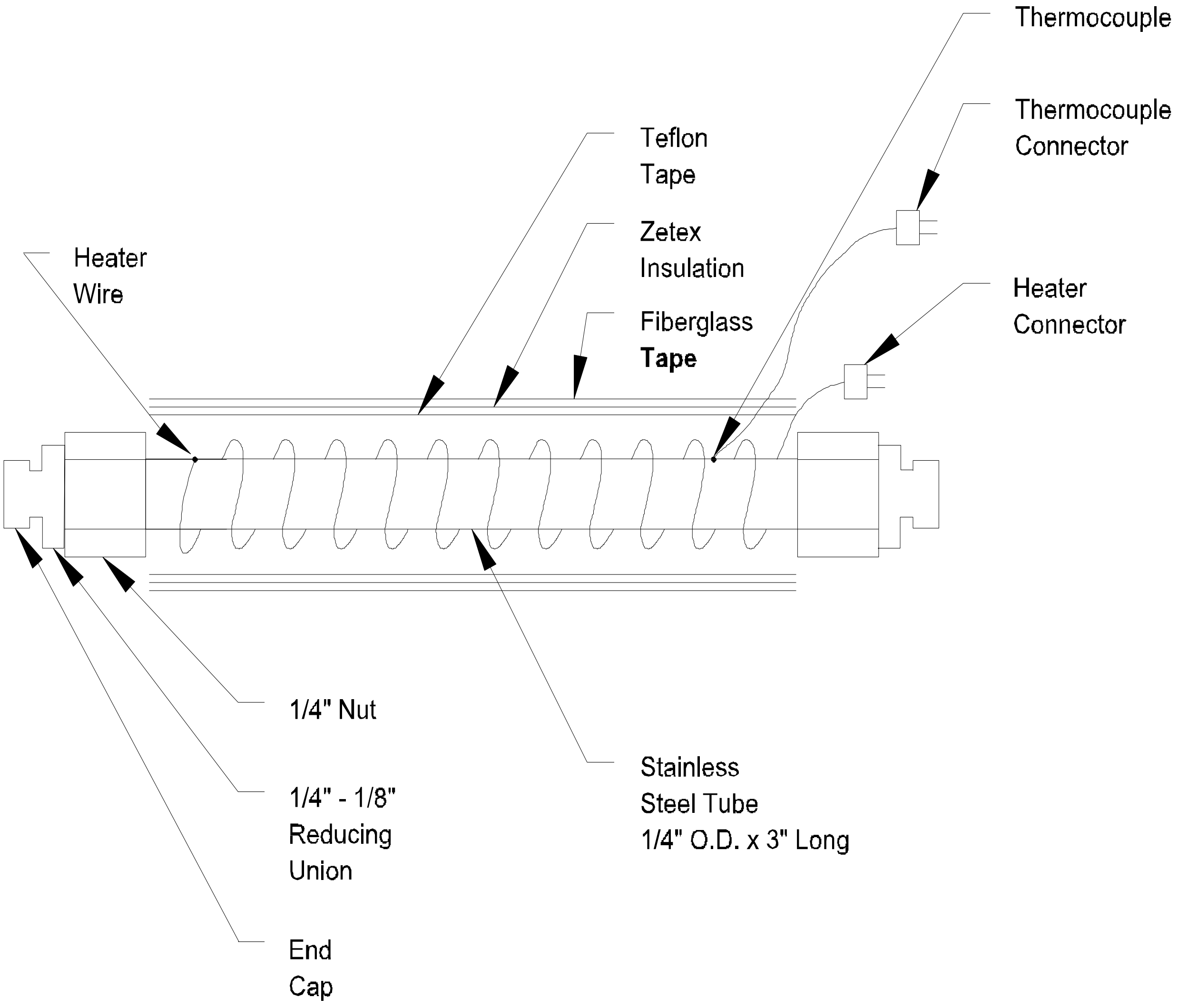


Figure 9-6. Carbon Molecular Sieve Trap (CMS) Construction

Source: Reference 289.

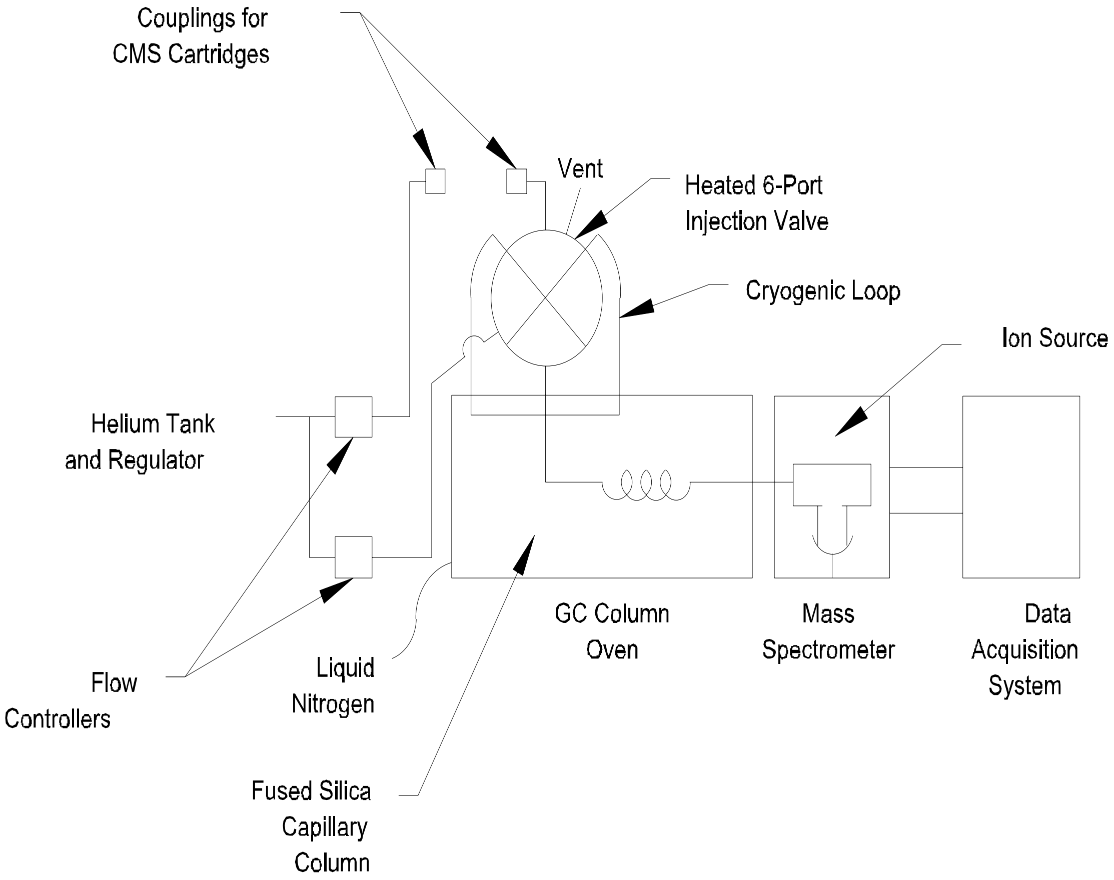


Figure 9-7. GC/MS Analysis System for CMS Cartridges

Source: Reference 289.

containing 0.4 g of a CMS adsorbent. The cartridge is analyzed in the laboratory by flushing with dry air to remove adsorbed moisture and purging the sample with helium while heating the cartridge to 350 to 400°C. The desorbed organics are collected in a cryogenic trap and flash-evaporated into a GC followed by an MS. Only capillary GC techniques should be used. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points. The MS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics. The most common interferences are structural isomers.

9.6 EPA METHOD TO-14[283,289]

Ambient air concentrations of benzene can also be measured using EPA Method TO-14 from *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*.[289] This method is based on collection of a whole-air sample in SUMMA® passivated stainless steel canisters and is used to determine semivolatile and volatile organic compounds.

This method is applicable to specific semivolatiles and VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Benzene has been successfully measured in the parts-per-billion- by-volume level using this method.

Figure 9-8 presents a diagram of the canister sampling system.[289] Air is drawn through a sampling train into a pre-evacuated sample SUMMA® canister. The canister is attached to the analytical system. Water vapor is reduced in the gas stream by a Nafion dryer and VOCs are concentrated by collection into a cryogenically cooled trap. The cryogen is removed and the temperature of the sample raised to volatilize the sample into a high-resolution GC column. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points into a detector.

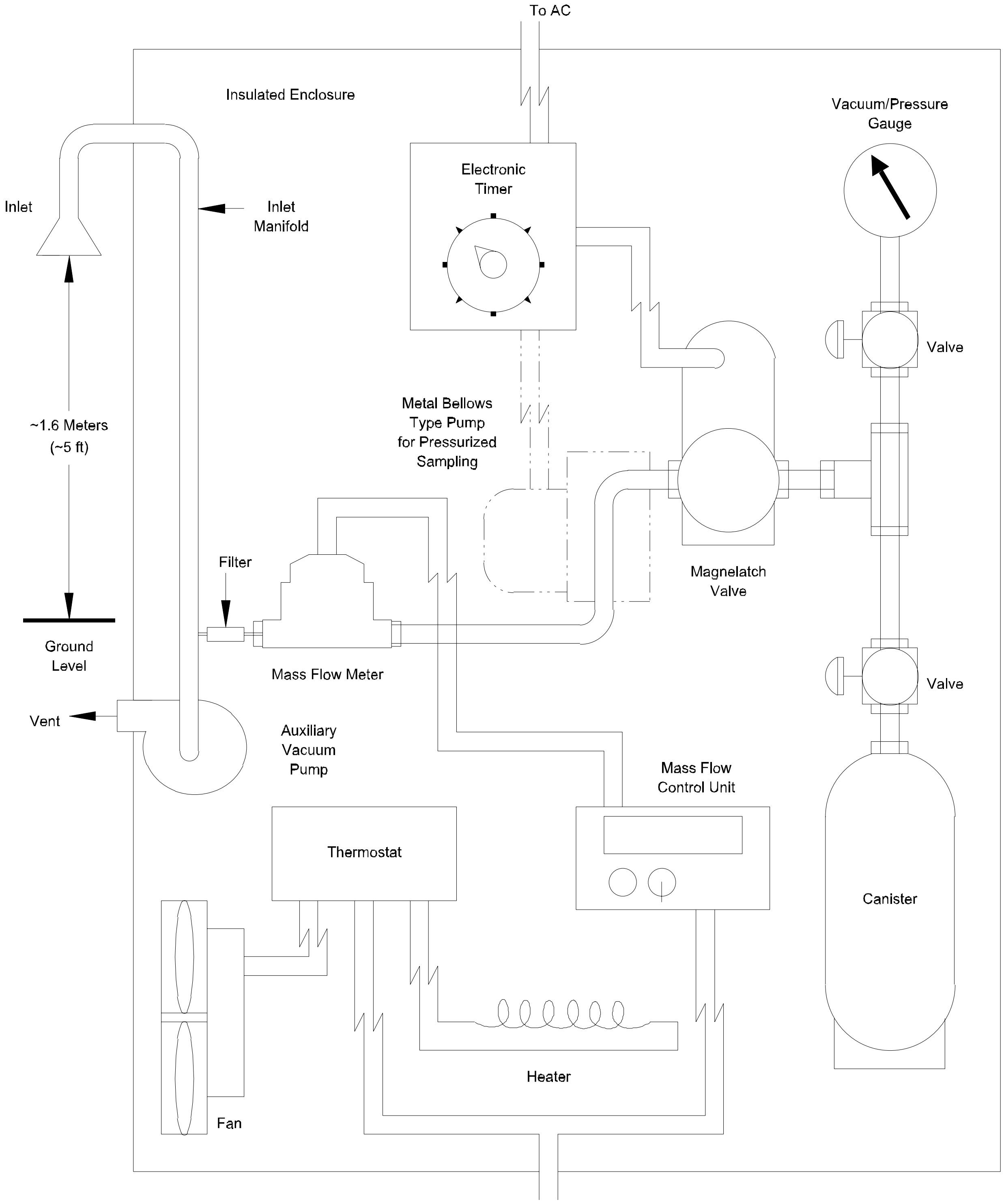


Figure 9-8. Sampler Configuration for EPA Method TO-14

Source: Reference 289.

The choice of detector depends on the specificity and sensitivity required by the analysis. Non-specific detectors suggested for benzene analysis include flame ionization detectors (FID) with detection limits of about 4 ppbv and photoionization detectors (PID), which are about 25 times more sensitive than FID. Specific detectors include an MS operating in the selected ion mode or the SCAN mode, or an ion trap detector. Identification errors can be reduced by employing simultaneous detection by different detectors. The recommended column for Method TO-14 is an HP OV-1 capillary type with 0.32 mm I.D. and a 0.88 µm cross-linked methyl silicone coating or equivalent. Samples should be analyzed within 14 days of collection. One of the advantages of Method TO-14 is that multiple analyses can be performed on one sample.

9.7 FEDERAL TEST PROCEDURE (FTP)

The most widely used test procedure for sampling emissions from vehicle exhaust is the FTP, which was developed in 1974.[290-292] The FTP uses the Urban Dynamometer Driving Schedule (UDDS), which is 1,372 seconds in duration. An automobile is placed on a chassis dynamometer, where it is run according to the following schedule: 505 seconds of a cold start; 867 seconds of hot transient; and 505 seconds of a hot start. (The definitions of the above terms can be found in the FTP description in the 40 CFR, Part 86).[290] The vehicle exhaust is collected in Tedlar® bags during the three testing stages.

The most widely used method for transporting vehicle exhaust from the vehicle to the bags is a dilution tube sampling arrangement identical to the system used for measuring criteria pollutants from mobile sources.[290,293] Dilution techniques are used for sampling auto exhaust because, in theory, dilution helps simulate the conditions under which exhaust gases condense and react in the atmosphere. Figure 9-9 shows a diagram of a vehicle exhaust sampling system.[290,294] Vehicle exhausts are introduced at an orifice where the gases are collected and mixed with a supply of filtered dilution air. The diluted exhaust stream flows at a measured velocity through the dilution tube and is sampled isokinetically.

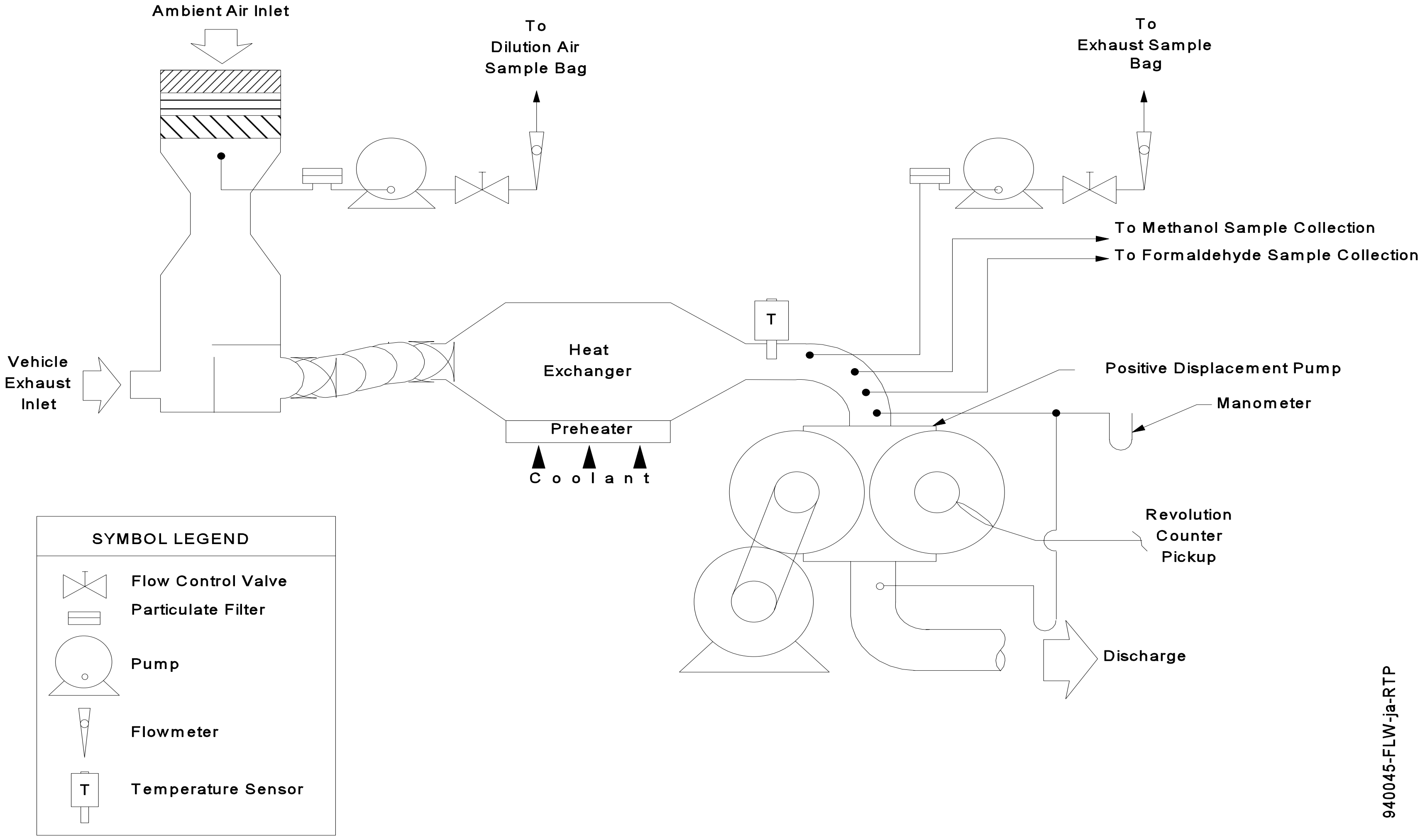


Figure 9-9. Vehicle Exhaust Gas Sampling System

Source: Reference 290.

The major advantage to using a dilution tube approach is that exhaust gases are allowed to react and condense onto particle surfaces prior to sample collection, providing a truer composition of exhaust emissions as they occur in the atmosphere. Another advantage is that the dilution tube configuration allows simultaneous monitoring of hydrocarbons, CO, CO_2, and NO_x. Back-up sampling techniques, such as filtration/adsorption, are generally recommended for collection of both particulate- and gas-phase emissions.[292]

9.8 AUTO/OIL AIR QUALITY IMPROVEMENT RESEARCH PROGRAM SPECIATION METHOD

Although there is no EPA-recommended analytical method for measuring benzene from vehicle exhaust, the AQIRP method for the speciation of hydrocarbons and oxygenates is widely used.[292,295] Initially, the AQIRP method included three separate analytical approaches for analyzing different hydrocarbons, but Method 3, the method designated for benzene, was dropped from use because of wandering retention times. Method 2 can be used to measure benzene from auto exhaust but some interferences, which will be discussed later, may occur.

This analytical method calls for analyzing the bag samples collected by the FTP method by injecting them into a dual-column GC with an FID. A recommended pre-column is a 2 m x 0.32 mm I.D. deactivated fused silica (J&W Scientific Co.) connected to an analytical column that is 60 m DB-1, 0.32 mm I.D., 1 µm film thickness.[295] The detection limit for benzene with this method is 0.005 ppmC.

The peak areas corresponding to the retention times of benzene are measured and compared to peak areas for a set of standard gas mixtures to determine the benzene concentrations. However, there is a problem with benzene co-eluting with 1-methylcyclopentene. Therefore, the analyst should be aware of this potential interference.

The amount of benzene in a sample is obtained from the calibration curve in units of micrograms per sample. Collected samples are sufficiently stable to permit 6 days of ambient sample storage before analysis. If samples are refrigerated, they are stable for 18 days.

SECTION 10.0

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APPENDIX A

SUMMARY OF EMISSION FACTORS

TABLE A-1. SUMMARY OF EMISSION FACTORS

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-01-197-45	Ethylene Manufacturing - Compressor Lube Oil Vent[a]	Compressor Lube Oil Vents	Uncontrolled	0.0006 lb/ton (0.0003 kg/Mg)	U
		Single Compressor Train	Uncontrolled	0.0004 lb/ton (0.0002 kg/Mg)	U
		Dual Compressor Train	Uncontrolled	0.0008 lb/ton (0.0004 kg/Mg)	U
3-01-197-42	Ethylene Manufacturing Pyrolysis Furnace Decoking[a]	Pyrolysis Furnace Decoking		No benzene emissions	
3-01-197-43	Ethylene Manufacturing - Acid Gas Removal[a]	Acid Gas Removal		No benzene emissions	
3-01-197-44	Ethylene Manufacturing - Catalyst Regeneration[a]	Catalyst Regeneration		No benzene emissions	
3-01-820-09	Ethylene Manufacturing-Secondary Sources[a]	Secondary Wastewater Treatment	Uncontrolled	0.0434 lb/ton (0.0217 kg/Mg)	U
3-01-197-49	Ethylene Manufacturing - Equipment Leak Emissions[a]	Equipment Leak Emissions	Detection/Correction of leaks	See Section 4.5.2	
			Uncontrolled	See Section 4.5.2	
3-01-197-99	Ethylene Manufacturing - Intermittent Emissions[a]	Intermittent Emissions[b]			
		Single Compressor Train	Flare	0.1584-0.0316 lb/ton (0.0792-0.0158 kg/Mg)	U
			Uncontrolled	1.584 lb/ton (0.7919 kg/Mg)	U
		Dual Compressor Train	Flare	0.0202-0.004 lb/ton (0.0101-0.002 kg/Mg)	U
			Uncontrolled	0.2022 lb/ton (0.1011 kg/Mg)	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Gas By-Product Plant (Furnace Coke)	Cooling Tower			
		-Direct Water	Uncontrolled	0.54 lb/ton (270 g/Mg)	E
		-Tar Bottom	Uncontrolled	0.14 lb/ton (70 g/Mg)	E
		Light-Oil Condenser Vent	Uncontrolled	0.18 lb/ton (89 g/Mg)	E
			Gas Blanketing	3.6×10^{-3} lb/ton (1.8 g/Mg)	E
		Naphthalene Separation and Processing	Uncontrolled	0.22 lb/ton (110 g/Mg)	E
			Activated Carbon	7.0×10^{-4}lb/ton (0.35g/Mg)	E
		Tar-Intercepting Sump	Uncontrolled	0.019 lb/ton (9.5 g/Mg)	E
		Tar Dewatering	Uncontrolled	0.042 lb/ton (21 g/Mg)	E
			Gas Blanketing	8.4×10^{-4} lb/ton (0.45 g/Mg)	E
		Tar Decanter	Uncontrolled	0.11 lb/ton (54 g/Mg)	E
			Gas Blanketing	22×10^{-3} lb/ton (1.1 g/Mg)	E
		Tar Storage	Uncontrolled	0.013 lb/ton (6.6 g/Mg)	E
			Gas Blanketing	7.6×10^{-4} lb/ton (0.38 g/Mg)	E
		Light-Oil Sump	Uncontrolled	0.03 lb/ton (15 g/Mg)	E
			Source Enclosure	6×10^{-4} lb/ton (0.3 g/Mg)	E
		Light-Oil Storage	Uncontrolled	0.012 lb/ton (5.8 g/Mg)	E
			Gas Blanketing	2.4×10^{-4} lb/ton (0.12 g/Mg)	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke-Gas By-Product Plant (Furance Coke) (continued)	BTX Storage	Uncontrolled	0.012 lb/ton (5.8 g/Mg)	E
			Gas Blanketing	2.4 x 10^{-4} lb/ton (0.12 g/Mg)	E
		Benzene Storage	Uncontrolled	0.0116 lb/ton (5.8 g/Mg)	E
			Nitrogen or Natural Gas Blanketing	2.4 x 10^{-4} lb/ton (0.12 g/Mg)	E
		Flushing-Liquor Circulation Tank	Uncontrolled	0.026 lb/ton (13 g/Mg)	E
			Gas Blanketing	5.2 x 10^{-4} lb/ton (0.26 g/Mg)	E
		Excess-Ammonia Liquor Tank	Uncontrolled	0.018 lb/ton (9 g/Mg)	E
			Gas Blanketing	5.6 x 10^{-4} lb/ton (0.028 g/Mg)	E
		Wash-Oil Decanter	Uncontrolled	7.6 x 10^{-3} lb/ton (3.8 g/Mg)	E
			Gas Blanketing	1.5 x 10^{-4} lb/ton (0.076 g/Mg)	E
		Wash-Oil Circulation Tank	Uncontrolled	7.6 x 10^{-3} lb/ton (3.8 g/Mg)	E
			Gas Blanketing	1.5 x 10^{-4} lb/ton (0.076 g/Mg)	E
3-03-003-15	By-Product Coke-Gas By-Product Plant (Foundry Coke)	Cooling Tower			
		-Direct Water	Uncontrolled	0.40 lb/ton (200 g/Mg)	E
		-Tar Bottom	Uncontrolled	0.10 lb/ton (51 g/Mg)	E
		Light-Oil Condenser Vent	Uncontrolled	0.096 lb/ton (48 g/Mg)	E
			Gas Blanketing	1.9 x 10^{-3} lb/ton (0.97 g/Mg)	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke-Gas By-Product Plant (Foundry Coke) (continued)	Naphthalene Separation and Processing	Uncontrolled	0.16 lb/ton (80 g/Mg)	E
			Activated Carbon	5.0 x 10^{-4}lb/ton (0.25 g/Mg)	E
		Tar-Intercepting Sump	Uncontrolled	0.009 lb/ton (4.5 g/Mg)	E
		Tar Dewatering	Uncontrolled	0.20 lb/ton (9.9 g/Mg)	E
			Gas Blanketing	4 x 10^{-4} lb/ton (0.2 g/Mg)	E
		Tar Decanter	Uncontrolled	0.05 lb/ton (25 g/Mg)	E
			Gas Blanketing	1.0 x 10^{-3} lb/ton (0.5 g/Mg)	E
		Tar Storage	Uncontrolled	6.2 x 10^{-3} lb/ton (3.1 g/Mg)	E
			Gas Blanketing	3.6 x 10^{-4} lb/ton (0.18 g/Mg)	E
		Light-Oil Sump	Uncontrolled	0.016 lb/ton (8.1 g/Mg)	E
			Gas Blanketing	3.2 x 10^{-4} lb/ton (0.16 g/Mg)	E
		Light-Oil Storage	Uncontrolled	6.2 x 10^{-3} lb/ton (3.1 g/Mg)	E
			Gas Blanketing	1.2 x 10^{-4} lb/ton (0.06 g/Mg)	E
		BTX Storage	Uncontrolled	6.2 x 10^{-3} lb/ton (3.1 g/Mg)	E
			Gas Blanketing	1.2 x 10^{-4} lb/ton (0.06 g/Mg)	E
		Benzene Storage	Uncontrolled	6.2 x 10^{-3} lb/ton (3.1 g/Mg)	E
			Nitrogen or Natural Gas Blanketing	1.2 x 10^{-4} lb/to (0.06 g/Mg)	E
		Flushing-Liquor Circulation Tank	Uncontrolled	0.019 lb/ton (9.5 g/Mg)	E
			Gas Blanketing	3.8 x 10^{-4} lb/ton (0.19 g/Mg)	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Gas By-Product Plant (Foundry Coke) (continued)	Excess-Ammonia Liquor Tank	Uncontrolled	2.0×10^{-3} lb/ton (1.0 g/Mg)	E
			Gas Blanketing	4.0×10^{-5} lb/ton (0.020 g/Mg)	E
		Wash-Oil Decanter	Uncontrolled	4.2×10^{-3} lb/ton (2.1 g/Mg)	E
			Gas Blanketing	8.2×10^{-5} lb/ton (0.041 g/Mg)	E
		Wash-Oil Circulation Tank	Uncontrolled	4.2×10^{-3} lb/ton (2.1 g/Mg)	E
			Gas Blanketing	8.2×10^{-5} lb/ton (0.041 g/Mg)	E
3-03-003-15	By-Product Coke - Furnace Coke By-Product Recovery (Light Oil BTX Recovery)	Valves	Uncontrolled	0.4 lb/day (0.18 kg/day)	U
			Quarterly Inspection	0.15 lb/day (0.07 kg/day)	U
			Monthly Inspection	0.11 lb/day (0.05 kg/day)	U
			Use Sealed Bellows Valves	--	
		Pumps	Uncontrolled	4.2 lb/day (1.9 kg/day)	U
			Quarterly Inspection	1.2 lb/day (0.55 kg/day)	U
			Monthly Inspection	0.71 lb/day (0.32 kg/day)	U
			Use of Dual Mechanical Seals	--	

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Furnace Coke By-Product Recovery (Light Oil BTX Recovery) (continued)	Exhausters	Uncontrolled	0.62 lb/day (0.28 kg/day)	U
			Quarterly Inspection	0.29 lb/day (0.13 kg/day)	U
			Monthly Inspection	0.22 lb/day (0.10 kg/day)	U
			Use of Degassing Reservoir Vents	--	
		Pressure Relief Devices	Uncontrolled	6.0 lb/day (2.7 kg/day)	U
			Quarterly Inspection	3.3 lb/day (1.5 kg/day)	U
			Monthly Inspection	2.9 lb/day (1.3 kg/day)	U
			Use of Rupture Disk System	--	
		Sampling Connections	Uncontrolled	0.55 lb/day (0.25 kg/day)	U
			Closed-purge Sampling	--	
		Open-ended Lines	Uncontrolled	0.084 lb/day (0.038 kg/day)	U
			Plug or Cap	--	
3-03-003-15	By-Product Coke - Furnace Coke Gas By-Product Recovery (Light Oil Recovery, Benzene Refining)	Valves	Uncontrolled	0.49 lb/day (0.22 kg/day)	U
			Quarterly Inspection	0.18 lb/day (0.08 kg/day)	U
			Monthly Inspection	0.13 lb/day (0.06 kg/day)	U
			Use of Sealed Bellows Valves	--	

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Furnace Coke By-Product Recovery (Light Oil Recovery, Benzene Refining) (continued)	Pumps	Uncontrolled	5.1 lb/day (2.3 kg/day)	U
			Quarterly Inspection	1.5 lb/day (0.67 kg/day)	U
			Monthly Inspection	0.86 lb/day (0.39 kg/day)	U
			Use of Dual Mechanical Seals	--	
		Exhausters	Uncontrolled	0.62 lb/day (0.28 kg/day)	U
			Quarterly Inspection	0.29 lb/day (0.13 kg/day)	U
			Monthly Inspection	0.22 lb/day (0.10 kg/day)	U
			Use of Degassing Reservoir Vents	--	
		Pressure Relief Devices	Uncontrolled	7.5 lb/day (3.4 kg/day)	U
			Quarterly Inspection	4.2 lb/day (1.9 kg/day)	U
			Monthly Inspection	3.5 lb/day (1.6 kg/day)	U
			Use of Rupture Disk System	--	
		Sampling Connections	Uncontrolled	0.68 lb/day (0.31 kg/day)	U
			Closed-purge Sampling	--	
		Open-ended Lines	Uncontrolled	0.104 lb/day (0.047 kg/day)	U
			Plug or Cap	--	

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Foundry By-Product Recovery (Light Oil BTX Recovery)	Valves	Uncontrolled	0.35 lb/day (0.16 kg/day)	U
			Quarterly Inspection	0.13 lb/day (0.06 kg/day)	U
			Monthly Inspection	0.09 lb/day (0.04 kg/day)	U
			Use of Sealed Bellows Valves	--	
		Pumps	Uncontrolled	3.7 lb/day (1.7 kg/day)	U
			Quarterly Inspection	1.1 lb/day (0.5 kg/day)	U
			Monthly Inspection	0.66 lb/day (0.3 kg/day)	U
			Use of Dual Mechanical Seals	--	
		Exhausters	Uncontrolled	0.55 lb/day (0.25 kg/day)	U
			Quarterly Inspection	0.24 lb/day (0.11 kg/day)	U
			Monthly Inspection	0.20 lb/day (0.09 kg/day)	U
			Use of Degassing Reservoir Vents	--	
		Pressure Relief Devices	Uncontrolled	5.5 lb/day (2.5 kg/day)	U
			Quarterly Inspection	3.1 lb/day (1.4 kg/day)	U
			Monthly Inspection	2.6 lb/day (1.2 kg/day)	U
			Use of Rupture Disk System	--	
		Sampling Connections	Uncontrolled	0.51 lb/day (0.23 kg/day)	U
			Plug or Cap	--	

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Foundry By-Product Recovery (Light Oil BTX Recovery) (continued)	Open-ended Lines	Uncontrolled	0.077 lb/day (0.035 kg/day)	U
			Closed-purge Sampling	--	
3-03-003-15	By-Product Coke - Foundry By-Product Recovery (Light Oil Recovery Benzene Refining)	Valves	Uncontrolled	0.44 lb/day (0.20 kg/day)	U
			Quarterly Inspection	0.15 lb/day (0.07 kg/day)	U
			Monthly Inspection	0.13 lb/day (0.06 kg/day)	U
		Valves	Use of Sealed Bellows Valves	--	
		Pumps	Uncontrolled	4.6 lb/day (2.1 kg/day)	U
			Quarterly Inspection	1.3 lb/day (0.6 kg/day)	U
			Monthly Inspection	0.88 lb/day (0.4 kg/day)	U
			Use of Dual Mechanical Seals	--	
		Exhausters	Uncontrolled	0.55 lb/day (0.25 kg/day)	U
			Quarterly Inspection	0.24 lb/day (0.11 kg/day)	U
			Monthly Inspection	0.20 lb/day (0.09 kg/day)	U
			Use of Degassing Reservoir Vents	--	

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-03-003-15	By-Product Coke - Foundry By-Product Recovery (Light Oil Recovery Benzene Refining) (continued)	Pressure Relief Devices	Uncontrolled	6.8 lb/day (3.1 kg/day)	U
			Quarterly Inspection	3.7 lb/day (1.7 kg/day)	U
			Monthly Inspection	3.3 lb/day (1.5 kg/day)	U
			Use of Rupture Disk System	--	
		Sampling Connections	Uncontrolled	0.62 lb/day (0.28 kg/day)	U
			Plug or Cap	--	
		Open-ended Lines	Uncontrolled	0.95 lb/day (0.043 kg/day)	U
			Close-purge Sampling	--	
3-01-169-02	Ethylbenzene Manufacturing - Alkylation Reactor Vent[c]	Alkylation Reactor Vent	Process Heater	0.0006 lb/ton (0.0003 kg/Mg)	U
			Uncontrolled	0.6 lb/ton (0.3 kg/Mg)	U
3-01-169-03	Ethylbenzene Manufacturing - Benzene Drying Column[c]	Atmospheric/Pressure Column Vents[d]	Flare	0.024 - 0.96 lb/ton (0.012 - 0.48 kg/Mg)	U
			Uncontrolled	2.4 lb/ton (1.2 kg/Mg)	U
3-01-169-06	Ethylbenzene Manufacturing - Polyethylbenzene Recovery Column[c]	Other Vacuum Vents[e]	Flare	0.0010 - 0.004 lb/ton (0.005 - 0.002 kg/Mg)	U
			Uncontrolled	0.10 lb/ton (0.05 kg/Mg)	U
3-01-206-02	Styrene Manufacturing - Styrene Purification Vents[c]	Benzene-Toluene Vacuum Vent	Flare	0.06 - 2.4 lb/ton (0.03 - 1.2 kg/Mg)	U
			Uncontrolled	6.0 lb/ton (3.0 kg/Mg)	U
3-01-206-03	Styrene Manufacturing - Hydrogen Separation Vent[c]	Hydrogen Separation Vent	Flare	0.00006 - 0.0024 lb/ton (0.00003 -0.0012 kg/Mg)	U
			Uncontrolled	0.006 lb/ton (0.003 kg/Mg)	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-01-169-80/ 3-01-206-80	Ethylbenzene/Styrene Manufacturing - Equipment Leaks[c]	Equipment Leaks	Detection and Correction	See Section 4.5.2	
			Uncontrolled		
4-07-196-02/ 4-07-196-13	Ethylbenzene/Styrene Manufacturing - Storage and Handling[c]	Storage and Handling	Floating Roof, Vented to Flare, Refrigerated Vent Condenser , and Uncontrolled	See Section 4.5.3	
3-01-156-02	Cumene Manufacturing - Benzene Drying Column	Process Vent	Flare	2.00×10^{-3} lb/ton (1.00×10^{-3} kg/Mg)	U
			Uncontrolled	4.00×10^{-2} lb/ton (2.00×10^{-2} kg/Mg)	U
3-01-156-03	Cumene Manufacturing - Catalyst Mix Tank Scrubber Vent	Process Vent	Flare	1.59×10^{-2} lb/ton (7.95×10^{-3} kg/Mg)	U
			Uncontrolled	3.18×10^{-1} lb/ton (1.59×10^{-1} kg/Mg)	U
3-01-156-04	Cumene Manufacturing - Wash-Decant System Vent	Process Vent	Flare	7.84×10^{-4} lb/ton (3.92×10^{-4} kg/Mg)	U
			Uncontrolled	1.57×10^{-2} lb/ton (7.85×10^{-3} kg/Mg)	U
3-01-156-05	Cumene Manufacturing - Benzene Recovery Column	Process Vent	Flare	1.70×10^{-3} lb/ton (8.50×10^{-4} kg/Mg)	U
			Uncontrolled	3.40×10^{-2} lb/ton (1.70×10^{-2} kg/Mg)	U
3-01-202-02	Phenol Manufacturing - Cumene Oxidation	Process Vent	Uncontrolled[f]	4.00×10^{-3} lb/ton (2.00×10^{-3} kg/Mg)	U
3-01-202-02	Phenol Manufacturing - Cumene Oxidation	Process Vent	Thermal Oxidizer	1.16×10^{-4} lb/ton (5.82×10^{-5} kg/Mg)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-01-195-01	Nitrobenzene - General	Small Benzene Storage (Point G)	Uncontrolled	0.156 lb/ton (0.078 g/kg)	U
				0.154 lb/ton (0.077 g/kg)	U
		Benzene Storage (Point G)	Uncontrolled	0.566 lb/ton (0.283 g/kg)	U
				0.562 lb/ton (0.281 g/kg)	U
			Internal Floating Roof	0.085 lb/ton (0.0425 g/kg)	U
		Secondary (Point J)	Uncontrolled	0.20 lb/ton (0.10 g/kg)	U
		Total Plant	Uncontrolled	4.9 lb/ton (2.45 g/kg)	U
				4.4 lb/ton (2.19 g/kg)	U
			Vent Adsorber	0.78 lb/ton (0.39 g/kg)	U
				0.64 lb/ton (0.32 g/kg)	U
			Thermal Oxidizer	0.44 lb/ton (0.22 g/kg)	U
				0.52 lb/ton (0.26 g/kg)	U
3-01-195-03	Nitrobenzene - Acid Stripper Vent	Waste-Acid Stripper (Point B)	Uncontrolled	0.034 lb/ton (0.170 g/kg)	U
3-01-195-04	Nitrobenzene - Washer/Neutralizer Vent	Wash and Neutralization (Point C)	Uncontrolled	0.0162 lb/ton (0.0081 g/kg)	U
			Vent Adsorber	0.155 lb/ton (0.0776 g/kg)	U
3-01-195-05	Nitrobenzene - Nitrobenzene Stripper Vent	Nitrobenzene Stripper (Point D)	Uncontrolled	0.34 lb/ton (0.170 g/kg)	U
			Thermal Oxidizer	0.0288 lb/ton (0.0144 g/kg)	U
3-01-195-06	Nitrobenzene - Waste Acid Storage	Wash Acid Storage (Point G)	Uncontrolled	0.102 lb/ton (0.051 g/kg)	U
				0.96 lb/ton (0.048 g/kg)	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-01-195-80	Nitrobenzene - Fugitive Emissions	Process Pumps and Valves[g]	Uncontrolled	1.26 lb/ton (0.63 g/kg)	U
				0.76 lb/ton (0.38 g/kg)	U
			LD&R Plus Mechanical Seals	0.33 lb/ton (0.165 g/kg)	U
				0.198 lb/ton (0.099 g/kg)	U
3-01-301-01	Chlorobenzene Manufacturing - Tail-Gas Scrubber[h]	Tail-Gas Scrubber Treatment	Carbon Adsorption	0.0134 lb/ton (0.0067 kg/Mg)	U
			Uncontrolled	1.04 lb/ton (0.52 kg/Mg)	U
3-01-301-02	Chlorobenzene Manufacturing - Benzene Dry Distillation[h]	Atmospheric Distillation Vents[i]	Carbon Adsorption	0.0084 lb/ton (0.0042 kg/Mg)	U
			Uncontrolled	0.64 lb/ton (0.32 kg/Mg)	U
3-01-301-04	Chlorobenzene Manufacturing - Heavy Ends Processing[h]				
3-01-301-05	Chlorobenzene Manufacturing - Monochlorobenzene Distillation[h]				
3-01-301-03	Chlorobenzene Manufacturing - Benzene Recovery[h]	Atmospheric Distillation Vent - Benzene Recovery	Carbon Adsorption	0.00104 lb/ton (0.00052 kg/Mg)	U
			Uncontrolled	0.08 lb/ton (0.04 kg/Mg)	U
3-01-301-80	Chlorobenzene Manufacturing - Equipment Leaks[h]	Equipment Leaks	Detection and Repair of Major Leaks	See Section 4.5.2	
			Uncontrolled	See Section 4.5.2	
4-07-196-01	Chlorobenzene Manufacturing - Benzene Storage[h]	Benzene Storage Vessel	Internal Floating Roof	See Section 4.5.3	
			Uncontrolled	See Section 4.5.3	
3-01-211-02	Linear Alkylbenzene - Benzene Drying[j]	Benzene Azeotropic Column Vent (Point A)	Uncontrolled	7.4×10^{-3} lb/ton (3.7 g/Mg)	U
			Used as Fuel	1.5×10^{-6} lb/ton (7.4×10^{-4} g/Mg)	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-01-21103	Linear Alkylbenzene HFl Scrubber Vent[j]	Hydrogen Fluoride Scrubber Column Vent (Point B)	Uncontrolled	0.022 lb/ton (11 g/Mg)	U
			Used as Fuel	4.4×10^{-6} lb/ton (2.2×10^{-3} g/Mg)	U
			Flare	2.2×10^{-3} lb/ton (1.1 g/Mg)	U
3-01-211-02	Linear Alkylbenzene - Benzene Drying[k]	Benzene Azeotropic Column Vent (Point A)	Uncontrolled	7.4×10^{-3} lb/ton (3.7 g/Mg)	U
			Used as Fuel	1.5×10^{-6} lb/ton (7.4×10^{-4} g/Mg)	U
3-01-211-23	Linear Alkylbenzene - HCl Adsorber Vent[k]	Hydrochloric Acid Adsorber Vent (Point B)	Uncontrolled	0.5 lb/ton (250 g/Mg)	U
			Used as Fuel	1×10^{-4} lb/ton (0.05 g/Mg)	U
3-01-211-24	Linear Alkylbenzene - Atmospheric Wash/Decanter Vent[k]	Atmospheric Wash/Decanter Vent (Point C)	Uncontrolled	0.0246 lb/ton (12.3 g/Mg)	U
			Used as Fuel	5×10^{-6} lb/ton (2.5×10^{-3} g/Mg)	U
3-01-211-25	Linear Alkylbenzene - Benzene Strip Column[k]	Benzene Stripping Column Vent (Point D)	Uncontrolled	7.4×10^{-3} lb/ton (3.7 g/Mg)	U
			Used as Fuel	1.48×10^{-6} lb/ton (7.4×10^{-4} g/Mg)	U
3-01-060-01	Pharmaceuticals - General Process - Vacuum Dryers	Vacuum Dryer Vent	Venturi Scrubber	2.1 lb/1,000 gal (0.25 g/L)	B
3-10-001-01	Oil and Gas Production - Oil Wellheads	Equipment Leaks	Uncontrolled	1.27×10^{-7} lb/hr (5.77×10^{-8} kg/hr)	D
			Uncontrolled	3.9×10^{-8} lb/hr (1.77×10^{-8} kg/hr)	D
			Uncontrolled	6.25×10^{-9} lb/hr (2.84×10^{-9} kg/hr)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-10-003-01	Glycol Dehydration Units - TEG Units	Reboiler Still Vent	Uncontrolled	0.93 tpy of BTEX/MMscfd (29.79 x 10^3 kg/yr of BTEX/MMscmd)	U
3-10-003-04	Glycol Dehydration Units - EG Units	Reboiler Still Vent	Uncontrolled	0.12 tpy of BTEX/MMscfd (3.84 x 10^3 kg/yr of BTEX/MMscmd)	U
3-06-005-08	Oil/Water Separators	Oil/Water Separator	Uncontrolled	1.3 lb of Benzene/10^6 gal of feed water (0.16 kg of Benzene/10^6 l of feed water)	E
3-06-005-20	Air Flotation Systems	Air Flotation Systems[l]	Uncontrolled	4 lb of Benzene/10^6 gal of feed water (0.48 kg of Benzene/10^6 l of feed water)	E
5-01-007-07	Solid Waste Disposal - Sewage Treatment	Comminutor	Wet scrubber	6.50 x 10^{-3} lb/million gal (7.79 x 10^{-4} kg/million liters)	E
5-01-007-15	Solid Waste Disposal - Sewage Treatment	Aerated Grit Chamber	Uncontrolled	3.56 x 10^{-3} lb/million gal (4.27 x 10^{-4} kg/million liters)	C
5-01-007-20	Solid Waste Disposal - Sewage Treatment	Primary Sedimentation Tank	Uncontrolled	5.50 x 10^{-4} lb/million gal (6.59 x 10^{-5} kg/million liters)	C
5-01-007-31	Solid Waste Disposal - Sewage Treatment	Diffused Air Activated Sludge	Uncontrolled	6.67 x 10^{-4} lb/million gal (7.99 x 10^{-5} kg/million liters)	B
5-01-007-33	Solid Waste Disposal - Sewage Treatment	Pure Oxygen Activated Sludge	Uncontrolled	3.80 x 10^{-6} lb/million gal (4.55 x 10^{-7} kg/million liters)	B
5-01-007-34	Solid Waste Disposal - Sewage Treatment	Trickling Filter	Uncontrolled	1.60 x 10^{-3} lb/million gal (1.92 x 10^{-4} kg/million liters)	C
5-01-007-40	Solid Waste Disposal - Sewage Treatment	Secondary Clarifier	Uncontrolled	1.40 x 10^{-4} lb/million gal (1.68 x 10^{-5} kg/million liters)	C

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
5-01-007-50	Solid Waste Disposal - Sewage Treatment	Tertiary Filter	Uncontrolled	4.00 x 10^{-6} lb/million gal (4.79 x 10^{-7} kg/million liters)	B
5-01-007-60	Solid Waste Disposal - Sewage Treatment	Chlorine Contact Tank	Uncontrolled	1.39 x 10^{-4} lb/million gal (1.67 x 10^{-5} kg/million liters)	E
5-01-007-61	Solid Waste Disposal - Sewage Treatment	Dechlorination	Uncontrolled	7.50 x 10^{-1} lb/million gal (7.50 x 10^{-1} kg/million liters)	B
5-01-007-71	Solid Waste Disposal - Sewage Treatment	Gravity Sludge Thickener	Uncontrolled	2.09 x 10^{-4} lb/million gal (2.50 x 10^{-5} kg/million liters)	B
5-01-007-72	Solid Waste Disposal - Sewage Treatment	Dissolved Air Floatation Thickener	Uncontrolled	3.00 x 10^{-3} lb/million gal (3.59 x 10^{-4} kg/million liters)	B
5-01-007-81	Solid Waste Disposal - Sewage Treatment	Anaerobic Digester	Uncontrolled	3.08 x 10^{-1} lb/million gal (3.69 x 10^{-2} kg/million liters)	B
5-01-007-91	Solid Waste Disposal - Sewage Treatment	Belt Filter Press	Uncontrolled	5.00 x 10^{-2} lb/million gal (5.99 x 10^{-3} kg/million liters)	B
5-01-007-92	Solid Waste Disposal - Sewage Treatment	Sludge Centrifuge	Uncontrolled	2.05 x 10^{-3} lb/million gal (2.46 x 10^{-4} kg/million liters)	B
5-01-007-93	Solid Waste Disposal - Sewage Treatment	Sludge Drying Bed	Uncontrolled	2.80 x 10^{-3} lb/million gal (3.36 x 10^{-4} kg/million liters)	B
5-02-006-01	Solid Waste Disposal - Landfill Dump	Waste Gas Flares	Uncontrolled	7.10 x 10^{-6} lb/MMBtu (3.05 x 10^{-9} g/kJ)	D
3-04-008-53	Synthetic Graphite	Mixing Cylinder (Vent A)	Uncontrolled	2.82 x 10^{-4} lb/lb (1.41 x 10^{-4} g/kg)	D
3-04-008-50	Synthetic Graphite	Cooling Cylinder (Vent B)	Uncontrolled	3.70 x 10^{-4} lb/lb (1.8 x 10^{-4} g/kg)	D
3-01-005-04	Carbon Black	Oil Furnace Process	Uncontrolled	6.23 x 10^{-4} lb/lb	U
3-01-025-01	Rayon-based Carbon Fibers	Carbon Fabric Dryer	Uncontrolled	7.17 x 10^{-7} lb/lb (7.17 x 10^{-4} g/kg)	B

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-04-001-99	Secondary Metals - Secondary Aluminum - Not Classified	General Facility (Vents A, D, E, F, and H)	Uncontrolled	7.08×10^{-2} lb/ton (3.54×10^{-2} kg/Mg)	D
		General Facility (Vents A, B, D, E, and G)	Uncontrolled	7.47×10^{-2} lb/ton (3.73×10^{-2} kg/Mg)	D
3-04-001-14	Secondary Metals - Secondary Aluminum - Pouring/Casting	Casting Shakeout Operation	Catalytic Incinerator	6.09×10^{-3} lb/ton (3.45×10^{-3} kg/Mg)	D
			Uncontrolled	5.48×10^{-3} lb/ton (2.74×10^{-2} kg/Mg)	D
3-05-001-01	Petroleum Industry - Asphalt Roofing -Asphalt Blowing - Saturant	Blowing Stills or Saturators	Uncontrolled	52 lb/ton (26 kg/Mg)	E
5-02-005-05	Solid Waste Disposal - Pathological Incinerator	Incinerator	Uncontrolled	4.92×10^{-3} lb/ton (2.46×10^{-3} kg/Mg)	D
5-01-005-15	Solid Waste Disposal - Sludge Incinerator	Multiple Hearth Furnace	Uncontrolled	1.2×10^{-2} lb/ton (5.8 g/Mg)	D
			Cyclone/Venturi Scrubbers	7.0×10^{-4} lb/ton (3.5×10^{-1} g/Mg)	E
			Venturi Scrubber	2.8×10^{-2} lb/ton (1.4 g/Mg)	E
			Venturi/Impingement Scrubbers	1.3×10^{-2} lb/ton (6.3 g/Mg)	D
			Venturi/Impingement Scrubbers and Afterburner	3.4×10^{-4} lb/ton (1.7×10^{-1} g/Mg)	E
5-01-005-16	Solid Waste Disposal - Fluidized Bed Incinerator	Fluidized Bed Incinerator	Venturi/Impingement Scrubbers	4.0×10^{-4} lb/ton (2.0×10^{-1} g/Mg)	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
5-01-005-15	Solid Waste Disposal - Multiple Hearth Incinerator	Multiple Hearth Incinerator	Uncontrolled	1.73 x 10^{-2} lb/ton (8.61 g/Mg)	D
			Venturi/Impingement Scrubbers	1.34 x 10^{-2} lb/ton (6.66 g/Mg)	D
			Elevated Operating Temperature	2.65 x 10^{-3} lb/ton (1.32 g/Mg)	D
			Elevated Operating Temperature/ Afterburner	1.41 x 10^{-3} lb/ton (7.02 x 10^{-1} g/Mg)	D
			Elevated Operating Temperature/ Afterburner/Venturi and Impingement Scrubbers	3.35 x 10^{-4} lb/ton (1.67 x 10^{-1} g/Mg)	D
5-03-005-01	Solid Waste Disposal - Hazardous Waste Incinerator	Liquid Injection Incinerator	Uncontrolled[m]	4.66 x 10^{-5} lb/ton (2.33 x 10^{-5} kg/Mg)	U
		Liquid Injection Incinerator	Various Control Devices[n]	1.23 x 10^{-3} lb/ton (6.16 x 10^{-4} kg/Mg)	U
1-01-002-03	External Combustion Boiler - Electric Generation	Cyclone Boiler - Coal	Baghouse/SCR/ Sulfuric Acid Condenser	5.58 x 10^{-6} lb/MMBtu (2.40 x 10^{-6} µg/J)	D
			Electrostatic Precipitator	7.90 x 10^{-6} lb/MMBtu (3.40 x 10^{-6} µg/J)	D
1-01-003-02	External Combustion Boiler - Electric Generation	Tangentially - Fired Boiler - Lignite	Electrostatic Precipitator/Scrubber	3.95 x 10^{-5} lb/MMBtu (1.70 x 10^{-5} µg/J)	D
1-01-006-01	External Combustion Boiler - Electric Generation	Opposed-wall Boiler - Natural Gas	Flue Gas Recirculation	1.40 x 10^{-6} lb/MMBtu (6.02 x 10^{-7} µg/J)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
1-01-006-04	External Combustion Boiler - Electric Generation	Tangentially - Fired Boiler - Natural Gas	Flue Gas Recirculation	4.00 x 10^{-7} lb/MMBtu (1.72 x 10^{-7} µg/J)	D
1-01-009-01	External Combustion Boiler - Electric Generation	Boiler - Bark Fuel	Uncontrolled	3.60 x 10^{-3} lb/ton (1.80 x 10^{-3} kg/Mg)	E
1-02-004-01	External Combustion Boiler - Industrial	Boiler - No. 6 Fuel Oil	Uncontrolled	9.38 x 10^{-5} lb/MMBtu (4.04 x 10^{-5} µg/J)	D
1-02-007-99	External Combustion Boiler - Industrial	Boiler - Landfill Gas Fuel	Uncontrolled	3.78 x 10^{-4} lb/MMBtu (1.63 x 10^{-4} µg/J)	D
1-02-008-04	External Combustion Boiler - Industrial	Boiler - Coke and Coal Fuel	Baghouse	2.68 x 10^{-5} lb/MMBtu (1.15 x 10^{-5} µg/J)	D
1-02-009-01	External Combustion Boiler - Industrial	Boiler - Bark Fuel	ESP	6.90 x 10^{-4} lb/MMBtu (2.97 x 10^{-4} µg/J)	E
1-02-009-03	External Combustion Boiler - Industrial	Boiler - Wood Fuel	Wet Scrubber	4.20 x 10^{-3} lb/MMBtu (1.81 x 10^{-3} µg/J)	E
			Multiple Cyclone/ESP	5.12 x 10^{-4} lb/MMBtu (2.20 x 10^{-4} µg/J)	E
			Multiple Cyclone	1.04 x 10^{-3} lb/MMBtu (4.46 x 10^{-4} µg/J)	E
		FBC Boiler - Wood Fuel	Multiple Cyclone/ESP	2.70 x 10^{-5} lb/MMBtu (1.16 x 10^{-5} µg/J)	E
1-02-009-05	External Combustion Boiler - Industrial	Boiler - Wood and Bark	Multiple Cyclone/Wet Scrubber	1.01 x 10^{-3} lb/MMBtu (4.35 x 10^{-4} µg/J)	E
1-02-009-06	External Combustion Boiler - Industrial	Spreader-stoker Boiler - Wood Fuel	Multiple Cyclone	2.43 x 10^{-4} lb/MMBtu (1.05 x 10^{-4} µg/J)	D
			Mechanical Dust Collector	1.67 x 10^{-4} lb/MMBtu (7.18 x 10^{-5} µg/J)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
1-02-012-01	External Combustion Boiler - Industrial	Boiler - Almond Shells and Wood	Baghouse	5.29 x 10^{-3} lb/MMBtu (2.28 x 10^{-3} µg/J)	D
1-03-007-01	External Combustion Boiler - Commercial/ Institutional	Boiler - POTW Digester Gas	Uncontrolled	3.50 x 10^{-3} lb/MMBtu (1.50 x 10^{-3} µg/J)	C
21-04-008-030	Stationary Source Combustion - Residential	Catalytic Woodstove	Uncontrolled	1.46 lb/ton (7.30 x 10^{-1} kg/Mg)	E
21-04-008-051	Stationary Source Combustion - Residential	Non-Catalytic Woodstove	Uncontrolled	1.94 lb/ton (9.70 x 10^{-1} kg/Mg)	E
2-02-001-02	Internal Combustion Engine - Industrial	Reciprocating Distillate Oil-fueled Engine	Uncontrolled	9.33 x 10^{-4} lb/MMBtu (4.01 x 10^{-1} ng/J)	E
2-02-001-04	Internal Combustion Engine - Industrial/Reciprocating Cogeneration	Cogeneration Distillate Oil-fueled Engine	Uncontrolled	5.36 x 10^{-4} lb/MMBtu (2.30 x 10^{-1} ng/J)	D
2-02-002-02	Internal Combustion Engine - Industrial/Reciprocating	2-cycle Lean Burn Natural Gas-fueled Engine	Uncontrolled	2.20 x 10^{-3} lb/MMBtu (9.46 x 10^{-1} ng/J)	E
		4-cycle Lean Burn Natural Gas-fueled Engine	NSCR	7.1 x 10^{-4} lb/MMBtu (3.05 x 10^{-1} ng/J)	E
2-02-004-01	Internal Combustion Engine - Industrial	Large Bore Diesel-fueled Engine	Uncontrolled	7.76 x 10^{-4} lb/MMBtu (3.34 x 10^{-1} ng/J)	E
2-02-004-02	Internal Combustion Engine - Industrial	Large Bore Oil- and Natural Gas-fueled Engine (Dual Fuel)	Uncontrolled	4.45 x 10^{-3} lb/MMBtu (1.91 ng/J)	E
2-03-007-02	Internal Combustion Engine - Commercial/Institutional	Reciprocating POTW Digester Gas-fueled Engine	Uncontrolled	6.90 x 10^{-4} lb/MMBtu (2.97 x 10^{-1} ng/J)	C
2-01-001-01	Internal Combustion Engine - Electric Generation	Gas Turbine Fueled with Distillate Oil	Afterburner	9.13 x 10^{-5} lb/MMBtu (3.92 x 10^{-2} ng/J)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
2-01-002-01	Internal Combustion Engine - Electric Generation	Gas Turbine Fueled with Natural Oil	Catalytic Reduction	1.10×10^{-4} lb/MMBtu (4.73×10^{-2} ng/J)	E
3-04-004-03	Secondary Metals - Secondary Lead Production	Blast Furnace (Cupola)	Uncontrolled	4.08×10^{-1} lb/ton (2.04×10^{-1} kg/Mg)	D
			Afterburner	2.47×10^{-2} lb/ton (1.23×10^{-2} kg/Mg)	D
3-04-004-04	Secondary Metals - Secondary Lead Production	Rotary Sweating Furnace	Uncontrolled	1.66×10^{-1} lb/ton (8.30×10^{-2} kg/Mg)	D
3-04-003-98	Secondary Metals - Gray Iron Foundries	Sand Cooling and Belts	Baghouse	6.99×10^{-4} lb/ton (3.50×10^{-4} kg/Mg)	D
3-05-007-06	Cement Manufacturing - Wet Process - Kilns	Kiln--Burning Hazardous Waste Exclusively, or with Coal or Coke	ESP	3.7×10^{-3} lb/ton (1.8×10^{-3} kg/Mg)	B
		Kiln--Burning Hazardous Waste and Natural Gas as Fuel	ESP	7.5×10^{-3} lb/ton (3.7×10^{-3} kg/Mg)	D
		Kiln--Burning Hazardous Waste and Coal at High Combustion Temperature	ESP	3.9×10^{-6} lb/ton (1.9×10^{-6} kg/Mg)	D
3-05-006-06	Cement Manufacturing - Dry Process	Kiln--Burning Coal in Precalciner Process	FF	1.6×10^{-2} lb/ton (8×10^{-3} kg/Mg)	E
		Kiln--Burning Coal and 20 Percent TDF	FF	0.17 g/MMBtu	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
3-05-002-01	Petroleum Industry - Asphalt Concrete - Rotary Dryer	Rotary Dryer, LPG-fired	Uncontrolled	5.35 x 10^{-4} lb/ton (2.68 x 10^{-4} kg/Mg)	C
		Rotary Dryer, Oil-fired	Multiple Cyclone	7.7 x 10^{-5} lb/ton (3.85 x 10^{-5} kg/Mg)	C
		Rotary Dryer, Natural Gas- or Oil-fired	Baghouse with Single Cyclone, Knock-out Box, or Multiple Cyclone	2.08 x 10^{-4} lb/ton (1.04 x 10^{-4} kg/Mg)	B
		Rotary Dryer, Natural Gas- or Diesel-fired	Wet scrubber	1.95 x 10^{-5} lb/ton (9.75 x 10^{-6} kg/Mg)	C
3-05-002-08	Petroleum Industry - Asphalt Concrete - Asphalt heater - Distillate oil	Asphalt Heater, Diesel-fired	Uncontrolled	1.50 x 10^{-4} lb/ton (7.5 x 10^{-5} kg/Mg)	D
26-10-030-00	Waste Disposal - On-Site Incineration - Residential	Yard Waste Burning	Uncontrolled	1.10 lb/ton (5.51 x 10^{-1} kg/Mg)	U
28-01-500-000	Agricultural Production - Field Burning	Land Clearing/Burning	Uncontrolled	9.06 x 10^{-1} lb/ton (4.53 x 10^{-1} kg/Mg)	U
28-10-005-000	Other Combustion - Managed Slash Burning	Slash (Pile) Burning	Uncontrolled	9.06 x 10^{-1} lb/ton (4.53 x 10^{-1} kg/Mg)	U
28-10-001-000	Other Combustion - Forest Wildfires	Forest Fires - Fire Wood	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Forest Fires - Small Wood	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Forest Fires - Large Wood (Flaming)	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Forest Fires - Large Wood (Smoldering)	Uncontrolled	2.52 lb/ton (1.26 kg/Mg)	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
28-10-001-000	Other Combustion - Forest Wildfires (continued)	Forest Fires - Live Vegetation	Uncontrolled	1.48 lb/ton (7.4 x 10^{-1} kg/Mg)	U
		Forest Fires - Duff (Flaming)	Uncontrolled	2.52 lb/ton (1.26 kg/Mg)	U
28-10-015-000	Other Combustion - Managed Prescribed Burning	Prescribed Burning (Broadcast) - Fire Wood	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Prescribed Burning (Broadcast) - Small Wood	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Prescribed Burning (Broadcast) - Large Wood (Flaming)	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Prescribed Burning (Broadcast) - Large Wood (Smoldering)	Uncontrolled	2.52 lb/ton (1.26 kg/Mg)	U
		Prescribed Burning (Broadcast) - Live Vegetation	Uncontrolled	1.48 lb/ton (7.4 x 10^{-1} kg/Mg)	U
		Prescribed Burning (Broadcast) - Duff (Flaming)	Uncontrolled	6.6 x 10^{-1} lb/ton (3.3 x 10^{-1} kg/Mg)	U
		Prescribed Burning (Broadcast) - Duff (Smoldering)	Uncontrolled	2.52 lb/ton (1.26 kg/Mg)	U
5-03-002-03	Solid Waste Disposal, Open Burning - Autobody Components	Chunk Tires	Uncontrolled	3.05 lb/ton (1.53 kg/Mg)	C
		Shredded Tires	Uncontrolled	3.86 lb/ton (1.93 kg/Mg)	C

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
5-03-002-02	Solid Waste Disposal, Open Burning - Refuge	Unused Plastic Burning	Uncontrolled	9.55×10^{-5} lb/ton (4.77×10^{-5} kg/Mg)	C
			Forced Air	5.75×10^{-5} lb/ton (2.87×10^{-5} kg/Mg)	C
		Used Plastic Burning	Uncontrolled	2.47×10^{-5} lb/ton (1.23×10^{-5} kg/Mg)	C
			Forced Air	4.88×10^{-5} lb/ton (2.44×10^{-5} kg/Mg)	C
4-06-002-36	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship Loading - Uncleaned Tanks	Uncontrolled	0.023 lb/1000 gal (2.8 mg/liter)	D
4-06-002-37	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ocean Barges Loading - Uncleaned Tanks	Uncontrolled	0.023 lb/1000 gal (2.8 mg/liter)	D
4-06-002-34	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship Loading - Ballasted Tank	Uncontrolled	0.015 lb/1000 gal (1.8 mg/liter)	D
4-06-002-035	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ocean Barges Loading - Ballasted Tank	Uncontrolled	0.015 lb/1000 gal (1.8 mg/liter)	D
4-06-002-36	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship Loading - Cleaned Tanks	Uncontrolled	0.014 lb/1000 gal (1.6 mg/liter)	D
4-06-002-31	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ocean Barges Loading - Cleaned Tanks	Uncontrolled	0.014 lb/1000 gal (1.6 mg/liter)	D
4-06-002-31	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship Loading - Cleaned and Vapor-Free Tanks	Uncontrolled	0.006 lb/1000 gal (0.77 mg/liter)	D
4-06-002-32	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ocean Barges Loading - Cleaned and Vapor-Free Tanks	Uncontrolled	0.006 lb/1000 gal (0.77 mg/liter)	D

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
4-06-002-43	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship/Ocean Barges Loading- Any Condition-Nonvolatile Previous Cargo	Uncontrolled	0.006 lb/1000 gal (0.77 mg/liter)	D
4-06-002-43	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ship Loading- Typical Condition - Any Cargo	Uncontrolled	0.016 lb/1000 gal (1.9 mg/liter)	D
4-06-002-40	Transportation of Petroleum Products - Marine Vessels	Gasoline: Ocean Barge Loading- Typical Condition - Any Cargo	Uncontrolled	0.016 lb/1000 gal (1.9 mg/liter)	D
4-06-002-38	Transportation of Petroleum Products - Marine Vessels	Gasoline: Barge Loading - Uncleaned Tanks	Uncontrolled	0.035 lb/1000 gal (4.2 mg/liter)	D
4-06-002-33	Transportation of Petroleum Products - Marine Vessels	Gasoline: Barge Loading - Cleaned and Vapor-Free Tanks	Uncontrolled	0.018 lb/1000 gal (2.2 mg/liter)	D
4-06-002-39	Transportation of Petroleum Products - Marine Vessels	Gasoline: Tanker Ship Loading - Ballasted Condition	Uncontrolled	0.007 lb/1000 gal (0.9 mg/liter)	D
4-06-002-42	Transportation of Petroleum Products - Marine Vessels	Gasoline: Transit Loss	Uncontrolled	0.024 lb/week-1000 gal (2.8 mg/week-liter)	D
4-04-002-01	Storage Tanks - Fixed Roof - Breathing Loss		Uncontrolled	0.5 lb/1000 gal. (5.4 mg/liter)	E
4-04-002-04	Storage Tanks - Fixed Roof - Working Loss				
					E
	Filling		Uncontrolled	0.086 lb/1000 gal (10.3 mg/liter)	E
	Emptying		Uncontrolled	0.034 lb/1000 gal (4.1 mg/liter)	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
4-04-002-50	Bulk Terminals/Plants - Loading Racks	Splash Loading-Normal Service	Uncontrolled	0.11 lb/1000 gal (12.9 mg/liter)	E
		Submerged Loading-Normal Service	Uncontrolled	0.044 lb/1000 gal (5.3 mg/liter)	E
		Balance Service Loading	Vapor Balancing	0.002 lb/1000 gal (0.4 mg/liter)	E
4-06-003-01	Petroleum Products Marketing - Underground Storage Tanks	Filling Losses - Splash Fill	Uncontrolled	0.104 lb/1000 gal (12.4 mg/liter)	E
4-06-003-02	Petroleum Products Marketing - Underground Storage Tanks	Filling Losses - Submerged Fill	Uncontrolled	0.066 lb/1000 gal (7.9 mg/liter)	E
4-06-003-06	Petroleum Products Marketing - Underground Storage Tanks	Filling Losses - Balanced Submerged Fill	Vapor Balancing	0.003 lb/1000 gal (0.40 mg/liter)	E
4-06-003-07	Petroleum Products Marketing - Underground Storage Tanks	Underground Tank Breathing Losses	Uncontrolled	0.009 lb/1000 gal (1.1 mg/liter)	E
4-06-004-01	Petroleum Products Marketing - Vehicle Refueling	Displacement Losses			
		Controlled	Stage II	0.0099 lb/1000 gal (1.2 mg/liter)	E
		Uncontrolled	Uncontrolled	0.099 lb/1000 gal (11.9 mg/liter)	E
4-06-004-02	Petroleum Products Marketing - Vehicle Refueling	Spillage	Uncontrolled	0.0063 lb/1000 gal (0.76 mg/liter)	E
3-06-010-01	Sludge dewatering units	Sludge dewatering unit[p]	Uncontrolled	660 lb of TOC/10^6 lb sludge (660 kg of TOC/10^6 kg sludge)	C
4-06-002-XX	Ocean Going Commercial	Motor Propulsion - All Underway Modes	Uncontrolled	0.25 lb/1000 gal fuel	E
		Auxilary Diesel Generators 500 KW (50% load)	Uncontrolled	0.87 lb/1000 gal fuel	E

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
4-06-002-XX	Commercial Marine Vessels-Harbor and Fishing	Diesel Engines			
		<500 hp			
		Full	Uncontrolled	0.22 lb/1000 gal fuel	E
		Cruise	Uncontrolled	0.54 lb/1000 gal fuel	E
		Slow	Uncontrolled	0.60 lb/1000 gal fuel	E
		500-1000 hp			
		Full	Uncontrolled	0.25 lb/1000 gal fuel	E
		Cruise	Uncontrolled	0.18 lb/1000 gal fuel	E
		Slow	Uncontrolled	0.18 lb/1000 gal fuel	E
		1000-1500 hp			
		Full	Uncontrolled	0.25 lb/1000 gal fuel	E
		Cruise	Uncontrolled	0.25 lb/1000 gal fuel	E
		Slow	Uncontrolled	0.25 lb/1000 gal fuel	E
		1500-2000 hp			
		Full	Uncontrolled	0.18 lb/1000 gal fuel	E
		Cruise	Uncontrolled	0.25 lb/1000 gal fuel	E
		Slow	Uncontrolled	0.25 lb/1000 gal fuel	E
		2000 + hp			
		Full	Uncontrolled	0.23 lb/1000 gal fuel	E
		Cruise	Uncontrolled	0.18 lb/1000 gal fuel	E
		Slow	Uncontrolled	0.24 lb/1000 gal fuel	E
		Gasoline Engines - all hp ratings			
		Exhaust (g/bhp-hr)	Uncontrolled	0.35 lb/1000 gal fuel	E
		Evaporative (g/hr)	Uncontrolled	0.64 lb/1000 gal fuel	E
A22-85-002-005	Line Haul Locomotive		Uncontrolled	0.00022 lb/gal	U
A22-85-002-010	Yard Locomotive		Uncontrolled	0.00054 lb/gal	U

(continued)

TABLE A-1. CONTINUED

SCC/AMS Code	Description	Emission Source	Control Device	Emission Factor	Factor Rating
28-10-040-000	Rocket Engines	Booster rocket engines using RP-1 (kerosene) and liquid oxygen as fuel	Uncontrolled	0.431 lb/ton (0.215 kg/Mg)	C

[a] Data are for a hypothetical plant using 50 percent naphtha/50 percent gas oil as feed and having an ethylene capacity of 1,199,743 lb/yr (544.2 Gg/yr).

[b] Intermittent emissions have been reported from the activation of pressure relief devices and the depressurization and purging of equipment for maintenance purposes.

[c] Emission factors are for a model plant with capacity 661 million lbs (300 million kg) per year. Actual emission factors may vary with throughput and control measures and should be determined through direct contacts with plant personnel. Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylbenzene/styrene produced.[1]

[d] Includes the following vents: benzene drying column, benzene recovery column, and ethylbenzene recovery column.

[e] Includes the following vents: polyethylbenzene recovery column at ethylbenzene plants; and benzene recycle column and styrene purification vents at styrene plants.

[f] Measured at post oxidizer condenser vent.

[g] Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility. All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in this table are based on the factors given in Section 4.5.2.

[h] These emission factors are based on a hypothetical plant producing 74,956 tons (68 Gg) monochlorobenzene, 13,669 tons (12.4 Gg) o-dichlorobenzene, and 17,196 tons (15.6 Gg) p-dichlorobenzene. The reader is urged to contact a specific plant as to process, products made, and control techniques used before applying these emission factors.

[i] Includes the following vents: benzene dry distillation, heavy ends processing, and monochlorobenzene distillation.

[j] Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant using the Olefin Process.

[k] Emission factor estimates based on a 198 million lb/yr (90,000 Mg/yr) hypothetical plant using the Chlorination Process.

[l] Includes dissolved air flotation (DAF) or induced air flotation (IAF) systems.

[m] The liquid injection incinerator has a built-in afterburner chamber.

[n] The incinerators tested had the following control devices: venturi, packed, and ionized scrubbers; carbon bed filters; and HEPA filters.

[o] Emission factor is based on the detection limit because no benzene was detected above the detector limit.

[p] Based on a 2.2 meter belt filter press dewatering oil/water separator bottoms, DAF float, and biological sludges at an average temperature of 125°F.[2]

"--" = Data not available.

(continued)

TABLE A-1. CONTINUED

REFERENCES

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2. Research Triangle Institute. *Summary Report TSDF Dewatering Organic Air Emission Factors*. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, May 1991.

(continued)

APPENDIX B

UNITED STATES PETROLEUM REFINERIES: LOCATION BY STATE

TABLE B-1. UNITED STATES PETROLEUM REFINERIES: LOCATION BY STATE

State	Company	Location
ALABAMA	Coastal Mobil Refining Co.	Mobile Bay
ALABAMA	Gamxx Energy, Inc.	Theodore
ALABAMA	Hunt Refining Co.	Tuscaloosa
ALABAMA	Louisiana Land & Exploration Co.	Saraland
ALASKA	ARCO	Kuparuk
ALASKA	ARCO	Prudhoe Bay
ALASKA	Mapco Alaska Petroleum	North Pole
ALASKA	Petro Star Inc.	North Pole
ALASKA	Tesoro Petroleum Corp.	Kenai
ARIZONA	Intermountain Refining CI	Fredonia
ARIZONA	Sunbelt Refining Co.	Randolph
ARKANSAS	Berry Petroleum Co.	Stevens
ARKANSAS	Cross Oil & Refining Co. Inc.	Smackover
ARKANSAS	Lion Oil Co.	El Dorado
CALIFORNIA	Anchor Refining CI	McKittrick
CALIFORNIA	Atlantic Richfield Co.	Carson
CALIFORNIA	Chemoil Refining Corp.	Signal Hill
CALIFORNIA	Chevron USA Inc.	El Segundo
CALIFORNIA	Chevron USA Inc.	Richmond
CALIFORNIA	Conoco Inc.	Santa Maria
CALIFORNIA	Edgington Oil CI	Long Beach
CALIFORNIA	Exxon Co.	Benicia
CALIFORNIA	Fletcher Oil & Refining Co.	Carson
CALIFORNIA	Golden West Refining Co.	Santa Fe Springs
CALIFORNIA	Huntway Refining Co.	Benicia
CALIFORNIA	Huntway Refining Co.	Wilmington
CALIFORNIA	Kern Oil & Refining Co.	Bakersfield
CALIFORNIA	Lunday-Thagard Co.	South Gate
CALIFORNIA	Mobil Oil Corp.	Torrance
CALIFORNIA	Pacific Refining Co.	Hercules
CALIFORNIA	Paramount Petroleum Corp.	Paramount
CALIFORNIA	Powerine Oil Co.	Santa Fe Springs
CALIFORNIA	San Joaquin Refining CI	Bakersfield
CALIFORNIA	Shell Oil Co.	Martinez
CALIFORNIA	Shell Oil Co.	Wilmington (Carson)
CALIFORNIA	Sunland Refining Corp.	Bakersfield

TABLE B-1. UNITED STATE PETROLEUM REFINERIES: LOCATION BY STATE (CONTINUED)

State	Company	Location
CALIFORNIA	Ten By, Inc.	Oxnard
CALIFORNIA	Texaco Refining & Marketing Inc.	Bakersfield
CALIFORNIA	Texaco Refining & Marketing Inc.	Wilmington
CALIFORNIA	Tosco Corp.	Martinez
CALIFORNIA	Ultramar	Wilmington
CALIFORNIA	Unocal Corp.	Los Angeles
CALIFORNIA	Unocal Corp.	San Francisco (includes Santa Maria)
CALIFORNIA	Witco Chemical Corp, Golden Bear Div.	Oildale
COLORADO	Colorado Refining Co.	Commerce City
COLORADO	Conoco Inc.	Denver
COLORADO	Landmark Petroleum Inc.	Fruita
DELAWARE	Star Enterprise	Delaware City
GEORGIA	Amoco Oil Co.	Savannah
GEORGIA	Young Refining Corp.	Douglasville
HAWAII	Chevron USA Inc.	Barber's Point
HAWAII	Hawaiian Independent Refinery Inc.	Ewa Beach
ILLINOIS	Clark Oil & Refining Corp.	Blue Island
ILLINOIS	Clark Oil & Refining Corp.	Hartford
ILLINOIS	Indian Refining Co.	Lawrenceville
ILLINOIS	Marathon Oil Co.	Robinson
ILLINOIS	Mobil Oil Corp.	Joliet
ILLINOIS	Shell Oil Co.	Wood River
ILLINOIS	The UNO-VEN Co.	Lemont
INDIANA	Amoco Oil Co.	Whiting
INDIANA	Countrymark Cooperative, Inc.	Mt. Vernon
INDIANA	Laketon Refining Corp.	Laketon
INDIANA	Marathon Oil Co.	Indianapolis
KANSAS	Coastal Refining and Marketing Inc.	Augusta
KANSAS	Coastal Refining & Marketing Inc.	El Dorado
KANSAS	Coastal Refining & Marketing Inc.	Wichita
KANSAS	Farmland Industries Inc.	Coffeyville
KANSAS	Farmland Industries Inc.	Phillipsburg
KANSAS	National Cooperative Refinery Association	McPherson
KANSAS	Texaco Refining & Marketing Inc.	El Dorado

TABLE B-1. UNITED STATE PETROLEUM REFINERIES: LOCATION BY STATE (CONTINUED)

State	Company	Location
KANSAS	Total Petroleum Inc.	Arkansas City
KENTUCKY	Ashland Petroleum Co.	Catlettsburg
KENTUCKY	Somerset Refinery Inc.	Somerset
LOUISIANA	American International Refining, Inc.	Lake Charles
LOUISIANA	Atlas Processing Co. Div. of Pennzoil	Shreveport
LOUISIANA	BP Oil Co.	Belle Chasse
LOUISIANA	Calcasieu Refining Co.	Lake Charles
LOUISIANA	Calumet Lubricants Co.	Princeton
LOUISIANA	Canal Refining Co.	Church Point
LOUISIANA	CAS Refining, Inc.	Mermentau
LOUISIANA	Citgo Petroleum Corp.	Lake Charles
LOUISIANA	Conoco Inc.	Lake Charles
LOUISIANA	Exxon Co.	Baton Rouge
LOUISIANA	Kerr McGee Refining Corp.	Cotton Valley
LOUISIANA	Marathon Oil Co.	Garyville
LOUISIANA	Mobil Oil Corp.	Chalmette
LOUISIANA	Murphy Oil USA Inc.	Meraux
LOUISIANA	Phibro Refining Inc.	Krotz Springs
LOUISIANA	Phibro Refining Inc.	St. Rose
LOUISIANA	Placid Refining Co.	Port Allen
LOUISIANA	Shell Oil Co.	Norco
LOUISIANA	Star Enterprise	Convent
MICHIGAN	Crystal Refining Co.	Carson City
MICHIGAN	Lakeside Refining Co.	Kalamazoo
MICHIGAN	Marathon Oil Co.	Detroit
MICHIGAN	Total Petroleum Inc.	Alma
MINNESOTA	Ashland Petroleum Co.	St. Paul Park
MINNESOTA	Koch Refining Co.	Rosemount
MISSISSIPPI	Amerada-Hess Corp.	Purvis
MISSISSIPPI	Chevron USA Inc.	Pascagoula
MISSISSIPPI	Ergon Refining Inc.	Vicksburg
MISSISSIPPI	Southland Oil Co.	Lumberton
MISSISSIPPI	Southland Oil Co.	Sandersville
MONTANA	Cenex	Laurel
MONTANA	Conoco Inc.	Billings

TABLE B-1. UNITED STATE PETROLEUM REFINERIES: LOCATION BY STATE (CONTINUED)

State	Company	Location
MONTANA	Exxon Co.	Billings
MONTANA	Montana Refining Co.	Great Falls
NEVADA	Petro Source Refining Partners	Tonopah
NEW JERSEY	Amerada-Hess Corp.	Port Reading
NEW JERSEY	Chevron USA Inc.	Perth Amboy
NEW JERSEY	Coastal Eagle Point Oil Co.	Westville
NEW JERSEY	Exxon Co.	Linden
NEW JERSEY	Mobil Oil Corp.	Paulsboro
NEW JERSEY	Seaview Petroleum Co. LP	Thorofare
NEW MEXICO	Bloomfield Refining Co.	Bloomfield
NEW MEXICO	Giant Industries Inc.	Gallup
NEW MEXICO	Navajo Refining Co.	Artesia
NEW MEXICO	Triftway Marketing Corp.	Farmington
NEW YORK	Cibro Petroleum Products Co.	Albany
NORTH DAKOTA	Amoco Oil Co.	Mandan
OHIO	Ashland Petroleum Co.	Canton
OHIO	BP Oil Co.	Lima
OHIO	BP Oil Co.	Toledo
OHIO	Sun Refining & Marketing Co.	Toledo
OKLAHOMA	Barrett Refining Corp.	Thomas
OKLAHOMA	Conoco Inc.	Ponca City
OKLAHOMA	Cyril Petrochemical Corp.	Cyril
OKLAHOMA	Kerr-McGee Refining Corp.	Wynnewood
OKLAHOMA	Sinclair Oil Corp.	Tulsa
OKLAHOMA	Sun Refining & Marketing Co.	Tulsa
OKLAHOMA	Total Petroleum Inc.	Ardmore
OREGON	Chevron USA Inc.	Portland
PENNSYLVANIA	BP Oil Co.	Marcus Hook
PENNSYLVANIA	Chevron USA Inc.	Philadelphia
PENNSYLVANIA	Pennzoil Products Co.	Rouseville
PENNSYLVANIA	Sun Refining & Marketing Co.	Marcus Hook
PENNSYLVANIA	Sun Refining & Marketing Co.	Philadelphia
PENNSYLVANIA	United Refining Co.	Warren
PENNSYLVANIA	Witco Chemical Co., Kendall-Amalie Div.	Bradford
TENNESSEE	Mapco Petroleum Inc.	Memphis

TABLE B-1. UNITED STATE PETROLEUM REFINERIES: LOCATION BY STATE (CONTINUED)

State	Company	Location
TEXAS	Amoco Oil Co.	Texas City
TEXAS	Chevron USA Inc.	El Paso
TEXAS	Chevron USA Inc.	Port Arthur
TEXAS	Citgo	Corpus Christi
TEXAS	Coastal Refining & Marketing Inc.	Corpus Christi
TEXAS	Crown Central Petroleum Corp.	Houston
TEXAS	Diamond Shamrock Corp.	Sunray
TEXAS	Diamond Shamrock Corp.	Three Rivers
TEXAS	El Paso Refining CL	El Paso
TEXAS	Exxon Co. USA	Baytown
TEXAS	Fina Oil & Chemical Co.	Big Spring
TEXAS	Fina Oil & Chemical Co.	Port Arthur
TEXAS	Howell Hydrocarbons Inc.	San Antonio
TEXAS	Koch Refining Co.	Corpus Christi
TEXAS	LaGloria Oil & Gas Co.	Tyler
TEXAS	Leal Petroleum Corp.	Nixon
TEXAS	Liquid Energy Corp.	Bridgeport
TEXAS	Lyondell Petrochemical Co.	Houston
TEXAS	Marathon Oil Co.	Texas City
TEXAS	Mobil Oil Corp.	Beaumont
TEXAS	Phibro Refining Inc.	Houston
TEXAS	Phibro Refining Inc.	Texas City
TEXAS	Phillips 66 Co.	Borger
TEXAS	Phillips 66 Co.	Sweeny
TEXAS	Pride Refining Inc.	Abilene
TEXAS	Shell Oil Co.	Deer Park
TEXAS	Shell Oil Co.	Odessa
TEXAS	Southwestern Refining Co., Inc.	Corpus Christi
TEXAS	Star Enterprise	Port Arthur
TEXAS	Trifinery	Corpus Christi
TEXAS	Valero Refining Co.	Corpus Christi
UTAH	Amoco Oil Co.	Salt Lake City
UTAH	Big West Oil Co.	Salt Lake City
UTAH	Chevron USA	Salt Lake City
UTAH	Crysen Refining Inc.	Woods Cross

TABLE B-1. UNITED STATE PETROLEUM REFINERIES: LOCATION BY STATE (CONTINUED)

State	Company	Location
UTAH	Pennzoil Products Co.	Roosevelt
UTAH	Phillips 66 Co.	Woods Cross
VIRGINIA	Amoco Oil Co.	Yorktown
WASHINGTON	Atlantic Richfield Co.	Ferndale
WASHINGTON	BP Oil Co.	Ferndale
WASHINGTON	Chevron USA Inc.	Seattle
WASHINGTON	Shell Oil Co.	Anacortes
WASHINGTON	Sound Refining Inc.	Tacoma
WASHINGTON	Texaco Refining & Marketing Inc.	Anacortes
WASHINGTON	U.S. Oil & Refining Co.	Tacoma
WEST VIRGINIA	Phoenix Refining Co.	St. Mary's
WEST VIRGINIA	Quaker State Oil Refining Corp.	Newell
WISCONSIN	Murphy Oil USA Inc.	Superior
WYOMING	Frontier Oil & Refining Co.	Cheyenne
WYOMING	Little America Refining Co.	Casper
WYOMING	Sinclair Oil Corp.	Sinclair
WYOMING	Wyoming Refining Co.	Newcastle

Source: 1/1/92 issue of *Oil and Gas Journal*

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR QUALITY PLANNING AND STANDARDS

Public Information and Clearance Record

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Clearance (check)

- ☐ Technical paper for presentation before scientific groups
- ☐ Speech
- ☐ Article for publication in scientific or technical journal
- ☐ Hearings and testimony before legislative, judicial, or administrative proceedings
- ☐ Training materials
- ☐ Motion picture, filmstrip or slide presentation
- ☐ Proposed *Federal Register* Notice
- ☐ Reports to Congress
- ☐ Questionnaire - Federal Reports Act
- ☐ Public statements of Agency position or policy
- ☐ Reprints, posters and related items
- X Other (specify below)

Date and place for presentation of material:

Describe briefly the nature and content of material. (Attach 2 copies of the material.)

Locating and Estimating Air Emissions from Sources of Benzene, EPA-454/R-98-011. This document assists groups interested in inventorying air emissions of Benzene. It presents information on (1) the types of sources that may emit Benzene; (2) process variations and release points for these sources; and (3) available emissions information indicating the potential for releases of Benzene into the air from each operation.

This volume is part of a widely used series of documents.

Clearance Signatures:

Group Leader: David Misenheimer ____________ Date: ____________

Division Director: William F. Hunt, Jr. ____________ Date: ____________

Other (technical review): ____________ Date: ____________

Clearance Officer, OAQPS: Henry Thomas ____________ Date: ____________

Comments: This report has been reviewed within the EPA by personnel of the Emissions, Monitoring and Analysis Division, Emission Standards Division and Office of Mobile Sources. It has been externally reviewed by numerous industrial trade associations including the National Solid Waste Management Association, Electric Power Research Institute and the Chemical Manufacturers Association.

EPA(DUR)229 REV. 7/73

IMPLANTACIÓN DE UN PROGRAMA LDAR

Las emisiones de COV's pueden tener tres orígenes distintos, siendo éstos:

- Fuentes constantes: se agrupan aquellas que conllevan una emisión constante, como pueden ser los tanques de ventilación continua, balsas o sumideros. Dentro de esta clasificación podrían incluirse los focos de emisión de proceso (chimeneas y antorchas).

- Fuentes de equipos de proceso: bajo este nombre se designan las emisiones debidas a anomalías en el correcto funcionamiento de las Unidades, como pueden ser fugas en sellos de bombas, bridas, compresores, etc.

- Fuentes puntuales y periódicas: la diferencia entre este tipo de fuente y la anterior radica principalmente en que en este caso las emisiones fugitivas son generadas por el propio desarrollo de un trabajo en condiciones normales (toma de muestras, drenajes de botellones, cargaderos u operaciones de mantenimiento).

La implantación de un programa de detección y reparación de fugas (LDAR) repercute por un lado en la reducción de la emisión de Compuestos Orgánicos Volátiles (COV) procedentes de los diferentes equipos de las Unidades de proceso y por otro lado, en los beneficios económicos derivados de la reducción de pérdidas de producto y de la mejora en el rendimiento general de los procesos productivos.

El programa LDAR está destinado a la detección y progresiva reducción de las emisiones gaseosas (COV) de carácter difuso que tienen su origen en las pérdidas que se producen en los diferentes elementos que componen las Unidades de proceso (bombas, válvulas, compresores, bridas, etc.).

Las etapas de que consta un programa LDAR son:

- Se identifican en la planta los equipos que fugan utilizando para ello el Método 21 de la EPA (establece no sólo el método a emplear para llevar a cabo las mediciones en campo sino que define las características de los elementos a emplear y el método de calibración de los mismos).

- Se procede a la medición en los equipos identificados mediante el uso de detectores de ionización, ya sean tipo FID (ionización de llama) o PID (fotoionización).

- En los equipos que emiten más de cierto valor (típicamente 10.000 ppm) se intenta corregir la fuga.

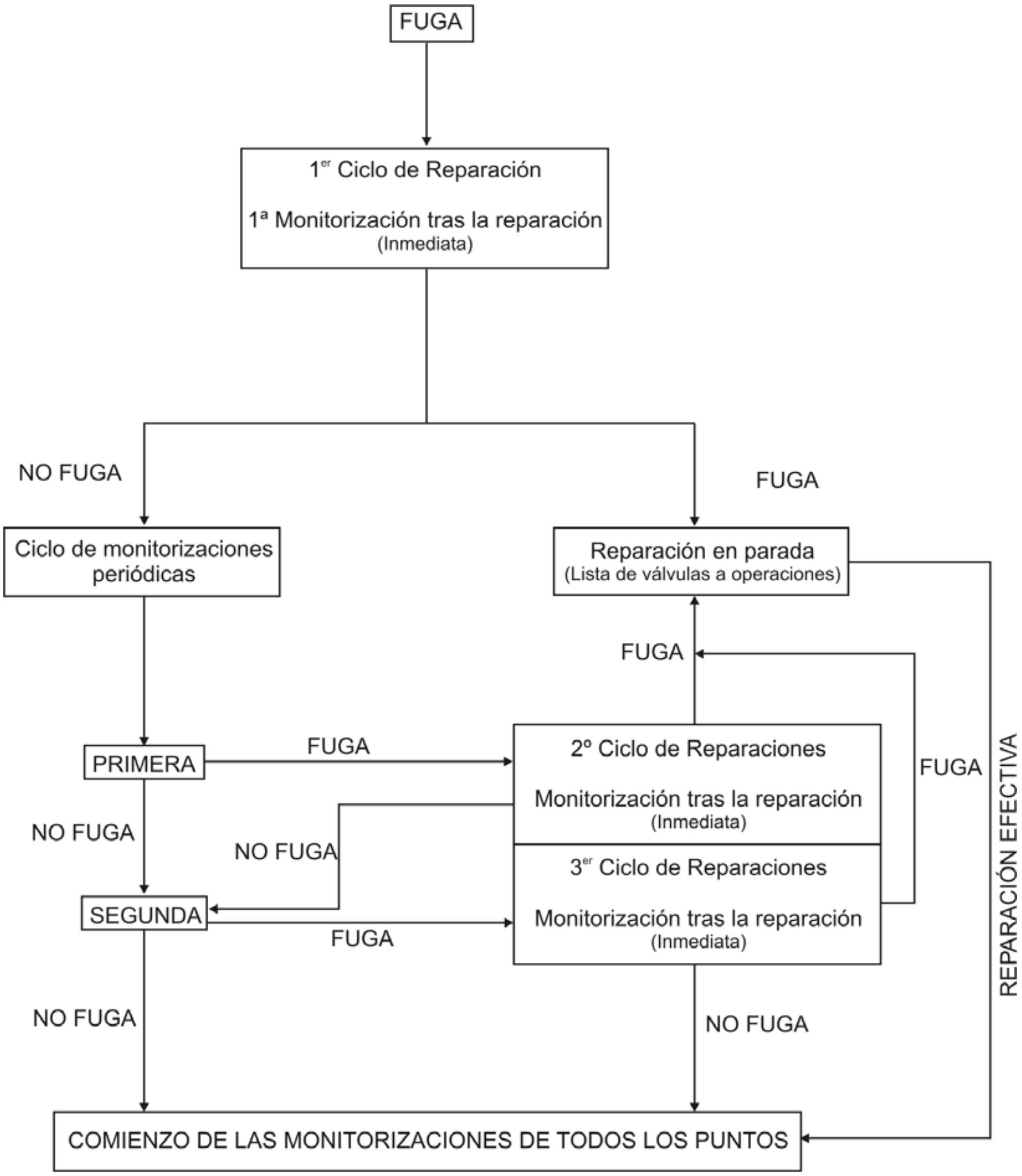
- Se establecen los plazos para llevar a cabo el ajuste, reparación o sustitución del elemento con fuga. Los plazos se fijan en función de las características del elemento o equipo, de la magnitud de la fuga y sin afectar al funcionamiento normal de la

Planta. Con estos criterios se fija un programa de reinserción de los elementos o equipos reparados, así como un calendario de seguimiento.

- En una segunda fase, se repetiría todo el proceso estableciendo nuevos valores de fuga.

El desarrollo de un programa LDAR suele llevarse a cabo con la ayuda de una herramienta informática que sirva de base de datos y permita el conocimiento sobre el estado de cada equipo en cada etapa del programa. Finalmente, se presenta de forma simplificada el diagrama de bloques típico que resume la implantación de uno de estos sistemas.

ESQUEMA IMPLANTACIÓN DEL SISTEMA LDAR



METHOD 21 - DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application.

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC)	No CAS number assigned

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method.

2.1 A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions.

3.1 *Calibration gas* means the VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a known concentration approximately equal to the leak definition concentration.

3.2 *Calibration precision* means the degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

3.3 *Leak definition concentration* means the local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

3.5 *Reference compound* means the VOC species selected as the instrument calibration basis for specification of the leak definition concentration. (For example, if a leak definition concentration is 10,000 ppm as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument meter calibrated with methane would be classified as a leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

3.7 *Response time* means the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

4.0 Interferences. [Reserved]

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in Section 16.0.

6.0 Equipment and Supplies.

A VOC monitoring instrument meeting the following specifications is required:

6.1 The VOC instrument detector shall respond to the compounds being processed. Detector types that may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

6.2 The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension for sampling not to exceed 6.4 mm (1/4 in) in outside diameter, with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards.

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport.

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1-3 of Section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to Section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I - Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange.

Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II - "No Detectable Emission". Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in Section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in Section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in Section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of Section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of Section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control.

Section	Quality Control Measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard
10.0	Instrument calibration	

10.0 Calibration and Standardization.

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures. [Reserved]

12.0 Data Analyses and Calculations. [Reserved]

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References.

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81051. September 1981.

2. Brown, G.E., *et al*. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81-022. May 1981.

3. DuBose, D.A. *et al*. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental

Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81-110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data.

[Reserved]

BROMODIFENILÉTERES (PBDE)

Los difenileteres (poli)bromados (PBDEs) son un grupo de productos químicos con propiedades similares que se utilizan como mezclas en aplicaciones industriales. Representan en total 209 productos químicos individuales (“congéneres”) dentro de la familia de los PBDEs. Se pueden distinguir tres tipos principales, dependiendo del número de átomos de bromo presentes en cada molécula: Penta-BDE (5 átomos de bromo), Octa-BDE (8 átomos de bromo) y Deca-BDE (10 átomos de bromo). Estas tres sustancias son los únicos PBDEs disponibles comercialmente. El pentabromodifenileter (Penta-BDE) es por sí mismo una mezcla de sustancias relacionadas, que contiene de cuatro a seis átomos de bromo por molécula. El grado comercial se presenta como un líquido denso aceitoso y espeso de color ámbar o como un semisólido que se descompone al calentarse por encima de 200 ºC. Es completamente no inflamable y se utiliza como un retardante de la llama. Es insoluble en agua pero miscible con aceite de parafina y otros disolventes orgánicos. Casi siempre es completamente no volátil.

1. Producción y usos

En 1994 eran ocho los fabricantes de PBDE: Dead Sea Bromines/Eurobrome (Holanda), Atochem (Francia), Ethyl Corporation (USA), Great Lakes Chemical Corporation (USA), Tosoh (Japón), Matsunaga (Japón), Nippo (Japón), Great Lakes Chemical Ltd. (Reino Unido).

El consumo anual mundial de PBDE es de 40.000 t (Arias, 1992). Las cifras de producción e importación para la Comunidad Económica Europea se muestran en el siguiente cuadro:

	1986	**1987**	**1988**	**1989**
Producción	4.276	3.624	4.066	3.843
Importación	4.310	3.492	4.955	7.103
Total	**8.586**	**7.116**	**9.021**	**10. 946**

Debido a la significativa reducción del peligro de incendios causado por el uso de PBDE en numerosas aplicaciones, el consumo del mismo se ha incrementado notablemente en los últimos años.

El penta-BDE se utiliza principalmente como retardante de la llama en espuma de poliuretano flexible para muebles y tapizados en los EEUU y, en menor medida, en plásticos rígidos y adhesivos y puede representar hasta el 10 % en peso del producto acabado. La fabricación de penta-BDE en la UE cesó en 1997 y los porcentajes de utilización se han venido reduciendo constantemente en la última década. Los Octa-BDE y los Deca-BDE se utilizan junto con trióxido de antimonio como retardantes de la llama en plásticos rígidos utilizados en el sector del automóvil y en productos de consumo tales como aparatos eléctricos. En la Unión Europea está prohibida la comercialización y el uso de Penta-BDE y de Octa-BDE en todas las aplicaciones, con carácter efectivo, a partir del 15 de agosto de 2004.

2. Fuentes de emisión

Los PBDEs pueden liberarse en el medio ambiente durante la fabricación del propio producto químico, al incorporarlo en productos plásticos (en su mayor parte espuma de poliuretano), durante el procesamiento de la espuma en artículos acabados, durante la propia vida del artículo y, por último, al eliminarlos en vertederos o por incineración. En términos generales sólo se liberan pequeñas cantidades de la sustancia debido a su muy baja volatilidad y escasa solubilidad en el agua. El polvo producido a partir de los productos de espuma representa usualmente la forma principal de liberación de estos productos. El Penta-BDE se ha medido también en tejidos animales, aguas y sedimentos lejos de las fuentes de emisión, por lo que preocupa el posible impacto global de las emisiones.

La exposición excesiva a penta-BDE puede afectar al hígado de las personas. El penta-BDE es altamente tóxico para los animales acuáticos y puede producir efectos adversos a largo plazo para el medio acuático. El penta-BDE es altamente resistente y bioacumulativo. Se han comunicado efectos sobre el crecimiento y reproducción de animales acuáticos. La toxicidad acuática y el potencial de bioacumulación de los PBDEs se reduce a medida que aumenta el bromado, por lo que se considera poco probable que el Deca-PBDE presente efectos tóxicos para los invertebrados a concentraciones por debajo de su límite de solubilidad. Los PBDEs pueden descomponerse en caso de incendio generando productos químicos bromados altamente tóxicos. Los PBDEs figuran como sustancias prioritarias, y el Penta-BDE incluso como una sustancia peligrosa prioritaria según la Directiva Marco del Agua. Los Penta-, Octa- y Deca-BDE son todos ellos sustancias prioritarias según el Reglamento (CE) 793/93.

3. Referencias

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DDT (e isómeros)

El DDT es un insecticida de alta persistencia. El nombre químico del DDT es: 1,1,1-tricoloro-2, 2-bis (4-clorofenil) etano. Su fórmula es: $C_{14}H_9Cl_5$.

El DDT a temperatura ambiente es un sólido cristalino, blanco y casi inodoro. Es prácticamente insoluble en agua y muy soluble en disolventes orgánicos apolares. Su punto de fusión varía en torno a los 109 ºC y el punto de ebullición es 185 ºC.

Normalmente el término DDT se asigna al compuesto para,para'-DDT, el cual se produce y usa por sus propiedades como insecticida. Sin embargo, el DDT es un grupo de 14 compuestos químicos en el que un 65-80% es el compuesto activo para,para'-DDT y el resto son compuestos como el orto,para-DDT, el para,para'-TDE y el orto,para-DDE, entre otros.

El DDT es resistente a la luz y a su oxidación. El isómero para,para'-DDT se desclora a temperaturas por encima de su punto de fusión, dando como producto el DDE, que no tiene propiedades insecticidas. Esta reacción se cataliza con Fe^{3+} o con cloruro de aluminio, luz ultravioleta y en soluciones alcalinas; de aquí se deduce que el DDT no se debe almacenar en contenedores de hierro ni mezclarse con sales de hierro y aluminio o con soluciones alcalinas. Las temperaturas elevadas también deben evitarse.

1. Producción y usos

El DDT (mezcla de 14 compuestos) se obtiene por la condensación del ácido clorhídrico con clorobenceno en ácido sulfúrico concentrado.

Se sintetizó por primera vez en 1874, pero hasta 1939 no se descubrieron sus propiedades insecticidas.

El DDT es un insecticida de amplio espectro que fue muy popular debido a su efectividad, su persistencia y su bajo coste. El DDT empezó a usarse como insecticida en 1939 y se usó ampliamente hasta 1970, siendo prohibido posteriormente. Durante la segunda guerra mundial, se empleó para controlar la malaria, el tifus y otras enfermedades transmitidas por insectos. El DDT también se ha empleado en la agricultura para el control de insectos. También se ha usado como pesticida en bosques. En las casas se ha empleado como un agente antipolillas y para controlar los piojos. En regiones donde la malaria es endémica, se fumiga con DDT el interior de las superficies de las casas con el fin de controlar los mosquitos, para los cuales el DDT también es irritante y repelente.

2. Fuentes de emisión

La aplicación del DDT es la principal fuente de contaminación del suelo. De ésta ya se deriva la contaminación de aguas y atmósfera por arrastre de partículas y volatilización principalmente.

El DDT y sus productos de degradación son semivolátiles, por tanto tienen la capacidad e transportarse por aire, tanto en fase gaseosa como adsorbidos en las partículas que podrán depositarse vía seca o vía húmeda.

El DDT depositado en el suelo o en el agua se volatilizaría y en la atmósfera el insecticida adherido a partículas o en fase gaseosa se movería con las corrientes de aire hasta ser depositado por acción de la lluvia o por el peso de las partículas.

Además de mediante la deposición de partículas atmosféricas, el DDT también puede llegar al agua por derrames accidentales, por aplicación directa o por arrastre de partículas del suelo donde está adsorbido. Dada su baja solubilidad en agua y su elevada afinidad con las partículas del suelo, la sedimentación es el principal mecanismo por el que el DDT no se dispersa en el agua. La volatilidad disminuye en presencia de sedimentos. En soluciones acuosas puede sufrir fotólisis, en grado apreciable sólo en presencia de ciertas sustancias. La biodegradación en condiciones anaeróbicas puede ser importante tanto en el agua como en el suelo, incrementándose la cinética con el contenido en materia orgánica del suelo. La degradación aeróbica en el suelo es mucho más lenta.

3. Referencias

- IPCS INCHEM International Programme on Chemical Safety Poisons Information monograph 127. Chemical. DDT. Febrero 1990.

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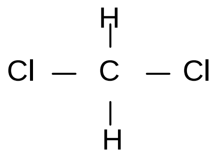
DICLOROMETANO (DCM)

El diclorometano es un hidrocarburo halogenado, alifático y saturado. Se trata de un líquido volátil incoloro con la siguiente estructura molecular:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ Cl & — & C & — & Cl \\ & & | & & \\ & & H & & \end{array}$$

El diclorometano se emite a la atmósfera durante su producción y uso. Según la EPA, el diclorometano puede considerarse excluido de las regulaciones sobre compuestos volátiles en cuanto a la formación de ozono. Sin embargo, se encuentra en la lista de los 189 HAP's (Hazardous air pollutants).

Para estimar la peligrosidad del diclorometano en cuanto a sus efectos en la salud humana, Australian National Pollutant Inventory (ANPI) propone el uso de una escala de 0-3, donde una puntuación de 3 representa un compuesto muy peligroso, una puntuación de 2 representa un compuesto peligroso y una puntuación de 1 representa un compuesto nocivo para la salud humana. En este sentido el diclorometano cuenta con una puntuación de 1,5.

Por otra parte, según RCRA (Resource Conservation and Recovery Act) el diclorometano debe ser tratado como residuo peligroso para la salud humana por sus efectos cancerígenos y neurotóxicos.

1. Producción y usos

La producción mundial del diclorometano ha descendido en los últimos años debido fundamentalmente a factores ambientales y de salud.

Los usos del diclorometano incluyen:

- ingrediente activo para disolventes de pinturas
- fabricación de resinas policarbonadas
- producción de triacetato de celulosa
- agente auxiliar para el moldeo de espumas
- soporte para recubrimientos de comprimidos farmacéuticos
- disolvente para procesos de limpieza de metales
- disolvente para aerosoles
- fabricación de paneles para circuitos electrónicos
- compuesto inerte en pesticidas
- agente de extracción en la recuperación de oleo-resinas, aceites, grasas y ceras

2. Fuentes de emisión

Todas las fuentes de emisión del diclorometano son antropogénicas; el diclorometano no se produce de forma natural.

2.1 Emisiones derivadas de la producción de diclorometano

El diclorometano se produce mediante dos procesos: cloración directa del metano para obtener cloruro de metilo o mediante hidrocloración del metanol para conseguir igualmente cloruro de metilo. El cloruro de metilo producto de ambos procesos se trata posteriormente con cloro para obtener diclorometano.

El diclorometano se almacena generalmente en tanques exteriores y se distribuye mediante camiones cisterna, barcos, ferrocarril, etc. El equipamiento para su producción incluye tanques de almacenamiento, reactores, columnas de destilación, scrubbers y torres de secado.

Las fuentes de emisión consideradas para el caso de la producción de diclorometano incluye:

- fugas en equipos
- tanques de almacenamiento
- emisiones en operaciones de transferencia del compuesto (carga/descarga)
- venteo de alivio
- apertura de equipos
- emisiones secundarias (por ejemplo, tratamiento de aguas residuales)

Debido a que el equipamiento para la producción de diclorometano es exterior, las pérdidas de diclorometano generalmente se dispersan directamente en la atmósfera.

2.2 Emisiones derivadas del uso del diclorometano

Los principales usos industriales del diclorometano incluyen la producción de disolventes de pinturas, plásticos, espumas de poliuretano, industria farmacéutica, desengrasantes y producción de aerosoles.

Otras aplicaciones secundarias son la producción de pesticidas y el procesado de películas fotográficas.

a) Producción y uso de disolventes de pinturas

Las emisiones consideradas contemplan tanto la formulación de disolventes de pinturas como su uso.

Las fuentes de emisión derivadas de la formulación de disolventes incluyen almacenamiento, manipulación, fugas de equipos y fuentes secundarias (asociadas a la eliminación de aguas residuales principalmente).

En cuanto al uso de disolventes de pinturas, las industriales emplean este tipo de compuestos principalmente para procesos de eliminación de pinturas de automóviles, aviones y mobiliario comercial, procesos de limpieza de suelos y paredes, etc.

En ese sentido, las fuentes de emisión son clasificadas conforme a tres categorías:

- aperturas de los edificios en general (puertas, ventanas, etc.) donde se efectúa el uso del disolvente
- procesos de purga de disolvente en procesos concretos de limpieza
- almacenamiento exterior del disolvente

Los datos referentes a emisiones en cuanto a la formulación del diclorometano como disolvente están definidos, no así para la cuantificación de las emisiones derivadas del uso de dicho disolvente.

b) Fabricación de plásticos

El diclorometano se emplea en la fabricación de resinas policarbonadas, fibras triacetato y otros plásticos.

- RESINAS POLICARBONADAS

  Las emisiones derivadas de la fabricación de resinas policarbonadas provienen de las operaciones de venteo, fugas en equipos, almacenamiento, manipulación, aperturas de equipos y fuentes secundarias de emisión.

  Entre estas fuentes secundarias se encuentra por ejemplo los efluentes de aguas residuales.

- FIBRA TRIACETATO

  El diclorometano se emplea como solvente en procesos de hilado de fibras de triacetato. Las fuentes de emisión en este caso se derivan de los procedimientos de almacenamiento, carga/descarga y fugas en equipos. Sin embargo, no se cuenta con datos referentes a la cantidad de diclorometano emitido para este uso concreto.

- OTROS PLÁSTICOS

  En 1983 la factoría de General Electric en Pittsfield (Massachusetts, EEUU) informó sobre el uso de diclorometano en operaciones de fabricación de plásticos. Sin embargo, la información concerniente a la descripción del proceso de fabricación y a los productos finales obtenidos fue considerada como confidencial y por tanto no se dispone de documentación.

Las emisiones consideradas proceden fundamentalmente de purgas y fugas así como de tanques de almacenamiento.

Otras fuentes secundarias a tener en cuenta son las corrientes de aguas residuales de la planta.

c) Producción de espumas flexibles de uretano

El diclorometano es el agente más empleado para la formulación de espumas flexibles de uretano.

Las fuentes primarias de emisión en la producción de espumas incluyen procesos de purga, fugas en equipos y tanques de almacenamiento.

El uso del diclorometano para este fin se ha visto incrementado en un 20% desde 1984 debido fundamentalmente a su uso como sustituto del clorofluorcarbono-11 en este proceso de fabricación.

d) Industria farmacéutica

La industria farmacéutica consume aproximadamente 11% del total de diclorometano producido. Se emplea como disolvente general y agente de extracción .

Las fuentes de emisión derivadas de su uso en los procesos de síntesis proceden de los procesos de secado, purificación, separación, reacción, operaciones de carga/descarga y almacenamiento. En general, las fuentes de emisión más significativas provienen de los secadores, reactores, sistemas de destilación y los sistemas de almacenamiento y transferencia (carga/descarga).

En cuanto al diclorometano emitido respecto a su empleo como recubrimiento de comprimidos, la mayoría de las emisiones corresponden a los procesos de purga, almacenamiento, operaciones de transferencia y emisiones fugitivas.

e) Procesos de limpieza

El diclorometano se emplea como disolvente en determinados procesos de limpieza tales como los previos a la aplicación de pinturas, reparación, ensamblaje, tratamientos con aplicación de calor. Las industrias que utilizan el diclorometano con este fin incluyen la producción de objetos metálicos, equipamiento eléctrico y electrónico, automóviles, herramientas de reparación, etc.

Las fuentes de emisión consideradas en este caso se derivan de emisiones fugitivas, almacenamiento y manipulación, operaciones de carga/descarga, destilaciones, descomposición del disolvente, efluentes de aguas residuales.

f) Envasado de aerosoles

Un aerosol es una suspensión de sólidos o partículas líquidas en un gas bifásico: fase líquida-vapor. En el envase de aerosol, se requiere un líquido propulsor que mantenga la presión constante dentro del recipiente, a medida que el producto se vaya consumiendo.

En este sentido, el diclorometano actúa por un lado como disolvente y portador del ingrediente activo y por otro lado como supresor de la presión de vapor del propulsor. Con ello se consigue disminuir la tendencia a la combustión y mejorar la dispersión del spray

Las emisiones consideradas en el caso de aerosoles provienen del proceso de envasado y dispersión del aerosol así como de su uso.

Durante el proceso de envasado, las emisiones de diclorometano pueden ocurrir durante su almacenamiento y manipulación, procedentes de fugas en equipos, efluentes de aguas residuales y emisiones accidentales.

g) Otros

Aproximadamente el 5% del total de diclorometano producido se emplea para distintos usos a los mencionados. Los usos incluyen la producción de pesticidas y procesado de películas fotográficas principalmente. Otras aplicaciones son el procesado de comida, cauchos, tintes, tratamiento de residuos sólidos.

- PRODUCCIÓN DE PESTICIDAS

  El diclorometano tiene varias aplicaciones en la fabricación de pesticidas, incluyendo su uso en los procesos de extracción, separación, purificación y cristalización. Sin embargo el empleo de diclorometano en la producción de pesticidas tiende a disminuir debido fundamentalmente al perjuicio que supone su uso para la salud humana.

  Las emisiones procedentes de la producción de pesticidas incluyen partículas, gases y vapores que emanan de los equipos en cada una de las etapas de fabricación.

- FABRICACIÓN DE PELÍCULAS FOTOGRÁFICAS

  El diclorometano es un componente clave para la fabricación de las películas fotográficas de celulosa. Se emplea para disolver los pellets de triacetato con el objeto de conseguir una capa fina y transparente, que se enrolla sobre papel fotográfico.

Las emisiones procedentes de la fabricación de películas fotográficas resultan de las tres fases básicas de producción: preparación, recubrimiento y destilación o reciclaje.

3. Referencias

- "Locating and estimating air emissions from sources of methylene chloride". Febrero 1993. Environmental Protection Agency (EPA).

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HEXAFLUORURO DE AZUFRE (SF_6)

El hexafluoruro de azufre (SF_6) es químicamente inerte, gaseoso incluso a bajas temperaturas, no inflamable, no tóxico y no corrosivo. Su composición química le proporciona numerosas ventajas debido a sus propiedades térmicas y eléctricas.

1. Producción y usos

El SF_6 fue fabricado por primera vez en 1902. Comercialmente, ha estado disponible desde 1948 como AccuDri SF_6 (AlliedSignal Inc.). Actualmente se produce en los EEUU, Alemania, Italia, Japón y Rusia.

La producción de gas SF_6 consiste básicamente en un proceso de cuatro etapas principales, a saber:

1. Producción de flúor gaseoso por procesos electrolíticos.

2. Fluoración del azufre para producir el gas SF_6.

3. Purificación del SF_6 donde todos los subproductos y demás impurezas son lavados a través de varias operaciones unitarias.

4. Condensación y recuperación del producto.

El SF_6 permite un diseño simplificado de interruptores eléctricos de medio y alto voltaje debido a la reducción de tamaño y peso, y al mantenimiento y manejo sencillo y fiable de estos. Propiedades excepcionales son su intensidad e inalterable constante dieléctrica comprendida entre 1 Hz hasta varios GHz así como sus propiedades para detener y prevenir la formación de arcos eléctricos.

Además, su alta capacidad térmica y su baja viscosidad le confieren una alta efectividad en la transferencia de calor.

La mezcla SF_6/O_2 de muy alta pureza se utiliza principalmente como gas de alimentación para el proceso de ataque químico empleado durante la fabricación de determinados semiconductores.

El SF_6 se emplea además en varias aplicaciones no eléctricas ni electrónicas. En procesos desarrollados para la fundición de magnesio en el que una atmósfera protectora de SF_6 previene la formación de productos indeseables. Otras aplicaciones son aquellas que emplean la mezcla N_2/SF_6 en la fundición de aluminio como agente desgasificante y en su refino.

Varias aplicaciones secundarias son su uso como sustancia trazadora de escapes, altavoces y láser.

2. Fuentes de emisión

En la Tabla 1 se muestran las principales fuentes de emisión de SF_6.

Las fuentes de emisión asociadas al proceso de producción de SF_6 suponen aproximadamente el 0,2% del total producido. Las emisiones proceden fundamentalmente de emisiones fugitivas durante la producción y distribución del compuesto.

Dentro del sector de la metalurgia, y principalmente en las industrias del aluminio, magnesio, acero y ferroaleaciones, el SF_6 es empleado para productos especiales de fundición. Dentro de estas industrias, se contabilizan además las emisiones de tetrafluoruro de carbono y hexafluoruro de carbono originadas en la producción de los ánodos durante la operación de las células electrolíticas. La determinación de las emisiones será función de la tecnología empleada.

Por otro lado se consideran los usos primarios del SF_6 en conmutadores eléctricos con aislamiento de gas e interruptores automáticos, extinción de incendios y protección contra explosivos así como medio aislante, sustancia trazadora de escapes y diferentes aplicaciones electrónicas.

En 1995 se emitieron en España 6.045 kilos de SF_6, 118.420 toneladas de CO_2 equivalente, y en 2000 las emisiones aumentaron hasta llegar a 245.700 toneladas de CO_2 equivalente. En este sentido las emisiones en 2000 representaron el 0,06 % de las emisiones totales brutas de gases invernadero en España, sin incluir sumideros.

TABLA 1
PRINCIPALES FUENTES DE EMISIÓN DE SF_6

Fuentes que emiten SF_6
Fabricación de equipos eléctricos
Uso de equipos eléctricos
Industria del magnesio
Fabricación de semiconductores
Aplicaciones por sus propiedades adiabáticas (uso en neumáticos de coches, suelas de zapatillas deportivas, etc.)
Usos varios(aislamiento de ventanas, desgasificación de aluminio.)

3. Referencias

- “Fluorine compounds, Inorganic, Sulphur” Francis E. Evans, Ganpat Mani, AlliedSignal Inc. Diciembre 2000. Kirk-Othmer Encyclopedia of Chemical Technology.

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- "Reduction of the emissions of HFC´s, PFC´s and SF_6 in the European Union (commissioned by the European Commission)" H.Heijnes, M. van Brummelen, K. Blok. Abril 1999.

- “Ways and Means of Limiting Emissions for Hydrofluorocarbons and Perfluorocarbons”. Noviembre 1999. United Nations Framework Convention on Climate Change.

- "Standard EDGAR 3 source reporting categories". National Institute of Public Health and the Environment of Nederland. http://arch.rivm.nl/env/int/coredata/edgar/edgar32-src-grouping-cnt-tables.doc

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HIDROCLOROFLUOROCARBUROS (HCFC)

Existe una gran variedad de hidroclorofuorocarburos (HCFC), pero de forma general los HCFC de bajo peso molecular se caracterizan por tener alta presión de vapor, densidad e índice de refracción y una baja viscosidad y tensión de vapor. En condiciones normales de presión y temperatura pueden ser gases inflamables o no inflamables, o líquidos volátiles no inflamables. Son incoloros y la mayoría de ellos inodoros o con un ligero olor a éter. Presentan ligera o moderada solubilidad en agua y son miscibles con algunos disolventes orgánicos.

1. Producción y usos

Los HCFC se obtienen haciendo reaccionar ácido fluorhídrico anhidro con el correspondiente hidrocarburo clorado (según el número de átomos de carbono que vaya a tener el HCFC) en fase líquida y en presencia de un catalizador de haluro de antimonio. Este proceso se está reemplazando por un proceso en continuo en fase vapor, empleando ácido fluorhídrico anhidro y gaseoso en presencia de un catalizador de óxido de cromo o su haluro (cloruro férrico o tetrafluoruro de torio).

Los HCFC aparecieron como los sustitutos de los CFC por causar menos impacto en el agujero de la capa de ozono y en el efecto invernadero y también por tener tiempos de residencia menores.

Los principales usos son como: refrigerante, disolvente, aerosol, propelente de gases y fluido de intercambio térmico en aplicaciones energéticas geotérmicas. La aplicación del HCFC es función de su composición y, por tanto, de sus características físico-químicas.

2. Fuentes de emisión

La emisión de HCFC al medio ambiente se debe principalmente a reparaciones de equipos, su mantenimiento y fugas.

3. Referencias

- IPCS International Programme on Chemical Safety Environmental Health Criteria 126. Partially halogenated chlorofluorocarbons (methane derivatives). World Health Organization. Geneva 1991.

- IPCS International Programme on Chemical Safety. Environmental Health Criteria 139. Partially halogenated chlorofluorocabons (ethane derivatives). World Health Organization. Geneva 1992.

HIDROFLUOROCARBUROS (HFC)

Los hidrofluorocarburos son alcanos cuyos átomos de hidrógeno han sido parcialmente reemplazados por átomos de flúor.

Las propiedades físicas de los HFCs reflejan su carácter polar y la importancia del enlace intermolecular del hidrógeno. Así pues presentan altos índices de refracción y constantes dieléctricas así como elevadas tensiones superficiales.

1. Producción y usos

El proceso de producción de los HFCs consiste en la fluoración directa de hidrocarburos con flúor elemental. Este proceso es extraordinariamente exotérmico y difícilmente controlable. Se han desarrollado varios métodos de control que incluyen “jet reactors” y alta dilución; sin embargo estas técnicas no son aún satisfactorias.

Los hidrofluorocarburos se producen además a partir de acetileno u olefinas y fluoruro de hidrógeno, o clorocarburos y fluoruro de hidrógeno anhidro, en presencia de catalizadores.

La importancia de los HFCs radica en su amplia difusión como sustitutos de los clorofluorocarburos (CFCs) a partir de la imposición de restricción, salvo para aplicaciones de uso esencial, de la que fueron objeto. El empleo de CFCs fue prohibido fundamentalmente por sus efectos perjudiciales para la capa de ozono. Sin embargo, con el uso de HFCs, nocivos para la capa de ozono, nos enfrentamos a la problemática de su importancia como gases potenciadores del efecto invernadero.

Al igual que en el pasado se eliminaron los CFCs, actualmente se intenta suprimir la producción y uso de los HFCs mediante su sustitución por otro tipo de compuestos que no supongan un riesgo tan elevado en cuanto a su impacto ambiental.

a) Refrigeración y acondicionamiento de aire

Los HFCs se emplean como refrigerantes en aplicaciones domésticas, comerciales e industriales. Además se incluye su uso para la refrigeración en transportes, aires acondicionados comerciales y residenciales así como en sistemas de acondicionamiento de aire y bombas de calor.

b) Producción de espumas

Se estima que el mayor uso de HFCs en unos años será la producción de espumas, como molde y aislante. La mayoría de los fabricantes de espumas de poliuretano, poliisociuranato, polietileno y poliestireno XPS se basan hoy día en tecnologías de HCFC (hidroclorofluorocarburos). Tras la revisión de la normativa actual EU 3093/94 respecto a las sustancias perjudiciales para la capa de ozono, las industrias de producción de espumas se están viendo presionadas para sustituir estos HCFCs por compuestos HFCs.

c) Aerosoles / Inhaladores

El HFC-134a y HFC-227ae se emplean como propulsores para inhaladores utilizados en el tratamiento de ciertas enfermedades respiratorias como el asma.

Los HFCs se usan además en aerosoles como propulsores, para fines domésticos (desodorantes, cremas de afeitar, limpiadores) e industriales (lubricantes, sprays limpiadores específicos).

d) Extinción de incendios

Ciertos tipos de HFCs se emplean como sustituyentes del halón en los sistemas contraincendio. Se estima que el 20% de los actuales sistemas contraincendio emplean HFCs en lugar de halón; el resto de sistemas están basados en equipos de detección de humos y con base un gas inerte o agua.

e) Disolvente

El CFC-113 y el metil cloroformo han sido utilizados como disolventes para procesos de producción, operaciones de limpieza específicas y desengrasante de metales. Actualmente estos compuestos se han sustituido por un HFC alternativo (HCF-43-10mee).

f) Producción de HCFC-22

El HFC-23 se genera durante el proceso de producción de HCFC-22. El HFC-23 se separa del HCFC-22 y se emite a la atmósfera, generalmente como un residuo. En algunos casos, estas emisiones se capturan para su posterior destrucción por vía térmica.

El HCFC-22 se produce en varios países de la Comunidad Europea, con una producción total en 1995 de 128000 toneladas.

2. Fuentes de emisión

Las emisiones de hidrofluorocarburos se asocian principalmente con su uso en refrigeración, aire acondicionado, producción de espumas y aerosoles.

Anteriormente a 1990, los HFCs no se utilizaban prácticamente en la Comunidad Europea. En efecto, las únicas emisiones a la atmósfera correspondían a la formación de HFC-23 como subproducto en la fabricación de HCFC-22. Sin embargo, a partir de 1990 se ha producido un aumento significativo del mercado de HFCs debido a su uso como sustitutos de clorofluorocarburos (CFCs) y hidroclorofluorocarburos (HCFCs).

En 1995, año base a efectos del Protocolo de Kioto, se emitieron en España 481,6 toneladas, 5.595.480 toneladas de CO_2 equivalente, mientras que en 2000 se llegó a 10.057.100 toneladas de CO_2 equivalente. En 2000 representaron el 2,5% de las emisiones totales brutas de gases de efecto invernadero en España. En la Tabla 1 se recogen las emisiones de HFCs en España en el período 1990-2000.

TABLA 1
EMISIONES DE COMPUESTOS HIDROFLUOROCARBUROS (HFC) EN ESPAÑA
(MILES DE TONELADAS DE CO2 EQUIVALENTE)

Año	1990	1991	1992	1993	1994	1995	1996	1997	198	1999	2000
Emisiones	2894	2575	2869	2258	3885	5596	6412	6923	7015	9146	10057

2.1. Emisiones derivadas de la producción de HFCs

Las emisiones de HFCs derivadas de su producción provienen de las emisiones fugitivas durante el proceso de generación y distribución del producto. En 1995 estas emisiones fugitivas supusieron el 0,2% del total de HFCs emitidos.

2.2. Emisiones derivadas del uso de HFCs

a) Refrigeración y acondicionamiento de aire

En 1995, las emisiones derivadas del uso de HFCs en refrigeración y acondicionamiento de aire supusieron el 10% de las emisiones totales de HFCs en la Comunidad Europea, siendo la segunda fuente de emisiones en importancia.

Las emisiones proceden de fugas en equipos, si bien debido a que el precio de los HFCs se ha visto incrementado considerablemente en los últimos años así como el interés por preservar el medio ambiente, los sistemas de refrigeración actuales presentan un menor número de fugas.

b) Producción de espumas

Las emisiones contabilizadas en 1995 indican que no existen emisiones de HFCs procedentes de la producción de espumas. Sin embargo, se estima un aumento muy considerable (10 millones de t de CO_2 equivalente en el año 2010) debido a la utilización de HFCs como sustitutos de los actualmente empleados para este proceso de producción (HCFCs).

c) Aerosoles / Inhaladores

La práctica totalidad de los HFCs empleados como propulsores se emiten a la atmósfera durante su aplicación.

Se estima que el 3% del total de HFCs emitidos en la Comunidad Europea procede de esta aplicación concreta.

d) Extinción de incendios

Las emisiones documentadas en 1995 indican que no existen emisiones de HFCs procedentes de los sistemas contraincendio. Se estima un aumento poco significativo (0,3 % del total de emisiones de HFCs en la Comunidad Europea) debido a su utilización como sustituto del halón.

e) Disolvente

En general las emisiones de HFC empleado como disolvente se deben a la evaporación del producto en las operaciones de limpieza en las que se utiliza.

f) Producción de HCFC-22

En 1995, la producción de HCFC-22 supuso la mayor fuente de emisiones de HFCs en la Comunidad Europea, con un 85% del total de emisiones de HFCs.

Debido a las normativas europeas en cuanto a las sustancias consideradas perjudiciales para la capa de ozono, las emisiones de HFCs han sufrido una reducción muy significativa.

La mayoría de las plantas han rediseñado sus instalaciones para reducir la generación de HFC-23 en la producción de HCFC-22, e incorporar sistemas de abatimiento de HFCs.

3. Referencias

- "Opportunities to minimise emissions of Hydrofluorocarbons (HFCs) from the European Union". Septiembre 1998. March Consulting Group, UK.

- "Fluorinated Aliphatic Compounds". Bruce E. Smart, Richard E. Fernandez, E. I. du Pont de Nemours & Co., Inc. Diciembre 2000. Kirk-Othmer Encyclopedia of Chemical Technology.

- "Evolución de los Gases de efecto invernadero en España 1990-2000". Santamarta, J.; Nieto, J.

- "Ways and Means of Limiting Emissions for Hydrofluorocarbons and Perfluorocarbons". Noviembre 1999. United Nations Framework Convention on Climate Change.

PENTACLOROBENCENO

El pentaclorobenceno, de fórmula molecular C_6HCl_5, pertenece al grupo de los clorobencenos.

Aparece en forma de cristales que varían de incoloro a blanco y presenta un olor característico. Su punto de ebullición es 275-277 ºC y su punto de fusión 86 ºC. No es soluble en agua. Su presión de vapor es alrededor de 2 Pa a 25 ºC.

El pentaclorobenceno es muy tóxico para los organismos acuáticos. Puede producirse una bioacumulación de esta sustancia en peces, en la leche, en los vegetales y en los mamíferos.

1. Producción y usos

Al igual que el resto de bencenos clorados, el pentaclorobenceno se produce mediante cloración continua del benceno en presencia de un catalizador de Friedel-Crafts. El catalizador más usado es el $FeCl_3$, el cual se puede añadir mezclado a la reacción o se puede generar in situ exponiendo una superficie de hierro con el líquido que está siendo clorado. Los compuestos puros se tienen por destilación y cristalización.

Ya que todos los clorobencenos se producen de igual forma, el grado de cloración del benceno se puede controlar según el catalizador que se use, la temperatura y el ratio benceno/cloro que se alimenta al reactor.

El pentaclorobenceno se utilizaba como plaguicida, agente retardante del fuego y en combinación con los PCB en fluidos dieléctricos. No se ha podido precisar si se sigue utilizando como plaguicida o agente pirorretardante por sí solo; no obstante, se puede hallar como impureza del pentacloronitrobenceno (quintoceno) y de otros plaguicidas. Actualmente ya no se fabrica quintoceno en la Unión Europea desde 2002 y tampoco existe registro de autorización para este producto en España. El pentaclorobenceno ya ha dejado de producirse comercialmente en los países europeos de la CEPE de las Naciones Unidas.

2. Fuentes de emisión

Actualmente no se tiene constancia de emisiones de pentaclorobenceno destacables. Puede emitirse desde fuentes no intencionales, en concreto:

- durante la incineración de materia orgánica y cloro.
- durante el proceso de blanqueo con cloro en la industria de papel.
- en la industria del acero.
- en el tratamiento de aguas residuales por fangos activados.

El pentaclorobenceno es persistente en el suelo, el agua y la atmósfera. El periodo de semidesintegración en el aire calculado es de 277 días. Por sus características físico-químicas se puede transportar largas distancias. Según CEPA (1993), se puede producir la fotooxidación del pentaclorobenceno en la atmósfera fundamentalmente por medio de reacciones con los radicales hidroxilo, su periodo de semidesintegración estimado varía entre 45-467 días.

En aguas superficiales también se puede fotodegradar, pero se ve disminuida por la gran adsorción a los sólidos. En aguas superficiales el periodo de semidesintegración varía entre 194-1250 días mientras que se estima un periodo de semidesintegración para la biodegradación anaeróbica en aguas profundas que varía entre 776-1380 días (CEPA, 1993).

En caso de emisiones de pentaclorobenceno en el suelo, se espera que éste lo absorba en su mayor parte, pero sin filtrarse a las aguas subterráneas. También es posible que no se produzca ni hidrólisis ni biodegradación importantes.

3. Referencias

- Programa de las Naciones Unidas para el Medio Ambiente. Examen de nuevas propuestas de inclusión de productos químicos en los anexos A, B o C del Convenio de Estocolmo: Pentaclorobenceno. Ginebra. Noviembre 2006.

- Plan Nacional de Aplicación del Convenio de Estocolmo y el Reglamento 850/2004, sobre Contaminantes Orgánicos Persistentes. (BORRADOR). Agosto 2006.

- Locating and Estimating Air Emissions from Sources of chlorobenzenes (Revised). EPA-454/R-93-044. Marzo 1994.

- International Chemical Safety Cards. Nº CAS 608-93-5.

TALIO

El talio es un metal pesado que existe en el ambiente principalmente combinado con otros elementos (fundamentalmente oxígeno, azufre y halógenos) formando compuestos inorgánicos. El talio es bastante estable en el ambiente.

Los compuestos de talio por lo general son solubles en agua, encontrándose dicho elemento sobre todo como ión monovalente (Tl^+). El talio tiende a ser a absorbido por el suelo y los sedimentos y a bioconcentrarse en plantas acuáticas, invertebrados y peces. Las plantas terrestres también pueden absorber talio del suelo.

1. Producción y usos

El talio se puede obtener como subproducto aprovechando las corrientes residuales provenientes de la fundición de zinc, cobre y plomo, mediante tratamientos de electrolisis, precipitación o reducción.

La principal aplicación del talio se encuentra en la industria de los semiconductores. Los compuestos de talio tienen diversas aplicaciones. El sulfato de talio se emplea en semiconductores y termómetros, sistemas ópticos y células fotoeléctricas y como compuesto intermedio para obtener otros compuestos de talio. El acetato de talio se emplea para preparar soluciones de alta densidad para separar por flotación los constituyentes de un mineral. El cloruro de talio se emplea como catalizador en cloración. El nitrato de talio se usa con otros compuestos y resinas para señales en el mar. También se emplea para la producción de vidrio de bajo punto de fusión, fotocélulas y como agente oxidante en síntesis orgánicas. El óxido de talio se usa en la fabricación de vidrio altamente refractario y en la producción de gemas artificiales. El talio y sus compuestos también se han empleado como pesticidas para el control de roedores e insectos.

2. Fuentes de emisión

Las mayores emisiones de talio al ambiente provienen de procesos como la combustión de carbón y fundición, en los cuales el talio es un contaminante traza de las materias primas, más que de instalaciones que produzcan o usen compuestos de talio.

- Emisiones al aire.

Principalmente el talio se emite a la atmósfera proveniente de centrales térmicas de carbón, fábricas de cemento y fundición de compuestos ferrosos y no ferrosos.

Algunos estudios en centrales térmicas de carbón sostienen que el contenido de talio en cenizas volantes va de los 29 a los 76 µg/g, aumentando la concentración de talio cuanto menor es el tamaño de las partículas.

Otras fuentes de talio en partículas son las fábricas de aleaciones, gemas artificiales, equipos electrónicos, vidrio óptico y producción de calor a nivel doméstico.

- Emisiones al agua.

Las principales fuentes de emisión de talio al agua son las aguas residuales procedentes de industrias cuya actividad implique el manejo de talio. La concentración de talio en estas aguas puede llegar a 2 g/l.

- Emisiones al suelo.

Las principales emisiones de talio al suelo proceden de residuos sólidos provenientes de operaciones de combustión de carbón y fundición. Aunque las emisiones directas de talio al suelo son pequeñas, la contaminación atmosférica por talio puede contribuir a la contaminación del suelo en áreas cercanas a las fuentes de emisión.

3. Referencias

- Toxicological profile for thallium. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Julio 1992.

TRICLOROBENCENOS (TCB)

Los derivados clorados del benceno, $C_6H_{(6-x)}Cl_x$, forman un grupo de compuestos estables, incoloros y de agradable olor. El cloro puede sustituir a los seis átomos de hidrógeno del anillo bencénico, formando doce compuestos clorados diferentes:

- monoclorobenceno
- orto-diclorobenceno
- meta-diclorobenceno
- para-diclorobenceno
- 1, 2, 3-triclorobenceno
- 1, 2, 4-triclorobenceno
- 1, 3, 5-triclorobenceno
- 1, 2, 3, 4-tetraclorobenceno
- 1, 3, 4, 5-tetraclorobenceno
- 1, 2, 4, 5-tetraclorobenceno
- pentaclorobenceno
- hexaclorobenceno

Únicamente los mono-, di- y triclorobenceno tienen aplicaciones industriales importantes.

En general los triclorobencenos son sólidos blancos cristalinos, excepto el 1, 2, 4–triclorobenceno que es un líquido incoloro. Sus solubilidades son similares, con insolubilidad en agua, y generalmente buena solubilidad en alcohol, éter, benceno y cloroformo.

1. Producción y usos

Como se ha mencionado anteriormente pueden formarse doce compuestos distintos mediante sustitución de alguno o todos los átomos de hidrógeno del anillo bencénico por átomos con cloro. Con la excepción de 1, 3-diclorobenceno, 1, 3, 5-triclorobenceno y 1, 2, 3, 5-tetraclorobenceno, los bencenos clorados son producidos en presencia de un catalizador de Friedel-Crafts. El catalizador usual es cloruro de hierro ($FeCl_3$), el cual puede ser añadido a la reacción mezclado o generado in situ por exposición de una superficie de hierro con el líquido que está siendo clorado. Los compuestos puros son obtenidos por destilación y cristalización.

Actualmente, la capacidad de las plantas de clorobencenos varía desde 500 a 80.000 toneladas. Sólo se producen comercialmente monoclorobenceno, o-diclorobenceno y p-diclorobenceno. No existen datos disponibles de producción de bencenos clorados superiores.

Los procesos de fabricación de clorobenceno incluyen métodos de separación, obteniéndose varios productos. El proceso usado actualmente es la cloración directa del benceno en presencia de un catalizador de $FeCl_3$ para producir monoclorobenceno. El monoclorobenceno reacciona con el cloro restante para formar diclorobencenos. El cloruro de hidrógeno es un subproducto en ambas reacciones. Además de los dos principales isómeros del diclorobenceno, orto y para, se forma una pequeña parte del isómero meta también. Como la cloración continúa, se forman además tri-, tetra-, penta- y hexaclorobencenos. Normalmente, el triclorobenceno es el único de los productos clorados superiores encontrados en cantidades significativas. El grado de cloración del benceno puede ser controlado mediante la elección del catalizador, temperatura y el ratio benceno/cloro en la alimentación al reactor. El cloruro de hidrógeno, un subproducto de la reacción, es procesado en condiciones anhidras después de ser absorbido en agua. La reacción y el proceso de recuperación, en la mayoría de los casos, son continuos.

El proceso más común por el cual se forman los triclorobencenos es la cloración catalítica de orto y para-diclorobenceno en presencia de cloruro férrico. Los productos son sometidos a una destilación fraccionada para obtener 1, 2, 4– y 1, 2, 3–triclorobenceno.

De la misma forma, el 1, 3, 5–triclorobenceno puede ser obtenido por la cloración del m–diclorobenceno.

La mayoría de los triclorobencenos se generan en las mismas plantas donde se producen los bencenos clorados inferiores. En estas instalaciones, los triclorobencenos se separan por destilación fraccional de los diclorobencenos.

Otros procesos de producción de triclorobenceno mencionados en la literatura:

1) La reacción de α-, β- o γ–hexaclorobenceno con sosa potásica a 100ºC.

2) La deshalogenación de α-hexaclorobenceno con piridina.

3) La reacción de α–hexaclorobenceno con hidróxido cálcico.

El 1, 2, 4–triclorobenceno se emplea principalmente como ingrediente de pesticidas (la producción de pesticida Banvel® consumió aproximadamente 8.000 toneladas de triclorobenceno en 1988). Además el 1, 2, 4–triclorobenceno se emplea como disolvente, intermediario químico, lubricante y como fluido térmico.

Benceno + cloro → Triclorobenceno →

- Producción de herbicidas (75%)
- Portador de tintes y otros usos (25%)

2. Fuentes de emisión

El 1, 2, 4–triclorobenceno se emite la atmósfera a través de su uso en la fabricación de portadores de tintes, herbicidas, bencenos clorados, fluidos dieléctricos y por otras aplicaciones. Reacciona con radicales hidroxilos y tiene una vida media estimada de 18,5 días. El 1, 3– y 1, 4–diclorobenceno se introducen en la atmósfera como subproductos de su fotodegradación.

El 1, 3, 5–triclorobenceno se emite a la atmósfera a través de su uso en la industria química, como intermediario químico, disolvente y emulsionante. Puede reaccionar con radicales hidroxilos, con una vida media estimada de 6,17 meses.

2.1. Emisiones derivadas de la producción de triclorobenceno

Las emisiones de triclorobenceno que se liberan durante el proceso de producción resultan del almacenamiento y manipulación de productos de triclorobenceno. Asimismo, las emisiones fugitivas de triclorobencenos pueden ocurrir debido a escapes en válvulas, bombas y demás equipos. También son posibles emisiones secundarias procedentes de la producción de monoclorobenceno, por la volatilización de triclorobenceno de aguas residuales que contienen benceno y otros compuestos volátiles disueltos así como residuos del catalizador.

2.2 Emisiones derivadas del uso de triclorobenceno

a) Uso de triclorobenceno como disolvente de proceso.

El triclorobenceno se emplea como disolvente del proceso de producción de un tinte comúnmente llamado Vat Green 1. (C.I.59825).

El nivel de las emisiones de clorobencenos de cualquier instalación con esta aplicación es función de variables como la capacidad y las medidas de control, y deberán ser determinadas a través de contacto directo con el personal de cada planta.

b) Uso de 1, 2, 4 – triclorobenceno como portador de tintes en la industria textil.

Las operaciones de las fábricas textiles en las cuales se emplea 1, 2, 4–triclorobenceno incluyen procesos finales como la limpieza de la lana, del tejido y la fabricación final de hilos. En la mayoría de los casos el 1, 2, 4–triclorobenceno se utiliza únicamente cuando se requieren determinados colores (usualmente oscuros para la fabricación artificial de fibras).

La cantidad típica de triclorobenceno presente en la formulación de los portadores de tintes varía entre 10 y 90 % del total.

Las fuentes potenciales de emisiones de 1, 2, 4–triclorobenceno en la industria textil incluyen operaciones de venteo en equipos de proceso, fugas en equipos, operaciones de secado y operaciones de transferencia y manipulación.

c) Uso de 1, 2, 4-triclorobenceno en la fabricación de herbicida Banvel®

El triclorobenceno se emplea en la formación del herbicida Banvel®. (CAS- 2300-66-5) que se emplea como herbicida en cultivos como maíz, grano y caña de azúcar.

El 1, 2, 4–triclorobenceno se utiliza como materia prima. En el proceso, el triclorobenceno y el hidróxido sódico se disuelven en metanol en presencia de dióxido de carbono y dimetil sulfato y son calentados a 190 ºC durante 4 horas. La mezcla resultante se enfría, filtra, seca y procesa para la producción de Banvel®.

Se estima que el 33 % de la cantidad total de triclorobenceno utilizado por la industria de los pesticidas se consume durante el proceso de fabricación.

En el primer paso de la producción de Banvel® el 90 % del 1, 2, 4–triclorobenceno se consume en la producción de 2, 5–diclorofenol. El restante 10% se asume que es emitido al medio ambiente.

d) Uso de triclorobenceno como disolvente orgánico para operaciones de limpieza.

Los clorobencenos se emplean como agentes limpiadores y desengrasantes en disolventes de operaciones de limpieza para eliminar sólidos insolubles en agua de metales, plásticos, fibras u otras superficies.

En particular, el triclorobenceno se emplea en fórmulas desengrasantes para láminas electrónicas en la industria de los componentes electrónicos y limpieza de maquinaria.

El tipo de emisiones producidas incluye aquellas generadas por evaporación del aire de los alrededores, del disolvente transportado de las zonas que se han limpiado, agitación, evaporación del disolvente sobrante y evaporación de los sprays. Algunas emisiones se deben a la evaporación de los disolventes durante la mezcla y manipulación.

e) Uso de tricolorobenceno como conservante de madera

El triclorobenceno se emplea como tratamiento sólido, como repelente o veneno para termitas alrededor de los cimientos de los edificios. Para ello se utiliza una mezcla de 1, 2, 3–triclorobenceno y 1, 2, 4–triclorobenceno.

El 1, 2, 4–triclorobenceno se emite a la atmósfera durante la aplicación y manipulación.

f) Otros usos de los triclorobencenos

El 1, 2, 4–triclorobenceno se emplea en la formulación de fluidos tales como líquidos dieléctricos y aceites de transformadores. El 1, 2, 4–triclorobenceno se usa también como disolvente en procesos de cristalización de productos de alto punto de fusión, en control térmico, fosas sépticas y como lubricante. Las emisiones ocurren durante la producción y uso de productos secundarios.

El 1, 3, 5–triclorobenceno se utiliza como disolvente para productos de elevados puntos de fusión. Además se emplean como refrigerante en instalaciones eléctricas y atemperación de cristales, fluido térmico, lubricante y aceites sintéticos de transformadores. Se usa en tratamientos de termitas y tintado del poliéster. El 1, 3, 5–triclorobenceno se emite a la atmósfera durante el proceso de producción y usos de estos productos.

El 1, 2, 3–triclorobenceno se emplea como intermediario orgánico y en aceites sintéticos de transformadores. Las emisiones proceden del uso general en laboratorios y de la aplicación como aceite de transformadores. Históricamente, el 1, 2, 3–triclorobenceno ha sido también utilizado como agente para el control de termitas; actualmente no se emplea con este fin.

g) Volatilización de clorobencenos en operaciones de tratamiento de aguas residuales

Una instalación típica de tratamiento de aguas residuales procedente de plantas que producen clorobencenos consiste en filtración, eliminación, clarificación primaria, uso de lodos activos con aireación y cloración. Debido a la naturaleza volátil de los clorobencenos, las emisiones al aire se deben principalmente a la clarificación y aireación. Medidas de la concentración de clorobencenos en los efluentes indican que entre el 40 y 90% de los clorobencenos, se emiten durante la aireación de lodos activos.

3. Referencias

- “Locating and Estimating air emissions from sources of chlorobenzenes”. Marzo 1994. Environmental Protection Agency (EPA).
- “Chlorinated Benzenes”. Ramesh Krishnamurti. Julio 2001. Kirk-Othmer Encyclopedia of Chemical Technology.

POTENTIAL SOURCE CATEGORIES OF CHLOROBENZENES EMISSIONS

1,2,3-triclorobenceno (87-61-6)	
SIC Code Source Description	**SIC Code Source Description**
5093 Scrap and waste materials	3679 Electronic components, nec
2211 Broadwoven fabric mills, cotton	

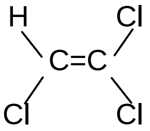
1,2,4-triclorobenceno (120-82-1)	
SIC Code Source Description	**SIC Code Source Description**
2221 Broadwoven fabric mills, manmade	2231 Broadwoven fabric mills, wool
2253 Knit outerwear mills	2254 Knit underwear mills
2257 Weft knit fabric mills	2258 Lace & warp knit fabric mills
2261 Finishing plants, cotton	2262 Finishing plants, manmade
2269 Finishing plants, nec	2273 Carpets and rugs
2491 Wood preserving	2812 Alkalies and chlorine
2816 Inorganic pigments	2819 Industrial inorganic chemicals, nec
2841 Soap and other detergents	2842 Polishes and sanitation goods
2843 Surface active agents	2861 Gum and wood chemicals
2865 Cyclic crudes and intermediates	2869 Industrial organic chemicals, nec
2873 Nitrogenous fertilizers	2879 Agricultural chemicals, nec
2899 Chemical preparations, nec	2992 Lubricating oils and greases
3251 Brick and structural clay tile	3253 Ceramic wall and floor tile
3291 Abrasive products	3357 Nonferrous wiredrawing & insulating
3449 Miscellaneous metal work	3479 Metal coating and allied services
3612 Transformers, except electronic	3621 Motors and generators
3674 Semiconductors and related devices	3679 Electronic components, nec
3699 Electrical equipment & supplies, nec	3812 Search and navigation equipment
3822 Environmental controls	3861 Photographic equipment and supplies
4953 Refuse systems	7342 Disinfecting & pest control services

TRICLOROETILENO

NOTA IMPORTANTE: El tricloroetileno NO es un producto de combustión. La inclusión de este contaminante en la sublista de Instalaciones de combustión parece ser debida a una anomalía en la base de datos de EPER. *Fuente: “Air Pollutant emission estimation methods for E-PRTR reporting by refineries. CONCAWE report no. 3/07*

En general el tricloroetileno es un líquido bajo condiciones normales de temperatura y presión, no inflamable e incoloro.

La estructura molecular del tricloroetileno se muestra a continuación:



El tricloroetileno es miscible con la mayoría de compuestos líquidos orgánicos (éter, alcohol, cloroformo, etc.) e inmiscible en agua. Por otro lado, se trata de un compuesto relativamente volátil.

El tricloroetileno se descompone mediante oxidación atmosférica y por degradación catalizada por el cloruro de aluminio. Los productos de la descomposición incluyen compuestos ácidos y corrosivos, como el ácido clorhídrico. Por este motivo el tricloroetileno comercial contiene estabilizadores tales como aminas, que previenen esta descomposición.

La vida media en la atmósfera estimada para el tricloroetileno es de cuatro días. Esta relativamente corta vida indica que no se trata de un compuesto persistente en la atmósfera.

Para estimar la peligrosidad del tricloroetileno en cuanto a sus efectos en la salud humana, Australian National Pollutant Inventory (ANPI) propone el uso de una escala de 0-3, donde una puntuación de 3 representa un compuesto muy peligroso, una puntuación de 2 representa un compuesto peligroso y una puntuación de 1 representa un compuesto nocivo para la salud humana. En este sentido el tricloroetileno cuenta con una puntuación de 1,3.

1. Producción y usos

El tricloroetileno se produce mediante dos procesos: la cloración directa del dicloroetileno y la oxicloración del dicloroetileno. En este sentido, el tricloroetileno puede producirse conjuntamente con el percloroetileno (tetracloroetileno), o bien por separado, ajustando la relación de compuestos en la alimentación.

Además el tricloroetileno puede producirse como un subproducto durante el proceso de formación del cloruro de vinilideno o del monómero de dicloroetileno/cloruro de vinilo

Los principales productos del proceso de cloración del dicloroetileno son el tricloroetileno y el percloroetileno mientras que del proceso de oxicloración se obtienen tricloroetileno, percloroetileno y agua.

La principal aplicación del tricloroetileno es como disolvente orgánico para su uso como desengrasante industrial. Por otro lado, se emplea como modificador de la longitud de las cadenas polímeras en la producción de PVC. Por último, el tricloroetileno también se usa como disolvente en otras aplicaciones tales como formulación de adhesivos o pinturas.

2. Fuentes de emisión

2.1. Emisiones derivadas de la producción de tricloroetileno

a) Producción a partir de la cloración directa del dicloroetileno

Las fuentes de emisión más importantes procedentes del proceso de cloración directa del dicloroetileno son los tanques de almacenamiento, fugas en equipos y operaciones de manipulación. Otras fuentes secundarias a considerar incluyen las operaciones de venteo, apertura de equipos, sistema de tratamiento de aguas residuales que contienen volátiles (en este caso el tricloroetileno) o la combustión de residuos sólidos resultantes en el proceso y que contengan tricloroetileno.

b) Producción a partir de la oxicloración del dicloroetileno

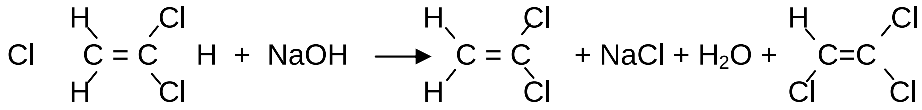
En cuanto al proceso de oxicloración del dicloroetileno, las fuentes a considerar son las fugas en equipos y las mismas fuentes de emisión secundarias señaladas para el proceso de cloración directa. Otras fuentes menos significativas provienen de los procesos de venteo, almacenamiento, operaciones de manipulación y de carga/descarga.

c) Producción de tricloroetileno como subproducto de otros procesos

Existen dos procesos en los cuales aparece el tricloroetileno como subproducto: producción de cloruro de vinilideno y de monómero de dicloroetileno/cloruro de vinilo.

- PRODUCCIÓN DE CLORURO DE VINILIDENO

  El cloruro de vinilideno se produce a partir de la deshidrocloración del 1,1,2-tricloroetano con hidróxido de calcio. El proceso es el siguiente:



1,1,2-tricloroetano Sosa Cloruro de vinilideno tricloroetileno

Las fuentes de emisión potenciales se refieren a la purga del reactor de deshidrocloración y de la columna de destilación. Otras fuentes corresponden a operaciones de manipulación, almacenamiento y emisiones fugitivas en válvulas, bombas, compresores.

- DICLOROETILENO/CLORURO DE VINILO MONOMEROS

  El proceso de producción del monómero puede considerarse en dos etapas. En la primera de ellas, el dicloroetileno se produce mediante la cloración directa del etileno con cloro o bien mediante la oxicloración del etileno con ácido clorhídrico. En la segunda etapa el dicloroetileno es deshidroclorado produciendo el cloruro de vinilo y ácido clorhídrico.

  Durante la primera etapa se producen tricloroetileno y percloroetileno como subproductos del proceso.

  Las fuentes de emisiones más importantes en este caso son las purgas tras el reactor de cloración directa y oxicloración. Otras emisiones provienen del almacenamiento, manipulación y fuentes secundarias de emisiones tales como el procesado de efluentes de aguas residuales.

2.2 Emisiones derivadas del uso de tricloroetileno

a) Producción de policloruros de vinilo (PVC)

El tricloroetileno se utiliza en la producción de PVC como agente de transferencia en las cadenas polímeras para conseguir polímeros de menor peso. El proceso de suspensión del PVC es el único proceso que emplea el tricloroetileno con este fin.

Las fuentes potenciales de emisión de tricloroetileno incluyen las siguientes:

- almacenamiento y descarga de tricloroetileno
- apertura de equipos para operaciones de limpieza y mantenimiento
- descargas de alivio
- purgas y operaciones de venteo
- fugas en válvulas, bombas, compresores, conectores, y demás sistemas
- fuentes secundarias de emisión tales como efluentes de aguas residuales

b) Desengrasante industrial

Los disolventes orgánicos empleados en operaciones de limpieza son parte integral de muchas industrias tales como la automovilística, fabricación de muebles, textiles, papel, plástico, cristal. Estos disolventes se utilizan para eliminar de la superficie del objeto los compuestos insolubles en agua (como aceites, grasas, depósitos de carbón, ceras) previamente a los procesos de aplicación de pintura, reparación, tratamientos, etc. El tricloroetileno es especialmente útil para la limpieza y secado de objetos metálicos.

Las principales fuentes de emisión de tricloroetileno incluyen las pérdidas de vapores en los tanques debidas a procesos de difusión y convención, así como el tricloroetileno evaporado de las superficies una vez limpiadas con dicho compuesto.

c) Pinturas, recubrimientos y adhesivos

El tricloroetileno se emplea como disolvente de pinturas, recubrimientos y adhesivos. Las emisiones del disolvente en este caso proceden de la evaporación de éste durante su aplicación. Por consiguiente se estima que todo el tricloroetileno empleado para este fin se emite finalmente a la atmósfera.

d) Distribución del tricloroetileno

Prácticamente todo el tricloroetileno producido se vende a través de distintos distribuidores. Las emisiones asociadas a esta actividad proceden del almacenamiento y manipulación (carga/descarga) del producto.

e) Otras fuentes de emisiones

El tricloroetileno se emplea en multitud de síntesis y aplicaciones como solvente. Por ejemplo, se utiliza tricloroetileno como reactivo para producir pesticidas. Además puede utilizarse en la síntesis de retardantes de llama, como disolvente en la industria farmacéutica, secado y refinado en la industria textil, como portador en la formulación de productos tales como insecticidas, fungicidas, correctores de escritura líquidos, como quitamanchas, etc.

Se estima que la totalidad del tricloroetileno empleado para estos fines se emite a la atmósfera, si bien trabajos llevados a cabo en los EEUU documentan que las emisiones procedentes de los pesticidas y la industria farmacéutica puede asumirse despreciable.

Por último, el tricloroetileno puede ser emitido a la atmósfera durante el tratamiento, almacenamiento y eliminación de residuos sólidos. En este sentido en los EEUU se han documentado emisiones de tricloroetileno procedentes de incineradoras de residuos de hospitales, combustión de residuos oleosos de desengrasado, sedimentos procedentes de la red de alcantarillado y vertederos.

3. Referencias

- "Locating and estimating air emissions from sources of perchloroethylene and trichloroethylene". Agosto 1989. Environmental Protection Agency (EPA).

- "National Pollutant Inventory Database Query 2000-2001". Environment Australia, Department of the Environmental and Heritage.
  www.aeat.co.uk/netcen/airqual/naei/home.html.

FICHAS
CONTAMINANTES ATMOSFÉRICOS

1/1 CH_4, combustión en hornos y calderas
1/2 CH_4, combustión en turbinas
1/3 CH_4, combustión en motores
1/4 CH_4, combustión
1/5 CH_4, antorchas
1/6 CH_4, cracking catalítico en lecho fluido
1/7 CH_4, destilación a vacío
1/8 CH_4, purgas
1/9 CH_4, planta de tratamiento de efluentes líquidos
1/10 CH_4, emisiones fugitivas (procesos)

2/1 CO, combustión
2/2 CO, combustión en hornos y calderas
2/3 CO, combustión en turbinas
2/4 CO, combustión en motores
2/5 CO, antorchas
2/6 CO, cracking catalítico en lecho fluido
2/7 CO, reformado catalítico

3/1 CO_2, combustión
3/2 CO_2, antorchas
3/3 CO_2, plantas de hidrógeno
3/4 CO_2, regeneración catalítica de unidades de cracking, otros tipos de regeneración catalítica y flexicoking

5/1 N_2O, combustión en hornos y calderas
5/2 N_2O, combustión en turbinas
5/3 N_2O, combustión en motores
5/4 N_2O, combustión
5/5 N_2O, cracking catalítico en lecho fluido

6/1 NH_3, combustión en hornos y calderas
6/2 NH_3, cracking catalítico en lecho fluido
6/3 NH_3, sistemas de reducción de NO_X
6/4 NH_3, sistemas de refrigeración

7/1 COVDM, combustión en hornos y calderas
7/2 COVDM, combustión en turbinas
7/3 COVDM, combustión en motores
7/4 COVDM, antorchas
7/5 COVDM, cracking catalítico en lecho fluido

7/6	COVDM, destilación a vacío
7/7	COVDM, planta de tratamiento de efluentes líquidos
7/8	COVDM, torres de refrigeración
7/9	COVDM, emisiones fugitivas (procesos)
7/10	COVDM, parque de almacenamiento
7/11	COVDM, purgas
8/1	NO_X, combustión
8/2	NO_X, combustión en hornos y calderas
8/3	NO_X, combusión en turbinas
8/4	NO_X, combustión motores
8/5	NO_X, antorchas
8/6	NO_X, cracking catalítico en lecho fluido
11/1	SO_X, combustión
11/2	SO_X, plantas de recuperación de azufre
11/3	SO_X, plantas antorchas
11/4	SO_X, cracking catalítico en lecho fluido
11/5	SO_X, reformado catalítico
17/1	As, combustión en hornos y calderas
17/2	As, combustión en turbinas
17/3	As, combustión
17/4	As, cracking catalítico en lecho fluido
18/1	Cd, combustión en hornos y calderas
18/2	Cd, combustión en turbinas
18/3	Cd, combustión
18/4	Cd, cracking catalítico en lecho fluido
19/1	Cr, combustión en hornos y calderas
19/2	Cr, combustión en turbinas
19/3	Cr, combustión
19/4	Cr, cracking catalítico en lecho fluido
20/1	Cu, combustión en hornos y calderas
20/2	Cu, combustión en turbinas
20/3	Cu, combustión
20/4	Cu, cracking catalítico en lecho fuido
21/1	Hg, combustión en hornos y calderas
21/2	Hg, combustión en turbinas
21/3	Hg, combustión
21/4	Hg, cracking catalítico en lecho fluido

22/1	Ni, combustión en hornos y calderas
22/2	Ni, combustión en turbinas
22/3	Ni, combustión
22/4	Ni, cracking catalítico en lecho fluido
23/1	Pb, combustión en hornos y calderas
23/2	Pb, combustión en turbinas
23/3	Pb, combustión
23/4	Pb, cracking catalítico en lecho fluido
24/1	Zn, combustión en hornos y calderas
24/2	Zn, combustión en turbinas
24/3	Zn, combustión
24/4	Zn, cracking catalítico en lecho fluido
47/1	Dioxinas y furanos, combustión
47/2	Dioxinas y furanos, regeneración de catalizador en reforming catalítico
62/1	Benceno, combustión en hornos y calderas
62/2	Benceno, combustión en turbinas
62/3	Benceno, combustión en motores
62/4	Benceno, antorchas
62/5	Benceno, destilación a vacío
62/6	Benceno, cracking catalítico
62/7	Benceno, purgas
62/8	Benceno, planta de tratamiento de efluentes líquidos
62/9	Benceno, emisiones fugitivas (procesos)
62/10	Benceno, parque de almacenamiento
72/1	HAP, combustión en hornos y calderas
72/2	HAP, combustión en turbinas
72/3	HAP, combustión en motores
72/4	HAP, antorchas
72/5	HAP, cracking catalítico en lecho fluido
72/6	HAP, planta de tratamiento de efluentes líquidos
76/1	COT, combustión en hornos y calderas
76/2	COT, combustión en turbinas
76/3	COT, combustión en motores
76/4	COT, antorchas
76/5	COT, cracking catalítico en lecho fluido
76/6	COT, destilación a vacío
76/7	COT, purgas
76/8	COT, planta de tratamiento de efluentes líquidos
76/9	COT, torres de refrigeración

76/10	COT, emisiones fugitivas (procesos)
76/11	COT, parque de almacenamiento
80/1	Cloro, combustión en hornos y calderas
80/2	Cloro, cracking catalítico en lecho fluido
86/1	PM_{10}, combustión
86/2	PM_{10}, combustión en hornos y calderas
86/3	PM_{10}, combustión en turbinas
86/4	PM_{10}, combustión en motores
86/5	PM_{10}, antorchas
86/6	PM_{10}, cracking catalítico en lecho fluido
86/7	PM_{10}, coquización fluida
92/1	PST, combustión
92/2	PST, combustión en hornos y calderas
92/3	PST, combustión en turbinas
92/4	PST, combustión en motores
92/5	PST, antorchas
92/6	PST, cracking catalítico en lecho fluido
94/1	Sb, combustión en hornos y calderas
94/2	Sb, cracking catalítico en lecho fluido
95/1	Co, combustión en hornos y calderas
95/2	Co, cracking catalítico en lecho fluido
96/1	Mn, combustión en hornos y calderas
96/2	Mn, combustión en turbinas
96/3	Mn, cracking catalítico en lecho fluido
97/1	V, combustión en hornos y calderas

CONTAMINANTE **Metano** CH_4	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

Hornos y calderas < 10 MW

(1) Gasoil: $6{,}98 \cdot 10^{-1}$ g/GJ

(2) Fueloil: 1,43 g/GJ

(3) LPG: $9{,}63 \cdot 10^{-1}$ g/GJ

(4) GN: 1,08 g/GJ

(5) Fuelgas (H_2<65% (v)): $3{,}26 \cdot 10^{-1}$ g/GJ

(6) Fuelgas (H_2≥65%(v)): $2{,}39 \cdot 10^{-1}$ g/GJ

Hornos y calderas de 10 a 100 MW

(7) Gasoil: $1{,}68 \cdot 10^{-1}$ g/GJ

(8) Fueloil: 3,02 g/GJ

(9) LPG: $9{,}63 \cdot 10^{-1}$ g/GJ

(10) GN: 1,08 g/GJ

(11) Fuelgas (H_2<65%(v)): $3{,}26 \cdot 10^{-1}$ g/GJ

(12) Fuelgas (H_2≥65%(v)): $2{,}39 \cdot 10^{-1}$ g/GJ

Hornos y calderas > 100 MW

(13) Gasoil: $9{,}05 \cdot 10^{-1}$ g/GJ

(14) Fueloil: $8{,}45 \cdot 10^{-1}$ g/GJ

(15) GN : 1,08 g/GJ

(16) Fuelgas (H_2<65% (v)): $3{,}26 \cdot 10^{-1}$ g/GJ

(17) Fuelgas (H_2≥65%(v)): $2{,}39 \cdot 10^{-1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

CONTAMINANTE **Metano** **CH_4**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **1/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Potencia sin especificar.

(18) Fueloil: 2,9 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(19) GN: 1,4 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(20) Fueloil: 1 lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-3, SCC 10200401

(21) GN: 2,3 lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-2, SCC 10200601

(22) Fueloil: 3 kg/TJ

(23) Gas/Diesel Oil: 0,2 kg/TJ

(24) GN: 1 kg/TJ

(25) LPG: 0,9 kg/TJ

Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

- **Cuantificación**

(1) a (19)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right)\times\frac{\text{kg}}{10^3\text{g}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

(20)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}00378\ \text{m}^3}\times\text{m}^3\ \text{fueloil}$$

(21)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right)\times\frac{0{,}45359\ \text{kg}}{\text{lb}}\times\frac{31{,}31467\,\text{ft}^3}{\text{m}^3}\times\text{m}^3\ \text{gas natural}$$

(22) a (25)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right)\times\frac{\text{TJ}}{10^3\ \text{GJ}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

- **Observaciones**

El índice de confianza de (20) es A y el de (21) es B, mientras que para el resto no se han localizado índices en la bibliografía analizada.

CONTAMINANTE Metano CH_4	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 1/2/1 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de CH_4	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: 4,11 g/GJ. Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(2) Fueloil: 3 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(3) Gasoil: 1÷8 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(4) GN: 2,5÷4 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) GN: $8{,}6 \cdot 10^{-3}$ lb/10^6 btu Fuente: EPA, SCC 20200201.

(6) GN (>3 MW): 4 kg/TJ. Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

- **Cuantificación**

(1) a (4)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(5)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg GN}$$

(6)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right) \times \frac{\text{TJ}}{10^3\,\text{GJ}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

No se han localizado índices de confianza para los factores (1) a (4). Para el factor (5) es C.

CONTAMINANTE
Metano
CH_4

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de CH_4

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
1/3/1
1(a), 1(c)

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: $5{,}97 \cdot 10^{2}$ g/GJ

(2) Diesel: 3,67 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Fueloil: 3 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(4) Gasoil: 1,5 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) GN (2-cycle, Lean Burn): 1,45 lb/106 btu Fuente: EPA, SCC 20200252
693 kg/TJ Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

(6) GN (4-cycle, Rich Burn): $2{,}3 \cdot 10^{-1}$ lb/10^{6} btu Fuente: EPA, SCC 20200253
110 kg/TJ Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

(7) GN (4-cycle, Lean Burn): 1,25 lb/10^{6} btu Fuente: EPA, SCC 20200254
597 kg/TJ Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

(8) Diesel (Large Bore Engine): 1,11 lb/10^{3} gal Fuente: EPA, SCC 20200401

(9) Diesel (Motor > 600 hp): 4 kg/TJ Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

Empleo de factores de emisión basados en la energía producida.

(10) Combustible mixto oil/gas (Large Bore Engine): 3,97 lb/10^{3} hp-hour producido
Fuente: EPA, SCC 20200402

CONTAMINANTE Metano CH_4	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **1/3/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de CH_4	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Cuantificación**

(1) a (4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right)\times\frac{\text{kg}}{10^3\text{g}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

(5) a (7)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{btu}}{0{,}251\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg GN}$$

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right)\times\frac{\text{TJ}}{10^3\,\text{GJ}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

(8)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}00378\,\text{m}^3}\times\text{m}^3\text{ diesel}$$

(9)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right)\times\frac{\text{TJ}}{10^3\,\text{GJ}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

(10)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{hp-hour}}\right)\times\frac{0{,}45359\text{ kg}}{\text{lb}}\times\frac{\text{hp-hour}}{0{,}7456999\,\text{kWh}}\times\text{kWh producidos}$$

- **Observaciones**

No se han localizado índices de confianza para los factores (1) a (4). El índice de confianza de (5), (6) y (7) es C, y el de (8) y (9) es E.

CONTAMINANTE **Metano** **CH_4**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Combustión

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gas/Diesel Oil: 3 kg/TJ.

(2) Residual Fuel Oil: 3 kg/TJ.

(3) LPG: 1 kg/TJ.

(4) Refinery Gas: 1 kg/TJ.

(5) Natural Gas: 1 kg/TJ.

Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy).

- **Cuantificación**

(1) a (5) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right)\times\frac{\text{TJ}}{10^3\ \text{GJ}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg}\,\text{combustible}$$

- **Observaciones**

No se han localizado índices de confianza para estos factores en la bibliografía analizada.

CONTAMINANTE **Metano** CH_4	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV's totales basados en el crudo procesado en Refinería.

(1) Factor: 0,8·lb/10^3 barril crudo Fuente: EPA, SCC 30600401

Empleo de factores de emisión para el cálculo de COV's totales basados en el gas de antorcha.

(2) Factor: 0,06 kg/GJ Fuente: Australian National Pollutant Inventory (Ref. US EPA 1997a)

(3) Factor: 5,6 lb/10^6 ft^3 Fuente: CORINAIR, Capítulo 923 (Ref. US EPA CHIEF database)

Se asume que el 20% de la emisión de COV's es metano (CORINAIR, Capítulo 923, Ref. US EPA CHIEF database)

Empleo de factores de emisión para el cálculo de CH_4 basados en el crudo procesado de Refinería.

(4) Factor: $2{,}28\cdot10^{-5}$ kg/m^3 crudo Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07.

Empleo de factores de emisión para el cálculo de CH_4, conocidas la masa y composición de la corriente a antorcha.

(5) Se asume que el 0,5% de los hidrocarburos queda sin quemar Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07.

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\frac{20}{100}\times\text{m}^3\,\text{crudo}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{GJ}}\right)\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\frac{20}{100}\times\text{kg gas}$$

$$(3)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{31{,}31467\,\text{ft}^3}{\text{m}^3}\times\frac{20}{100}\times\text{m}^3\,\text{gas}$$

$$(4)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right)\times\text{m}^3\,\text{crudo}$$

$$(5)\ \text{kg emitidos} = \text{kg gas}\times\frac{\%\text{CH}_4}{100}\times\frac{0{,}5}{100}$$

- **Observaciones**

El índice de confianza para el factor (1) es B, no habiéndose localizado para el resto en la bibliografía manejada.

CONTAMINANTE
Metano
CH_4

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de CH_4

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
1/6/1
1(a), 1(c)

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para COV's totales basados en la alimentación a la unidad.

Factor: 220 lb/10^3 barril. Fuente: CORINAIR, B411, Tabla 8.4 (Ref: EPA, SCC 30600201)

Posteriormente se considera que el 1% de los COV´s totales es metano (menos del 1%, según EPA, AP-42, Tabla 5.1-1).

No obstante, también se ha encontrado que el 36% de los COV's totales es metano (CORINAIR, B411, Tabla 9.3. Refinery Fluid Catalytic Cracker, Referencia US EPA).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\frac{1}{100}\times\text{m}^3\ \text{alimentados}$$

- **Observaciones**

El índice de confianza para el factor (1) es B, no habiéndose localizado para el resto en la bibliografía manejada.

El factor inicial para COV's totales tiene un índice de confianza B, mientras que para el porcentaje de metano de CORINAIR (36%) es C.

CONTAMINANTE Metano CH_4	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **1/7/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de CH_4	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 7 Destilación a vacío

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para COV's totales basados en la alimentación a la unidad.

(1) Factor: 50 lb/10^3 barril. Fuente: CORINAIR, B411, Tabla 8.4 (Ref : EPA SCC 30600602)

Empleo de factores de emisión para COV's totales basados en la alimentación a Refinería.

(2) Factor: 0,052 kg/m^3 crudo. Fuente: CORINAIR, Capítulo 411 (Ref. US EPA 1985a y 1995).

Posteriormente se considera que el 1% de los COV's totales es metano (menos del 1%, según EPA, AP-42, Tabla 5.1-1).

No obstante, también se ha encontrado que el 13% de los COV's totales es metano (CORINAIR, B411, Tabla 9.2, Ref. US EPA, Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\frac{1}{100}\times\text{m}^3\ \text{alimentados}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right)\times\frac{1}{100}\times\text{m}^3\ \text{crudo}$$

- **Observaciones**

El índice de confianza de (1) es C, no habiéndose encontrado para el factor (2).

El índice de confianza del porcentaje de metano de CORINAIR (13%) es E.

CONTAMINANTE **Metano** CH_4	## METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	**Nº** **1/8/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	## REFINO DE PETRÓLEO	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 8 Purgas

Metodología 1 Código C

- **Descripción**

En el caso de venteos a la atmósfera (sin recuperación ni envío a antorcha) se considera un factor de emisión de hidrocarburos totales de 1.662 kg/m^3 de alimentación a Refinería, siendo el contenido en metano < 1%.
(Fuente: CONCAWE. Ref: EPA, AP-42, Tabla 5.1-1).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \frac{1}{100} \times \text{m}^3\ \text{crudo}$$

- **Observaciones**

El índice de confianza del factor de emisión es C.

CONTAMINANTE
Metano
CH_4

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de CH_4

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
1/9/1
1(a), 1(c)

FUENTE DE EMISIÓN: 9 Planta de tratamiento de efluentes líquidos

Metodología 1 Código C

- **Descripción**

Empleo de ecuación de Litchfield para determinar COV's totales y posteriormente cálculo de metano a partir de porcentajes recogidos en bibliografía.

La ecuación de Litchfield expresa la emisión de COV's como porcentaje del total de aceites que entran a la planta de tratamiento:

% pérdidas = - 6,6339 + 0,0319 x (T_{amb} ºF) - 0,0286 x (10% Dist. Point ºF) + 0,2145 x (T_{agua} ºF)

Valores típicos
10% dist. Point = 250 ºF
Concentración aceites en agua a tratar = 2.000 mg/l

Fuente: CONCAWE, report Nº 87/52. "Cost-efectiveness of hydrocarbon emission controls in Refineries from crude oil receipt to product dispatch".

Esta ecuación no considera la existencia de balsas cubiertas y/o sistemas de recuperación de vapor. En caso de que existan medidas de control, debe considerarse aplicar el ratio 0,024/0,6 según se indica en US EPA AP-42, Tabla 5.1-2.

Sobre el valor total de COV's obtenido, se considera que el 13% es metano (CORINAIR, Tabla 9.2, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = Q_{\text{agua a planta}} \left(\frac{m^3}{\text{año}}\right) \times \frac{10^3 l}{m^3} \times 2.000 \frac{mg}{l} \times \frac{kg}{10^6 mg} \times \frac{\% \text{Litchfield}}{100} \times \frac{13}{100}$$

- **Observaciones**

No existen índices de confianza en la bibliografía manejada, observándose cómo parámetros como el área de balsas o velocidad de viento no entran en consideración en el cálculo.
El porcentaje de metano respecto a COV's totales es E.

CONTAMINANTE Metano CH_4	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **1/9/2** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de CH_4	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 9 Planta de tratamiento de efluentes líquidos

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en m^3 de agua tratada para determinar COV's totales y posteriormente cálculo de metano a partir de porcentajes recogidos en bibliografía.

Factores de emisión (US EPA, AP-42, Tabla 5.1-2):
0,6 kg/m^3 agua tratada (sin medidas correctoras)
0,024 kg/m^3 agua tratada (balsas cubiertas y/o sistemas de recuperación de vapor)

Sobre el valor total de COV's obtenido, se considera que el 13% es metano (CORINAIR, Tabla 9.2, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = m^3\ \text{agua tratada} \times \text{Factor de emisión}\left(\frac{\text{kg}}{m^3}\right) \times \frac{13}{100}$$

- **Observaciones**

El índice de confianza para los factores de emisión ofrecidos por EPA es D. El correspondiente al porcentaje de metano es E.

CONTAMINANTE **Metano** CH_4	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/9/3** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Planta de tratamiento de efluentes líquidos

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados áreas de balsas existentes para determinar COV's totales.

Factores:

20 g/(m^2.h)	para separadores de aceite sin cubrir
2 g/(m^2.h)	para separadores de aceite cubiertos
2 g/(m^2.h)	para flotación
0,2 g/(m^2.h)	para tratamientos biológicos

Fuente: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries.

Sobre el valor total de COV's obtenido, se considera que el 13% es metano (CORINAIR, Tabla 9.2, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = \Sigma\ \text{Factor}_i \left(\frac{g}{m^2 \times h}\right) \times m^2\ \text{equipo}_i \times \text{horas de operación}_i \times \frac{kg}{10^3 g} \times \frac{13}{100}$$

- **Observaciones**

La bibliografía manejada no aporta índices de confianza para los factores suministrados. Debe destacarse cómo estos factores son de una gran generalidad, sin tener en cuenta las condiciones climáticas del emplazamiento de la planta.

El índice de confianza para el metano presente en COV's totales es E.

CONTAMINANTE
Metano
CH_4

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de CH_4

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
1/10/1
1(a), 1(c)

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 1 Código C

- **Descripción**

Determinación de metano a partir de factores de emisión de NMCOV's específicos para elementos: válvulas, conexiones, drenajes...

Estos factores se afectan posteriormente por el nº de elementos estimados en cada unidad de Refinería (ver Anexo 12).

Una vez obtenidos los valores de NMVOC's, se calcula el metano correspondiente, según las especiaciones recogidas en CORINAIR (Tablas 9.4 a 9.8):

	CH_4 (% p) en COV's totales	índice de confianza
- Drenajes:	2,90	C
- Sellos de compresores:	13,30	D
- Válvulas de seguridad:	0	D
- Válvulas y conexiones:	28,6	C
- Sellos de bombas:	3,30	C

Los factores empleados son:

Tipo de equipo	Servicio	Factor de emisión kg/h/elemento
Válvulas	Gas (a)	0,0268
	Líquido ligero (a)	0,0109
	Líquido pesado (b)	0,0000987
Sellos de bombas	Líquido ligero (a)	0,114
	Líquido pesado (b)	0,00349
Sellos de compresores	Gas (a)	0,636
Válvulas de alivio de presión	Gas (a)	0,16
Conexiones	Para todos (a)	0,00025
Finales de línea	Para todos (a)	0,0023
Conexiones de muestreo	Para todos (a)	0,0150
Drenajes	Para todos (a)	0,032

(a) US EPA (1995 A)
(b) Taback (1996)
Nota: todos los valores se corresponden para Centros sin programas de inspección y mantenimiento.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{n° elementos} \times \text{h}} \right) \times \text{n° elementos}_i \times \text{n°horas}_i \times \frac{\%_i}{100 - \%_i}$$

- **Observaciones**

El índice de confianza para la mayoría de los elementos (fuente US EPA) es U. En relación con la fiabilidad del método, deben considerarse la calidad en la contabilización del nº de elementos.

CONTAMINANTE **Metano** **CH_4**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/10/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 2 Código E

- **Descripción**

Extrapolación de resultados a partir de las emisiones típicas de una Refinería (Fuente: US EPA, AP-42, Tabla 5.1-2):

Fuente	Número	Emisiones NMCOV's(kg/día)
- Válvulas:	11.500	3.100
- Bridas:	46.500	300
- Sellos de bombas:	350	590
- Sellos de compresores:	70	500
- Válvulas de seguridad:	100	200
- Drenajes:	650	450

Las emisiones del cuadro se corresponden a una Refinería con una capacidad de 330.000 barriles/día, sin programas de inspección y mantenimiento. Estos valores se corresponden a NMVOC's, por lo que los resultados deberán ser afectados por los porcentajes presentados en metodología 1/10/1 para obtener metano.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{nº elementos} \times \text{h}} \right) \times \text{nº elementos}_i \times \text{nºhoras}_i \times \frac{\%_i}{100 - \%_i}$$

- **Observaciones**

La fiabilidad del método no es alta, ya que no considera las unidades particulares que integran la Refinería.

CONTAMINANTE **Metano** CH_4	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **1/10/3** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CH_4**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 3 Código M

· Descripción

Implantación de un programa de detección y reparación de fugas (LDAR). El programa LDAR está destinado a la detección y progresiva reducción de las emisiones gaseosas de compuestos orgánicos volátiles (COV) de carácter difuso que tienen su origen en las pérdidas que se producen en los diferentes elementos que componen las unidades de proceso (bombas, válvulas, compresores, bridas, etc.).

Este programa se basa en los estándares del Método 21 de la US EPA, el cual establece no sólo el método a emplear para llevar a cabo las mediciones en campo sino que también define las características de los elementos a emplear y el método de calibración de los mismos. Mediante el programa LDAR, se identifican en planta los equipos que fugan, se procede a la medición de los mismos y, para aquellos que superan un cierto valor, se establecen plazos para llevar a cabo el ajuste, reparación o sustitución y se fija un calendario de seguimiento.

Seguidamente, se obtiene el contenido de metano según las especiaciones recogidas en CORINAIR:

	CH_4 (%p) en COV`s totales	Índice de confianza
- Drenajes	2,90	C
- Sellos de compresores	13,30	D
- Válvulas de seguridad	0	D
- Válvulas y conexiones	28,6	C
- Sellos de bombas	3,30	C

Nota: Obviamente, en caso de que el programa LDAR llevara a cabo mediciones de metano no sería necesario aplicar los porcentajes anteriores.

· Cuantificación

$$\text{kg emitidos} = \sum \text{Medida LDAR}_i\,(\text{kg}) \text{ x } \frac{\%\,CH_4}{100}\,_i$$

Donde i es cada elemento que fuga

· Observaciones

La fiabilidad de las medidas de COV's obtenidas mediante un sistema LDAR se considera superior a los cálculos basados en factores de emisión.

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante análisis de la composición del combustible y a partir de éste, a través de la aplicación de la Orden de 26 de diciembre de 1995 (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3)** x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

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* C y Q expresados en igual base y al mismo oxígeno de referencia

** Usualmente, CO se expresa en ppm. 1 ppm = $1{,}25.10^{-6}$ kg/Nm^3

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/1/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código M

- **Descripción**

Determinación a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3)* x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores el índice de confianza se considera alto.

* Usualmente, CO se expresa en ppm. 1 ppm = 1,25.10^{-6} kg/Nm^3

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

Hornos y calderas < 10 MW

(1) Gasoil: 1,62 · 10^1 g/GJ

(2) Fueloil: 1,51 · 10^1 g/GJ

(3) LPG: 9,40 g/GJ

(4) GN: 3,93 · 10^1 g/GJ

Hornos y calderas de 10 a 100 MW

(5) Gasoil: 1,62 · 10^1 g/GJ

(6) Fueloil: 1,51 · 10^1 g/GJ

(7) LPG: 1,58 · 10^1 g/GJ

(8) GN: 3,93 · 10^1 g/GJ

Hornos y calderas > 100 MW

(9) Gasoil: 1,62 · 10^1 g/GJ

(10) Fueloil: 1,51 · 10^1 g/GJ

(11) LPG: 3,47 · 10^1 g/GJ

(12) GN: 3,93 · 10^1 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

Potencia sin especificar

(13)	Fueloil: 5 lb/10^3 gal	Fuente: EPA, AP-42, Tabla 1.3-1, SCC 30600103
(14)	GN: 84 lb/10^6 ft^3	(todas las configuraciones, excepto quemadores tangenciales) Fuente: EPA, AP-42, Tabla 1.4-1, SCC 10200601, SCC 10200602
(15)	GN: 24 lb/10^6 ft^3	(quemadores tangenciales) Fuente: EPA, AP-42, Tabla 1.4-1, SCC 10100604
(16)	Fueloil: 15 g/GJ	Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111
(17)	Gasoil: 12 g/GJ	Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111
(18)	GN: 17 ó 13 g/GJ	Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111

- **Cuantificación**

(1) a (12) y (16) a (18)

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\,PCI\left(\frac{kcal}{kg}\right) x\,kg\,combustible$$

(13)

$$\text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^3\,gal}\right) x \frac{0,45359\,kg}{lb} x \frac{gal}{0,00378\,m^3} x\,m^3\ fueloil$$

(14) y (15)

$$\text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^6\,ft^3}\right) x \frac{0,45359\,kg}{lb} x \frac{ft^3}{0,028\,m^3} x\,m^3\ GN$$

- **Observaciones**

Los índices de confianza de (13), (14) y (15) son A, B y C respectivamente. Para el resto de factores no se han encontrado índices de confianza en la bibliografía manejada.

CONTAMINANTE Monóxido de carbono **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **2/3/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 500.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de CO	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 3 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido

(1) Gasoil: 1,49 g/GJ

(2) GN: $3{,}92 \cdot 10^{1}$ g/GJ

Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 10-15 g/GJ

(4) Gasoil: 10-20 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

- **Cuantificación**

(1) a (4) $\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\,PCI\left(\frac{kcal}{kg}\right) x\,kg\,combustible$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido

(1) GN: $2,66 \cdot 10^2$ g/GJ

(2) Diésel: $3,85 \cdot 10^2$ g/GJ

Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 100 g/GJ

(4) Gasoil: 12-1130 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

- **Cuantificación**

(1) a (4)

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\, PCI\left(\frac{kcal}{kg}\right) x\, kg\, combustible$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en la cantidad de crudo tratado.

(1) Factor: 4,3 lb/10^3 barril Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1, SCC 30600401)

Empleo de factores de emisión basados en el poder calorífico del gas a antorcha

(2) Factor: 177 g/GJ Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Factor: 159 g/GJ Fuente: Australian National Pollutant Inventory (Ref: USEPA 1997a)

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right) \text{x} \frac{0{,}4539\,\text{kg}}{\text{lb}} \text{x} \frac{\text{barril}}{0{,}159\,\text{m}^3} \text{x}\, \text{m}^3 \text{ de crudo}$$

(2) y (3) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\, \text{kg gas}$$

- **Observaciones**

El índice de confianza de (1) es C, no habiéndose encontrado en la bibliografía manejada los de (2) y (3).

CONTAMINANTE Monóxido de carbono **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/5/2** 1(a), 1(c)
VALOR UMBRAL (kg/año) 500.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de CO	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 2 Código M

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores y los controles bienales realizados.

El factor de emisión empleado originalmente es función del gas incinerado (Q, Nm3/h):

Factor original = Factores (2) ó (3) de 2/5/1.

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor original}\left(\frac{g}{GJ}\right) x\ \text{factor de experiencia}(a\dim)\ x\ \frac{kg}{10^3\ g}\ x\ \frac{GJ}{239.005\ kcal}\ x$$

$$x\ Q\left(\frac{Nm^3}{h}\right) x\ \text{densidad gas}\left(\frac{kg}{Nm^3}\right) x\ \text{PCI gas}\left(\frac{kcal}{kg}\right)\ x\ \text{nº de horas}$$

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor original. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE Monóxido de carbono **CO**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 2/6/1 1(a), 1(c)
VALOR UMBRAL (kg/año) 500.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de CO	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en la alimentación a la unidad.

Factor: 1,37 · 10^4 lb/10^3 barril alimentado. Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1, SCC 30600201 (sin precipitador electrostático ni caldera de CO auxiliar))

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor original}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right) x \frac{0,45359\,\text{kg}}{\text{lb}} x \frac{\text{barril}}{0,159\,\text{m}^3} x\, \text{m}^3\ \text{alimentados}$$

- **Observaciones**

La fiabilidad del factor se corresponde con la categoría B.

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/6/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 2 Código E

- **Descripción**

Empleo de factores de emisión basados en emisiones facilitadas por determinadas refinerías con combustión completa de CO

Factor: 20 g/t INFORME CORINE-AIRE 1997-2000

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{t}\right) x \frac{kg}{10^3\, g} x\, t\ \text{alimentación}$$

- **Observaciones**

La fiabilidad del método viene muy determinada por la calidad de la medida de los valores de CO en emisiones.

CONTAMINANTE
Monóxido de carbono
CO

VALOR UMBRAL (kg/año)
500.000

EXPRESADO COMO
kg de CO

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
2/6/3
1(a), 1(c)

ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 3 Código M

- **Descripción**

  Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores de emisión y los controles bienales realizados

- **Cuantificación**

  Factor de emisión corregido = Factor de emisión x Factor de experiencia.
  (El factor de emisión corregido es empleado como ha sido visto en 2/6/1).

- **Observaciones**

  El resultado global obtenido mejora el índice de confianza del factor de emisión. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/6/4** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 4 Código M

- **Descripción**

Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante el empleo de correlaciones (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3)** x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

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* C y Q expresadas en igual base y al mismo oxígeno de referencia

** Usualmente, CO se expresa en ppm. 1 ppm= 1,25.10^{-6} kg/Nm^3

CONTAMINANTE **Monóxido de carbono** **CO**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **2/6/5** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **500.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 5 Código M

- **Descripción**

Determinación a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3)* x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores el índice de confianza se considera alto.

* Usualmente, CO se expresa en ppm. 1 ppm= 1,25.10^{-6} kg/Nm^3

CONTAMINANTE
Monóxido de carbono
CO

VALOR UMBRAL (kg/año)
500.000

EXPRESADO COMO
kg de CO

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
2/7/1
1(a), 1(c)

FUENTE DE EMISIÓN: 7 Reformado catalítico

Metodología 1 Código C

Descripción

Factor de emisión basado en el volumen alimentado a la unidad.

Factor: $4{,}16 \cdot 10^{-2}$ kg/m^3 alimentado a la unidad

Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07. (Ref: Bertrand, R.R. and Siegell, J.H. (2003) Emission of trace compounds from catalytic reforming units. Environmental Progress 22, 1, 74-77).

Cuantificación

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{ x m}^3 \text{ alimentado a la unidad.}$$

Observaciones

Este factor de emisión se ha obtenido a partir de unidades con diferentes sistemas de abatimiento, por lo que puede no representar fielmente las emisiones incontroladas.

CONTAMINANTE
Dióxido de carbono
CO_2

VALOR UMBRAL (kg/año)
100.000.000

EXPRESADO COMO
kg de CO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
3/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Según la Decisión 2007/589/CE, las emisiones de gases de efecto invernadero (GEI) pueden determinarse con una metodología basada en la medición utilizando sistemas de medición continua de emisiones (SMCE). Tal como se recoge en el Anexo XII de dicha Decisión, las emisiones de GEI se obtendrán a partir de dos parámetros: concentración de GEI y flujo de gases de combustión.

Concentración de GEI
La concentración de gases de efecto invernadero en el gas de combustión se determina mediante la medición continua en un punto representativo.

Flujo de gases de combustión
El flujo de gases de combustión secos puede determinarse mediante uno de los métodos siguientes.

Método A: El flujo Q_e de gases de combustión se calcula mediante un planteamiento de balance de masas teniendo en cuenta todos los parámetros significativos, como cargas de material de entrada, flujo de aire de entrada, eficacia del proceso, etc., y, en cuanto a la producción, la salida del producto, la concentración de O_2, las concentraciones de SO_2 y NO_x, etc.
La autoridad competente aprobará el método específico de cálculo dentro de la evaluación del plan de seguimiento y de la metodología de seguimiento incluida en ese plan.

Método B: El flujo de gases de combustión Q_e se determina mediante la medición continua del flujo en un punto representativo.

- **Cuantificación**

kg emitidos = $\sum^{\text{horas func.anuales}}$ concentración de GEI x flujo de gases de combustión

- **Observaciones**

Los procedimientos aplicados para medir concentraciones y flujos de masa o volumen se ajustarán a un método normalizado, de haberlo, que limite el margen de error en el muestreo y la medición y cuya incertidumbre de medición sea conocida. Se utilizarán las normas CEN (es decir, las publicadas por el Comité Europeo de Normalización), de haberlas. En caso contrario, se aplicarán las normas ISO (es decir, las publicadas por la Organización Internacional de Normalización) o las normas nacionales adecuadas. Cuando no existan normas aplicables, los procedimientos podrán ajustarse, cuando sea posible, a proyectos de normas adecuadas o directrices sobre mejores prácticas de la industria.

En todo caso, habrán de seguirse los requisitos establecidos en la Autorización de Emisión de GEI de cada Instalación.

CONTAMINANTE **Dióxido de carbono** **CO_2**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **3/1/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código C

- **Descripción**

Las emisiones de CO_2 de instalaciones de combustión se calcularán multiplicando el contenido de energía de cada combustible utilizado (dato de actividad) por un factor de emisión y un factor de oxidación, tal como se expone en el apartado de cuantificación.

Los datos de actividad se expresan en general como el contenido de energía neto del combustible consumido.

Dato de actividad = VCN x consumo de combustible

donde VCN es el valor calorífico neto del combustible.

- **Cuantificación**

Emisiones de CO_2 = Dato de actividad x factor de emisión x factor de oxidación

- **Observaciones**

Los factores implicados en el cálculo (combustible consumido, valor calorífico neto, factor de emisión y factor de oxidación) se ajustarán a los requisitos establecidos en la Autorización de Emisión de GEI de cada Instalación.

Con carácter general, los requisitos para Refinerías tipo C (emisiones anuales superiores a 500.000 t) implican la determinación del VCN y contenido en carbono del combustible utilizado; para Refinerías tipo B (emisiones entre 50.000 y 500.000 t) se podría optar por valores de VCN y factores de emisión del último inventario nacional.

CONTAMINANTE Dióxido de carbono CO_2	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **3/2/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de CO_2	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 2 Antorchas

Metodología 1 Código C

- **Descripción**

Las emisiones de antorchas incluirán las rutinarias y las operacionales (disparos, arranque y parada), así como descargas de emergencia.

Las emisiones de CO_2 se calcularán multiplicando un dato de actividad por un factor de emisión y un factor de oxidación, tal como se expone en el apartado de cuantificación.

En este caso el dato de actividad es la cantidad de gas quemado en la antorcha.

- **Cuantificación**

Emisiones de CO_2 = dato de la actividad x factor de emisión x factor de oxidación

- **Observaciones**

Los factores implicados en el cálculo (cantidad de gas quemado, factor de emisión y factor de oxidación) se ajustarán a los requisitos establecidos en la Autorización de Emisión GEI de cada Instalación.

CONTAMINANTE **Dióxido de carbono** **CO_2**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **3/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de CO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Plantas de hidrógeno

Metodología 1 Código C

- **Descripción**

El CO_2 emitido procederá del contenido de carbono del gas entrante, descontando en su caso el contenido en carbono de las corrientes de salida. Se hará un cálculo de las emisiones de CO_2 aplicando la fórmula de cálculo que se indica en el apartado de cuantificación.

En este caso, el dato de actividad es la cantidad de hidrocarburo entrante procesada y la cantidad de las diferentes corrientes de salida.

- **Cuantificación**

$$\text{Emisiones de } CO_2 = (\text{dato de actividad}_{\text{entrada}} \times \text{factor de emisión}_{\text{entrada}}) - (\text{dato de actividad}_{\text{salida}} \times \text{factor de emisión}_{\text{salida}})$$

- **Observaciones**

La Decisión 2007/589/CE no recoge la posibilidad de que las corrientes de salida contengan carbono. No obstante, si esta cuestión queda recogida en la Autorización de Emisión de GEI, podría ser aplicada.

Los factores implicados en el cálculo (datos de actividad y factores de emisión) se ajustarán a los requisitos establecidos en la Autorización de Emisión de GEI de cada Instalación.

CONTAMINANTE
Dióxido de carbono
CO_2

VALOR UMBRAL (kg/año)
100.000.000

EXPRESADO COMO
kg de CO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
3/4/1
1(a), 1(c)

FUENTE DE EMISIÓN: **4 Regeneración catalítica de unidades de cracking, otros tipos de regeneración catalítica y flexicoking**

Metodología 1 Código C

Descripción

El coque depositado en el catalizador como subproducto del proceso de cracking se quemará en el regenerador con el fin de restablecer la actividad del catalizador. Otros procesos de refinería emplean un catalizador que necesita ser regenerado, por ejemplo, reformado catalítico.

Las emisiones de CO_2 se calcularán aplicando la fórmula que se recoge en el apartado de cuantificación. En este caso, el dato de actividad es la cantidad de coque quemado en el regenerador.

Las emisiones se calcularán mediante un balance de materiales, teniendo en cuenta el estado del aire de entrada y el gas de combustión. Todo el CO presente en el gas de combustión se contabilizará como CO_2 (aplicando la relación de masas: t CO_2 = t CO x 1,571)

El análisis del aire de entrada y de los gases de combustión así como la elección de niveles se harán de acuerdo con lo dispuesto en la sección 13 del anexo I de la Decisión 2007/589/CE. La autoridad competente aprobará el método específico de cálculo dentro de la evaluación del plan de seguimiento y de la metodología de seguimiento incluida en ese plan.

Cuantificación

Emisiones de CO_2 = dato de actividad x factor de emisión

Observaciones

Los factores implicados en el cálculo (cantidad de coque quemado y factor de emisión) se ajustarán a los requisitos establecidos en la Autorización de Emisión de GEI de cada Instalación.

CONTAMINANTE
Óxido nitroso
N_2O

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de N_2O

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
5/1/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos

(1) Gasoil: 8,40 · 10^{-1} g/GJ

(2) Fueloil: 1,60 g/GJ

(3) LPG: 4,33 g/GJ

(4) GN: 1,03 g/GJ

(5) GN (con quemador de bajo NO_x): 3,00 · 10^{-1} g/GJ

Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07 (Ref: API (2004) Compendium of greenhouse gas emissions estimation methodologies for the oil and gas industries)

(6) Fueloil: 46,5 g/GJ

(7) Gasoil: 15,7 g/GJ

(8) GN: 2,4 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(9) Fueloil: 0,53 lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-8, SCC 10200401

(10) GN: 2,2 lb/10^6 ft^3. Fuente: EPA AP-42, Tabla 1.4-2, SCC 10200601

(11) GN (con quemadores de bajo NO_x): 0,64 lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-2, SCC 10200601

(12) Fueloil: 0,3 kg/TJ

(13) Gas/Diesel Oil: 0,4 kg/TJ

(14) GN: 1 kg/TJ

(15) LPG: 4 kg/TJ

Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy)

CONTAMINANTE
Óxido nitroso
N_2O

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de N_2O

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
5/1/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Cuantificación**

(1) a (8)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

(9)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\,\text{m}^3} \text{x}\,\text{m}^3\ \text{fueloil}$$

(10) y (11)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{35{,}31467\,\text{ft}^3}{\text{m}^3} \text{x}\,\text{m}^3\ \text{gas natural}$$

(12) a (15)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right) \text{x} \frac{\text{TJ}}{10^3\,\text{GJ}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

- **Observaciones**

El índice de confianza de (9), (10) y (11) es E, no estando disponible en la bibliografía manejada para el resto de factores.

CONTAMINANTE **Óxido nitroso** **N_2O**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **5/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de N_2O**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: 1,43 g/GJ. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07 (Ref: API (2004) Compendium of greenhouse gas emissions estimation methodologies for the oil and gas industries)

(2) Fueloil: 2,5 ÷ 14 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(3) Gasoil: 2 ÷ 3 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(4) GN: $3 \cdot 10^{-3}$ lb/10^6 btu. Fuente: EPA, SCC 20200201

(5) GN (>3 MW): 1 kg/TJ. Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy)

- **Cuantificación**

(1) a (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0,251\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{GN}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right) \text{X} \frac{\text{TJ}}{10^3\,\text{GJ}} \text{X} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

- **Observaciones**

El índice de confianza de (4) es E, no estando disponibles en la bibliografía manejada para el resto de factores.

CONTAMINANTE **Óxido nitroso** **N_2O**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **5/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de N_2O**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Diesel: 2,21 g/GJ. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07 (Ref: API (2004) Compendium of greenhouse gas emissions estimation methodologies for the oil and gas industries)

(2) Fueloil: 2,5 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(3) Gasoil: 2,5 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

- **Cuantificación**

$$\text{(1) a (3)} \quad \text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

- **Observaciones**

Los índices de confianza de los factores anteriores no están disponibles en la bibliografía manejada.

CONTAMINANTE
Óxido nitroso
N_2O

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de N_2O

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
5/4/1
1(a), 1(c)

FUENTE DE EMISIÓN: 4 Combustión

Metodología 1 Código C

Descripción

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gas/Diesel Oil: 0,6 kg/TJ

(2) Residual Fuel Oil: 0,6 kg/TJ

(3) LPG: 0,1 kg/TJ

(4) Refinery Gas: 0,1 kg/TJ

(5) Natural Gas: 0,1 kg/TJ

Fuente: 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Volume 2, Energy)

Cuantificación

(1) a (5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{TJ}}\right) \text{x} \frac{\text{TJ}}{10^3\,\text{GJ}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

Observaciones

No se han localizados índices de confianza para estos factores en la bibliografía analizada.

CONTAMINANTE **Óxido nitroso** **N_2O**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **5/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de N_2O**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Cracking catalítico en lecho fluido

Metodología 1 Código E

- **Descripción**

Factor deducido en función del dato de coque retenido en el catalizador de las unidades. Se considera que la eliminación del coque retenido en el catalizador puede ser equiparable a un proceso de combustión. Asumiendo este presupuesto, se deduce un factor de 298 g/t coque (Fuente: Informe CORINE-AIRE 1.997-2.000).

- **Cuantificación**

$$\text{Kg emitidos} = \text{Factor}\left(\frac{g}{t}\right) x \frac{kg}{10^3 g} x\, t\, \text{coque}$$

- **Observaciones**

No existen índices de confianza en la bibliografía manejada.

CONTAMINANTE **Amoniaco** **NH_3**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **6/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de amoniaco**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

(1) Fueloil: 0,8 lb/10^3 gal. Fuente: EPA SCC 10200401

(2) GN: 3,2 lb/10^6 ft^3. Fuente: EPA SCC 10200601

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{gal}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}00378\ \text{m}^3}\times\text{m}^3\ \text{fueloil}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{ft}^3}{0{,}028\ \text{m}^3}\times\text{m}^3\ \text{GN}$$

- **Observaciones**

El índice de confianza para los factores empleados es E para (1) y C para (2).

CONTAMINANTE **Amoniaco** NH_3	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **6/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de amoniaco**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Factor: 54 lb/10^3 barril. Fuente: CONCAWE (Ref: EPA SCC 30600201)
(sin precipitador electrostático ni caldera auxiliar de CO).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\text{m}^3\text{alimentados}$$

- **Observaciones**

El factor de emisión ofrecido por EPA tiene un índice de confianza B.

CONTAMINANTE
Amoniaco
NH_3

VALOR UMBRAL (kg/año)
10.000

EXPRESADO COMO
kg de amoniaco

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
6/3/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 3 Sistemas de reducción de NO_x

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

SNCR

(1) Fueloil: 2,9 lb/10^3 gal. Fuente: CONCAWE (Ref: EPA SCC 10200401)

(2) GN: 18 lb/10^6 ft^3. Fuente: CONCAWE (Ref : EPA SCC 10200601)

SCR

(3) Fueloil: 1,4 lb/10^3 gal. Fuente: CONCAWE (Ref : EPA SCC 10200401)

(4) GN: 9,1 lb/10^6 ft^3. Fuente: CONCAWE (Ref : EPA SCC 10200601)

Empleo de factores de emisión basados en el flue gas, tanto para SNCR como para SCR.

(5) 3,8 mg/m^3. Fuente: Libro Guía EMEP/CORINAIR, Capítulo 111

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{gal}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}0378\ \text{m}^3}\times\text{m}^3\ \text{fueloil}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{ft}^3}{0{,}028\ \text{m}^3}\times\text{m}^3\text{gas natural}$$

$$(3)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{gal}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}0378\ \text{m}^3}\times\text{m}^3\ \text{fueloil}$$

$$(4)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{ft}^3}{0{,}028\ \text{m}^3}\times\text{m}^3\text{gas natural}$$

$$(5)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{mg}}{\text{m}^3}\right)\times\frac{1\text{kg}}{10^6\ \text{mg}}\times\text{m}^3\ \text{flue gas}$$

- **Observaciones**

El índice de confianza de todos los factores empleados es C, excepto para el último factor, del que no se encuentra disponible en la bibliografía manejada.

CONTAMINANTE **Amoniaco** **NH_3**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **6/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de amoniaco**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Sistemas de refrigeración

Metodología 1 Código M

- **Descripción**

Se asume que las emisiones de NH_3 empleado como refrigerante son iguales a la cantidad de NH_3 con la que se rellenan los sistemas de refrigeración como consecuencia de las pérdidas por fugas (CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07).

- **Cuantificación**

kg emitidos = kg de NH_3 usados para rellenar los sistemas de refrigeración.

- **Observaciones**

El índice de confianza se considera alto, siempre que la medida del NH_3 de relleno sea fiable.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

Hornos y calderas < 10 MW

(1) Gasoil: 1,1 g/GJ

(2) Fueloil: 3,41 g/GJ

(3) LPG: 1,48 g/GJ

(4) GN: 2,58 g/GJ

Hornos y calderas de 10 a 100 MW

(5) Gasoil: $6,47 \cdot 10^{-1}$ g/GJ

(6) Fueloil: $8,45 \cdot 10^{-1}$ g/GJ

(7) LPG: 1,48 g/GJ

(8) GN: 2,58 g/GJ

Hornos y calderas > 100 MW

(9) Gasoil: 2,46 g/GJ

(10) Fueloil: 2,29 g/GJ

(11) LPG: 2,27 g/GJ

(12) GN: 2,58 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

Hornos y calderas < 50 MW

(13) Gasoil: 15 g/GJ

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Hornos y calderas ≥ 50 MW

(14) Fueloil: 10 g/GJ

(15) Gasoil: 5 g/GJ

(16) GN: 5 g/GJ

(17) Fuelgas: 25 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

Potencia sin especificar

(18) Fueloil: $2{,}8\cdot10^{-1}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-3, SCC 10200401

(19) GN: 3,2 lb/10^6 ft^3. (Obtenido como COV-Metano = 5,5-2,3 lb/10^6 ft3, Fuente: EPA, AP-42, Tabla 1.4-2, SCC 10200601).

- **Cuantificación**

$$\text{(1) a (17)}\quad \text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right)\text{x}\frac{\text{kg}}{10^3\text{g}}\text{x}\frac{\text{GJ}}{239.005\,\text{kcal}}\text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\text{x}\,\text{kg}\,\text{combustible}$$

$$\text{(18)}\qquad \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right)\text{x}\frac{0{,}45359\,\text{kg}}{\text{lb}}\text{x}\frac{\text{gal}}{0{,}00378\,\text{m}^3}\text{x}\,\text{m}^3\ \text{fueloil}$$

$$\text{(19)}\qquad \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right)\text{x}\frac{0{,}45359\,\text{kg}}{\text{lb}}\text{x}\frac{\text{ft}^3}{0{,}028\,\text{m}^3}\text{x}\,\text{m}^3\ \text{GN}$$

- **Observaciones**

El índice de confianza de (18) es A. Los índices de confianza de los factores de emisión de los que se obtiene (19) son B para el metano y C para COV. Del resto de factores, no se han localizado índices de confianza en la bibliografía manejada.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil : $1{,}86 \cdot 10^{-1}$ g/GJ

(2) GN : 1 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 3 g/GJ

(4) Gasoil: 5 g/GJ ó 1,5 ÷ 2 g/GJ (según fuente bibliográfica)

(5) GN: 5 g/GJ ó 2,5 ÷ 4 g/GJ (según fuente bibliográfica)

(6) Fuelgas: 2,5 g/GJ

Fuente: Libro Guía EMEP/CORINAIR, Capítulo 111

- **Cuantificación**

(1) a (6)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\ \text{kcal}} \text{x}\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\, \text{kg combustible}$$

- **Observaciones**

No se han encontrado índices de confianza de los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: $5{,}64 \cdot 10^{1}$ g/GJ

(2) Diesel: $3{,}71 \cdot 10^{1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 50 g/GJ

(4) Gasoil: 1,5 ÷ 100 g/GJ

(5) GN: 200 g/GJ

Fuente: Libro Guía EMEP/CORINAIR, Capítulo 111

- **Cuantificación**

(1) a (6)

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^{3} g} x \frac{GJ}{239.005\,kcal} x\,PCI\left(\frac{kcal}{kg}\right) x\,kg\,combustible$$

- **Observaciones**

No se han encontrado índices de confianza de los factores anteriores en la bibliografía manejada.

CONTAMINANTE Compuestos Orgánicos Volátiles Distintos del Metano **COVDM**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **7/4/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de COVDM	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV's totales basados en el crudo procesado en Refinería.

(1) Factor: 0,8 lb/10^3 barril crudo. EPA SCC 30600401

Se asume que el 20% de la emisión de COV's es metano (CORINAIR, ref. US EPA CHIEF database).

Empleo de factores de emisión para el cálculo de COVDM basados en el crudo procesado en Refinería.

(2) Factor: $2 \cdot 10^{-3}$ kg/m^3. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07

Empleo de factores de emisión para el cálculo de COVDM conocidas la masa y composición de la corriente a antorcha.

(3) Se asume que el 0,5 % de los hidrocarburos queda sin quemar. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no.3/07

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{barril}}{0{,}159\,\text{m}^3} \times \frac{100\text{-}20}{100} \times \text{m}^3\,\text{de crudo}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \text{m}^3\,\text{de crudo}$$

(3) $$\text{kg emitidos} = \text{kg gas} \times \frac{\%\,\text{COVDM}}{100} \times \frac{0{,}5}{100}$$

- **Observaciones**

El índice de confianza para el factor de emisión (1) es B.

No aparece en la bibliografía manejada el índice de confianza para el resto de factores ni para el porcentaje de metano.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV's totales basados en la alimentación a la unidad.

Factor: 220 lb/10^3 barril. Fuente: CONCAWE (Ref: EPA, Tabla 5.1-1 SCC 30600201)

Posteriormente se considera que el 1% de los COV's totales es metano (menos del 1%, según EPA, AP-42, Tabla 5.1-1).

No obstante, también se ha encontrado que el 36% de los COV’s totales es metano (CORINAIR, B411, Tabla 9.3 Refinery Fluid Catalytic Cracking, Referencia US EPA).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{-3}\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159}\times\frac{1}{100}\times \text{m}^3\ \text{alimentados}$$

- **Observaciones**

El factor inicial para COV's totales tiene un índice de confianza B, mientras que para el porcentaje de metano de CORINAIR (36%) es C.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/6/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Destilación a Vacío

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para COV's totales basados en la alimentación a la unidad.

(1) Factor: 50 lb/10^3 barril Fuente: CORINAIR, Capítulo 411 (Ref: EPA SCC 30600602)

Empleo de factores de emisión para COV's totales basados en la alimentación a Refinería.

(2) Factor: 0,052 kg/m^3 crudo. Fuente: CORINAIR, Capítulo 411 (Ref. US EPA 1985 a y 1995).

Posteriormente se considera que el 1% de los COV's totales es metano (menos del 1%, según EPA, AP-42, Tabla 5.1-1).

No obstante, también se ha encontrado que el 13% de los COV's totales es metano (CORINAIR, B411, Tabla 9.2, Ref. US EPA, Petroleum Refinery Speciation Profile).

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\frac{100-1}{100}\times\text{m}^3\text{alimentados}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right)\times\frac{100-1}{100}\times\text{m}^3\,\text{crudo}$$

- **Observaciones**

El índice de confianza de (1) es C, no habiéndose encontrado para el factor (2).

El índice de confianza del porcentaje de metano de CORINAIR (13%) es E.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/7/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 7 Planta de tratamiento de efluentes líquidos

Metodología 1 Código C

- **Descripción**

Empleo de la ecuación de Litchfield para determinar COV's totales y posteriormente cálculo de NMCOV's a partir del porcentaje en metano.

La ecuación de Litchfield expresa la emisión de NMCOV's como porcentaje del total de aceites que entran a la planta de tratamiento:

- % pérdidas = -6,6339 + 0,0319 x (T_{amb} ºF) - 0,0286 x (10% Dist. Point ºF) + 0,2145 x (T_{agua} ºF)

- Valores típicos 10% dist. point = 250 ºF
  Concentración aceites en agua a tratar = 2.000 mg/l

Fuente CONCAWE, report Nº 87/52. “Cost-efectiveness of hydrocarbon emission controls in Refineries from crude oil receipt to product dispatch”.

Esta ecuación no considera la existencia de balsas cubiertas y/o sistemas de recuperación de vapor. En caso de que existan estas medidas de control, debe considerarse aplicar el ratio 0,024/0,6 según se indica en US EPA AP-42, Tabla 5.1-2.

Sobre el total de COV’s obtenidos, se considera que el 13% es metano (CORINAIR, Tabla 9.2, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = Q_{\text{agua a planta}}\left(\frac{m^3}{\text{año}}\right) \times \frac{10^3\,l}{m^3} \times 2.000\,\frac{mg}{l} \text{ x } \frac{kg}{10^6\,mg} \times \frac{\%\text{Litchfield}}{100} \text{ x } \frac{100-13}{100}$$

- **Observaciones**

No existen índices de confianza en la bibliografía manejada para el cálculo de COV's totales, observándose cómo parámetros como el área de balsas o velocidad de viento no entran en consideración en el cálculo.

El índice de confianza del porcentaje de metano respecto a COV's totales es E.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano
COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
7/7/2
1(a), 1(c)

FUENTE DE EMISIÓN: 7 Planta de tratamiento de efluentes líquidos

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en m^3 de agua tratada para determinar COV's totales y posteriormente cálculo de NMCOV's a partir del porcentaje en metano.

Factores de emisión: (US EPA, AP-42, Tabla 5.1-2)

· 0,6 kg/m^3 agua tratada	(sin medidas correctoras)
· 0,024 kg/m^3 agua tratada	(balsas cubiertas y/o sistemas de recuperación de vapor)

Sobre el valor total de COV's obtenido, se considera que el 13% es metano (CORINAIR, Tabla 9.2, ref. US EPA Petroleum Refinery Speciation profile).

- **Cuantificación**

$$\text{kg emitidos} = \ \text{m}^3\ \text{agua tratada} \times \text{factor de emisión}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x}\ \frac{100\text{-}13}{100}$$

- **Observaciones**

El índice de confianza para los factores de emisión ofrecidos por EPA es D. El correspondiente al porcentaje de metano es E.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano
COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
7/7/3
1(a), 1(c)

FUENTE DE EMISIÓN: 7 Planta de tratamiento de efluentes líquidos

Metodología 3 Código C

- **Descripción**

(1) Empleo de factores de emisión basados en áreas de balsas existentes para determinar COV's totales.

Factores:

- 20 g/(m^2·h) para separadores de aceite sin cubrir
- 2 g/(m^2·h) para separadores de aceite cubiertos
- 2 g/(m^2·h) para flotación
- 0,2 g/(m^2·h) para tratamientos biológicos

Fuente: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries.

Sobre el valor total de COV's obtenido, se considera que el 13% es metano (CORINAIR, Tabla 9.2, ref. US EPA Petroleum Refinery Speciation Profile).

(2) Para los separadores agua-aceite también se pueden emplear factores de emisión de COVDM basados en el volumen de agua tratada.

Factores:
- $1{,}11\cdot10^{-1}$ kg/m^3 para separadores por gravedad sin cubrir
- $3{,}30\cdot10^{-3}$ kg/m^3 para separadores por gravedad cubiertos
- 0 kg/m^3 para separadores por gravedad cubiertos y conectados a antorcha
- $4{,}00\cdot10^{-3}$ kg/m^3 para separadores DAF o IAF sin cubrir
- $1{,}20\cdot10^{-4}$ kg/m^3 para separadores DAF o IAF cubiertos
- 0 kg/m^3 para separadores DAF o IAF cubiertos y conectados a antorcha

NOTA: Los factores anteriores no incluyen la emisión de etano.
NOTA: Los factores para IAF y DAF son de aplicación cuando se instalan como tratamiento secundario.
FUENTE: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \sum \text{Factor}_i\left(\frac{g}{m^2\times h}\right)\times m^2\ \text{equipo}_i\times \text{horas de operación}_i\times\frac{kg}{10^3\ g}\times\frac{100\text{-}13}{100}$$

$$(2)\ \text{kg emitidos} = \sum \text{Factor}_i\left(\frac{kg}{m^3}\right)\times m^3\ \text{de agua tratada por el separador de aceite}$$

- **Observaciones**

La bibliografía manejada no aporta índices de confianza para los factores suministrados. Debe destacarse cómo estos factores son de una gran generalidad, sin tener en cuenta las condiciones climáticas del emplazamiento de la Planta.

El índice de confianza para el metano presente en COV's totales es E.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano
COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
7/8/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 8 Torres de refrigeración

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para determinar COV's totales basados en el volumen de agua circulante o cantidad de crudo procesada. Dado que en la bibliografía manejada no se ha localizado la presencia de metano en esta fuente, se asume que todos COV's calculados son NMCOV's.

(1) Factor = 6 lb/10^6 gal agua circulante. EPA SCC 30600701.
(2) Factor = 10 lb/1.000 barril crudo procesado. EPA SCC 30600702.

No obstante, según CONCAWE, las emisiones procedentes de torres de refrigeración pueden considerarse despreciables, ya que estos compuestos no llegan a las mismas. (Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07)

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{gal}}\right)\times\frac{0{,}45359\ \text{kg}}{\text{lb}}\times\frac{\text{gal}}{0{,}00378\ \text{m}^3}\times \text{m}^3\ \text{agua circulante}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{barril}}\right)\times\frac{0{,}45359\ \text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\ \text{m}^3}\times \text{m}^3\ \text{crudo procesado}$$

- **Observaciones**

Ambos factores tienen un índice de confianza D, prefiriéndose el empleo del primero al ser función directa del agua circulante. El empleo del segundo factor asume que el agua circulante se puede estimar como 40 veces el volumen de crudo procesado.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/9/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 1 Código C

- **Descripción**

Determinación de NMCOV's a partir de factores de emisión de NMCOV's específicos para elementos: válvulas, conexiones, drenajes, ...

Estos factores se afectan posteriormente por el nº de elementos estimados en cada unidad de Refinería (ver Anexo 12).

Los factores empleados son:

Tipo de equipo	Servicio	Factor de emisión kg/h/elemento
Válvulas	Gas (a)	0,0268
	Líquido ligero (a)	0,0109
	Líquido pesado (b)	0,0000987
Sellos de bombas	Líquido ligero (a)	0,114
	Líquido pesado (b)	0,00349
Sellos de compresores	Gas (a)	0,636
Válvulas de alivio de presión	Gas (a)	0,16
Conexiones	Para todos (a)	0,00025
Finales de línea	Para todos (a)	0,0023
Conexiones de muestreo	Para todos (a)	0,0150
Drenajes	Para todos (a)	0,032

(a): US EPA (1995 a)
(b): Taback (1996)
NOTA: Todos los valores se corresponden para centros sin programas de inspección y mantenimiento.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{nº elementos x h}} \right) \text{x nº elementos}_i \text{ x nº horas}_i$$

- **Observaciones**

El índice de confianza para la mayoría de los elementos (fuente US EPA) es U. En relación con la fiabilidad del método, debe considerarse la calidad en la contabilización del nº de elementos.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/9/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión generales, basados en la cantidad de crudo procesado. Así, CONCAWE en su report nº 3/07 (Air pollutant emission estimation methods for E-PRTR reporting by refineries) recoge un factor de emisión del 0,03% del total del crudo procesado por la Refinería.

- **Cuantificación**

kg emitidos = (0,03/100) x kg de crudo

- **Observaciones**

No se recogen índices de confianza. No obstante, no se considera un método de gran fiabilidad al no tener en cuenta la complejidad de la Refinería.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano

COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
7/9/3
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 3 Código E

- **Descripción**

Extrapolación de resultados a partir de las emisiones típicas de una Refinería (Fuente: US EPA, AP-42, Tabla 5.1-2):

Fuente	Número	Emisiones (NMCOV's) (kg/día)
- Válvulas:	11.500	3.100
- Bridas:	46.500	300
- Sellos de bombas:	350	590
- Sellos de compresores:	70	500
- Válvulas de seguridad:	100	200
- Drenajes:	650	450
- Válvulas:	11.500	3.100

Las emisiones del cuadro se corresponde a una Refinería con una capacidad de 330.000 barriles /día, sin programas de inspección y mantenimiento.

- **Cuantificación**

$$\text{kg emitidos} = \sum_{i} \text{emisiones elemento}_i \left(\frac{\text{kg}}{\text{d}}\right) \times \frac{\text{capacidad refino (barriles/día)}}{\text{330.000 barriles /día}} \times \text{nº de días}$$

- **Observaciones**

La fiabilidad del método no es alta, ya que no considera las unidades particulares que integran la Refinería.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano
COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
7/9/4
1(a), 1(c)

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 4 Código M

- **Descripción**

Implantación de un programa de detección y reparación de fugas (LDAR). El programa LDAR está destinado a la detección y progresiva reducción de las emisiones gaseosas de compuestos orgánicos volátiles (COV) de carácter difuso que tienen su origen en las pérdidas que se producen en los diferentes elementos que componen las unidades de proceso (bombas, válvulas, compresores, bridas, etc.).

Este programa se basa en los estándares del Método 21 de la US EPA, el cual establece no sólo el método a emplear para llevar a cabo las mediciones en campo sino que también define las características de los elementos a emplear y el método de calibración de los mismos. Mediante el programa LDAR, se identifican en planta los equipos que fugan, se procede a la medición de los mismos y, para aquellos que superan un cierto valor, se establecen plazos para llevar a cabo el ajuste, reparación o sustitución y se fija un calendario de seguimiento.

Seguidamente, se obtiene el contenido de COVDM según las especiaciones recogidas en CORINAIR:

	CH_4 (%p) en COV`s totales	Índice de confianza
- Drenajes	2,90	C
- Sellos de compresores	13,30	D
- Válvulas de seguridad	0	D
- Válvulas y conexiones	28,6	C
- Sellos de bombas	3,30	C

Nota: Obviamente, en caso de que el programa LDAR llevara a cabo mediciones de COVDM no sería necesario aplicar los porcentajes anteriores.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Medida LDAR}_i\,(\text{kg}) \times \left(\frac{100 - \%CH_4}{100}\right)_i$$

Donde i es cada elemento que fuga

- **Observaciones**

La fiabilidad de las medidas de COV's obtenidas mediante un sistema LDAR se considera superior a los cálculos basados en factores de emisión.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/10/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 10 Parque de almacenamiento

Metodología 1 Código C

- **Descripción**

Empleo del software "TANKS". TANKS es un procedimiento de cálculo desarrollado por US EPA que calcula las emisiones totales procedentes de tanques a partir del sistema de cálculo detallado en AP-42, sección 7.1, "Organic liquid storage tanks".

- **Cuantificación**

En función del tipo de tanque, sus dimensiones, naturaleza del producto y movimiento del mismo, características climatológicas de la zona, etc, se obtiene la emisión correspondiente a cada tanque en kg/año.

$$\text{kg emitidos} = \sum_i \text{kg emitidos tanque}_i$$

- **Observaciones**

Se considera como el método más preciso a la hora de evaluar las pérdidas en el parque de almacenamiento.

CONTAMINANTE
Compuestos Orgánicos Volátiles Distintos del Metano
COVDM

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de COVDM

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
7/10/2
1(a), 1(c)

FUENTE DE EMISIÓN: 10 Parque de almacenamiento

Metodología 2 Código E

- **Descripción**

Obtención de factores de emisión basados en datos reales y en CORINAIR (fuente Informe Corine-Aire, 1997-2000). Se parte de la información sobre factores de emisión para el almacenamiento de gasolina (tabla 8.3, B551, CORINAIR) aplicando a los distintos productos almacenados unos factores de conversión medios de acuerdo con la volatilidad de los mismos (valores medios obtenidos mediante estimación a partir de los datos facilitados por refinerías, al existir rangos de variación para un mismo producto incluso en una misma Refinería), tomando la volatilidad de la gasolina como 1 y calculando el factor relativo para los restantes productos. Los parámetros para la aplicación de este algoritmo de estimación, así como los factores de emisión deducidos para los distintos tipos de tanques se presentan seguidamente.

	Factores de emisión (gramos emitidos/tonelada almacenada)				
	Factor de conversión	Techo Externo Flotante (EFER)		Techo interno Flotante (IFC)	Techo Fijo
		Sello simple	Sello doble		
Gasolina	1	73	5	160	1.570
Crudo	0,5	36,5	2,5	80,0	785,0
Gasóleo	0,03	2,2	0,2	4,8	47,1
Queroseno	0,02	1,5	0,1	3,2	31,4
Nafta	1	73,0	5,0	160,0	1.570
Fuelóleo	0,02	1,5	0,1	3,2	31,4
GLP	1,35	98,6	6,8	216,0	2.119,5
Asfaltos	0,005	0,4	0,0	0,8	7,9
Aromáticos	0,02	1,5	0,1	3,2	31,4
Destilados medios	0,03	2,2	0,2	4,8	47,1
Destilados pesados	0,02	1,5	0,1	3	31,4

Fuente: Informe Corine-Aire. 1997-2000

- **Cuantificación**

$$\text{kg emitidos} = \sum_{i}^{\text{Producto}} \sum_{j}^{\text{Tipo tanque}} \text{Factor conversión}_{i} \times \text{Toneladas producto}_{i,j} \times \text{Factor emisión}_{i,j} \times 10^{-3}$$

donde el par “i, j” representa al producto “i” almacenado en el tanque tipo “j”.

- **Observaciones**

La fiabilidad del método es muy inferior a la de la metodología anterior (“TANKS”), al ser una estimación que no requiere conocimiento de la meteorología de la zona, el movimiento de productos, así como numerosas características constructivas de los tanques analizados.

CONTAMINANTE **Compuestos Orgánicos Volátiles Distintos del Metano** **COVDM**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **7/11/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de COVDM**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 11 Purgas

Metodología 1 Código C

- **Descripción**

En el caso de venteos a la atmósfera (sin recuperación ni envío a antorcha) se considera un factor de emisión de hidrocarburos totales de 1.662 kg/m^3 de alimentación a Refinería, siendo el contenido en metano <1 %.

Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x}\, \text{m}^3 \,\text{crudo}\, \text{x}\, \frac{100-1}{100}$$

- **Observaciones**

El índice de confianza del factor de emisión es C.

CONTAMINANTE **Óxidos de nitrógeno** **NO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Determinación a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudal de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3)* x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores el índice de confianza se considera alto.

* Usualmente, el NO_2 se expresa en ppm. 1 ppm = 2,05 · 10^{-6} kg/Nm^3

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/1/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código M

- **Descripción**

Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante análisis de la composición del combustible y a partir de éste a través de la aplicación de la Orden de 26 de diciembre de 1995 (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3)** x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

* C y Q expresados en igual base y al mismo oxígeno de referencia.

** Usualmente, el NO_2 se expresa en ppm. 1 ppm = 2,05 · 10^{-6} kg/Nm^3

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Cálculo de las emisiones de NO_X como suma del NO_X térmico y NO_X del combustible. Para ello se desarrolla la siguiente metodología:

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(1) Factor de NO_X térmico = F_{BASE} x F_{H2} x $F_{CONTROL}$ x $F_{PREHEAT}$ x F_{H2O} x F_{LOAD} x F_{BURN}

F_{BASE}: Factor del combustible. Tiene en cuenta la temperatura de la llama debido a la composición del combustible. Por tanto, depende del tipo de combustible.

COMBUSTIBLE	F_{BASE} (g/GJ)
Methane, Natural Gas, LPG	56
Refinery Fuel Gas	69
Low Joule Gas	30
Refinery Fuel Oil Distillates	56

F_{H2}: Factor de ajuste para la cantidad de gas hidrógeno en el combustible. Para todos los combustibles líquidos, metano, gas natural y LPG, F_{H2} = 1,0.

COMBUSTIBLE	Concentración de H_2 (% v)	F_{H2}
Refinery Fuel Gas	0-23	1,00
	33	1,04
	43	1,09
	53	1,25
	63	1,46
Low Joule Gas	0-14,7	1,00
	24,7	1,04
	34,7	1,09
	44,7	1,25
	54,7	1,46

CONTAMINANTE
Óxidos de nitrógeno
NO_X

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de NO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
8/2/1
1(a), 1(c)

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

$F_{CONTROL}$: Factor de ajuste para la tecnología de control empleada, incluyendo el tipo de quemador.

Tecnología de control		**$F_{CONTROL}$**
None		1,00
Low NO_X burner, staged fuel		0,33
Low NO_X burner, staged air		0,60
Ultra-low NO_X burner		0,30
Flue Gas Recirculation	0 %	1,00
	5 %	0,60
	10 %	0,40
	15 %	0,30
	20 %	0,20

$F_{PREHEAT}$: Factor de ajuste para la temperatura de precalentamiento del aire.

Temperatura de precalentamiento del aire (ºC)	**$F_{PREHEAT}$**
< 38	1,00
38	1,00
93	1,10
149	1,32
204	1,60
260	1,86

F_{H2O}: Factor de ajuste para el contenido de humedad en el aire de combustión.

Humedad (kg H_2O/kg aire seco)	**F_{H2O}**
0	1,00
0,01	0,79
0,02	0,67
0,03	0,53
0,04	0,41
0,05	0,29

F_{LOAD}: Factor de ajuste para el % de carga.

CARGA (% de diseño)	**F_{LOAD}**
40	0,55
60	0,70
80	0,85
100	1,00

CONTAMINANTE
Óxidos de nitrógeno
NO_X

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de NO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
8/2/1
1(a), 1(c)

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

F_{BURN}: Factor de ajuste para la intensidad, una medida del calor emitido por unidad de volumen. Si no se dispone de esta información, se considera que los packaged boilers y los hornos de pirólisis son de alta intensidad. Si se conoce el volumen de la sección radiante de un horno, se considera alta intensidad > 700 KW/m^3 y baja intensidad < 30 KW/m^3.

INTENSIDAD	**F_{BURN}**
Alta	1,8
Baja	1,0

(2) Factor de NO_X del combustible

Nitrógeno en el combustible (% p)	**$F_{N2CONTENT}$**	
	Uncontrolled Burner	**Low-NO_X Burner with staged air**
< 0,05	1,00	1,00
0,05	0,87	0,86
0,1	0,78	0,75
0,3	0,53	0,43
0,5	0,38	0,30
1,0	0,32	0,25

- **Cuantificación**

(1) kg de NO_X térmicos emitidos = Factor de NO_X térmico $\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x\, PCS \left(\frac{GJ}{kg}\right) x\, kg\, combustible$

PCS = 1,05 x PCI para combustibles líquidos
PCS = 1,11 x PCI para combustibles gaseosos

(2) kg de NO_X del combustible emitidos = kg combustible x $\frac{\%N}{100} x \frac{46}{14} x F_{N2CONTENT}$

kg emitidos = (1) + (2)

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/2/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

Potencia ≥ 300 MW

(1) Fueloil: 210 g/GJ (tangential firing)

(2) Fueloil: 260 g/GJ (wall firing)

(3) Fueloil: 155-296 g/GJ (configuración sin especificar)

(4) Gasoil: 68 g/GJ

(5) GN: 48-333 g/GJ

(6) Fuelgas: 88-333 g/GJ

Potencia entre 50 y 300 MW

(7) Fueloil: 150-170 g/GJ (tangential firing)

(8) Fueloil: 190-210 g/GJ (wall/bottom firing)

(9) Gasoil: 100 g/GJ

(10) GN: 125 g/GJ (50-100 MW)

(11) GN: 150 g/GJ (100-300 MW)

(12) GN: 48-333 g/GJ

(13) Fuelgas: 140 g/GJ

(14) Fuelgas: 88-333 g/GJ

Potencia < 50 MW

(15) Fueloil: 140 g/GJ (tangential firing)

(16) Fueloil: 180 g/GJ (wall/bottom firing)

CONTAMINANTE Óxidos de nitrógeno NO_X	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 8/2/2 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de NO_2	Asociación Española de Operadores de Productos Petrolíferos	ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 2 Código C

(17) Gasoil: 80-100 g/GJ

(18) GN: 100 g/GJ

(19) GN: 48-333 g/GJ

(20) Fuelgas: 140 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

Potencia >100 millones de btu/hora

(21) Fueloil: 47 lb/10^3 gal (combustión normal)

(22) Fueloil: 40 lb/10^3 gal (combustión normal, quemadores de bajo NO_X)

(23) Fueloil: 32 lb/10^3 gal (tangential firing)

(24) Fueloil: 26 lb/10^3 gal (tangential firing, quemadores de bajo NO_X)

(25) GN: 190 lb/10^6 ft^3

(26) GN: 140 lb/10^6 ft^3 (quemadores de bajo NO_X)

(27) GN: 100 lb/10^6 ft^3 (con recirculación de flue gas)

Potencia < 100 millones de btu/hora

(28) Fueloil: 55 lb/10^3 gal

(29) GN: 100 lb/10^6 ft^3

(30) GN: 50 lb/10^6 ft^3 (quemadores de bajo NO_X)

(31) GN: 32 lb/10^6 ft^3 (con recirculación de flue gas)

Potencia sin especificar (tangential firing)

(32) GN: 170 lb/10^6 ft^3

(33) GN: 76 lb/10^6 ft^3 (con recirculación de flue gas)

Fuente: EPA, AP-42, Tablas 1.3-1 y 1.4-1.

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/2/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 2 Código C

- **Cuantificación**

(1) a (20)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

(21) a (24) y (28)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\,\text{m}^3} \text{x}\,\text{m}^3\,\text{combustible}$$

(25) a (27) y (29) a (33)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{ft}^3}{0{,}028\,\text{m}^3} \text{x}\,\text{m}^3\,\text{combustible}$$

- **Observaciones**

Los índices de confianza de los factores EPA son los siguientes:

(21) A, (22) B, (23) A, (24) E, (25) A, (26) A, (27) D, (28) A, (29) B, (30) D, (31) C, (32) A, (33) D.

Del resto de factores no se han encontrado índices de confianza en la bibliografía manejada.

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: 153 g/GJ

(2) Gasoil: 398 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 250 g/GJ

(4) Gasoil: 120 g/GJ (turbinas modernas con premezclador)

(5) Gasoil: 350 g/GJ (sin especificar)

(6) Gasoil: 380 g/GJ (con quemadores de difusión)

(7) GN: 150 - 360 g/GJ

(8) Fuelgas: 150-151 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

- **Cuantificación**

$$\text{(1) a (8) kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\,PCI\left(\frac{kcal}{kg}\right) x\,kg\,combustible$$

- **Observaciones**

No se han encontrado en la bibliografía índices de confianza para los factores anteriores.

CONTAMINANTE Óxidos de nitrógeno **NO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gas: 405 g/GJ

(2) Diésel: 1.450 g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 1.090-1.200 g/GJ

(4) Gasoil: 100-1.200 g/GJ

(5) Gasoil o GN: 600 g/GJ (motor de compresión, precámara de inyección)

(6) Gasoil o GN: 1.200 g/GJ (motor de compresión, inyección directa)

(7) Gasoil o GN: 1.000 g/GJ (motor de chispa, 2 tiempos)

(8) Gasoil o GN: 1.800 g/GJ (motor de chispa, 4 tiempos)

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

- **Cuantificación**

$$\text{(1) a (8) kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Óxidos de nitrógeno** **NO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión en base al crudo procesado en Refinería.

(1) Factor = 18,9 lb/10^3 barril crudo. Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1, SCC 30600401)

Empleo de factores de emisión conocidas la masa y composición de la corriente a antorcha.

(2) Factor = 32,2 g/GJ. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{barril}}\right) x \frac{0,45359\,\text{kg}}{\text{lb}} x \frac{\text{barril}}{0,159\,\text{m}^3} x\, \text{m}^3\ \text{crudo}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) x \frac{\text{kg}}{10^3\ \text{g}} x \frac{\text{GJ}}{239.005\ \text{kcal}} x\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) x\, \text{kg gas}$$

- **Observaciones**

Para (1), se considera un índice de confianza C, debiendo tenerse en cuenta la generalidad del factor al partir de la capacidad de procesamiento de crudo.

Para (2) no se ha encontrado un índice de confianza en la bibliografía manejada.

CONTAMINANTE Óxidos de nitrógeno NO_x	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **8/5/2** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de NO_2	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 2 Código M

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores y los controles bienales realizados.

El factor de emisión empleado originalmente es función del gas incinerado (Q, Nm^3/h):

Factor original = 32,2 g/GJ

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor original}\left(\frac{g}{GJ}\right) x \text{ factor de experiencia (adim) } x \frac{kg}{10^3\ g} x \frac{GJ}{239.005\ kcal} x$$

$$x\, Q\left(\frac{Nm^3}{h}\right) x \text{ densidad gas}\left(\frac{kg}{Nm^3}\right) x \text{ PCI gas}\left(\frac{kcal}{kg}\right) x \text{ nº de horas}$$

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor original. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas “observaciones” que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE **Óxidos de nitrógeno** **NO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/5/3** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 3 Código M

- **Descripción**

Empleo de factor de emisión de NO_x emitido por volumen de fuelgas quemado, obtenido a partir de concentración medida en hornos que sólo queman fuelgas. Este valor se multiplica por el volumen de humo generado por unidad de fuelgas quemada (R, adim) y por la cantidad total de gas a antorcha (Q, Nm^3).

- **Cuantificación**

$$\text{kg emitidos = Factor original por medidas} \left(\frac{\text{kg}\,NO_2}{\text{Nm}^3\ \text{humos}}\right) x\, R \left(\frac{\text{Nm}^3\ \text{humos}}{\text{Nm}^3\ \text{fuelgas}}\right) x\, Q\left(\text{Nm}^3\ \text{a antorcha}\right)$$

- **Observaciones**

La fiabilidad del método está directamente relacionado con la calidad de la obtención del factor de emisión (realizada en base a mediciones). El valor global se obtiene por exceso debido a la mayor temperatura de llama en hornos que en antorcha. Este método sólo debe emplearse en aquellas Refinerías que sólo llevan a antorcha fuelgas.

CONTAMINANTE **Óxidos de nitrógeno** **NO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/6/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 1 Código M

- **Descripción**

Determinación a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3)* x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores el índice de confianza se considera alto.

* Usualmente, el NO_2 se expresa en ppm. 1 ppm = 2,05 · 10^{-6} kg/Nm^3

CONTAMINANTE **Óxidos de nitrógeno** **NO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **8/6/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de NO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

  Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm3)*. El caudal de humos (Q, Nm3/h)* se determina a partir de correlaciones (ver Anexo II).

- **Cuantificación**

  kg emitidos = C $(mg/Nm^3)^{**}$ x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

  El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

* C y Q expresados en igual base y al mismo oxígeno de referencia.

** Usualmente, el NO_2 se expresa en ppm. 1 ppm = $2{,}05 \cdot 10^{-6}$ kg/Nm^3

CONTAMINANTE Óxidos de nitrógeno NO_x	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **8/6/3** 1(a), 1(c)
VALOR UMBRAL (kg/año) 100.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de NO_2	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en la alimentación a la unidad.

Factor = 0,204 kg/m^3 alimentado. Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1, SCC 30600201) (Sin precipitador electrostático ni caldera auxiliar de CO)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{kg}{m^3}\right) x\, m^3 \text{ alimentados}$$

- **Observaciones**

El factor ofrecido presenta un índice de confianza B.

CONTAMINANTE
Óxidos de nitrógeno
NO_X

VALOR UMBRAL (kg/año)
100.000

EXPRESADO COMO
kg de NO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
8/6/4
1(a), 1(c)

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 4 Código M

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores EPA/CORINAIR y los controles bienales realizados.

- **Cuantificación**

Factor de emisión corregido = Factor de emisión x Factor de experiencia.

(El factor de emisión corregido es empleado como ha sido visto en método 8/6/3).

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor EPA/CORINAIR. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas “observaciones” que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE **Óxidos de azufre** **SO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante análisis de la composición del combustible y a partir de éste, a través de la aplicación de la Orden de 26 de diciembre de 1.995 (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/g) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

* C y Q expresados en igual base y al mismo oxígeno de referencia

CONTAMINANTE **Óxidos de azufre** **SO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/1/2**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	**1(a), 1(c)**
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código C

- **Descripción**

Determinación de SO_x por balance estequiométrico, a partir de combustibles empleados y contenido en azufre de los mismos. Se asume que el 100 % del azufre contenido en la alimentación está presente en humos de combustión como SO_2.

- **Cuantificación**

$$\text{kg emitidos} = \sum_{\text{comb.i}} \text{kg de combustible}_i \ \text{x} \ \frac{\text{\% de azufre}_i}{100} \ \text{x} \ \frac{64}{32}$$

- **Observaciones**

Se considera de una gran fiabilidad siempre y cuando el contenido de azufre sea lo suficientemente preciso. Debe recordarse que este parámetro está sujeto a variaciones destacables principalmente en el fuelgas.

CONTAMINANTE **Óxidos de azufre** **SO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/1/3** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en el contenido en azufre de los combustibles.

(1) Fueloil: 157 lb/10^3 gal Fuente: EPA, AP-42, Tabla 1.3-1, SCC 10200401

(2) GN: 0,6 lb/10^6 ft^3 (para un gas natural de 2.000 grains/$10^6 ft^3$) Fuente: EPA, AP-42, Tabla 1.4-2

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \times \%\,\text{de azufre} \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\,\text{m}^3} \times \text{m}^3\ \text{fueloil}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{ft}^3}{0{,}028\,\text{m}^3} \times \text{m}^3\ \text{GN}$$

- **Observaciones**

El índice de confianza de ambos factores es A.

El factor (2) está referido a un gas natural con un contenido en azufre de 2.000 grains/10^6 ft^3 (4,6 · 10^{-6} kg/m^3). En caso de que el gas natural tenga un contenido en azufre diferente, bastaría aplicar el ratio correspondiente para obtener un factor de emisión adecuado.

CONTAINANTE		
CONTAMINANTE **Óxidos de azufre** **SO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Plantas de recuperación de azufre

Metodología 1 Código C

- **Descripción**

Determinación de SO_2 en base al rendimiento real de las plantas y azufre elemental recuperado en las mismas.

- **Cuantificación**

$$\text{kg emitidos} = \left(\frac{100 - \text{rendimiento}(\%)}{\text{rendimiento}(\%)}\right) \times \text{kg azufre recuperado} \times \frac{64}{32}$$

- **Observaciones**

La fiabilidad de la determinación es muy elevada siempre y cuando la precisión de los parámetros empleados en el cálculo lo sea.

CONTAMINANTE **Óxidos de azufre** **SO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Antorchas

Metodología 1 Código M

- **Descripción**

Determinación analítica en continuo (monitorización) de valores tanto de caudal (Q, Nm^3/h)* como de contenido en ácido sulfhídrico (C, mg/Nm^3)* de gas a antorcha.

- **Cuantificación**

$$\text{kg emitidos} = Q\left(\frac{Nm^3}{h}\right) \times C\left(\frac{mg}{Nm^3}\right) \times \text{nº de horas} \times 10^{-6} \times \frac{64}{34}$$

- **Observaciones**

La fiabilidad de este método, al igual que la de todos aquellos que implican medidas, se encuentra directamente relacionada con la metodología y sistemática seguidas en la determinación. Debe destacarse la naturaleza de las combustiones llevadas a cabo en los sistemas de antorchas, caracterizadas por frecuentes variaciones tanto cuantitativas como cualitativas en el gas incinerado.

* C y Q expresados en igual base y al mismo oxígeno de referencia.

CONTAMINANTE **Óxidos de azufre** **SO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/3/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Antorchas

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en el crudo procesado.

Factor: 26,9 lb/10^3 barril. Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1, SCC 30600401)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right)\times\frac{0{,}45359\,\text{kg}}{\text{lb}}\times\frac{\text{barril}}{0{,}159\,\text{m}^3}\times\text{m}^3\ \text{de crudo}$$

- **Observaciones**

El índice de confianza del factor es C.

CONTAMINANTE **Óxidos de azufre** **SO_X**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código M

- **Descripción**

Determinación a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm3) y caudales de humos (Q, Nm3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores el índice de confianza se considera alto.

CONTAMINANTE Óxidos de azufre SO_X	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR REFINO DE PETRÓLEO Asociación Española de Operadores de Productos Petrolíferos	Nº 11/4/2 1(a), 1(c)
VALOR UMBRAL (kg/año) 150.000		
EXPRESADO COMO kg de SO_2		

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación a partir de medidas en continuo (monitorización). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante el empleo de correlaciones (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

* C y Q expresados en igual base y al mismo oxígeno de referencia.

CONTAMINANTE
Óxidos de azufre
SO_X

VALOR UMBRAL (kg/año)
150.000

EXPRESADO COMO
kg de SO_2

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
11/4/3

1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Factor = 493 lb/10^3 barril alimentado Fuente: CONCAWE (Ref: EPA, AP-42, Tabla 5.1-1 SCC 30600201)
(Sin precipitador electrostático ni caldera auxiliar de CO)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\text{barril}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{barril}}{0{,}159\,\text{m}^3} \times \text{m}^3 \text{ alimentados}$$

- **Observaciones**

El índice de confianza para el factor ofrecido es B.

CONTAMINANTE **Óxidos de azufre** **SO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/4/4** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 4 Código C

- **Descripción**

Cálculo de SO_2 emitido a partir de datos de diseño de la unidad, en concreto, el porcentaje de azufre alimentado que se encuentra presente en el gas efluente. Los resultados así obtenidos son posteriormente corregidos por el empleo de factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de los valores de diseño y los controles bienales realizados.

- **Cuantificación**

$$\text{kg emitidos} = \text{Alimentación al FCC (kg)} \times \frac{\text{\% azufre en alimentación}}{100} \times$$

$$\times \frac{\text{\% azufre que pasa a humos}}{100} \times \frac{64}{32} \times \text{Factor experiencia (adim)}$$

- **Observaciones**

Se considera una alta fiabilidad en el método, siempre que se consideren las mismas "observaciones" que en aquellas metodologías basadas en la determinación a partir de medidas periódicas.

CONTAMINANTE **Óxidos de azufre** **SO_x**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **11/5/1**
		1(a), 1(c)
VALOR UMBRAL (kg/año) **150.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de SO_2**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Reformado catalítico

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en el volumen alimentado a la unidad.

Factor: $3,63 \cdot 10^{-3}$ kg/m^3 alimentado a la unidad

Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07 (Ref: Bertrand, R.R. and Siegell, J.H. (2003) Emission of trace compounds from catalytic reforming units. *Environmental Progress 22, 1, 74-77)*

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \text{m}^3 \text{ alimentado a la unidad}$$

- **Observaciones**

Este factor de emisión se ha obtenido a partir de unidades con diferentes sistemas de abatimiento, por lo que puede no representar fielmente las emisiones incontroladas.

CONTAMINANTE **Arsénico y compuestos** **As**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **17/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **20**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de arsénico**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: 1,81 · 10^{-3} g/GJ

(2) Fueloil: 3,98 · 10^{-3} g/GJ

(3) Fuelgas y GN: 3,43 · 10^{-4} g/GJ

Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil: 0,5 g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) Combustibles gaseosos: 0,03 g/TJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 136.

(6) Fueloil: 1,32 · 10^{-3} lb/10^{3} gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(7) GN: 2 · 10^{-4} lb/10^{6} ft^{3}. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(8) Fueloil: 4 · 10^{-6} lb/10^{6} btu. Fuente: EPA, SCC 30600101

- **Cuantificación**

(1) a (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{Mg}}{10^3\,\text{kg}} \text{x}\,\text{kg fueloil}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{TJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005 \cdot 10^3\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

(6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\,\text{m}^3} \text{x}\,\text{m}^3\ \text{fueloil}$$

(7)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \text{x}\,\text{m}^3\ \text{gas natural}$$

(8)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg fueloil}$$

- **Observaciones**

Los índices de confianza de (1) a (5) no están disponibles. Los índices de confianza de (6), (7) y (8) son C, E y U respectivamente.

CONTAMINANTE **Arsénico y compuestos** **As**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **17/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **20**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de arsénico**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Diesel: < 1,1 · 10^{-5} lb/10^6 btu. Fuente: EPA, SCC 20200101

- **Cuantificación**

$$(1)\ \ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{btu}}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\ \text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg fueloil}$$

- **Observaciones**

El índice de confianza de (1) es D.

CONTAMINANTE Arsénico y compuestos **As**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **17/3/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 20	**REFINO DE PETRÓLEO**	
EXPRESADO COMO masa total de arsénico	Asociación Española de Operadores de Productos Petrolíferos	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de arsénico presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales x } \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de arsénico en las partículas. Esta determinación se puede llevar a cabo en un sólo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE Arsénico y compuestos **As**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **17/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **20**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de arsénico**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,002%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Arsénico y compuestos** **As**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **17/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **20**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de arsénico**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica del porcentaje de arsénico presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales x } \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE
Cadmio y compuestos
Cd

VALOR UMBRAL (kg/año)
10

EXPRESADO COMO
masa total de cadmio

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
18/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil : $1{,}36 \cdot 10^{-3}$ g/GJ

(2) Fueloil : $1{,}20 \cdot 10^{-3}$ g/GJ

(3) Fuelgas y GN: $7{,}12 \cdot 10^{-4}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil: 1g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) Combustibles gaseosos: 0,01 g/TJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 136.

(6) Fueloil: $3{,}98 \cdot 10^{-4}$ lb/10^{3} gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(7) GN: $1{,}1 \cdot 10^{-3}$ lb/10^{6} ft^{3}. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(8) Fueloil: $5{,}8 \cdot 10^{-6}$ lb/10^{6} btu. Fuente: EPA, SCC 30600101

(9) Fuelgas: $3 \cdot 10^{-8}$ lb/10^{6} btu. Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) a (3) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^{3}\,\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(4) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \times \frac{\text{kg}}{10^{3}\,\text{g}} \times \frac{\text{Mg}}{10^{3}\,\text{kg}} \times \text{kg fueloil}$$

(5) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{TJ}}\right) \times \frac{\text{kg}}{10^{3}\,\text{g}} \times \frac{\text{TJ}}{239.005 \cdot 10^{3}\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(6) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{3}\,\text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\,\text{m}^{3}} \times \text{m}^{3}\ \text{fueoil}$$

(7) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{ft}^{3}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{31{,}31467\,\text{ft}^{3}}{\text{m}^{3}} \times \text{m}^{3}\ \text{gas natural}$$

(8) y (9) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) a (5) no están disponibles. Los índices de confianza de (6) y (7) son C y D respectivamente y el de (8) y (9) es U.

CONTAMINANTE **Cadmio y compuestos** **Cd**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **18/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cadmio**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $2{,}17 \cdot 10^{-3}$ g/GJ

(2) Fuelgas y GN: $2{,}52 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Diesel: $4{,}8 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 20200101

(4) GN: $6{,}925 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 20200101

- **Cuantificación**

$$\text{(1) y (2) kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\,\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

$$\text{(3) y (4) kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) y (2) no están disponibles.
Los índices de confianza de (3) y (4) son D y U respectivamente.

CONTAMINANTE **Cadmio y compuestos** **Cd**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **18/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cadmio**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de cadmio presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de cadmio en las partículas. Esta determinación se puede llevar a cabo en un sólo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión**.**

CONTAMINANTE Cadmio y compuestos **Cd**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **18/4/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 10	REFINO DE PETRÓLEO	
EXPRESADO COMO masa total de cadmio	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,009%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE Cadmio y compuestos **Cd**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **18/4/2** 1(a), 1(c)
VALOR UMBRAL (kg/año) 10	**REFINO DE PETRÓLEO**	
EXPRESADO COMO masa total de cadmio	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica de porcentaje de cadmio presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de Cracking Catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de cadmio en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE
Cromo y compuestos
Cr

VALOR UMBRAL (kg/año)
100

EXPRESADO COMO
masa total de cromo

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
19/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil : $1{,}36 \cdot 10^{-3}$ g/GJ

(2) Fueloil : $1{,}48 \cdot 10^{-2}$ g/GJ

(3) Fuelgas y GN : $2{,}47 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air Pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil : 2,5 g/Mg Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) Combustibles gaseosos: 0,10 g/TJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 136.

(6) Fueloil: $8{,}45 \cdot 10^{-4}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(7) GN: $1{,}4 \cdot 10^{-3}$ lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(8) Fueloil: $1{,}7 \cdot 10^{-5}$ lb/10^6 btu. Fuente: EPA, SCC 30600101

(9) GN: $1{,}32 \cdot 10^{-7}$ lb/10^6 btu. Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) a (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{Mg}}{10^3\text{kg}} \times \text{kg fueloil}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{TJ}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{TJ}}{239.005 \cdot 10^3\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\ \text{m}^3} \times \text{m}^3\ \text{fueloil}$$

(7)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right) \times \frac{0{,}45359\ \text{kg}}{\text{lb}} \times \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \times \text{m}^3\ \text{gas natural}$$

(8) y (9)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) a (5) no están disponibles. Los índices de confianza de (6) y (7) son C y D respectivamente, mientras que el de (8) y (9) es U.

CONTAMINANTE
Cromo y compuestos
Cr

VALOR UMBRAL (kg/año)
100

EXPRESADO COMO
masa total de cromo

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
19/2/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil : $4{,}98 \cdot 10^{-3}$ g/GJ

(2) Fuelgas y GN : $6{,}26 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Diesel : $1{,}1 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 20200101

(4) GN : $1{,}329 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 20200201

- **Cuantificación**

$$\text{(1) y (2) kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^{3}\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg}\,\text{combustible}$$

$$\text{(3) y (4) kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg}\,\text{combustible}$$

- **Observaciones**

Los índices de confianza de (1) y (2) no están disponibles. Los índices de confianza de (3) y (4) son D y U respectivamente.

CONTAMINANTE **Cromo y compuestos** **Cr**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **19/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cromo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de cromo presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de cromo en las partículas. Esta determinación se puede llevar a cabo en un sólo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE **Cromo y compuestos** **Cr**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **19/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cromo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- Descripción

Empleo de factores de emisión en base al coque quemado.

Factor = 4,44·10^{-4} lb cromo/1.000 lb coque. Fuente: Environmental Progress (Vol. 21, No. 3, pp 163-167, 2.002)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{lb coque}}\right) \times \text{kg de coque quemado}$$

- **Observaciones**

El factor presentado se ha obtenido como valor medio de 48 muestras realizadas en otras tantas unidades de cracking catalítico.

CONTAMINANTE **Cromo y compuestos** **Cr**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **19/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cromo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica de porcentaje de cromo presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de cromo en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE Cobre y compuestos **Cu**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **20/1/1**
VALOR UMBRAL (kg/año) 100	**REFINO DE PETRÓLEO**	1(a), 1(c)
EXPRESADO COMO masa total de cobre	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $2{,}72 \cdot 10^{-3}$ g/GJ

(2) Fueloil: $1{,}19 \cdot 10^{-2}$ g/GJ

(3) Fuelgas y GN: $2{,}22 \cdot 10^{-3}$ g/GJ

Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil: 1 g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111

(5) Fueloil: $1{,}76 \cdot 10^{-3}$ lb/10^{3} gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(6) GN: $8{,}5 \cdot 10^{-4}$ lb/10^{6} ft^{3}. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(7) Fueloil: $1{,}8 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 30600101

(8) Fuelgas: $3{,}56 \cdot 10^{-7}$ lb/10^{6} btu. Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) a (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\, \text{kg combustible}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{Mg}}{10^3\,\text{kg}} \text{x}\, \text{kg fueloil}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\,\text{m}^3} \text{x}\, \text{m}^3 \text{ fueloil}$$

(6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \text{x}\, \text{m}^3 \text{ gas natural}$$

(7) y (8)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\,\text{kcal}} \text{x}\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\, \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) a (4) no están disponibles. El índice de confianza de (5) y (6) es C y el de (7) y (8) es U.

CONTAMINANTE **Cobre y compuestos** **Cu**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **20/2/1**
		1(a), 1(c)
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cobre**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Fuelgas y GN: 1,97· 10^{-2} g/GJ. Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(2) GN: 6,92· 10^{-5} lb/10^{6} btu. Fuente: EPA, SCC 20200201

- **Cuantificación**

(1)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^{3}\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

(2)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg GN}$$

- **Observaciones**

El índice de confianza de (1) no está disponible. El índice de confianza de (2) es U.

CONTAMINANTE **Cobre y compuestos** **Cu**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **20/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cobre**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de cobre presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de cobre en las partículas. Esta determinación se puede llevar a cabo en un sólo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE **Cobre y compuestos** **Cu**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **20/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cobre**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,02%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Cobre y compuestos** **Cu**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **20/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **100**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de cobre**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica de porcentaje de cobre presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE
Mercurio y compuestos
Hg

VALOR UMBRAL (kg/año)
10

EXPRESADO COMO
masa total de mercurio

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
21/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $1{,}36 \cdot 10^{-3}$ g/GJ

(2) Fuelgas y GN: $8{,}60 \cdot 10^{-5}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07

(3) Fueloil: 1 g/Mg Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111

(4) Fueloil: $1{,}13 \cdot 10^{-4}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(5) GN: $2{,}6 \cdot 10^{-4}$ lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(6) Fuelgas: $2{,}73 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) y (2)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{Mg}}{10^3\text{kg}} \times \text{kg fueloil}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\ \text{m}^3} \times \text{m}^3\ \text{fueloil}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right) \times \frac{0{,}45359\ \text{kg}}{\text{lb}} \times \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \times \text{m}^3\ \text{gas natural}$$

(6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg fuelgas}$$

- **Observaciones**

Los índices de confianza de (1) a (3) no están disponibles. Los índices de confianza de (4), (5) y (6) son C, D y U respectivamente.

CONTAMINANTE **Mercurio y compuestos** **Hg**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **21/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de mercurio**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $5{,}43 \cdot 10^{-4}$ g/GJ

(2) Fuelgas y GN: $7{,}31 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Diesel: $1{,}20 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 20200101

(4) GN: $6{,}63 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 20200201

- **Cuantificación**

$$\text{(1) y (2) kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\,\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

$$\text{(3) y (4) kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) y (2) no están disponibles. Los índices de confianza de (3) y (4) son D y U respectivamente.

CONTAMINANTE
Mercurio y compuestos
Hg

VALOR UMBRAL (kg/año)
10

EXPRESADO COMO
masa total de mercurio

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
21/3/1
1(a), 1(c)

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de mercurio presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de mercurio en las partículas. Esta determinación se puede llevar a cabo en un solo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE Mercurio y compuestos **Hg**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 21/4/1 1(a), 1(c)
VALOR UMBRAL (kg/año) 10	REFINO DE PETRÓLEO	
EXPRESADO COMO masa total de mercurio	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,01%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Mercurio y compuestos** **Hg**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **21/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **10**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de mercurio**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica del porcentaje de mercurio presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de mercurio en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE
Níquel y compuestos
Ni

VALOR UMBRAL (kg/año)
50

EXPRESADO COMO
masa total de níquel

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
22/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles empleados.

(1) Gasoil: 1,36· 10^{-3} g/GJ

(2) Fueloil: 1,03 g/GJ

(3) Fuelgas y GN: 3,60 · 10^{-3} g/GJ

Fuente:CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil: 35 g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111

(5) Fueloil: 8,45· 10^{-2} lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(6) GN: 2 ,1· 10^{-3} lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

(7) Fueloil: 2,4 · 10^{-3} lb/10^6 btu. Fuente: EPA, SCC 30600101

(8) Fuelgas: 4,33 · 10^{-7} lb/10^6 btu. Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) a (3) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

(4) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{Mg}}{10^3\,\text{kg}} \text{x}\,\text{kg fueloil}$$

(5) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0,00378\,\text{m}^3} \text{x}\,\text{m}^3\,\text{fueloil}$$

(6) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{31,31467\,\text{ft}^3}{\text{m}^3} \text{x}\,\text{m}^3\,\text{gas natural}$$

(7) y (8) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{btu}}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0,251\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) a (4) no están disponibles. El índice de confianza de (5) y (6) es C y el de (7) y (8) es U.

CONTAMINANTE **Níquel y compuestos** **Ni**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **22/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de níquel**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Fuelgas y GN: 7,93 · 10^{-2} g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(2) Diesel: < 4,6 · 10^{-6} lb/10^{6} btu. Fuente: EPA, SCC 20200101

(3) GN: 1,147· 10^{-4} lb/10^{6} btu. Fuente: EPA, SCC 20200201

- **Cuantificación**

(1)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^{3}\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x} \,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x} \,\text{kg combustible}$$

(2) y (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\,\text{kcal}} \text{x} \,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x} \,\text{kg combustible}$$

- **Observaciones**

El índice de confianza de (1) no esta disponible. Los índices de confianza de (2) y (3) son D y U respectivamente.

CONTAMINANTE **Níquel y compuestos** **Ni**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **22/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de níquel**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código C

- **Descripción**

Determinación analítica del porcentaje de níquel presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de níquel en las partículas. Esta determinación se puede llevar a cabo en un solo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE **Níquel y compuestos** **Ni**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **22/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de níquel**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,088%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Níquel y compuestos** **Ni**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **22/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de níquel**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica de porcentaje de níquel presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de níquel en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE **Plomo y compuestos** **Pb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **23/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de plomo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos**.**

(1) Gasoil: $4{,}07 \cdot 10^{-3}$ g/GJ

(2) Fueloil: $4{,}56\ 10^{-3}$ g/GJ

(3) Fuelgas y GN: $1{,}79 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil = 1,3 g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) Fueloil: $1{,}51 \cdot 10^{-3}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(6) GN: $5 \cdot 10^{-4}$ lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-2, SCC 10100601

(7) Fueloil: $2{,}1 \cdot 10^{-6}$ lb/10^6 btu. Fuente: EPA, SCC 30600101

- **Cuantificación**

(1) a (3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(4)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{Mg}}\right) \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{Mg}}{10^3\text{kg}} \times \text{kg fueloil}$$

(5)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\ \text{m}^3} \times \text{m}^3\ \text{fueloil}$$

(6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{ft}^3}\right) \times \frac{0{,}45359\ \text{kg}}{\text{lb}} \times \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \times \text{m}^3\ \text{gas natural}$$

(7)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\ \text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg fueloil}$$

- **Observaciones**

Los índices de confianza de (1) a (4) no están disponibles. Los índices de confianza de (5), (6) y (7) son C, D y U respectivamente.

CONTAMINANTE **Plomo y compuestos** **Pb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **23/2/1**
		1(a), 1(c)
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de plomo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos**.**

(1) Gasoil: $6{,}43 \cdot 10^{-3}$ g/GJ

(2) Fuelgas y GN: $1{,}36 \cdot 10^{-2}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Diesel: $1{,}4 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 20200101

- **Cuantificación**

(1) y (2)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \times \frac{\text{kg}}{10^{3}\,\text{g}} \times \frac{\text{GJ}}{239.005\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

(3)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{btu}}{0{,}251\,\text{kcal}} \times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \times \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (1) y (2) no están disponibles. El índice de confianza de (3) es C.

CONTAMINANTE **Plomo y compuestos** **Pb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **23/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de plomo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje de plomo presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de plomo en las partículas. Esta determinación se puede llevar a cabo en un solo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE Plomo y compuestos **Pb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **23/4/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 200	**REFINO DE PETRÓLEO**	
EXPRESADO COMO masa total de plomo	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,046%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Plomo y compuestos** **Pb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **23/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de plomo**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica de porcentaje de plomo presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de plomo en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE
Zinc y compuestos
Zn

VALOR UMBRAL (kg/año)
200

EXPRESADO COMO
masa total de zinc

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
24/1/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $1{,}81 \cdot 10^{-3}$ g/GJ

(2) Fueloil: $4{,}93\ 10^{-2}$ g/GJ

(3) Fuelgas y GN: $2{,}55 \cdot 10^{-2}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(4) Fueloil = 1 g/Mg. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111.

(5) Fueloil: $2{,}91 \cdot 10^{-2}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(6) GN: $2{,}9 \cdot 10^{-2}$ lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10100601

- **Cuantificación**

(1) a (3) $$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) \times \frac{kg}{10^3 g} \times \frac{GJ}{239.005\,kcal} \times PCI\left(\frac{kcal}{kg}\right) \times kg\,\text{combustible}$$

(4) $$\text{kg emitidos} = \text{Factor}\left(\frac{g}{Mg}\right) \times \frac{kg}{10^3 g} \times \frac{Mg}{10^3 kg} \times kg\,\text{fueloil}$$

(5) $$\text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^3\,gal}\right) \times \frac{0{,}45359\,kg}{lb} \times \frac{gal}{0{,}00378\ m^3} \times m^3\ \text{fueloil}$$

(6) $$\text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^6 ft^3}\right) \times \frac{0{,}45359\ kg}{lb} \times \frac{31{,}31467\,ft^3}{m^3} \times m^3\ \text{gas natural}$$

- **Observaciones**

Los índices de confianza de (1) a (4) no están disponibles. Los índices de confianza de (5) y (6) son D y E respectivamente.

CONTAMINANTE **Zinc y compuestos** **Zn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **24/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de zinc**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos**.**

(1) Fuelgas y GN: 2,38 g/GJ

Fuente: CONCAWE, Air Pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07**.**

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right)\times\frac{\text{kg}}{10^3\text{g}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times\text{kg combustible}$$

- **Observaciones**

El índice de confianza de (1) no está disponible.

CONTAMINANTE **Zinc y compuestos** **Zn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **24/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de zinc**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión

Metodología 1 Código M

- **Descripción**

Determinación analítica del porcentaje presente en las partículas totales en humos de combustión.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en humos de combustión. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de zinc en las partículas. Esta determinación se puede llevar a cabo en un solo foco de combustión que, por sus características, se considere suficientemente representativo de todos los focos presentes en Refinería.

Ver fichas correspondientes a determinación de partículas en combustión.

CONTAMINANTE **Zinc y compuestos** **Zn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **24/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de zinc**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 1 Código M

- **Descripción**

Determinación del metal a partir de la aplicación del porcentaje (según bibliografía) de esta sustancia presente en el total de partículas.

Porcentaje = 0,017%. Fuente: Australian National Pollutant Inventory (Ref. US EPA 93).

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas totales en la emisión del FCC. No existe índice de confianza para el porcentaje de metal presente.

Ver fichas correspondientes a determinación de partículas en Cracking catalítico.

CONTAMINANTE **Zinc y compuestos** **Zn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **24/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **200**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **masa total de zinc**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación analítica del porcentaje de zinc presente en las partículas totales del gas efluente de la unidad de cracking catalítico.

- **Cuantificación**

$$\text{kg emitidos} = \text{kg de partículas totales} \times \frac{\text{porcentaje}}{100}$$

- **Observaciones**

El índice de confianza de esta metodología está directamente relacionado con la metodología empleada en la determinación de partículas en el gas efluente de la unidad de cracking catalítico. Igualmente, se encuentra relacionado íntimamente con la sistemática empleada en la determinación de zinc en partículas.

Ver fichas correspondientes a determinación de partículas en Cracking Catalítico.

CONTAMINANTE **Dioxinas y Furanos** **PCDD+PCDF**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **47/1/1** **1(c)**
VALOR UMBRAL (kg/año) **0,0001**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **I-TEQ (equivalentes tóxicos)**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

(1) Fueloil: 3,72·10^{-10} kg/m^3. Fuente: Australian National Pollutant Inventory. Ref. US EPA 98a.

(2) Fueloil: 100 ng/t. Fuente: Estimación INFORME CORINE-AIRE 1997-2000 a partir de OSPARCOM-MELCOM-UNECE (1995). Tabla 4.5.1.

(3) Fueloil: 1,24·10^{-9} g I-TEQ/GJ. Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07 (Ref. API (1998) Air toxics emission factors for combustion sources using petroleum-based fuels)

Fuelgas: No aplicable.

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right)\times \text{m}^3\ \text{fueloil}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{ng}}{\text{t}}\right)\times\frac{\text{kg}}{10^{12}\text{ng}}\times \text{t fueloil}$$

(3) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right)\times\frac{\text{kg}}{10^3\ \text{g}}\times\frac{\text{GJ}}{239.005\,\text{kcal}}\times \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right)\times \text{kg fueloil}$$

- **Observaciones**

La emisión de dioxinas y furanos se encuentra únicamente ligada al consumo de fueloil (según la bibliografía manejada). No se ha determinado el índice de confianza ofrecido para los factores mostrados. Para una densidad y un PCI estándar en el fueloil, el factor (2) supondría 0,9·10^{-10} kg/m^3, aproximadamente cuatro veces menos que (1), y el factor (3) 0,4·10^{-10} kg/m^3, unas ochos veces menos que (1).

CONTAMINANTE **Dioxinas y Furanos** **PCDD+PCDF**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **47/2/1** **1(c)**
VALOR UMBRAL (kg/año) **0,0001**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **I-TEQ (equivalentes tóxicos)**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Regeneración de catalizador en Reforming Catalítico

Metodología 1 Código E

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Factor: 1,52 ng/barril alimentado. Fuente EPA, documento actualmente en preparación (DRAFT).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{ng}}{\text{barril}}\right) \times \frac{\text{kg}}{10^{12}\,\text{ng}} \times \frac{\text{barril}}{0{,}159\,\text{m}^3} \times \text{m}^3 \text{ alimentados}$$

- **Observaciones**

Atendiendo al origen del factor (aún en revisión), debe considerarse un bajo índice de confianza, por lo que ni siquiera se califica al método como “C: cálculo” sino como “E: estimación”.

CONTAMINANTE
Dioxinas y Furanos
PCDD+PCDF

VALOR UMBRAL (kg/año)
0,0001

EXPRESADO COMO
I-TEQ (equivalentes tóxicos)

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
47/2/2
1(c)

ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 2 Regeneración de catalizador en Reforming Catalítico

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Regeneración continua

(1) Factor: $1{,}91 \cdot 10^{-11}$ kg I-TEQ/m^3 alimentado

Semi-regenerativa

(2) Factor: $6{,}35 \cdot 10^{-15}$ kg I-TEQ/m^3 alimentado

Fuente (para ambos factores): CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries (Ref. EPA (2005) The inventory of sources and environmental releases of dioxin-like compounds in the United States: the year 2000 update)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \text{m}^3 \text{ alimentados}$$

- **Observaciones**

No se dispone de índices de confianza para los factores anteriores. El factor de la ficha anterior (1,52 ng/barril) equivale a la mitad del factor (1).

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
62/1/1
1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Fueloil: $6{,}47 \cdot 10^{-4}$ g/GJ

(2) Gas: $2{,}13 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Fueloil: $2{,}14 \cdot 10^{-4}$ lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-9, SCC 10100401

(4) GN: $2{,}1 \cdot 10^{-3}$ lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-3, SCC 10100601

- **Cuantificación**

(1) y (2)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

(3)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\,\text{m}^3} \text{x m}^3 \text{ fueloil}$$

(4)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{31{,}31467\,\text{ft}^3}{\text{m}^3} \text{x m}^3 \text{ gas natural}$$

- **Observaciones**

El índice de confianza del factor (3) es C, del (4) es B; para el resto de factores no se encuentran disponibles en la bibliografía manejada.

CONTAMINANTE Benceno C_6H_6	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 62/2/1 1(a), 1(c)
VALOR UMBRAL (kg/año) 1.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de benceno	Asociación Española de Operadores de Productos Petrolíferos	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: $2{,}49 \cdot 10^{-2}$ g/GJ

(2) Gas Natural: $5{,}73 \cdot 10^{-3}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) Diesel: $5{,}5 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 20200101

(4) GN: $1{,}2 \cdot 10^{-5}$ lb/10^{6} btu. Fuente: EPA, SCC 20200201

- **Cuantificación**

(1) y (2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^{3}\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

(3) y (4) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\,\text{btu}}\right) \text{x} \frac{0{,}45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

- **Observaciones**

En la bibliografía manejada no existen índices de confianza para los factores (1) y (2); los de los factores (3) y (4) son C y A respectivamente.

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
62/3/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gas: $6,21 \cdot 10^{-1}$ g/GJ

(2) Gasoil: $3,22 \cdot 10^{-1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

(3) GN (2-cycle, Lean Burn):$1,94 \cdot 10^{-3}$ lb/10^6 btu. Fuente: EPA, SCC 20200252

(4) GN (4-cycle, Rich Burn): $1,58 \cdot 10^{-3}$ lb/10^6 btu. Fuente: EPA, SCC 20200253

(5) GN (4-cycle, Lean Burn): $4,4 \cdot 10^{-4}$ lb/10^6 btu. Fuente: EPA, SCC 20200254

(6) Diesel (Large Bore Engine): $7,76 \cdot 10^{-4}$ lb/10^6 btu. Fuente: EPA, SCC 20200401

Empleo de factores de emisión basados en la energía producida.

(7) Combustible mixto oil/gas (Large Bore Engine): $4,45 \cdot 10^{-3}$ lb/10^6 btu. Fuente: EPA, SCC 20200402

- **Cuantificación**

(1) y (2) $$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3 g} x \frac{GJ}{239.005\,kcal} x\, PCI\left(\frac{kcal}{kg}\right) x\, \text{kg combustible}$$

(3) a (7) $$\text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^6\,btu}\right) x \frac{0,45359\,kg}{lb} x \frac{btu}{0,251\,kcal} x\, PCI\left(\frac{kcal}{kg}\right) x\, \text{kg combustible}$$

- **Observaciones**

Los índices de confianza de (3), (4), (5), (6) y (7) son A, B, A, E y U respectivamente. Para los factores (1) y (2) no se han encontrado índices de confianza en la bibliografía manejada.

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
62/4/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 4 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV’s totales basados en el crudo procesado en Refinería.

(1) Factor: 0,8 lb/10^3 barril. Fuente: EPA SCC 30600401

Se asume que el 0,083 % de la emisión de COV’s es benceno (Australian National Pollutant Inventory, Ref. Taback 1996).

Empleo de factores de emisión para el cálculo de benceno basados en el crudo procesado en Refinería.

(2) Factor: 0,00166 kg/m^3. Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

Empleo de factores de emisión para el cálculo de benceno conocidas la masa y composición de la corriente a antorcha.

(3) Se asume que el 0,5 % de los hidrocarburos queda sin quemar. Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{barril}}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{barril}}{0,159\,\text{m}^3} \text{x} \frac{0,083}{100} \text{x}\,\text{m}^3\,\text{crudo}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x}\,\text{m}^3\,\text{crudo}$$

(3) $$\text{kg emitidos} = \text{kg gas}\,\text{x} \frac{\%\text{CH}_4}{100} \text{x} \frac{0,5}{100}$$

- **Observaciones**

El índice de confianza para el factor de emisión (1) es B.

No aparece en la bibliografía manejada el índice de confianza para el resto de factores ni para el porcentaje de benceno.

CONTAMINANTE **Benceno** C_6H_6	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **62/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de benceno**	**Asociación Española de Operadores de Productos Petrolíferos**	ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Destilación a vacío

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para COV's totales basados en la alimentación a la unidad.

Factor: 50 lb/10^3 barril. Fuente: CORINAIR, B411, Tabla 8.4 (Ref: EPA SCC 30600602)

Posteriormente se considera que el 0,38% es benceno (CORINAIR, ref. US EPA, Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{barril}}\right) x \frac{0{,}45359\ \text{kg}}{\text{lb}} x \frac{\text{barril}}{0{,}159\ \text{m}^3} x \frac{0{,}38}{100} x\ \text{m}^3\ \text{alimentados}$$

- **Observaciones**

El factor inicial para COV's totales tiene un índice de confianza C, mientras que para el porcentaje de benceno, el índice es E.

CONTAMINANTE Benceno C_6H_6	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **62/6/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 1.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de benceno	Asociación Española de Operadores de Productos Petrolíferos	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 6 Cracking catalítico

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en la cantidad de coque quemado.

Factor: $1{,}05 \cdot 10^{-3}$ kg/t coque

Fuente: CONCAWE, Air pollutant emission estimation methods for E-PRTR reporting by refineries, report no. 3/07. (Ref. Bertrand, R.R. and Siegell, J.H. (2002) Emission of trace compounds from catalytic cracking regenerators. Environmental Progress 21, 3, 163-167).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{t}}\right) \text{x t coque}$$

- **Observaciones**

No se ha encontrado índice de confianza para este factor.

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
62/7/1
1(a), 1(c)

FUENTE DE EMISIÓN: 7 Purgas

Metodología 1 Código C

- **Descripción**

En el caso de venteos a la atmósfera (sin recuperación ni envío a antorcha) se considera un factor de emisión de hidrocarburos totales de 1.662 kg/m^3 de alimentación a Refinería (Fuente: EPA, AP-42, Tabla 5.1-1).

Se asume que la fracción de benceno es 0,38 %. (CORINAIR, Ref. US EPA, Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x} \frac{0,38}{100} \text{x}\, \text{m}^3 \text{ crudo}$$

- **Observaciones**

El índice de confianza del factor de emisión es C, y el del porcentaje de benceno es E.

CONTAMINANTE **Benceno** C_6H_6	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **62/8/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de benceno**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 1 Código C

- **Descripción**

Empleo de la ecuación de Litchfield para determinar COV's totales y posteriormente cálculo de benceno a partir de porcentajes presentes en bibliografía manejada.

La ecuación de Litchfield expresa la emisión de NMCOV's como porcentaje del total de aceites que entran a la planta de tratamiento:

% pérdidas = -6,6339 + 0,0319 x (T_{amb} ºF) -0,0286 x (10% Dist. Point ºF) + 0,2145 x (T_{agua} ºF)

Valores típicos 10% dist. point = 250 ºF

Concentración aceites en agua a tratar = 2.000 mg/l

Fuente: CONCAWE, report Nº 87/52. "Cost-efectiveness of hydrocarbon emission controls in Refineries from crude oil receipt to product dispatch”.

Esta ecuación no considera la existencia de balsas cubiertas y/o sistemas de recuperación de vapor. En caso de que existan estas medidas de control, debe considerarse aplicar el ratio 0,024/0,6 según se indica en US EPA AP-42, Tabla 5.1-2.

Sobre el valor total de COV's obtenido, se considera que el 0,38% es benceno (CORINAIR, ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\mathrm{kg\,emitidos} = Q_{\mathrm{agua\,a\,planta}}\left(\frac{m^3}{\mathrm{año}}\right) \mathrm{x} \frac{10^3\,l}{m^3} \mathrm{x}\, 2.000\frac{mg}{l} \mathrm{x} \frac{kg}{10^6\,mg} \mathrm{x} \frac{\%\mathrm{Litchfield}}{100} \mathrm{x} \frac{0,38}{100}$$

- **Observaciones**

No existen índices de confianza para el cálculo de COV's en la bibliografía manejada, observándose cómo parámetros como el área de balsas o velocidad de viento no entran en consideración en el cálculo.

El índice para el porcentaje de benceno es E.

CONTAMINANTE Benceno C_6H_6	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 62/8/2
		1(a), 1(c)
VALOR UMBRAL (kg/año) 1.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de benceno	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en m^3 de agua tratada para determinar COV's totales y posteriormente cálculo de benceno a partir del porcentaje de benceno indicado (0,38%).

Factores de emisión: (US EPA, AP-42, Tabla 5.1-2)

- 0,6 kg/m^3 agua tratada (sin medidas correctoras)
- 0,024 kg/m^3 agua tratada (balsas cubiertas y/o sistema de recuperación de vapor)

Sobre el valor total de COV's obtenido, se considera que el 0,38% es benceno (CORINAIR, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = m^3 \text{ agua tratada x Factor de emisión}\left(\frac{kg}{m^3}\right) x \frac{0{,}38}{100}$$

- **Observaciones**

El índice de confianza para los factores de emisión ofrecidos por EPA es D. El contenido en benceno respecto a COV’s totales tiene un índice E.

CONTAMINANTE Benceno C_6H_6	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 62/8/3 1(a), 1(c)
VALOR UMBRAL (kg/año) 1.000	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de benceno	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en áreas de balsas existentes para determinar COV's totales.

Factores:

- 20 g/(m^2·h) para separadores de aceite sin cubrir
- 2 g/(m^2·h) para separadores de aceite cubiertos
- 2 g/(m^2·h) para flotación
- 0,2 g/(m^2·h) para tratamientos biológicos

Fuente: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries.

Sobre el valor total de COV's obtenido, se considera que el 0,38% es benceno (CORINAIR, Ref. US EPA Petroleum Refinery Speciation Profile).

- **Cuantificación**

$$\text{kg emitidos} = \Sigma\,\text{Factor}_i \left(\frac{g}{m^2 \text{ x h}}\right) \text{x } m^2 \text{ equipo}_i \text{ x horas de operación x } 10^{-3} \text{ x } \frac{0{,}38}{100}$$

- **Observaciones**

La bibliografía manejada no aporta índices de confianza para los factores suministrados. Debe destacarse cómo estos factores son de una gran generalidad, sin tener en cuenta las condiciones climáticas del emplazamiento de la Planta.

El índice para el porcentaje de benceno sobre COV's totales es E.

CONTAMINANTE **Benceno** C_6H_6	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **62/9/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de benceno**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 1 Código C

- **Descripción**

Determinación de benceno a partir de factores de emisión de NMCOV's específicos para elementos: válvulas, conexiones, drenajes, ...

Estos factores se afectan posteriormente por el nº de elementos estimados en cada unidad de Refinería (Ver Anexo 12)

Una vez obtenidos los valores de NMCOV's, se calculan los COV's totales, según las especiaciones recogidas en CORINAIR (Tablas 9.4 a 9.8):

	CH_4 (% p) en COV's totales	índice de confianza
- Drenajes:	2,90	C
- Sellos de compresores:	13,30	D
- Válvulas de seguridad:	0	D
- Válvulas y conexiones:	28,6	C
- Sellos de bombas:	3,30	C

Seguidamente, se obtiene el contenido en benceno según las especiaciones de la referencia anterior, pero para benceno:

	C_6H_6 (%p) en COV's totales	índice de confianza
- Drenajes	2,40	C
- Sellos de compresores	0	D
- Válvulas de seguridad	0	D
- Válvulas y conexiones	0,10	C
- Sellos de bombas	0,50	C

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
62/9/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 1 Código C

- **Descripción**

Los factores empleados son:

Tipo de equipo	Servicio	Factor de emisión kg/h/elemento
Válvulas	Gas (a)	0,0268
	Líquido ligero (a)	0,0109
	Líquido pesado (b)	0,0000987
Sellos de bombas	Líquido ligero (a)	0,114
	Líquido pesado (b)	0,00349
Sellos de compresores	Gas (a)	0,636
Válvulas de alivio de presión	Gas (a)	0,16
Conexiones	Para todos (a)	0,00025
Finales de línea	Para todos (a)	0,0023
Conexiones de muestreo	Para todos (a)	0,0150
Drenajes	Para todos (a)	0,032

(a) US EPA (1995 A)
(b) Taback (1996)
Nota: todos los valores se corresponden para Centros sin programas de inspección y mantenimiento.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{nºelementos x h}} \right) \text{x Nº elementos}_i \text{ x nº horas}_i \text{ x } \frac{100}{100 - \%CH_{4_i}} \text{ x } \frac{\%C_6H_{6_i}}{100}$$

- **Observaciones**

El índice de confianza para la mayoría de los elementos (fuente US EPA) es U. En relación con la fiabilidad del método, debe considerarse la calidad en la contabilización del nº de elementos.

CONTAMINANTE **Benceno** **C_6H_6**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **62/9/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **1.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de benceno**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 2 Código C

- **Descripción**

Extrapolación de resultados a partir de las emisiones típicas de una Refinería (Fuente: US EPA, AP-42, Tabla 5.1-3):

Fuente	Número	Emisiones NMCOV's (kg/día)
- Válvulas:	11.500	3.100
- Bridas:	46.500	300
- Sellos de bombas:	350	590
- Sellos de compresores:	70	500
- Válvulas de seguridad:	100	200
- Drenajes:	650	450

Las emisiones del cuadro se corresponden a una refinería con una capacidad de 330.000 barriles/día, sin programas de inspección y mantenimiento. Estos valores se corresponden a NMCOV's, por lo que los resultados deberán ser afectados por los porcentajes presentados en metodología 62/9/1 para obtener benceno.

- **Cuantificación**

$$\text{kg emitidos} = \sum_i \text{emisiones elemento}_i \left(\frac{\text{kg}}{\text{d}}\right) \text{x} \frac{\text{capacidad refino (barril/día)}}{330.000 \text{ barril/día}} \text{x Nº de días x} \frac{100}{100 - \%CH_{4i}} \text{x} \frac{\%C_6H_{6i}}{100}$$

- **Observaciones**

La fiabilidad del método no es alta, ya que no considera las unidades particulares que integran la Refinería.

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
62/9/3
1(a), 1(c)

FUENTE DE EMISIÓN: 9 Emisiones fugitivas (procesos)

Metodología 3

Código M

- **Descripción**

Implantación de un programa de detección y reparación de fugas (LDAR). El programa LDAR está destinado a la detección y progresiva reducción de las emisiones gaseosas de compuestos orgánicos volátiles (COV) de carácter difuso que tienen su origen en las pérdidas que se producen en los diferentes elementos que componen las unidades de proceso (bombas, válvulas, compresores, bridas, etc.).

Este programa se basa en los estándares del Método 21 de la US EPA, el cual establece no sólo el método a emplear para llevar a cabo las mediciones en campo sino que también define las características de los elementos a emplear y el método de calibración de los mismos. Mediante el programa LDAR, se identifican en planta los equipos que fugan, se procede a la medición de los mismos y, para aquellos que superan un cierto valor, se establecen plazos para llevar a cabo el ajuste, reparación o sustitución y se fija un calendario de seguimiento.

Seguidamente, se obtiene el contenido en benceno según las especiaciones recogidas en CORINAIR:

	C_6H_6 (%p) en COV`s totales	Índice de confianza
- Drenajes	2,40	C
- Sellos de compresores	0	D
- Válvulas de seguridad	0	D
- Válvulas y conexiones	0,10	C
- Sellos de bombas	0,50	C

Nota: Obviamente, en caso de que el programa LDAR llevara a cabo mediciones de benceno no sería necesario aplicar los porcentajes anteriores.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{MedidaLDAR}_i\,(\text{kg}) \times \left(\frac{\%C_6H_6}{100}\right)_i$$

Donde i es cada elemento que fuga

- **Observaciones**

La fiabilidad de las medidas de COV's obtenidas mediante un sistema LDAR se considera superior a los cálculos basados en factores de emisión.

CONTAMINANTE
Benceno
C_6H_6

VALOR UMBRAL (kg/año)
1.000

EXPRESADO COMO
kg de benceno

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

Nº
62/10/1
1(a), 1(c)

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

FUENTE DE EMISIÓN: 10 Parque de almacenamiento

Metodología 1 Código C

- **Descripción**

Empleo del software "TANKS" aplicado a tanques de benceno. TANKS es un procedimiento de cálculo desarrollado por US EPA que calcula las emisiones totales procedentes de tanques a partir del sistema de cálculo detallado en AP-42, sección 7.1, "Organic liquid storage tanks".

- **Cuantificación**

En función del tipo de tanque, sus dimensiones, naturaleza del producto y movimiento del mismo, características climatológicas de la zona, etc, se obtiene la emisión correspondiente a cada tanque en kg/año.

$$\text{kg emitidos} = \sum_i \text{kg emitidos tanque}_i$$

- **Observaciones**

Se considera como el método más preciso a la hora de evaluar las pérdidas en el parque de almacenamiento.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos

(1) Fueloil: $3{,}67 \cdot 10^{-6}$ g/GJ

(2) Gas: $3{,}07 \cdot 10^{-6}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

- **Cuantificación**

(1) y (2) $\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos

(1) Gas: $3{,}53 \cdot 10^{-6}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\, g} x \frac{GJ}{239.005\, kcal} x\, PCI\left(\frac{kcal}{kg}\right) x\, kg\, \text{combustible}$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/3/1**
		1(a), 1(c)
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos

(1) Gas (motor de 4 tiempos): 4,60 · 10^{-4} g/GJ

(2) Gasoil: 8,79 · 10^{-4} g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07.

- **Cuantificación**

(1) y (2)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\,\text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores en la bibliografía manejada.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Antorchas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV’s totales basados en crudo procesado en Refinería.

Factor: 0,8 lb/10^3 barril. Fuente: EPA SCC 30600401

Determinación de HAP como porcentaje del total de COV’s emitidos.

Porcentaje = 0,020%. Fuente: Australian National Pollutant Inventory. Ref. Taback 1996

- **Cuantificación**

$$\text{Kg emitidos} = \text{Factor de COV's totales}\left(\frac{\text{lb COV's}}{10^3\ \text{barril}}\right) x \frac{0{,}45359\ \text{kg}}{\text{lb}} x \frac{0{,}020}{100} x \frac{\text{barril}}{0{,}159\ \text{m}^3} x\ \text{m}^3\ \text{de crudo}$$

- **Observaciones**

El porcentaje de HAP aplicado se refiere a todos los HAP, no sólo a los 4 especificados en E-PRTR: benzo (a) pireno, benzo (b) fluoranteno, benzo (k) fluoranteno e indeno (1,2,3-cd) pireno. Así pues, esta metodología sobreestima las emisiones de HAP, según lo exigido por el Reglamento E-PRTR.

No aparece índice de confianza para el porcentaje de HAP en la bibliografía, destacándose la generalidad del factor. El índice de confianza para la emisión de COV’s es B.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/4/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Antorchas

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV’s totales basados en el gas a antorcha.

Factor: 0,06 kg/GJ. Fuente: Australian National Pollutant Inventory. (Ref. US EPA 1997 a).

Determinación de HAP como porcentaje del total de COV’s emitidos.

Porcentaje = 0,020 %. Fuente: Australian National Pollutant Inventory. Ref. Taback 1996.

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor de COV's totales}\left(\frac{\text{kg}}{\text{GJ}}\right) \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x} \frac{0{,}020}{100} \text{x kg de gas a antorcha}$$

- **Observaciones**

No aparecen en la bibliografía manejada índices de confianza para los factores anteriores.

El porcentaje de HAP aplicado se refiere a todos los HAP, no sólo a los 4 especificados en E-PRTR: benzo (a) pireno, benzo (b) fluoranteno, benzo (k) fluoranteno e indeno (1,2,3-cd) pireno. Así pues, esta metodología sobreestima las emisiones de HAP, según lo exigido por el Reglamento E-PRTR.

CONTAMINANTE **Hidrocarburos aromáticos policíclicos** **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en la cantidad de coque que se quema durante la regeneración.

Factor: 1,17 · 10^{-5} kg/t de coque

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07. (Ref: Bertrand, R.R. and Siegell, J.H. (2002) Emission of trace compounds from catalytic cracking regenerators. *Environmental Progress 21, 3, 163-167*)

- **Cuantificación**

$$\text{Kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{t}}\right) \text{x t de coque}$$

- **Observaciones**

No se ha encontrado índice de confianza para el factor anterior en la bibliografía manejada.

CONTAMINANTE
Hidrocarburos aromáticos policíclicos
HAP

VALOR UMBRAL (kg/año)
50

EXPRESADO COMO
kg de HAP

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
72/5/2
1(a), 1(c)

FUENTE DE EMISIÓN: 5 Cracking catalítico en lecho fluido

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión para el cálculo de COV’s totales basados en la alimentación a la unidad.

Factor: 0,63 kg/m^3 Fuente: Australian National Pollutant Inventory (Ref. US EPA 1997 a)

Determinación de HAP como porcentaje del total de COV’s emitidos.

Porcentaje = 0,15 % Fuente: Australian National Pollutant Inventory. (Ref. US EPA 1993).

- **Cuantificación**

$$\text{Kg emitidos} = \text{Factor de COV's totales}\left(\frac{kg}{m^3}\right) x \frac{0,15}{100} x\, m^3 \text{ alimentados a la unidad.}$$

- **Observaciones**

No aparecen en la bibliografía manejada índices de confianza para los factores anteriores.

El porcentaje de HAP aplicado se refiere a todos los HAP, no sólo a los 4 especificados en E-PRTR: benzo (a) pireno, benzo (b) fluoranteno, benzo (k) fluoranteno e indeno (1,2,3-cd) pireno. Así pues, esta metodología sobreestima las emisiones de HAP, según lo exigido por el Reglamento E-PRTR.

CONTAMINANTE Hidrocarburos aromáticos policíclicos **HAP**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **72/6/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de HAP**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 6 Planta de tratamiento de efluentes líquidos

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el agua tratada.

(1) Factor = 0,65 kg/10^6 gal agua tratada. Fuente: Locating and estimating air emissions from sources of polycyclic organic matter. EPA-454/R-98-014.

(2) Factor = 127 mg/m^3 agua tratada. Fuente: Compilation of emission factors for POP’s, a case study of Czech and Slovak Republics.

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{10^6\ \text{gal}}\right) x \frac{\text{gal}}{0{,}00378\,\text{m}^3} x\, \text{m}^3\ \text{agua tratada}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{mg}}{\text{m}^3}\right) x \frac{\text{kg}}{10^6\ \text{mg}} x\, \text{m}^3\ \text{agua tratada}$$

- **Observaciones**

La bibliografía manejada no señala el índice de confianza para el factor propuesto en (1). Para (2), el índice de confianza es D.

Es de destacar que a pesar del origen tan distinto de los factores propuestos, el valor de los mismos es relativamente próximo (127 mg/m^3 = 0,48 kg/10^6 gal).

Obsérvese que las emisiones calculadas van más allá de los 4 compuestos HAP especificados en el Reglamento E-PRTR: benzo (a) pireno, benzo (b) fluoranteno, benzo (k) fluoranteno e indeno (1,2,3-cd) pireno. Así pues, esta metodología sobreestima las emisiones de HAP solicitadas por E-PRTR.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/1/1**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	**RD 508/2007**
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/1/1
- Factores de emisión para COVDM: Ver Ficha 7/1/1

Peso Molecular de COVDM: 59,38 (obtenido de CORINAIR, B411, Tabla 9.1).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times$$

$$\times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de emisión correspondientes al cálculo de las emisiones de CH_4 y COVDM se especifican en las Fichas 1/1/1 y 7/1/1, respectivamente.

CONTAMINANTE
Carbono Orgánico Total
COT

VALOR UMBRAL (kg/año)
-

EXPRESADO COMO
kg de C total

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
76/2/1

RD 508/2007

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/2/1
- Factores de emisión para COVDM: Ver Ficha 7/2/1

Peso Molecular de COVDM: 59,38 (obtenido de CORINAIR, B411, Tabla 9.1).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times$$
$$\times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de CH_4 y COVDM se especifican en las Fichas 1/2/1 y 7/2/1, respectivamente.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES** **PRTR**	**Nº** **76/3/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión en Motores

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/3/1
- Factores de emisión para COVDM: Ver Ficha 7/3/1

Peso Molecular de COVDM: 59,38 (obtenido de CORINAIR, B411, Tabla 9.1).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times$$
$$\times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de CH_4 y COVDM se especifican en las Fichas 1/3/1 y 7/3/1, respectivamente.

CONTAMINANTE Carbono Orgánico Total **COT**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **76/4/1** RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de C total	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 4 Antorchas

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/5/1
- Factores de emisión para COVDM: Ver Ficha 7/4/1

Peso Molecular de COVDM: 34,13 (obtenido de CORINAIR, B923, Ref.: USEPA CHIEF database).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times$$
$$\times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de CH_4 y COVDM se especifican en las Fichas 1/4/1 y 7/4/1, respectivamente.

CONTAMINANTE **Carbono Orgánico Total** **COT**	# METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	**Nº** **76/5/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	## REFINO DE PETRÓLEO	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/6/1
- Factores de emisión para COVDM: Ver Ficha 7/5/1

Peso Molecular de COVDM: 34,60 (obtenido de CORINAIR, B411, Tabla 9.3).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times$$

$$\times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de CH_4 y COVDM se especifican en las Fichas 1/5/1 y 7/5/1, respectivamente.

CONTAMINANTE
Carbono Orgánico Total
COT

VALOR UMBRAL (kg/año)
-

EXPRESADO COMO
kg de C total

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
76/6/1

RD 508/2007

FUENTE DE EMISIÓN: 6 Destilación a vacío

Metodología 1 Código C

- **Descripción**

El cálculo de las emisiones de COT al aire se realizará sumando las emisiones obtenidas de CH_4 y COVDM.

- Factores de emisión para CH_4: Ver Ficha 1/7/1
- Factores de emisión para COVDM: Ver Ficha 7/6/1

Peso Molecular de COVDM: 52,40 (obtenido de CORINAIR, B411, Tabla 9.2).

- **Cuantificación**

$$\text{kg emitidos} = (\text{kg emitidos de } CH_4) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de } CH_4} + (\text{kg emitidos de COVDM}) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COVDM}}$$

- **Observaciones**

Los índices de confianza de los factores de CH_4 y COVDM se especifican en las Fichas 1/6/1 y 7/6/1, respectivamente.

CONTAMINANTE Carbono Orgánico Total COT	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 76/7/1
		RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de C total	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 7 Purgas

Metodología 1 Código C

- **Descripción**

En el caso de venteos a la atmósfera (sin recuperación ni envío a antorcha) se considera un factor de emisión de hidrocarburos totales de 1.662 kg/m^3 de alimentación a Refinería. (Fuente: EPA, AP-42, Tabla 5.1-1).

Peso Molecular de hidrocarburos: 40,48 (obtenido de CORINAIR, B411, Tabla 9.2).

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \text{m}^3\ \text{crudo} \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de los hidrocarburos}}$$

- **Observaciones**

El índice de confianza del factor de emisión es C.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/8/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 1 Código C

- **Descripción**

Empleo de la ecuación de Litchfield para determinar COV’s totales.

La ecuación de Litchfield expresa la emisión de COV’s como porcentaje del total de aceites que entran a la planta de tratamiento:

% pérdidas = - 6,6339 + 0,0319 x (T_{amb} ºF) - 0,0286 x (10% Dist. Point ºF) + 0,2145 x (T_{agua} ºF)

Valores típicos | 10% dist. Point = 250 ºT
Concentración aceites en agua a tratar = 2.000 mg/l

Fuente: CONCAWE, report Nº 87/52. “Cost-efectiveness of hydrocarbon emission controls in Refineries from crude oil receipt to product dispatch”.

Esta ecuación no considera la existencia de balsas cubiertas y/o sistemas de recuperación de vapor. En caso de que existan medidas de control, debe considerarse aplicar el ratio 0,024/0,6 según se indica en US EPA AP-42, Tabla 5.1-2.

Peso Molecular de COV’s: 40,48 (obtenido de CORINAIR, B411, Tabla 9.2).

- **Cuantificación**

$$\text{kg emitidos} = Q_{\text{agua a planta}}\left(\frac{m^3}{\text{año}}\right) \times \frac{10^3 l}{m^3} \times 2.000\frac{mg}{l} \times \frac{kg}{10^6\,mg} \times \frac{\%\,\text{Litchfield}}{100} \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

- **Observaciones**

No existen índices de confianza en la bibliografía manejada, observándose cómo parámetros como el área de balsas o velocidad de viento no entran en consideración en el cálculo.

CONTAMINANTE Carbono Orgánico Total **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **76/8/2** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 2 Código C

- **Descripción**

Empleo de factores de emisión basados en m^3 de agua tratada para determinar COV's totales.

Factores de emisión (US EPA, AP-42, Tabla 5.1-2):
0,6 kg/m^3 agua tratada (sin medidas correctoras)
0,024 kg/m^3 agua tratada (balsas cubiertas y/o sistemas de recuperación de vapor)

Peso Molecular de COV's: 40,48 (obtenido de CORINAIR, B411, Tabla 9.2).

- **Cuantificación**

$$\text{kg emitidos} = \text{m}^3\ \text{agua tratada} \times \text{Factor de emisión}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

- **Observaciones**

El índice de confianza para los factores de emisión ofrecidos por EPA es D.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/8/3** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 8 Planta de tratamiento de efluentes líquidos

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en áreas de balsas existentes para determinar COV's totales.

Factores:

20 g/(m^2.h)	para separadores de aceite sin cubrir
2 g/(m^2.h)	para separadores de aceite cubiertos
2 g/(m^2.h)	para flotación
0,2 g/(m^2.h)	para tratamientos biológicos

Fuente: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries.

Peso Molecular de COV's: 40,48 (obtenido de CORINAIR, B411, Tabla 9.2).

- **Cuantificación**

$$\text{kg emitidos} = \Sigma\ \text{Factor}_i \left(\frac{\text{g}}{\text{m}^2 \times \text{h}}\right) \times \text{m}^2\ \text{equipo}_i \times \text{horas de operación}_i \times \frac{\text{kg}}{10^3\text{g}} \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

- **Observaciones**

La bibliografía manejada no aporta índices de confianza para los factores suministrados. Debe destacarse cómo estos factores son de una gran generalidad, sin tener en cuenta las condiciones climáticas del emplazamiento de la planta.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/9/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 9 Torres de refrigeración

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión para determinar COV's totales basados en el volumen de agua circulante o cantidad de crudo procesada.

(1) Factor = 6 lb/10^6 gal agua circulante. EPA SCC 30600701.
(2) Factor = 10 lb/1.000 barril crudo procesado. EPA SCC 30600702.

Peso Molecular de COV's: 59,38 (obtenido de CORINAIR, B411, Tabla 9.1).

- **Cuantificación**

$$(1) \quad \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\,\text{m}^3} \times \text{m}^3\ \text{agua circulante} \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

$$(2) \quad \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{barril}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{barril}}{0{,}159\,\text{m}^3} \times \text{m}^3\ \text{crudo procesado} \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

- **Observaciones**

Ambos factores tienen un índice de confianza D, prefiriéndose el empleo del primero al ser función directa del agua circulante. El empleo del segundo factor asume que el agua circulante se puede estimar como 40 veces el volumen de crudo procesado.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/10/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 1 Código C

Descripción

Determinación de COV's a partir de factores de emisión de NMCOV's específicos para elementos: válvulas, conexiones, drenajes...

Estos factores se afectan posteriormente por el nº de elementos estimados en cada unidad de Refinería (ver Anexo 12).

Una vez obtenidos los valores de NMVOC's, se calculan los COV's correspondientes, según las especiaciones de metano recogidas en CORINAIR (B411, Tablas 9.4 a 9.8):

	CH_4 (% p) en COV's totales	índice de confianza	Peso Molecular de COV's
- Drenajes:	2,90	C	65,63
- Sellos de compresores:	13,30	D	40,47
- Válvulas de seguridad:	0	D	43,20
- Válvulas y conexiones:	28,6	C	33,06
- Sellos de bombas:	3,30	C	74,07

Los factores empleados son:

Tipo de equipo	Servicio	Factor de emisión kg/h/elemento
Válvulas	Gas (a)	0,0268
	Líquido ligero (a)	0,0109
	Líquido pesado (b)	0,0000987
Sellos de bombas	Líquido ligero (a)	0,114
	Líquido pesado (b)	0,00349
Sellos de compresores	Gas (a)	0,636
Válvulas de alivio de presión	Gas (a)	0,16
Conexiones	Para todos (a)	0,00025
Finales de línea	Para todos (a)	0,0023
Conexiones de muestreo	Para todos (a)	0,0150
Drenajes	Para todos (a)	0,032

(a) US EPA (1995 A)
(b) Taback (1996)
Nota: todos los valores se corresponden para Centros sin programas de inspección y mantenimiento.

Cuantificación

$$\text{kg emitidos} = \sum \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{nº elementos} \times \text{h}}\right) \times \text{nº elementos}_i \times \text{nºhoras}_i \times \frac{100}{100 - \%_i} \times \left(\frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}\right)_i$$

Observaciones

El índice de confianza para la mayoría de los elementos (fuente US EPA) es U. En relación con la fiabilidad del método, deben considerarse la calidad en la contabilización del nº de elementos.

CONTAMINANTE **Carbono Orgánico Total** **COT**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **76/10/2** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de C total**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 2 Código E

- **Descripción**

Extrapolación de resultados a partir de las emisiones típicas de una Refinería (Fuente: US EPA, AP-42, Tabla 5.1-2):

	Fuente	Número	Emisiones NMCOV's(kg/día)	Peso Molecular de COV's
-	Válvulas:	11.500	3.100	33,06
-	Bridas:	46.500	300	33,06
-	Sellos de bombas:	350	590	74,07
-	Sellos de compresores:	70	500	40,47
-	Válvulas de seguridad:	100	200	43,20
-	Drenajes:	650	450	65,63

Las emisiones del cuadro se corresponden a una Refinería con una capacidad de 330.000 barriles/día, sin programas de inspección y mantenimiento. Estos valores se corresponden a NMVOC's, por lo que para estimar los COV's deberán tenerse en cuenta los porcentajes de metano presentados en la metodología 76/10/1.

- **Cuantificación**

$$\text{kg emitidos} = \sum_i \text{Factor elemento}_i \left(\frac{\text{kg}}{\text{día}}\right) \times \frac{100}{100 - \%_i} \times \frac{\text{capacidad refino (barriles día)}}{330.000\,(\text{barriles día})} \times \text{nº de días} \times \left(\frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}\right)_i$$

- **Observaciones**

La fiabilidad del método no es alta, ya que no considera las unidades particulares que integran la Refinería.

CONTAMINANTE Carbono Orgánico Total **COT**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **76/10/3** RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de C total	Asociación Española de Operadores de Productos Petrolíferos	AOP

FUENTE DE EMISIÓN: 10 Emisiones fugitivas (procesos)

Metodología 3 Código M

- **Descripción**

Implantación de un programa de detección y reparación de fugas (LDAR). El programa LDAR está destinado a la detección y progresiva reducción de las emisiones gaseosas de compuestos orgánicos volátiles (COV) de carácter difuso que tienen su origen en las pérdidas que se producen en los diferentes elementos que componen las unidades de proceso (bombas, válvulas, compresores, bridas, etc.).

Este programa se basa en los estándares del Método 21 de la US EPA, el cual establece no sólo el método a emplear para llevar a cabo las mediciones en campo sino que también define las características de los elementos a emplear y el método de calibración de los mismos. Mediante el programa LDAR, se identifican en planta los equipos que fugan, se procede a la medición de los mismos y, para aquellos que superan un cierto valor, se establecen plazos para llevar a cabo el ajuste, reparación o sustitución y se fija un calendario de seguimiento.

Como Pesos Moleculares de COV’s en cada elemento se tomarán los presentados en las metodologías 76/10/1 y 76/10/2.

- **Cuantificación**

$$\text{kg emitidos} = \sum \text{Medida LDAR}_i\,(\text{kg}) \times \left(\frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}} \right)_i$$

Donde i es cada elemento que fuga

- **Observaciones**

La fiabilidad de las medidas de COV’s obtenidas mediante un sistema LDAR se considera superior a los cálculos basados en factores de emisión.

CONTAMINANTE Carbono Orgánico Total **COT**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **76/11/1** RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de C total	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 11 Parque de almacenamiento

Metodología 1 Código C

- **Descripción**

Empleo del software "TANKS". TANKS es un procedimiento de cálculo desarrollado por US EPA que calcula las emisiones totales procedentes de tanques a partir del sistema de cálculo detallado en AP-42, sección 7.1, "Organic liquid storage tanks".

Peso Molecular de COV's: 59,38 (obtenido de CORINAIR, B411, Tabla 9.1).

- **Cuantificación**

En función del tipo de tanque, sus dimensiones, naturaleza del producto y movimiento del mismo, características climatológicas de la zona, etc, se obtiene la emisión correspondiente a cada tanque en kg/año.

$$\text{kg emitidos} = \sum_i \text{kg de COV's emitidos tanque}_i \times \frac{\text{Peso Molecular de C}}{\text{Peso Molecular de COV's}}$$

- **Observaciones**

Se considera como el método más preciso a la hora de evaluar las pérdidas en el parque de almacenamiento.

CONTAMINANTE
Cloro y compuestos inorgánicos
Cl

VALOR UMBRAL (kg/año)
10.000

EXPRESADO COMO
kg de ácido clorhídrico

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
80/1/1

1(a), 1(c)

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

Fueloil: $3{,}47 \cdot 10^{-1}$ lb/10^{3} gal. Fuente: EPA SCC 10100401

Fuelgas: No aplicable

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{3}\text{gal}}\right) \times \frac{0{,}45359\,\text{kg}}{\text{lb}} \times \frac{\text{gal}}{0{,}00378\,\text{m}^{3}} \times \text{m}^{3}\ \text{fueloil}$$

- **Observaciones**

Las emisiones de cloro en procesos de combustión vienen ligadas exclusivamente al consumo de fueloil, no habiéndose localizado en la bibliografía manejada emisiones de cloro asociadas al fuelgas o incluso gas natural. El índice de confianza para el factor antes expuesto es D.

CONTAMINANTE Cloro y compuestos inorgánicos **Cl**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **80/2/1** 1(a), 1(c)
VALOR UMBRAL (kg/año) 10.000	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de ácido clorhídrico	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 2 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión en base al coque quemado:

- Cloro: 1,29 · 10^{-3} lb/10^{3} lb coque. Fuente: Environmental Progress (Vol. 21, nº 3)
- Ácido Clorhídrico: 1,06 · 10^{-1} lb/10^{3} lb coque. Fuente: Environmental Progress (Vol. 21, nº 3, pp 163-167, 2.002).

- **Cuantificación**

$$\text{kg emitidos} = (\text{Factor cloro} \times \frac{36,5}{35,5} + \text{Factor ClH}) \left(\frac{\text{lb}}{10^{3}\ \text{lb coque}} \right) \times \text{kg coque}$$

- **Observaciones**

El factor de cloro es la media de dos medidas reales, mientras que el de clorhídrico es la media de 10 medidas reales.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/1/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Determinación de PM_{10} a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

CONTAMINANTE Partículas PM_{10}	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº 86/1/2 1(a), 1(c)
VALOR UMBRAL (kg/año) 50.000	REFINO DE PETRÓLEO	
EXPRESADO COMO Peso total partículas PM_{10}	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código M

- **Descripción**

Determinación de PM totales a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q Nm^3/h, secos), ambos al oxígeno de emisión. Posteriormente, se afectan por el ratio PM_{10}/PM totales en función del combustible empleado:

· Ratio para fueloil	= 7,4/12	EPA SCC 30600103
· Ratio para fuelgas	= 3/3	EPA SCC 30600106

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6} x ratio (adim)

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

El índice de confianza para los factores de emisión de donde se ha obtenido el ratio PM_{10}/PM totales es U para fueloil y B para fuelgas.

CONTAMINANTE **Partículas** **PM$_{10}$**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/1/3** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM$_{10}$**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 3 Código M

- **Descripción**

Determinación de PM$_{10}$ a partir de medidas en continuo (como correlación extinción-concentración de PM$_{10}$). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) [*]. El caudal de humos (Q, Nm^3/h)[*] se determina mediante análisis de la composición del combustible y a partir de éste, a través de la aplicación de la Orden de 26 de diciembre de 1995 (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

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[*] C y Q expresados en igual base y al mismo oxígeno de referencia.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/1/4** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 4 Código M

- **Descripción**

Determinación de PM totales a partir de medidas en continuo (como correlaciones extinción-concentración). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante análisis de la composición del combustible y a partir de éste, a través de la aplicación de la Orden de 26 de diciembre de 1995 (ver Anexo II). El resultado final se afecta del ratio PM_{10}/PM totales en función del combustible empleado:

· Ratio para fueloil	= 7,4/12	EPA SCC 30600103
· Ratio para fuelgas	= 3/3	EPA SCC 30600106

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6} x ratio (adim)

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

El índice de confianza para los factores de emisión de donde se ha obtenido el ratio PM_{10}/PM totales es U para fueloil y B para fuelgas.

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[*] C y Q expresados en igual base y al mismo oxígeno de referencia.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/1/5** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 5 Código C

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores EPA/CORINAIR y los controles bienales realizados.

- **Cuantificación**

Factor de emisión corregido = Factor de emisión x Factor de experiencia.
(el factor de emisión corregido es empleado como se muestra en 86/2/1, 86/3/1 y 86/4/1).

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor EPA/CORINAIR. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

Potencia < 10 MW

(1) Gasoil: 3,49 g/GJ

(2) Fueloil: (17,47 x % S) + 5,772 g/GJ

(3) GN: $8,90 \cdot 10^{-1}$ g/GJ

Potencia entre 10 y 100 MW

(4) Gasoil: 3,23 g/GJ

(5) Fueloil: (24,229 x % S) + 8,004 g/GJ

(6) GN: $8,90 \cdot 10^{-1}$ g/GJ

Potencia > 100 MW

(7) Gasoil: 3,23 g/GJ

(8) Fueloil: (19,937 x % S) +6,586 g/GJ

(9) GN: $8,90 \cdot 10^{-1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07. (Ref. EPA)

Potencia < 50 MW

(10) GN: 0,9 g/GJ

(11) Fueloil pesado: 40 g/GJ

(12) Otros combustibles líquidos: 40 g/GJ

CONTAMINANTE **Partículas** **PM$_{10}$**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/2/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM$_{10}$**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Potencia > 50 MW

(13) GN: 0,9 g/GJ

(14) Fueloil pesado (1% S): 18 g/GJ

(15) Fueloil pesado (3% S): 45 g/GJ

(16) Otros combustibles líquidos: 2,0 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulos 111(S1) y 111 (S2).

(17) Fueloil: 7,4 x % S lb/10^3 gal Fuente : EPA, SCC 30600103

(18) Fuelgas: 3 lb/10^6 ft^3 Fuente: EPA, SCC 30600106

- **Cuantificación**

(1) a (16)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\ \text{g}} \text{x} \frac{\text{GJ}}{239.005\ \text{kcal}} \text{x}\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\, \text{kg combustible}$$

(17)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{gal}}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\ \text{m}^3} \text{x}\ \text{m}^3\ \text{fueloil}$$

(18)

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{ft}^3}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{ft}^3}{0{,}028\ \text{m}^3} \text{x}\ \text{m}^3\ \text{fuelgas}$$

- **Observaciones**

El índice de confianza para (17) es U y para (18) es B.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/3/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Gasoil: 1,95 g/GJ

(2) GN: $9{,}08 \cdot 10^{-1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07. (Ref. EPA)

(3) GN: 0,9 g/GJ

(4) Otros combustibles líquidos: 2,0 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S3)

- **Cuantificación**

(1) a (4)

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\ PCI\left(\frac{kcal}{kg}\right) x\, kg\, combustible$$

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/4/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 4 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: $3{,}68 \cdot 10^{-2}$ g/GJ

(2) GN: $2{,}24 \cdot 10^{1}$ g/GJ

Fuente: CONCAWE, Air pollutant emission methods for E-PRTR reporting by refineries, report no. 3/07. (Ref. EPA)

(3) GN (2 tiempos): 18 g/GJ

(4) GN (4 tiempos): 0,04 g/GJ

(5) Fueloil pesado: 23 g/GJ

(6) Otros combustibles líquidos: 23 g/GJ

Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S3)

- **Cuantificación**

(1) a (6)

$$\text{kg emitidos} = \text{Factor}\left(\frac{g}{GJ}\right) x \frac{kg}{10^3\,g} x \frac{GJ}{239.005\,kcal} x\ \text{PCI}\left(\frac{kcal}{kg}\right) x\,\text{kg combustible}$$

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/5/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 1 Código C

- **Descripción**

Factores de emisión basados en el gas a antorcha y en la calidad de la combustión.

(1) Antorcha no humeante: 0 kg/m^3

(2) Antorcha ligeramente humeante: 40 · 10^{-6} kg/m^3

(3) Antorcha normalmente humeante: 177 · 10^{-6} kg/m^3

(4) Antorcha muy humeante: 274 · 10^{-6} kg/m^3

Fuente: Australian National Pollutant Inventory, Ref. US EPA (1997 a)

- **Cuantificación**

(1) a (4) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right)\text{x m}^3 \text{ gas a antorcha}$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/6/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 1 Código M

- **Descripción**

Determinación de PM_{10} a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/6/2** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación de PM totales a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión. Posteriormente, se afectan por el ratio PM_{10}/PM totales = 0,549/0,695 (Fuente: CONCAWE, Ref. Australian National Pollutant Inventory, Ref. EPA para PM_{10} y EPA SCC 30600201 para PM totales).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6} x ratio (adim)

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

El índice de confianza para el valor referenciado como emisión de partículas totales (0,695 kg/m^3, EPA SCC 30600201) es B.

CONTAMINANTE Partículas PM_{10}	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **86/6/3** 1(a), 1(c)
VALOR UMBRAL (kg/año) 50.000	REFINO DE PETRÓLEO	
EXPRESADO COMO Peso total partículas PM_{10}	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 3 Código M

- **Descripción**

Determinación de PM_{10} a partir de medidas en continuo (como correlaciones extinción-concentración de PM_{10}). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante el empleo de correlaciones (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}.

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

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[*] C y Q expresados en igual base y al mismo oxígeno de referencia

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/6/4** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 4 Código M

- **Descripción**

Determinación de PM totales a partir de medidas en continuo (como correlaciones extinción-concentración). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante el empleo de correlaciones (ver Anexo II). El resultado final se afecta del ratio PM_{10}/PM totales = 0,549/0,695 (Fuente: CONCAWE, Ref. Australian National Pollutant Inventory, Ref. EPA para PM_{10} y EPA SCC 30600201 para PM totales).

- **Cuantificación**

Kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6} x ratio

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

El índice de confianza para el valor referenciado como emisión de partículas totales (0,695 kg/m^3, EPA SCC 30600201) es B.

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* C y Q expresados en igual base y al mismo oxígeno de referencia

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/6/5** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 5 Código C

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Factor: 0,549 kg/m^3 Fuente: CONCAWE, Ref. Australian National Pollutant Inventory, Ref. US EPA (97a). Sin precipitador electrostático ni caldera auxiliar de CO.

- **Cuantificación**

$$\text{kg emitidos} = 0{,}549\left(\frac{\text{kg}}{\text{m}^3}\right) x\, \text{m}^3 \text{ alimentado}$$

- **Observaciones**

No se dispone de índice de confianza para el factor de emisión utilizado.

CONTAMINANTE **Partículas** **PM_{10}**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/6/6** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM_{10}**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 6 Código C

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores EPA/CORINAIR y los controles bienales realizados.

- **Cuantificación**

Factor de emisión corregido = Factor de emisión x Factor de experiencia (el factor de emisión corregido es empleado como ha sido visto en 86/6/5).

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor EPA/CORINAIR. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE **Partículas** **PM$_{10}$**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **86/7/1** **1(a), 1(c)**
VALOR UMBRAL (kg/año) **50.000**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **Peso total partículas PM$_{10}$**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 7 Coquización fluida

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en el volumen alimentado a la unidad.

Factor: 0,765 kg/m^3 alimentado a la unidad. Fuente: CONCAWE, Ref. Australian National Pollutant Inventory, Ref. US EPA (1997 a).

- **Cuantificación**

$$\text{Kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \times \text{m}^3 \text{ alimentados a la unidad.}$$

- **Observaciones**

No se ha encontrado en la bibliografía manejada índice de confianza para el factor de emisión anterior.

Obsérvese que el factor anterior está indicado para coquización fluida. En España, las dos unidades de coquizado existentes son del tipo retardada (Guía de Mejores Técnicas Disponibles en España del sector refino de petróleo).

CONTAMINANTE **Partículas totales en suspensión** **PST(ver NOTA)**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/1/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 1 Código M

- **Descripción**

Determinación de PST a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

NOTA: Así es como aparece este contaminante en el RD 508/2007, motivo por el cual se ha utilizado esta nomenclatura en la presente ficha. No obstante, parece obvio que si el análisis se está realizando en emisión, la totalidad de las partículas emitidas sean en suspensión, no siendo por tanto apropiado señalar: PST, partículas totales en suspensión (a diferencia de lo que pasa en inmisión, donde la diferencia entre partículas en suspensión o sedimentables sí puede ser de interés).

CONTAMINANTE
Partículas totales en suspensión
PST

VALOR UMBRAL (kg/año)
-

EXPRESADO COMO
kg de PST

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
92/1/2

RD 508/2007

FUENTE DE EMISIÓN: 1 Combustión

Metodología 2 Código M

- **Descripción**

Determinación de PST a partir de medidas en continuo (como correlación extinción-concentración de PST). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) [*]. El caudal de humos (Q, Nm^3/h)[*] se determina mediante análisis de la composición del combustible y a partir de éste, a través de la aplicación de la Orden de 26 de diciembre de 1995 (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

[*] C y Q expresados en igual base y al mismo oxígeno de referencia.

CONTAMINANTE Partículas totales en suspensión **PST**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **92/1/3** RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO kg de PST	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 1 Combustión

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores EPA/CORINAIR y los controles bienales realizados.

- **Cuantificación**

Factor de emisión corregido = Factor de emisión x Factor de experiencia.
(el factor de emisión corregido es empleado como se muestra en 92/2/1, 92/3/1 y 92/4/1).

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor EPA/CORINAIR. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE
Partículas totales en suspensión
PST

VALOR UMBRAL (kg/año)
-

EXPRESADO COMO
kg de PST

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
92/2/1

RD 508/2007

FUENTE DE EMISIÓN: 2 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Fueloil: 12 x % S lb/10^3 gal Fuente: EPA, SCC 30600103
(2) Fuelgas: 3 lb/10^6 ft^3 Fuente: EPA, SCC 30600106

Potencia < 50 MW

(3) GN: 0,9 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S1)
(4) Fueloil: 50 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S1)

Potencia > 50 MW

(5) GN: 0,9 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S2)
(6) Fueloil (1% S): 25 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S2)
(7) Fueloil (3% S): 64 g/GJ Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S2)

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0{,}00378\ \text{m}^3} \text{x}\ \text{m}^3\ \text{fueloil}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{ft}^3}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{ft}^3}{0{,}028\ \text{m}^3} \text{x}\ \text{m}^3\ \text{fuelgas}$$

(3) a (7) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^3\ \text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg}\,\text{combustible}$$

- **Observaciones**

El índice de confianza para (1) es U y para (2) es B. No se han encontrado en la bibliografía analizada índices de confianza para el resto de factores.

CONTAMINANTE Partículas totales en suspensión **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **92/3/1**
		RD 508/2007
VALOR UMBRAL (kg/año) -	**REFINO DE PETRÓLEO**	
EXPRESADO COMO kg de PST	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 3 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Diesel (con inyección de vapor o agua): 4,300 · 10^{-3} lb/10^{6} btu. Fuente: EPA, SCC 20200101

(2) GN: 0,9 g/GJ. Fuente: Libro Guía EMEP/CORINAIR Capítulo 111(S3)

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{6}\text{btu}}\right) \text{x} \frac{0{,}45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0{,}251\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) \text{x} \frac{\text{kg}}{10^{3}\ \text{g}} \text{x} \frac{\text{GJ}}{239.005\,\text{kcal}} \text{x PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x kg combustible}$$

- **Observaciones**

El índice de confianza de (1) es C. No se ha encontrado índice de confianza para (2).

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/4/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 4 Combustión en Motores

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) GN: 1,000 · 10^1 lb/10^6 ft^3 Fuente: EPA, SCC 20200202

(2) Diesel (Large Bore Engine): 1,370 · 10^1 lb/10^3 gal. Fuente: EPA, SCC 20200401

(3) Dual fuel (oil/gas) (Large Bore Engine): 6,200 · 10^{-2} lb/10^6 btu. Fuente: EPA, SCC 20200402

(4) GN (2-cycle, Lean Burn): 18 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S3)

(5) GN (4-cycle, Lean Burn): 0,04 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S3)

(6) Fueloil (motor diesel): 28 g/GJ. Fuente: Libro Guía EMEP/CORINAIR. Capítulo 111 (S3)

- **Cuantificación**

(1)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{ft}^3}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{\text{ft}^3}{0{,}028\,\text{m}^3} x\,\text{m}^3\ \text{combustible}$$

(2)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{gal}}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{\text{gal}}{0{,}00378\,\text{m}^3} x\ \text{m}^3\ \text{combustible}$$

(3)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{btu}}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{\text{btu}}{0{,}251\,\text{kcal}} x\ \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) x\,\text{kg}\,\text{combustible}$$

(4) a (6)
$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{g}}{\text{GJ}}\right) x \frac{\text{kg}}{10^3\text{g}} x \frac{\text{GJ}}{239.005\,\text{kcal}} x\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) x\,\text{kg}\,\text{combustible}$$

- **Observaciones**

El índice de confianza de (1) es U y el de (2) y (3) es E. No se han encontrado en la bibliografía analizada índices de confianza para el resto de factores.

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/5/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 5 Antorchas

Metodología 1 Código C

- **Descripción**

Dadas las características de las corrientes enviadas a antorcha, se considera que todas las partículas emitidas son PM_{10}. Por tanto se emplearán los mismos factores que se indican en la ficha 86/5/1 para PM_{10}.

Factores de emisión basados en el gas a antorcha y en la calidad de la combustión.

(1) Antorcha no humeante: 0 kg/m^3

(2) Antorcha ligeramente humeante: $40 \cdot 10^{-6}$ kg/m^3

(3) Antorcha normalmente humeante: $177 \cdot 10^{-6}$ kg/m^3

(4) Antorcha muy humeante: $274 \cdot 10^{-6}$ kg/m^3

Fuente: Australian National Pollutant Inventory, Ref. US EPA (1997 a)

- **Cuantificación**

(1) a (4) $$\text{kg emitidos} = \text{Factor} \left(\frac{kg}{m^3}\right) \times m^3 \text{ gas a antorcha}$$

- **Observaciones**

No se han encontrado índices de confianza para los factores anteriores.

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/6/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 1 Código M

- **Descripción**

Determinación de PST a partir de medidas periódicas efectuadas por Entidad Acreditada o bien autocontroles propios del Centro de Refino. Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3) y caudales de humos (Q, Nm^3/h, secos), ambos al oxígeno de emisión.

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se encuentra en relación directa con el método y sistemática empleados para la determinación. Este método de cuantificación debe emplearse en focos cuyas condiciones de operación no estén sometidas a variaciones significativas. En los supuestos anteriores, el índice de confianza es alto.

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/6/2**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	AOP ASOCIACIÓN ESPAÑOLA DE OPERADORES DE PRODUCTOS PETROLÍFEROS

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 2 Código M

- **Descripción**

Determinación de PST a partir de medidas en continuo (como correlaciones extinción-concentración de PST). Los resultados así obtenidos se corresponden con valores de concentración (C, mg/Nm^3)*. El caudal de humos (Q, Nm^3/h)* se determina mediante el empleo de correlaciones (ver Anexo II).

- **Cuantificación**

kg emitidos = C (mg/Nm^3) x Q (Nm^3/h) x horas de operación x 10^{-6}

- **Observaciones**

El índice de confianza del valor suministrado se considera muy elevado, siempre y cuando se constate la calidad de la calibración y la estimación del caudal sea suficientemente precisa.

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/6/3**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	**RD 508/2007**
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 3 Código C

- **Descripción**

Empleo de factores de emisión basados en alimentación a la unidad.

Factor: 0,695 kg/m^3. Fuente: EPA, AP-42, Tabla 5.1-1, SCC 30600201.

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x}\, \text{m}^3 \text{ alimentado}$$

- **Observaciones**

El índice de confianza del factor de emisión utilizado es B.

CONTAMINANTE **Partículas totales en suspensión** **PST**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **92/6/4**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **kg de PST**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 6 Cracking catalítico en lecho fluido

Metodología 4 Código C

- **Descripción**

Empleo de factores de emisión corregidos por factores de experiencia propios. Estos factores corrigen las desviaciones encontradas entre la aplicación de factores EPA/CORINAIR y los controles bienales realizados.

- **Cuantificación**

Factor de emisión corregido = Factor de emisión x Factor de experiencia (el factor de emisión corregido es empleado como ha sido visto en 92/5/3).

- **Observaciones**

El resultado global obtenido mejora el índice de confianza del factor EPA/CORINAIR. Dado que la corrección se realiza en base a medidas periódicas, deben considerarse las mismas "observaciones" que en las metodologías basadas en la determinación a partir de dichas medidas.

CONTAMINANTE Antimonio **Sb**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	Nº **94/1/1** RD 508/2007
VALOR UMBRAL (kg/año) -	**REFINO DE PETRÓLEO**	
EXPRESADO COMO peso total de antimonio	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

Fueloil: 5,25 · 10^{-3} lb/10^{3} gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^{3}\ \text{gal}}\right) \text{x} \frac{0,45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0,00378\ \text{m}^{3}} \text{x}\ \text{m}^{3}\ \text{fueloil}$$

- **Observaciones**

El índice de confianza del factor de emisión es E.

CONTAMINANTE Antimonio **Sb**	METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR	Nº **94/2/1** RD 508/2007
VALOR UMBRAL (kg/año) -	REFINO DE PETRÓLEO	
EXPRESADO COMO peso total de antimonio	Asociación Española de Operadores de Productos Petrolíferos	

FUENTE DE EMISIÓN: 2 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en la emisión de partículas y posterior aplicación del porcentaje de antimonio en las partículas.

Factor de emisión de partículas (TSP): 0,695 kg/m^3 alimentado a la unidad
Fuente: EPA, AP-42, Tabla 5.1-1.

Porcentaje de antimonio: 0,035 %
Fuente: Australian National Pollutant Inventory (Ref. US EPA 1997a)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor de partículas}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x} \frac{0{,}035}{100} \text{x m}^3 \text{ alimentados}$$

- **Observaciones**

El índice de confianza del factor de emisión de partículas es B, mientras que no se ha localizado el correspondiente al porcentaje de antimonio.

CONTAMINANTE
Cobalto
Co

VALOR UMBRAL (kg/año)
-

EXPRESADO COMO
peso total de cobalto

METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR

REFINO DE PETRÓLEO

Asociación Española de Operadores de Productos Petrolíferos

Nº
95/1/1
RD 508/2007

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

(1) Fueloil: 6,02 · 10^{-3} lb/10^3 gal. Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401
(2) GN: 8,4 · 10^{-5} lb/10^6 ft^3. Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10200601

- **Cuantificación**

(1) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\ \text{gal}}\right) \text{x} \frac{0,45359\ \text{kg}}{\text{lb}} \text{x} \frac{\text{gal}}{0,00378\,\text{m}^3} \text{x}\, \text{m}^3\ \text{fueloil}$$

(2) $$\text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\ \text{ft}^3}\right) \text{x} \frac{0,45359\ \text{kg}}{\text{lb}} \text{x} \frac{35,31467\,\text{ft}^3}{\text{m}^3} \text{x}\, \text{m}^3\ \text{GN}$$

- **Observaciones**

El índice de confianza de (1) y (2) es D.

CONTAMINANTE **Cobalto** **Co**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **95/2/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **peso total de cobalto**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en la emisión de partículas y posterior aplicación del porcentaje de cobalto en las partículas.

Factor de emisión de partículas (TSP): 0,695 kg/m^3 alimentado a la unidad
Fuente: EPA, AP-42, Tabla 5.1-1.

Porcentaje de cobalto: 0,002 %
Fuente: Australian National Pollutant Inventory (Ref. US EPA 1997a)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor de partículas}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x} \frac{0{,}002}{100} \text{x m}^3 \text{ alimentados}$$

- **Observaciones**

El índice de confianza del factor de emisión de partículas es B, mientras que no se ha localizado el correspondiente al porcentaje de cobalto.

CONTAMINANTE **Manganeso** **Mn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **96/1/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **peso total de manganeso**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Fueloil: $3 \cdot 10^{-3}$ lb/10^3 gal Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(2) GN: $3{,}8 \cdot 10^{-4}$ lb/10^6 ft^3 Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10200601

(3) Fueloil: $1{,}3 \cdot 10^{-5}$ lb/10^6 btu Fuente: EPA SCC 30600101

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^3\,\text{gal}}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{\text{gal}}{0{,}00378\,\text{m}^3} x\, \text{m}^3\ \text{fueloil}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\,\text{ft}^3}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{35{,}31467\,\text{ft}^3}{\text{m}^3} x\, \text{m}^3\ \text{GN}$$

$$(3)\ \text{kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{btu}}\right) x \frac{0{,}45359\,\text{kg}}{\text{lb}} x \frac{\text{btu}}{0{,}251\,\text{kcal}} x\, \text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) x\, \text{kg fueloil}$$

- **Observaciones**

Los índices de confianza de (1), (2) y (3) son C, D y U respectivamente.

CONTAMINANTE **Manganeso** **Mn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **96/2/1**
		RD 508/2007
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **peso total de manganeso**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 2 Combustión en Turbinas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en combustibles consumidos.

(1) Diesel: 7,9 · 10^{-4} lb/10^6 btu Fuente: EPA, SCC 20200101

(2) GN: 8,02 · 10^{-5} lb/10^6 btu Fuente: EPA, SCC 20200201

- **Cuantificación**

$$\text{(1) y (2) kg emitidos} = \text{Factor}\left(\frac{\text{lb}}{10^6\text{btu}}\right) \text{x} \frac{0,45359\,\text{kg}}{\text{lb}} \text{x} \frac{\text{btu}}{0,251\,\text{kcal}} \text{x}\,\text{PCI}\left(\frac{\text{kcal}}{\text{kg}}\right) \text{x}\,\text{kg combustible}$$

CONTAMINANTE **Manganeso** **Mn**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **96/3/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **peso total de manganeso**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 3 Cracking catalítico en lecho fluido

Metodología 1 Código C

- **Descripción**

Factor de emisión basado en la emisión de partículas y posterior aplicación del porcentaje de manganeso en las partículas.

Factor de emisión de partículas (TSP): 0,695 kg/m^3 alimentado a la unidad Fuente: EPA, AP-42, Tabla 5.1-1

Porcentaje de manganeso: 0,022 % Fuente: Australian National Pollutant Inventory (Ref. US EPA 1997a)

- **Cuantificación**

$$\text{kg emitidos} = \text{Factor de partículas}\left(\frac{\text{kg}}{\text{m}^3}\right) \text{x} \frac{0{,}022}{100} \text{x}\, \text{m}^3 \text{ alimentados}$$

- **Observaciones**

El índice de confianza del factor de emisión de partículas es B, mientras que no se ha localizado el correspondiente al porcentaje de manganeso.

CONTAMINANTE **Vanadio** **V**	**METODOLOGÍA CUANTIFICACIÓN EMISIONES PRTR**	**Nº** **97/1/1** **RD 508/2007**
VALOR UMBRAL (kg/año) **-**	**REFINO DE PETRÓLEO**	
EXPRESADO COMO **peso total de vanadio**	**Asociación Española de Operadores de Productos Petrolíferos**	

FUENTE DE EMISIÓN: 1 Combustión en hornos y calderas

Metodología 1 Código C

- **Descripción**

Empleo de factores de emisión basados en el combustible consumido.

Hornos y calderas ≥ 300 MW

(1) Fueloil: 4,4 g/Mg Fuente: Libro Guía EMEP/CORINAIR, Capítulo 111

Potencia sin especificar

(2) Fueloil: $3{,}18 \cdot 10^{-2}$ lb/10^3 gal Fuente: EPA, AP-42, Tabla 1.3-11, SCC 10100401

(3) GN: $2{,}3 \cdot 10^{-3}$ lb/10^6 ft^3 Fuente: EPA, AP-42, Tabla 1.4-4, SCC 10200601

- **Cuantificación**

$$(1)\ \text{kg emitidos} = \text{Factor}\left(\frac{g}{Mg}\right) x \frac{kg}{10^3 g} x \frac{Mg}{10^3 kg} x\, \text{kg fueloil}$$

$$(2)\ \text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^3 gal}\right) x \frac{0{,}45359\, kg}{lb} x \frac{gal}{0{,}00378\, m^3} x\, m^3\ \text{fueloil}$$

$$(3)\ \text{kg emitidos} = \text{Factor}\left(\frac{lb}{10^6\, ft^3}\right) x \frac{0{,}45359\, kg}{lb} x \frac{35{,}31467\, ft^3}{m^3} x\, m^3\ \text{GN}$$

- **Observaciones**

El índice de confianza de (2) y (3) es D. No se ha encontrado índice de confianza para (1) en la bibliografía manejada.