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AIR

EPA

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.

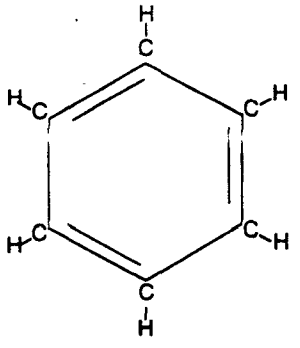


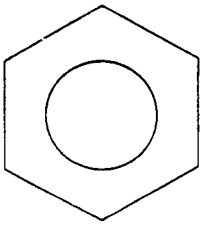
TABLE 3-1. CHEMICAL IDENTIFICATION OF BENZENE

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 1.1×10^{-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]

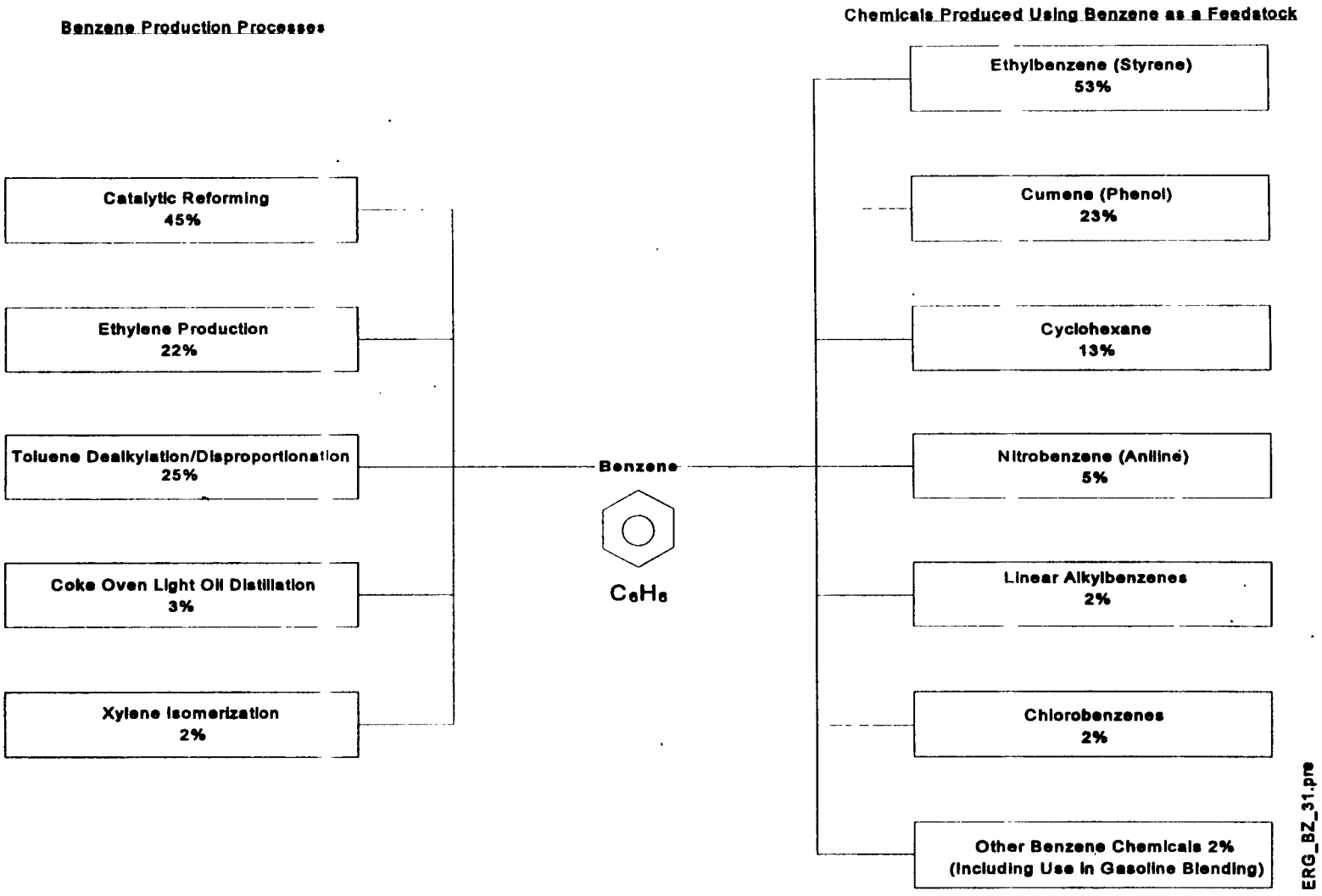


Figure 3-1. Production and Use Tree for Benzene

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 Hess Oil Virgin Islands Corporation, subsidiary	St. Croix, Virgin Islands	75 (284)	Catalytic reformate; toluene; no captive use
American Petrofina, Incorporated Fina Oil and Chemical Company, subsidiary	Port Arthur, Texas	33 (125) 31 (117)	Catalytic reformate; partly captive Toluene; partly captive
Amoco Corporation Amoco Oil Company, subsidiary	Texas City, Texas	85 (322) 25 (95) 12 (45)	Catalytic reformate; partly captive Pyrolysis gasoline; partly captive Xylene isomerization
Aristech Chemical Corporation	Clairton, Pennsylvania	45 (170)	Coke-oven light oil
Ashland Oil, Incorporated Ashland Chemical Company, division Petrochemicals Division	Catlettsburg, Kentucky	55 (208) 2 (8)	Coke-oven light oil; captive Catalytic reformate; captive
Atlantic Richfield Corporation Lyondell Petrochemical Company, subsidiary	Channelview, Texas Houston, Texas	90 (341) 35 (132) 15 (57)	Pyrolysis gasoline; captive Catalytic reformate; no captive use 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	Corpus Christi, Texas	50 (189)	Pyrolysis gasoline
Exxon Chemical Company, division		30 (114)	Toluene
Exxon Chemical Americas	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	Corpus Christi, Texas	17 (64)	Catalytic reformate; no captive use
Southwestern Refining Company, Incorporated, subsidiary			
Koch Industries, Incorporated	Corpus Christi, Texas	25 (95)	Catalytic reformate; captive
Koch Refining Company, subsidiary		55 (208)	Toluene; captive
		10 (38)	Xylene isomerization
		50 (189)	Toluene
Mobil Corporation	Beaumont, Texas	90 (341)	Catalytic reformate; no captive use
Mobil Oil Corporation		10 (38)	Pyrolysis gasoline
Mobil Chemical Company, division		20 (76)	Catalytic reformate; no captive use
Petrochemicals Division	Chalmette, Louisiana		
U.S. Marketing and Refining Division			

(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]

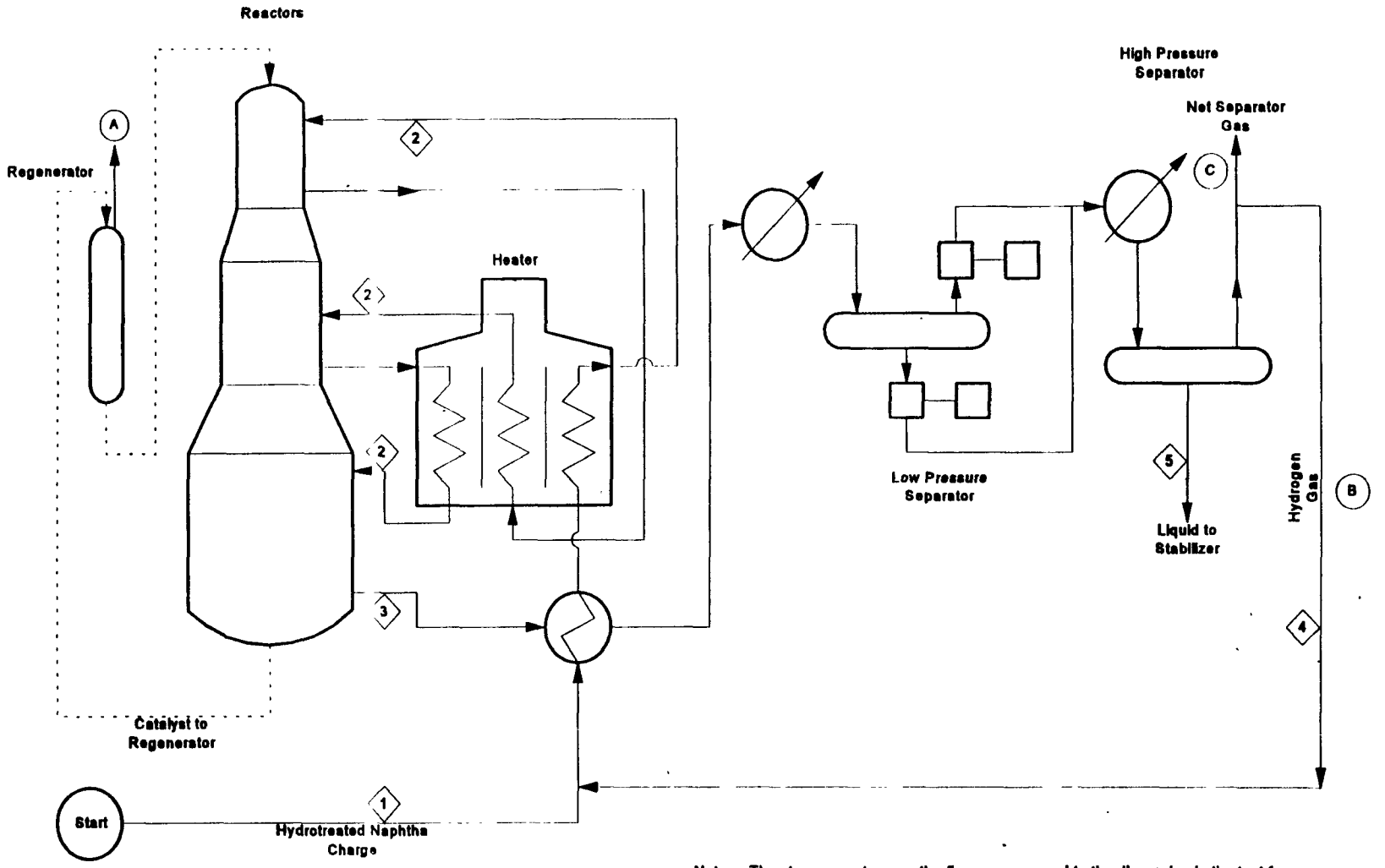


Figure 4-1. Universal Oil Products Platforming (Reforming) Process

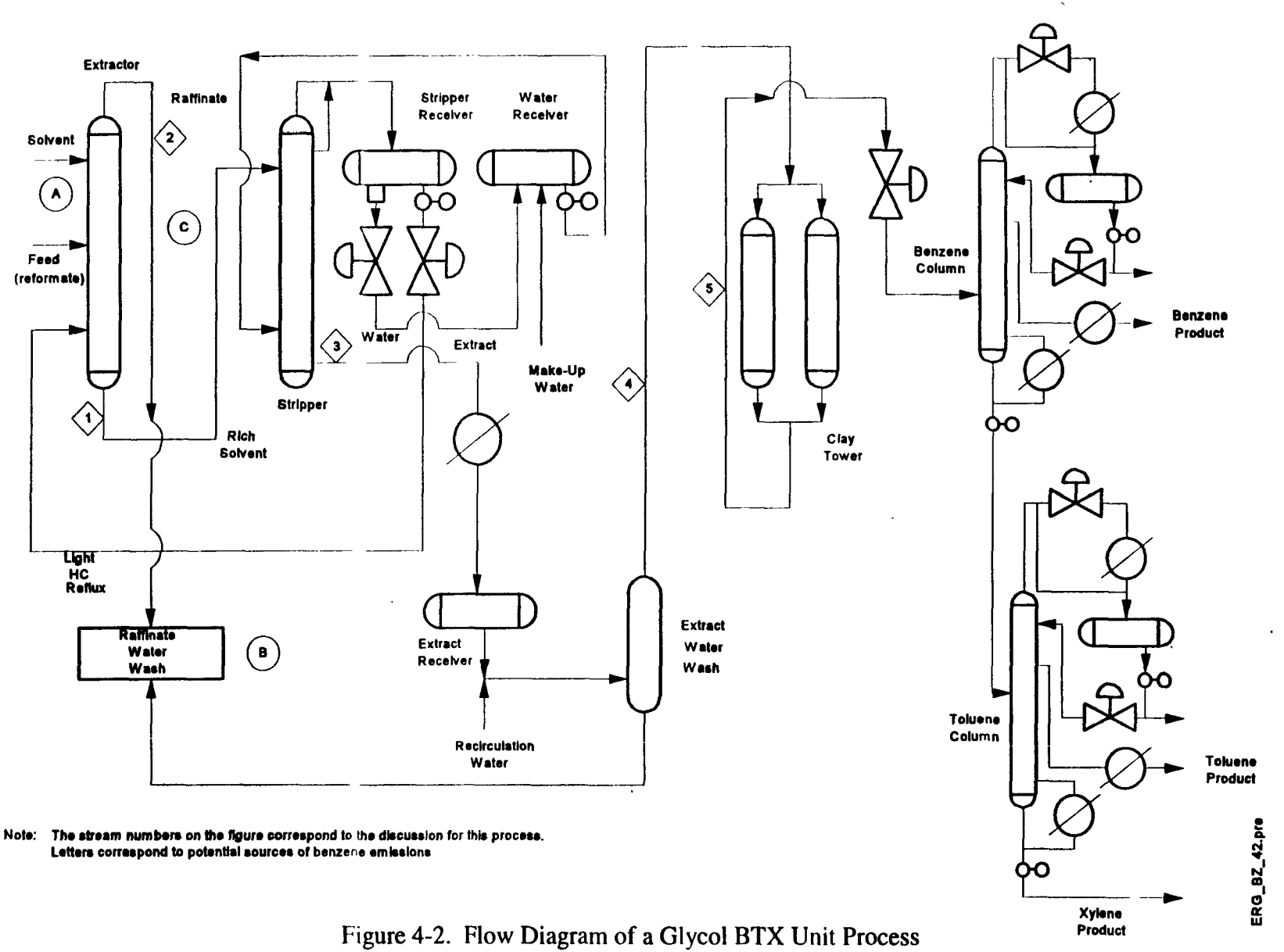
Source: Reference 22.

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]

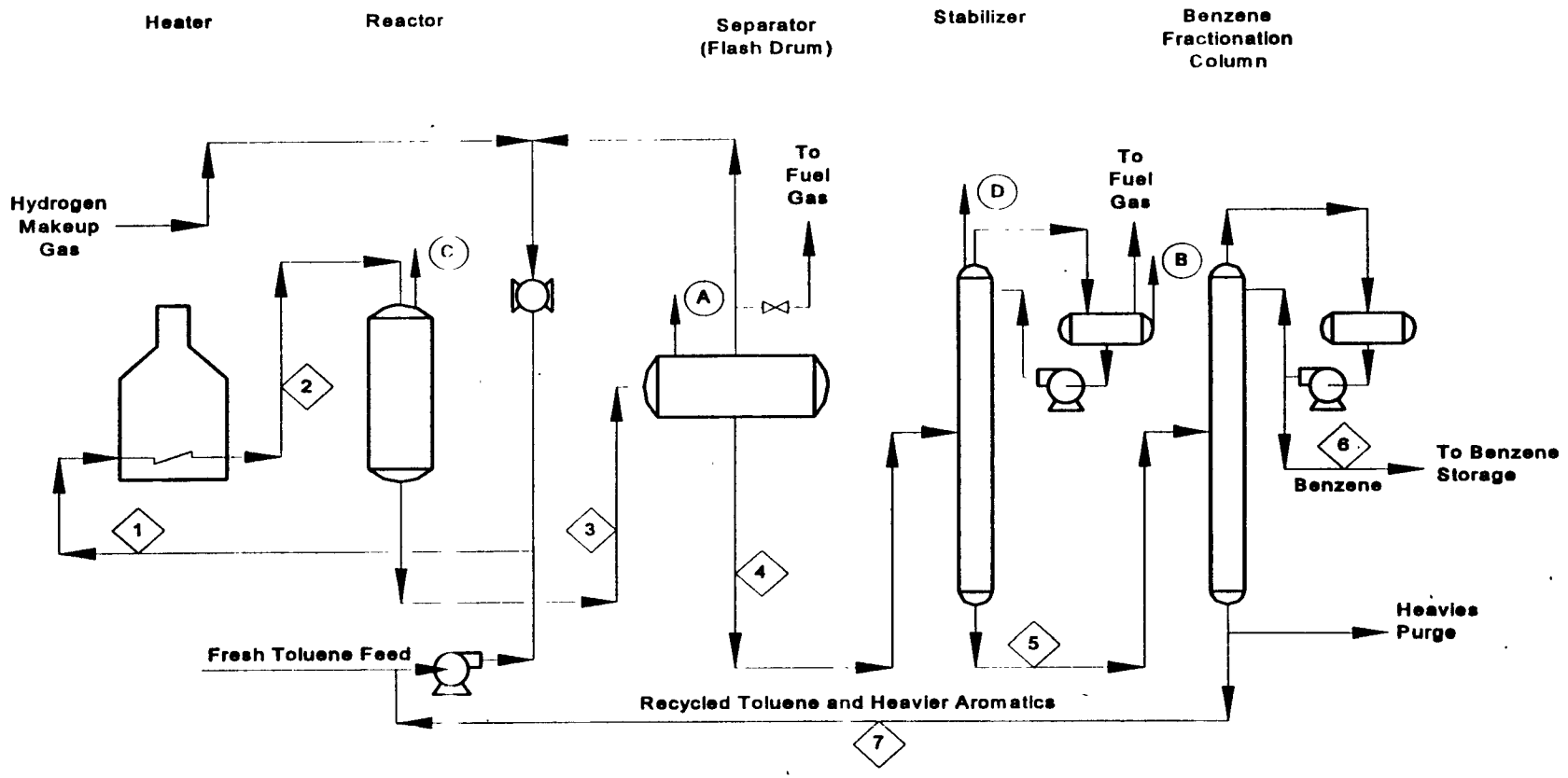
4.2.2 Toluene Disproportionation

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.

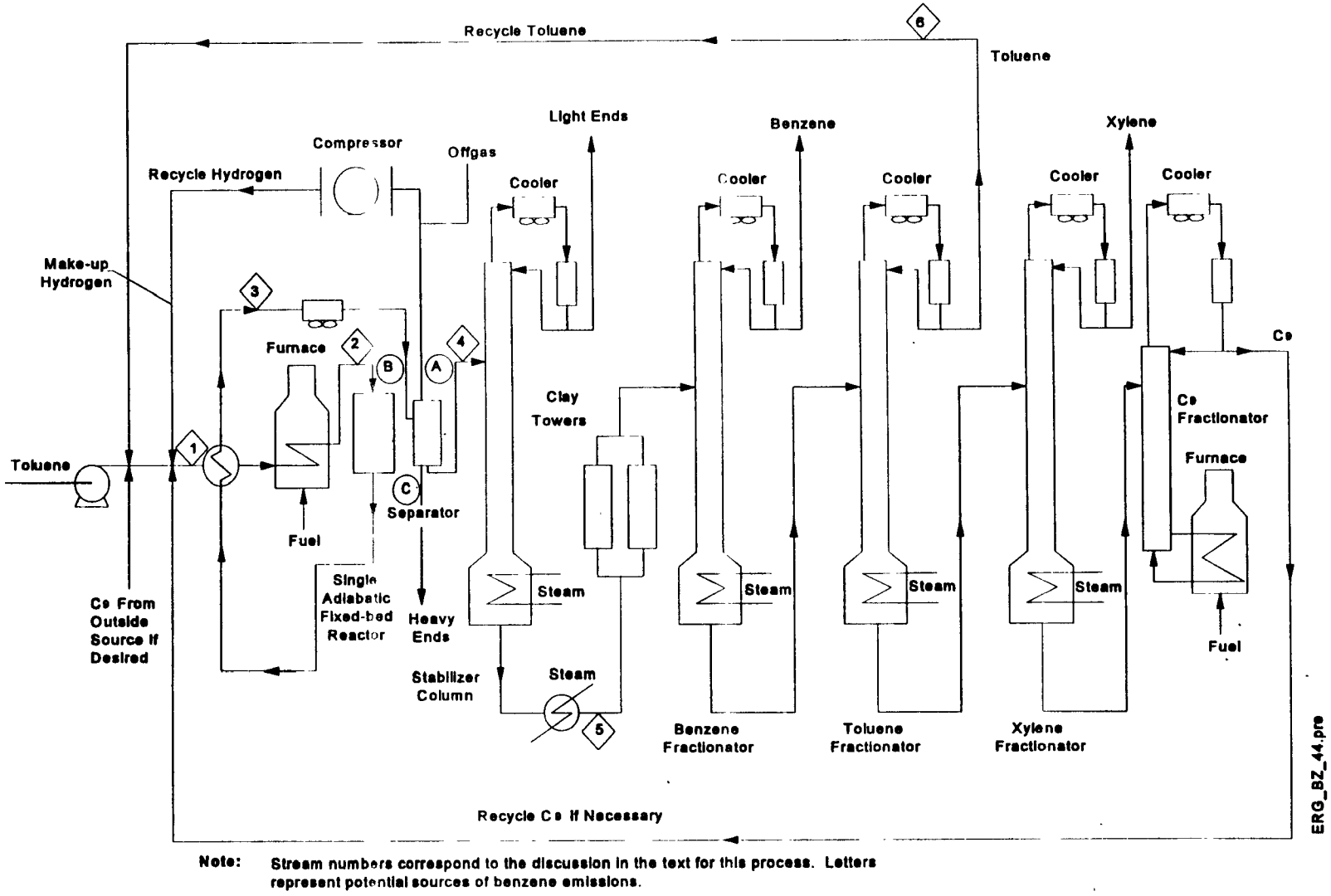


Figure 4-4. Toluene Disproportionation Process Flow Diagram (Tatoray Process)

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	Seadrift, Texas	880 (399)	Captive
Industrial Chemicals Division	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.

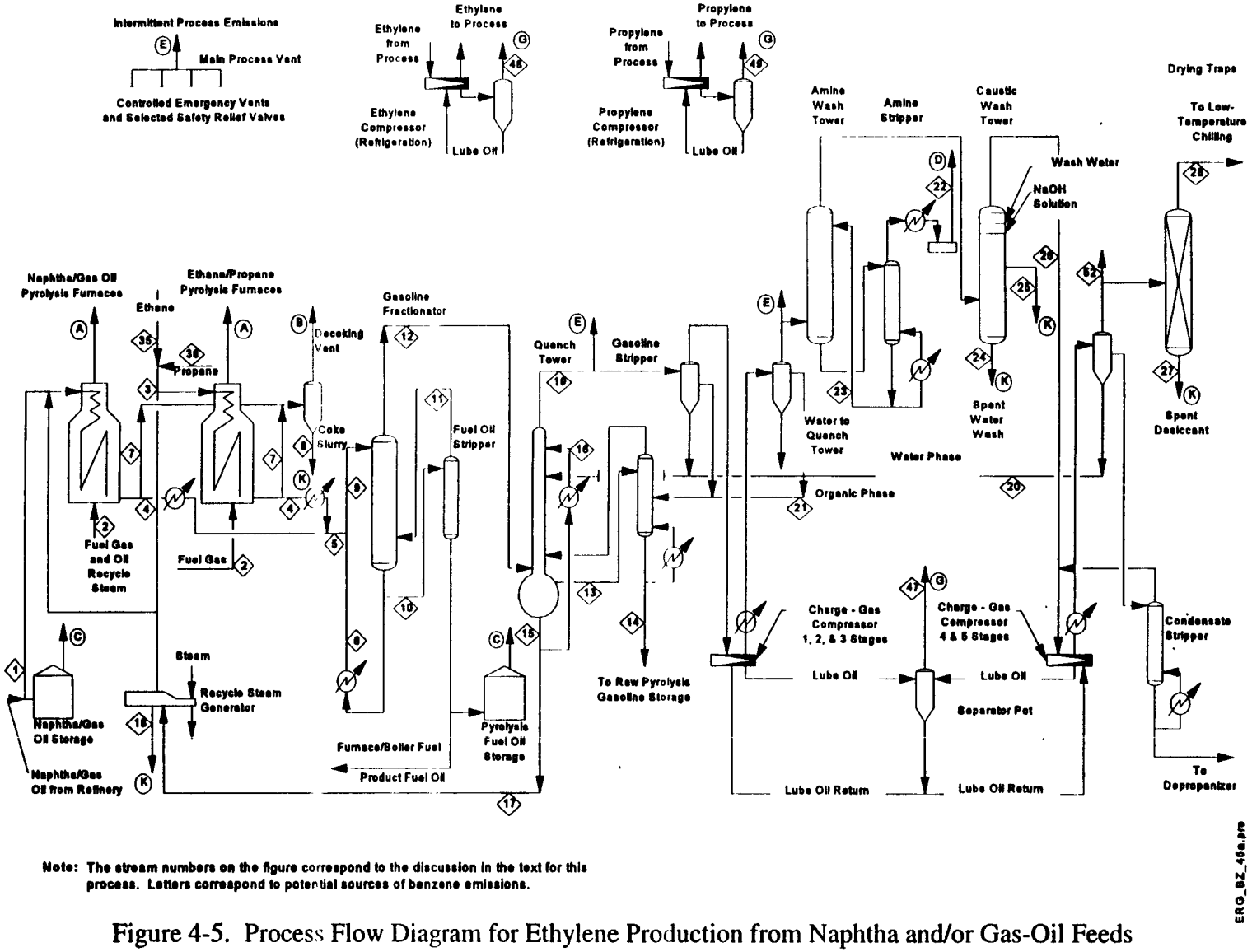
Ethylene/Pyrolysis Gasoline Production

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.

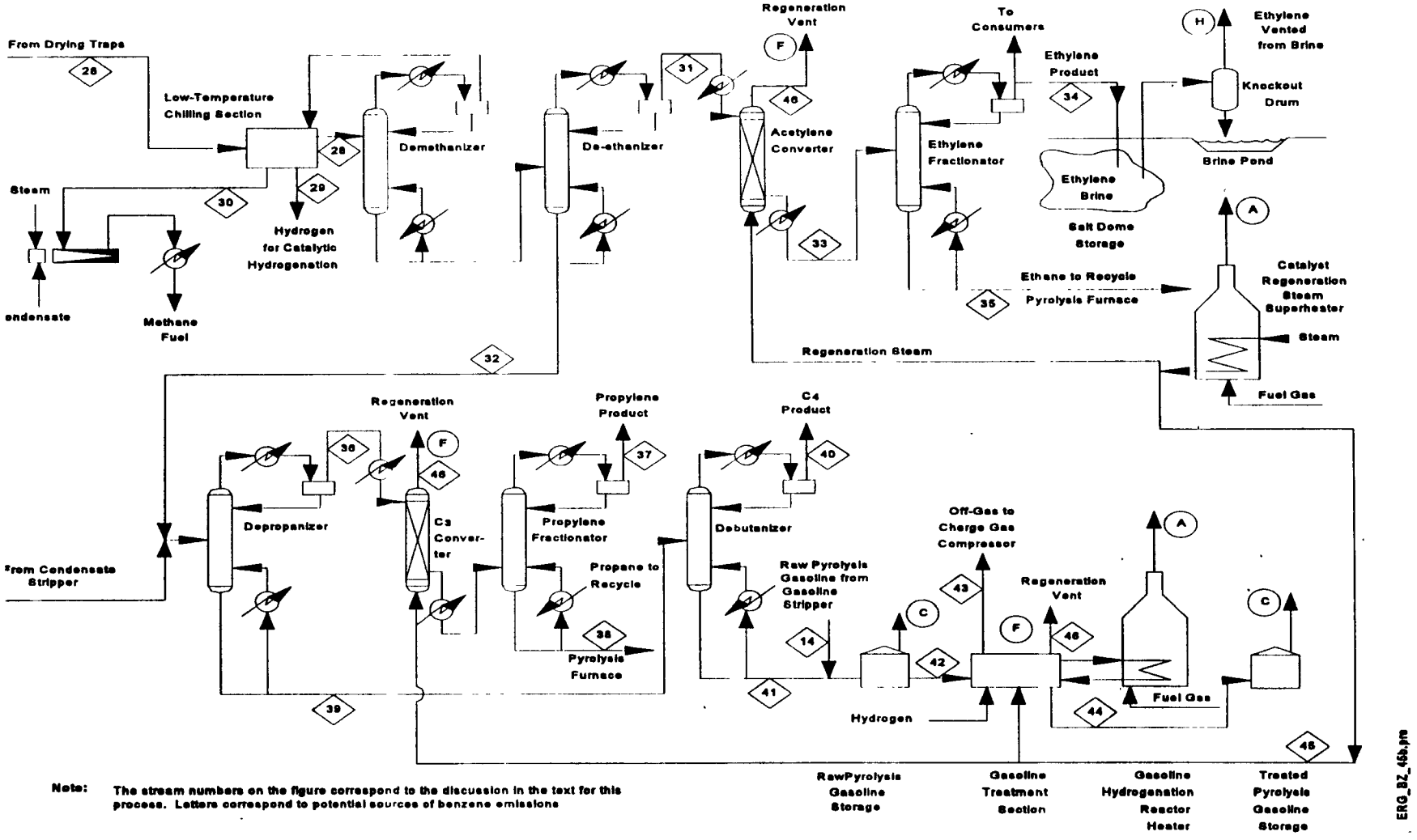


Figure 4-5. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds, continued

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

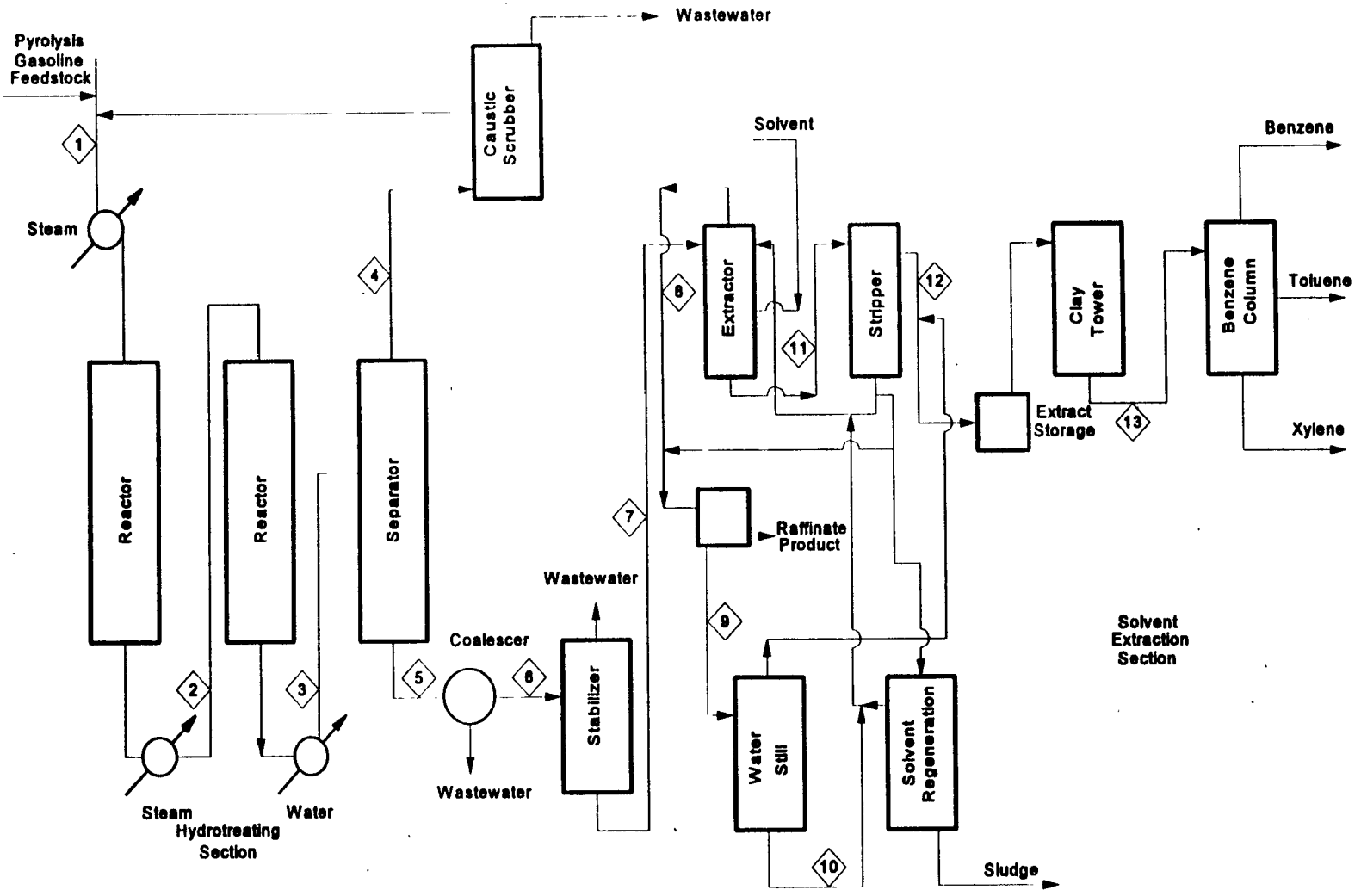
A process flow diagram for a plant producing benzene, toluene, and xylenes by hydrogenation of pyrolysis gasoline is presented in Figure 4-6. Pyrolysis gasoline is fed with make-up hydrogen into the first stage hydrogenation reactor (Stream 1), where olefins are hydrogenated. The reaction conditions 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	Intermittent Emissions[c]			
Ethylene Manufacturing-Intermittent Emissions	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

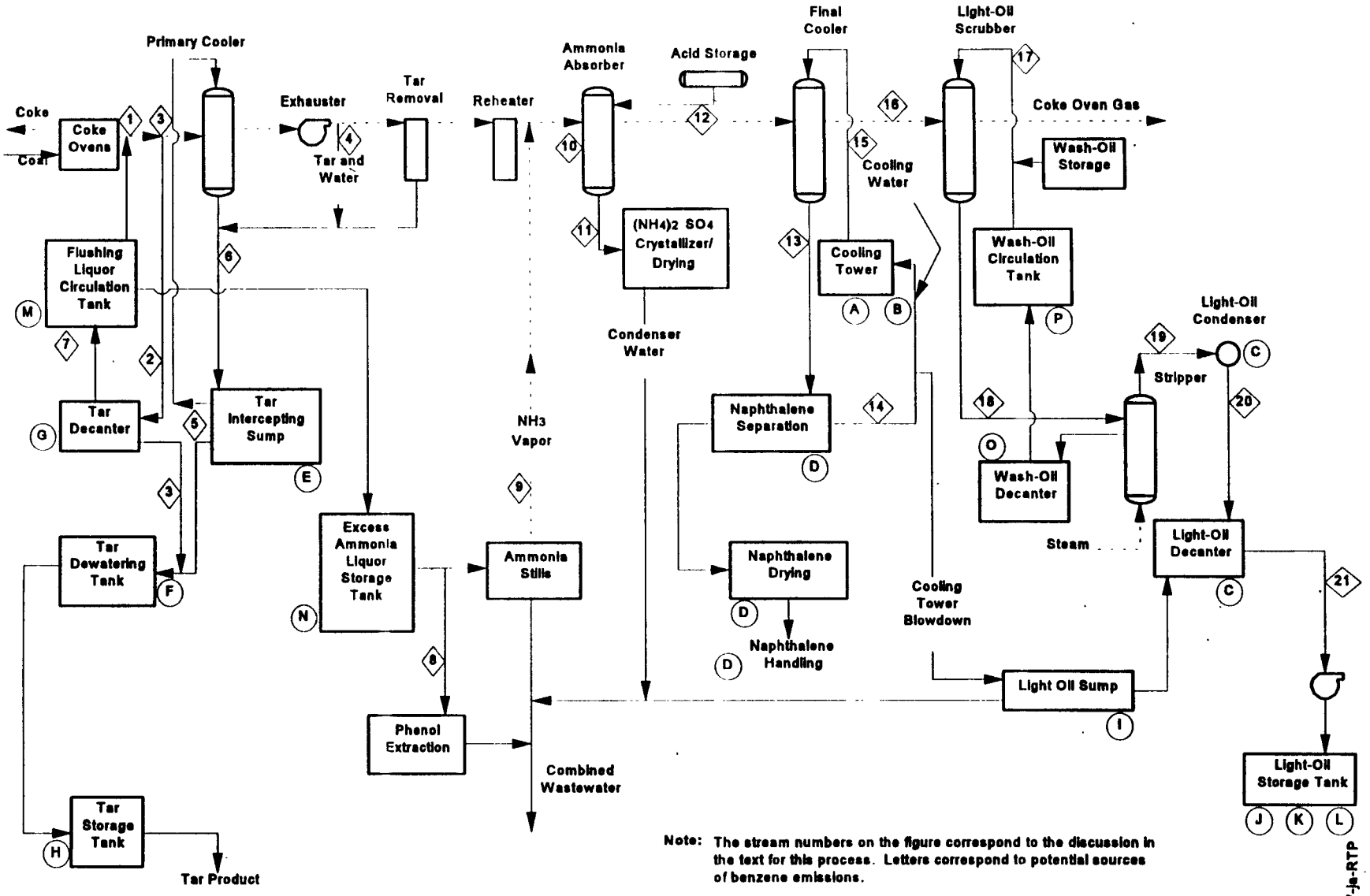


Figure 4-7. Coke Oven By-Product Recovery, Representative Plant

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).

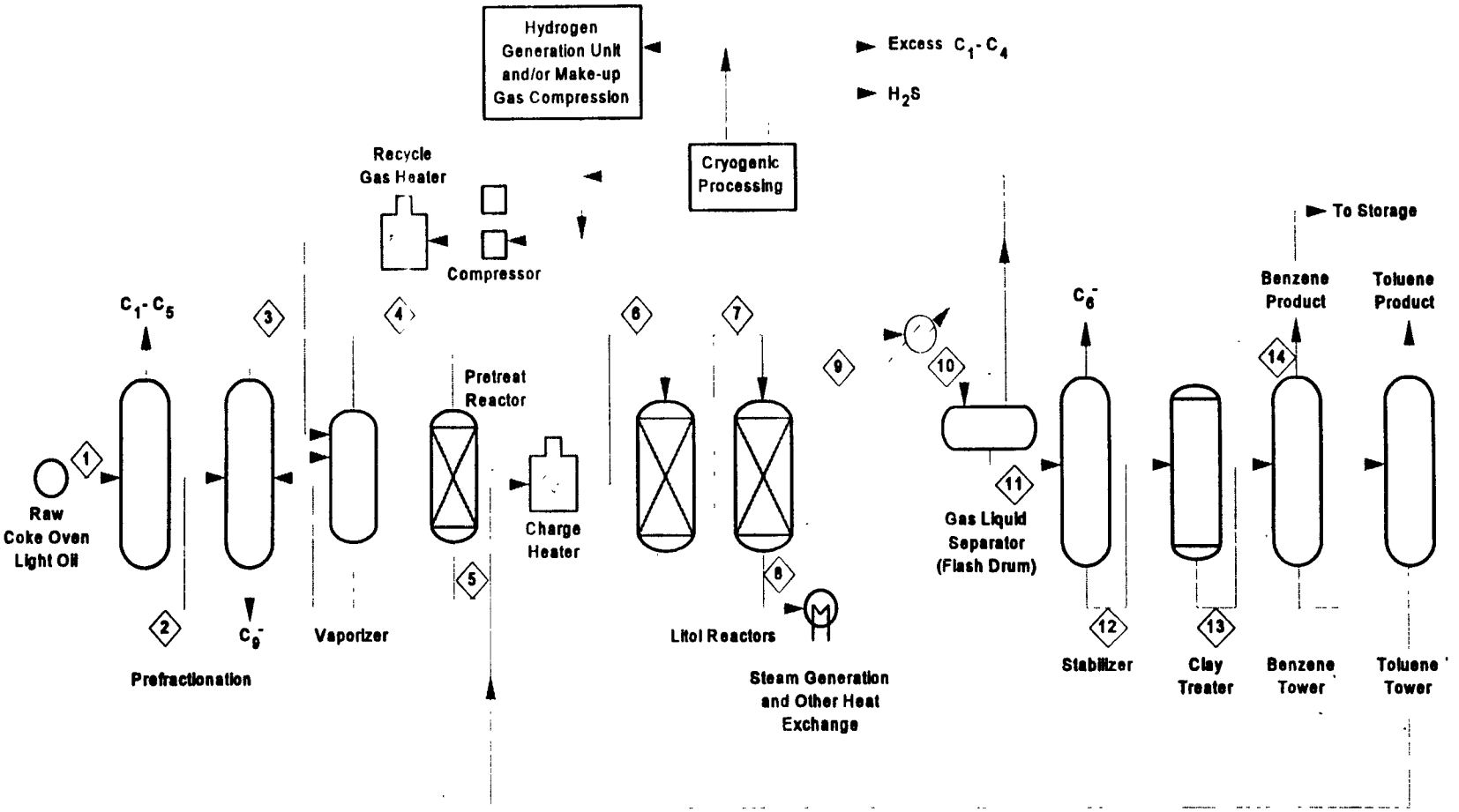
Depending on plant design, the heavy and light tar streams (Streams 2 and 5) may be merged or separated. The tar is separated from the flushing liquor by gravity in the tar decanter. Recovered flushing liquor is returned to the Flushing Liquor Circulation Tank (Stream7) and re-used. Tar from the decanter 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] Furnace Coke	Emission Factor lb/ton (g/Mg)[b] Foundry Coke	Factor Rating
	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] Furnace Coke	Emission Factor lb/ton (g/Mg)[b] Foundry Coke	Factor Rating
	Flushing-Liquor Circulation Tank (M)	Uncontrolled	0.026 (13)	0.019 (9.5)	E
		Gas Blanketing	5.2×10^{-4} (0.26)	3.8×10^{-4} (0.19)	E
	Excess-Ammonia Liquor Tank (N)	Uncontrolled	2.8×10^{-3}	2.0×10^{-3}	E
		Gas Blanketing	5.6×10^{-5} (0.028)	4.0×10^{-5} (0.020)	E
	Wash-Oil Decanter (O)	Uncontrolled	7.6×10^{-3} (3.8)	4.2×10^{-3} (2.1)	E
		Gas Blanketing	1.5×10^{-4} (0.076)	8.2×10^{-5} (0.041)	E
	Wash-Oil Circulation Tank (P)	Uncontrolled	7.6×10^{-3} (3.8)	4.2×10^{-3} (2.1)	E
		Gas Blanketing	1.5×10^{-4} (0.076)	8.2×10^{-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

SCC and Description	Emissions Source	Control (% efficiency)		Emission Factor lb/source day (kg/source day)[a,b] 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

SCC and Description	Emissions Source	Control (% efficiency)	Emission Factor lb/source day (kg/source day)[a,b] 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

SCC and Description	Emissions Source	Control (% efficiency)		Emission Factor lb/source day (kg/source day)[a,b] 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

SCC and Description	Emissions Source	Control (% efficiency)	Emission Factor lb/source day (kg/source day)[a,b] 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	<50,000	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:

$$\left[\begin{array}{c}\text{No. of}\\ \text{equipment}\\ \text{components}\end{array}\right] \times \left[\begin{array}{c}\text{Weight \%}\\ \text{benzene}\\ \text{in the stream}\end{array}\right] \times \left[\begin{array}{c}\text{Component-}\\ \text{specific}\\ \text{emission factor}\end{array}\right] \times \left[\begin{array}{c}\text{No. hr/yr in}\\ \text{benzene service}\end{array}\right]$$

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	$1.3x10^{-5}$
	Light Liquid	$4.3x10^{-5}$
Pump seals	Gas	$6.5x10^{-5}$
	Light Liquid	$5.4x10^{-4}$
Others (compressors and others)[b]	Gas	$1.2x10^{-4}$
	Light Liquid	$1.3x10^{-4}$
Fittings (connectors and flanges)[c]	Gas	$4.2x10^{-5}$
	Light Liquid	$8.0x10^{-6}$

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	1.3×10^{-5}
	Light Liquid	2.3×10^{-2}	1.5×10^{-5}
Pump seals	Light Liquid	7.7×10^{-2}	2.4×10^{-4}
Others (compressors and others)[b]	Gas	NA	1.2×10^{-4}
	Light Liquid	3.4×10^{-2}	2.4×10^{-5}
Fittings (connectors and flanges)[c]	Gas	3.4×10^{-2}	5.9×10^{-6}
	Light Liquid	6.5×10^{-3}	7.2×10^{-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	9.8×10^{-2}	2.5×10^{-5}
	Heavy Oil	NA	8.4×10^{-6}
	Light Oil	8.7×10^{-2}	1.9×10^{-5}
	Water/Oil	6.4×10^{-2}	9.7×10^{-6}
Pump seals	Gas	7.4×10^{-2}	3.5×10^{-4}
	Heavy Oil	NA	NA
	Light Oil	1.0×10^{-1}	5.1×10^{-4}
	Water/Oil	NA	2.4×10^{-5}
Others[c]	Gas	8.9×10^{-2}	1.2×10^{-4}
	Heavy Oil	NA	3.2×10^{-5}
	Light Oil	8.3×10^{-2}	1.1×10^{-4}
	Water/Oil	6.9×10^{-2}	5.9×10^{-5}
Connectors	Gas	2.6×10^{-2}	1.0×10^{-5}
	Heavy Oil	NA	7.5×10^{-6}
	Light Oil	2.6×10^{-2}	9.7×10^{-6}
	Water/Oil	2.8×10^{-2}	1.0×10^{-5}
Flanges	Gas	8.2×10^{-2}	5.7×10^{-6}
	Heavy Oil	NA	3.9×10^{-7}
	Light Oil	7.3×10^{-2}	2.4×10^{-6}
	Water/Oil	NA	2.9×10^{-6}
Open-ended lines	Gas	5.5×10^{-2}	1.5×10^{-5}
	Heavy Oil	3.0×10^{-2}	7.2×10^{-6}
	Light Oil	4.4×10^{-2}	1.4×10^{-5}
	Water/Oil	3.0×10^{-2}	3.5×10^{-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

Company	Location	Ethylbenzene Process	Ethylbenzene Capacity million lb (million kg)	Styrene Process	Styrene 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,c] (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.

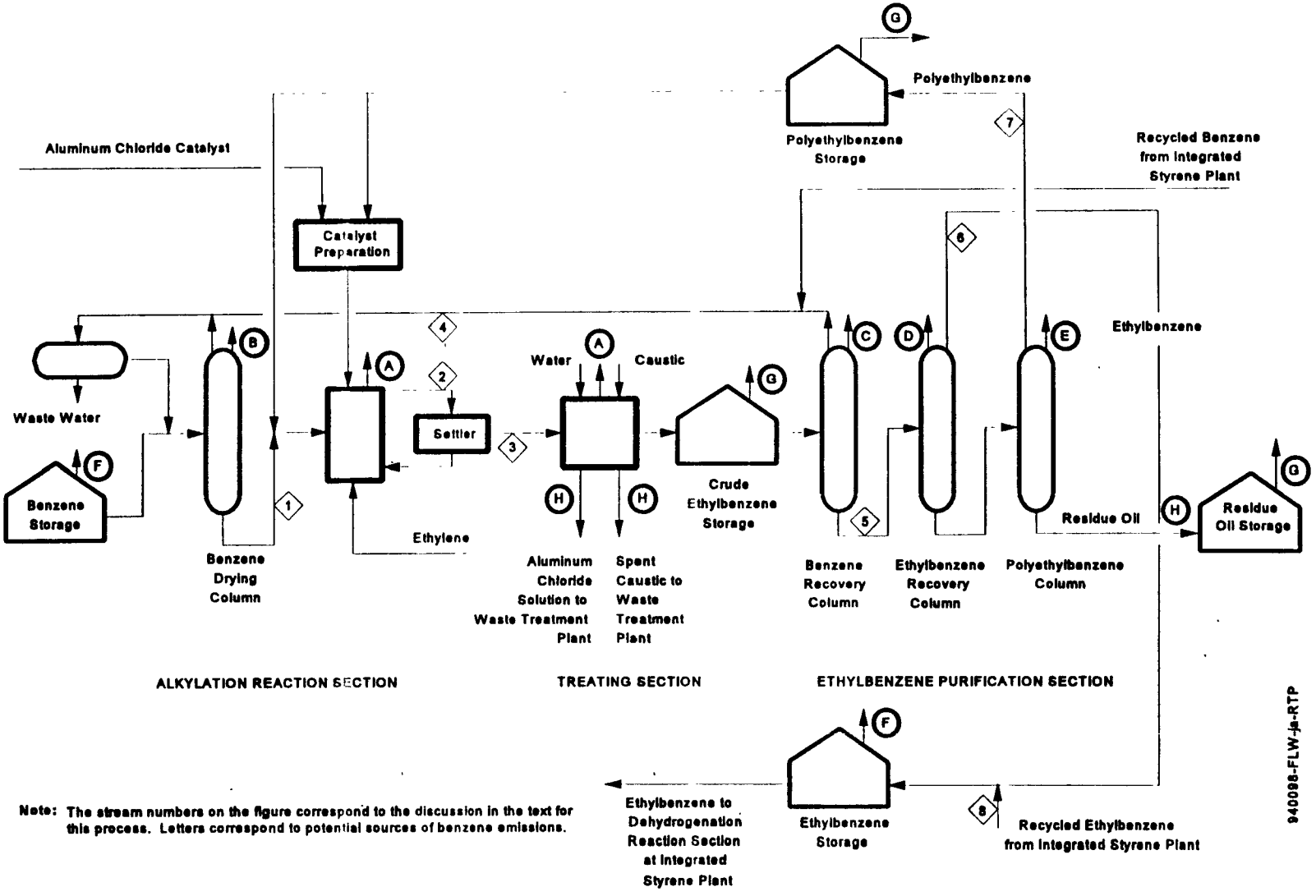


Figure 5-1. Basic Operations that may be used in the Production of Ethylbenzene by Benzene Alkylation with Ethylbenzene

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.

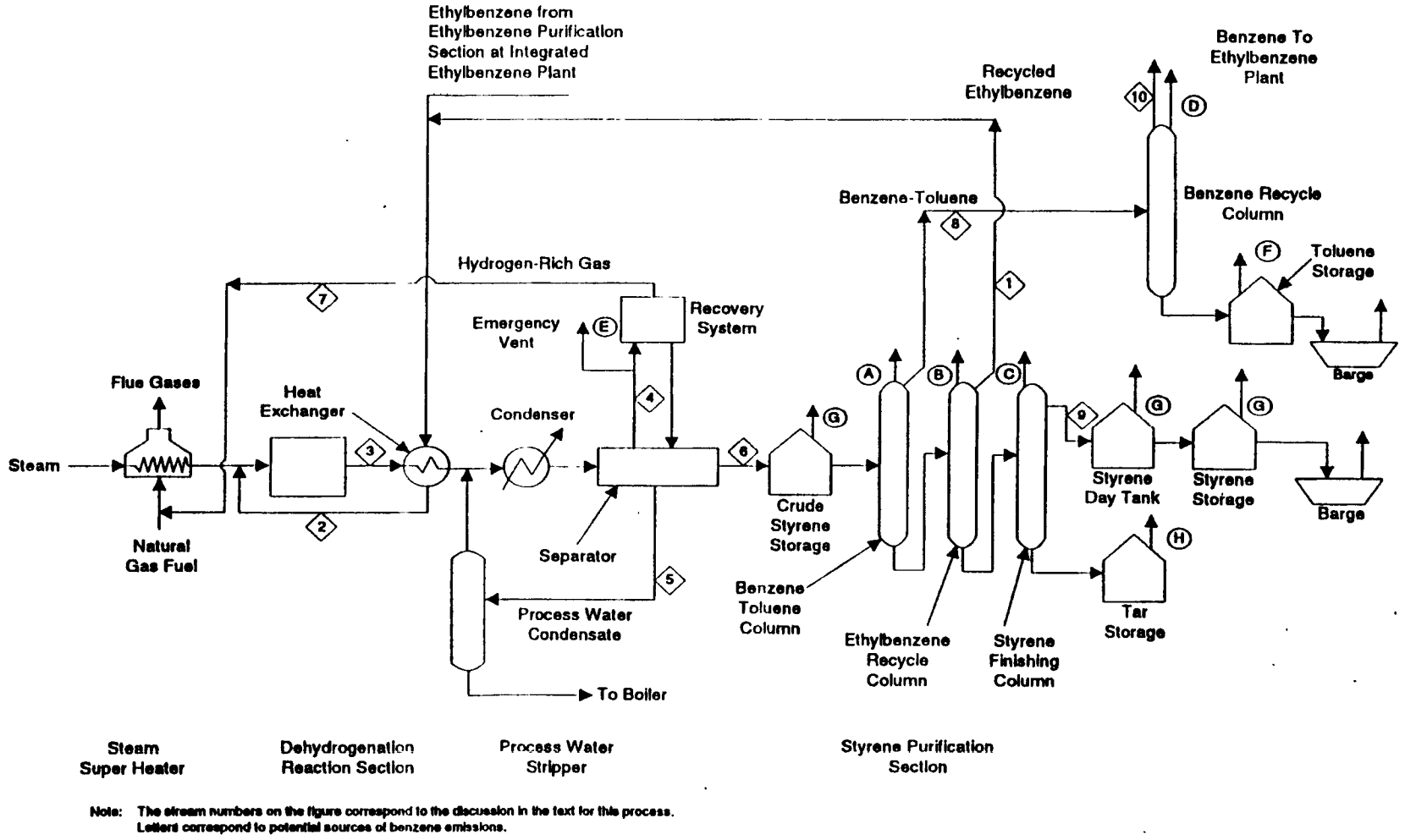


Figure 5-2. Basic Operations that may be used in the Production of Styrene by Ethylbenzene Dehydrogenation

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.

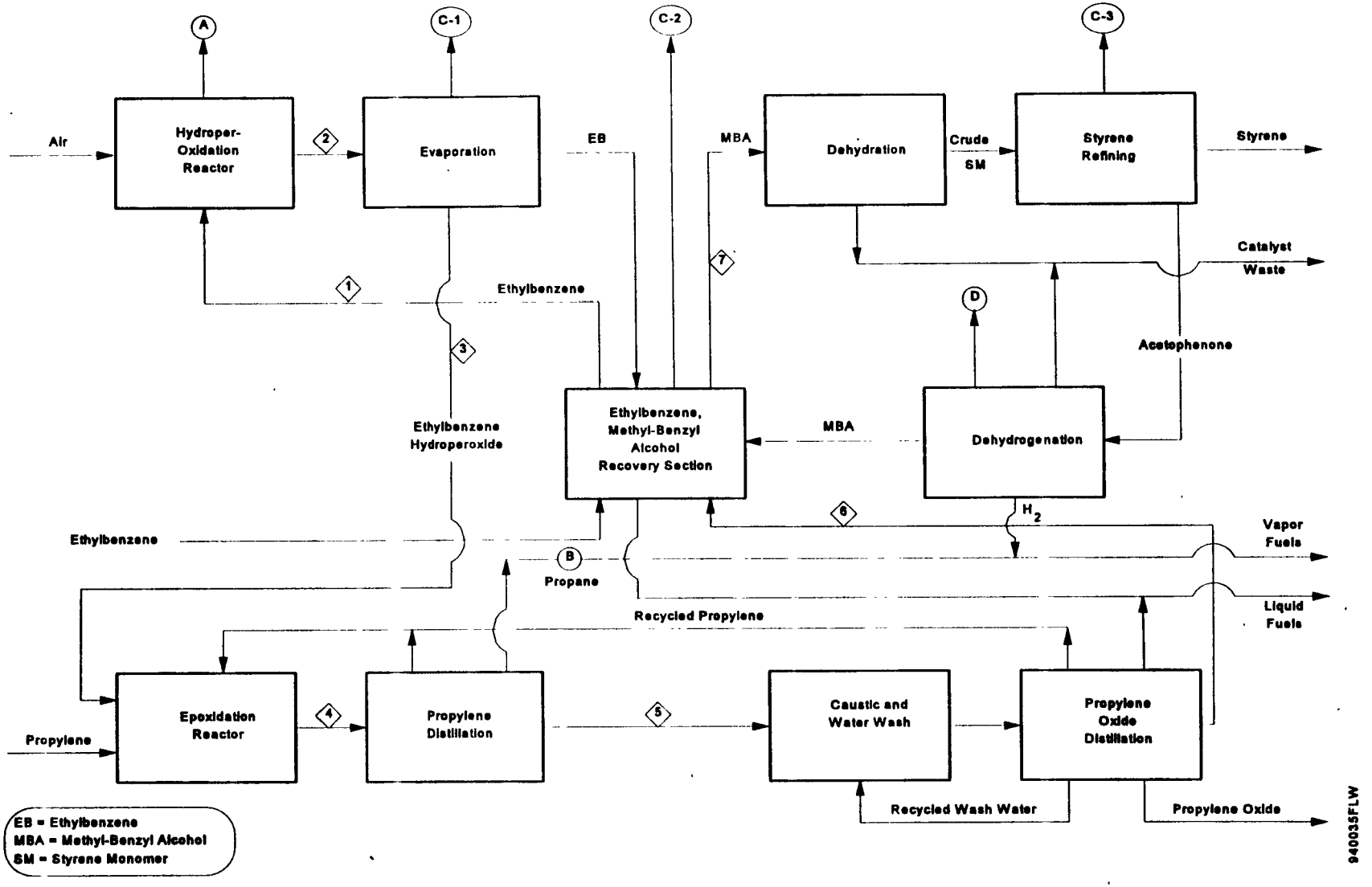
5.1.3 Process Description for Styrene Production from Ethylbenzene Hydroperoxidation

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.

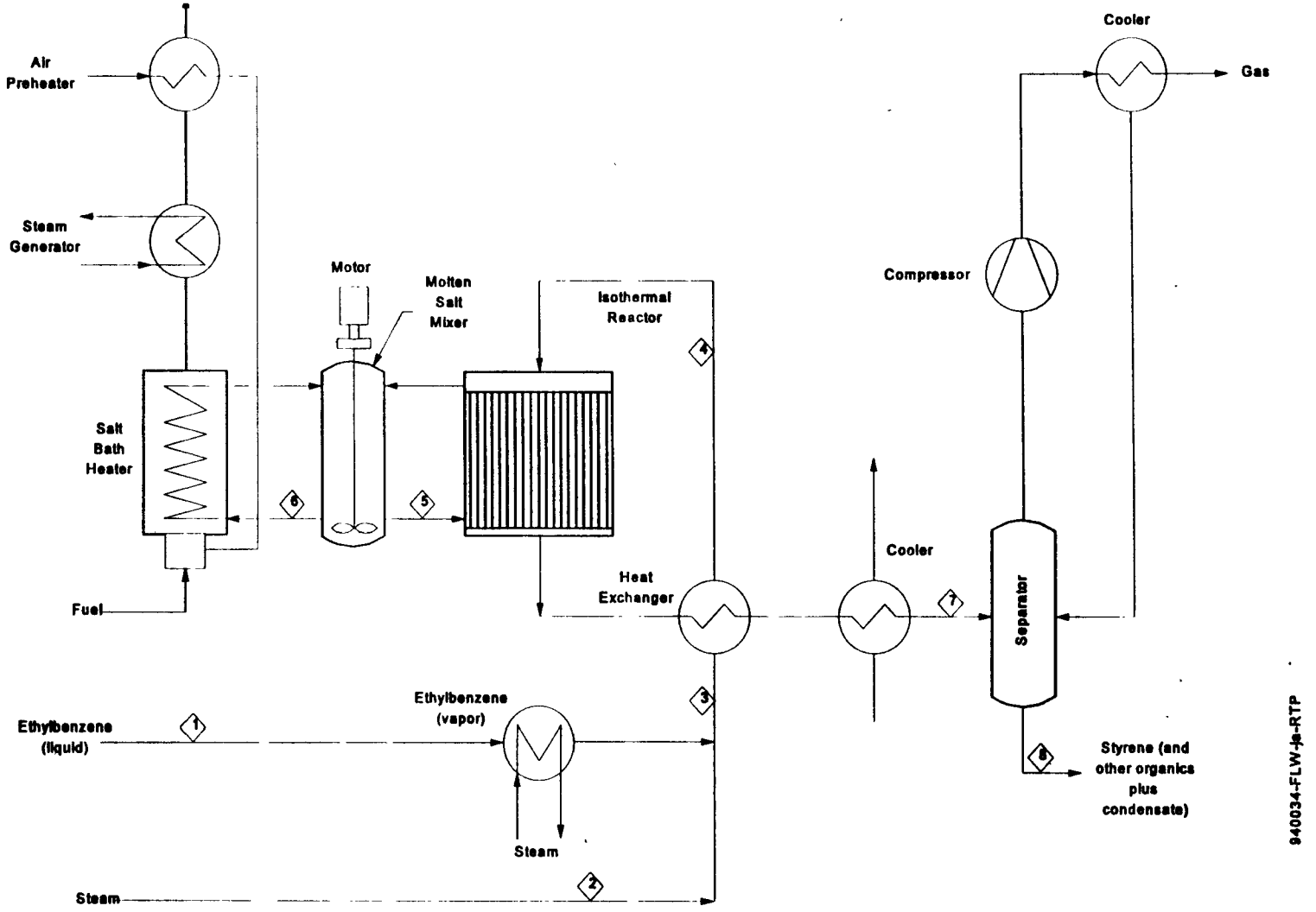
The mixed stream of α-methyl-benzyl alcohol and acetophenone (Stream 7) is then dehydrated over a solid catalyst to produce styrene. Residual catalyst solids and high-boiling impurities are separated and collected for disposal. The crude styrene goes to a series of distillation columns, where the pure 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[c]	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	See Section 4.5.2	
		Uncontrolled		
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

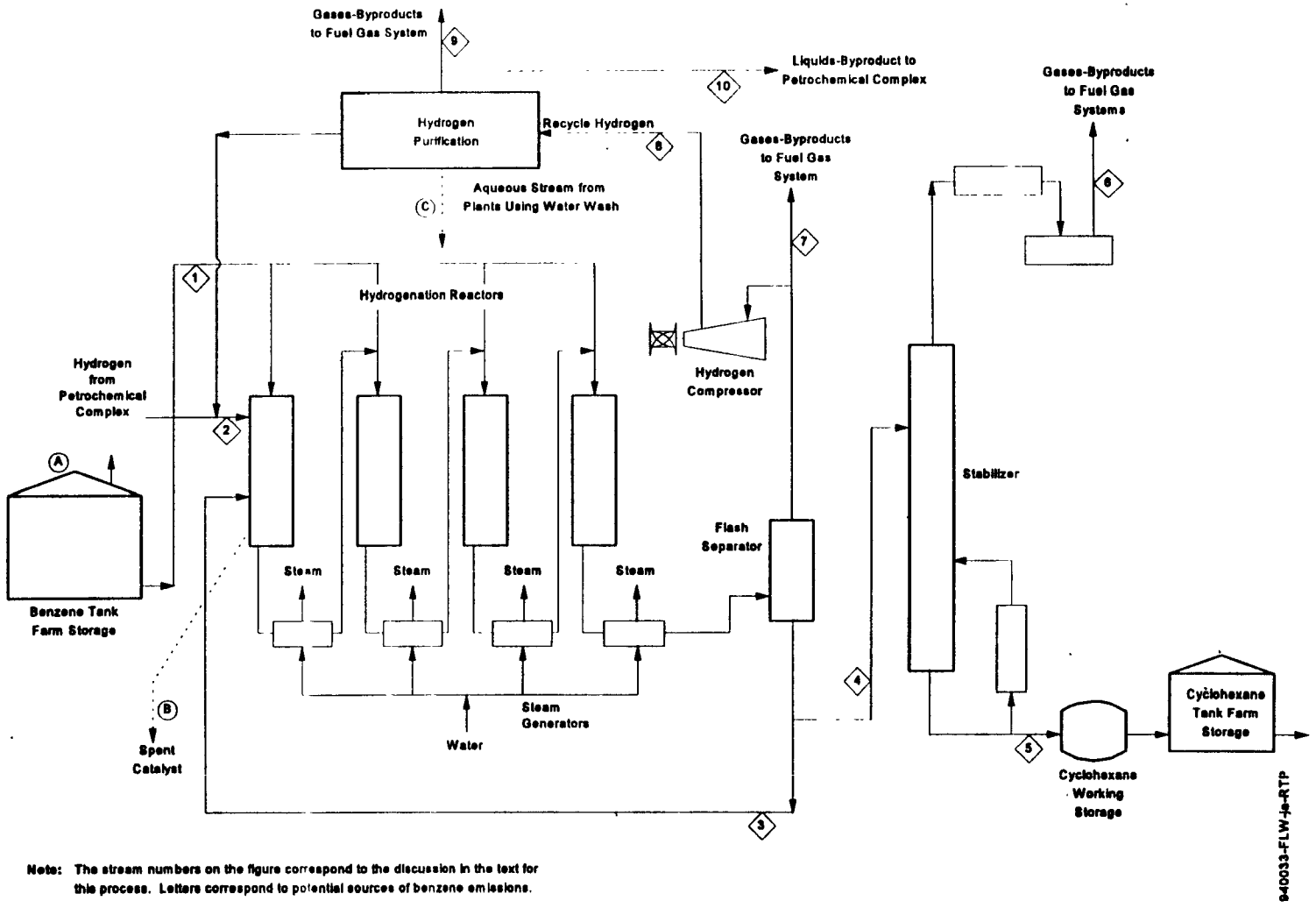
Company	Location	Annual Capacity millions of gal (l)
Chevron Chemical Company	Port Arthur, TX	38 (144)
Phillips Petroleum Company		
Specialty Chemicals Branch	Borger, TX	35 (132)
Olefins and Cyclics Branch	Sweeny, TX	90 (341)
Phillips Puerto Rico Core, Inc.	Guayama, PR	100 (379)
Texaco Chemical Company	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.

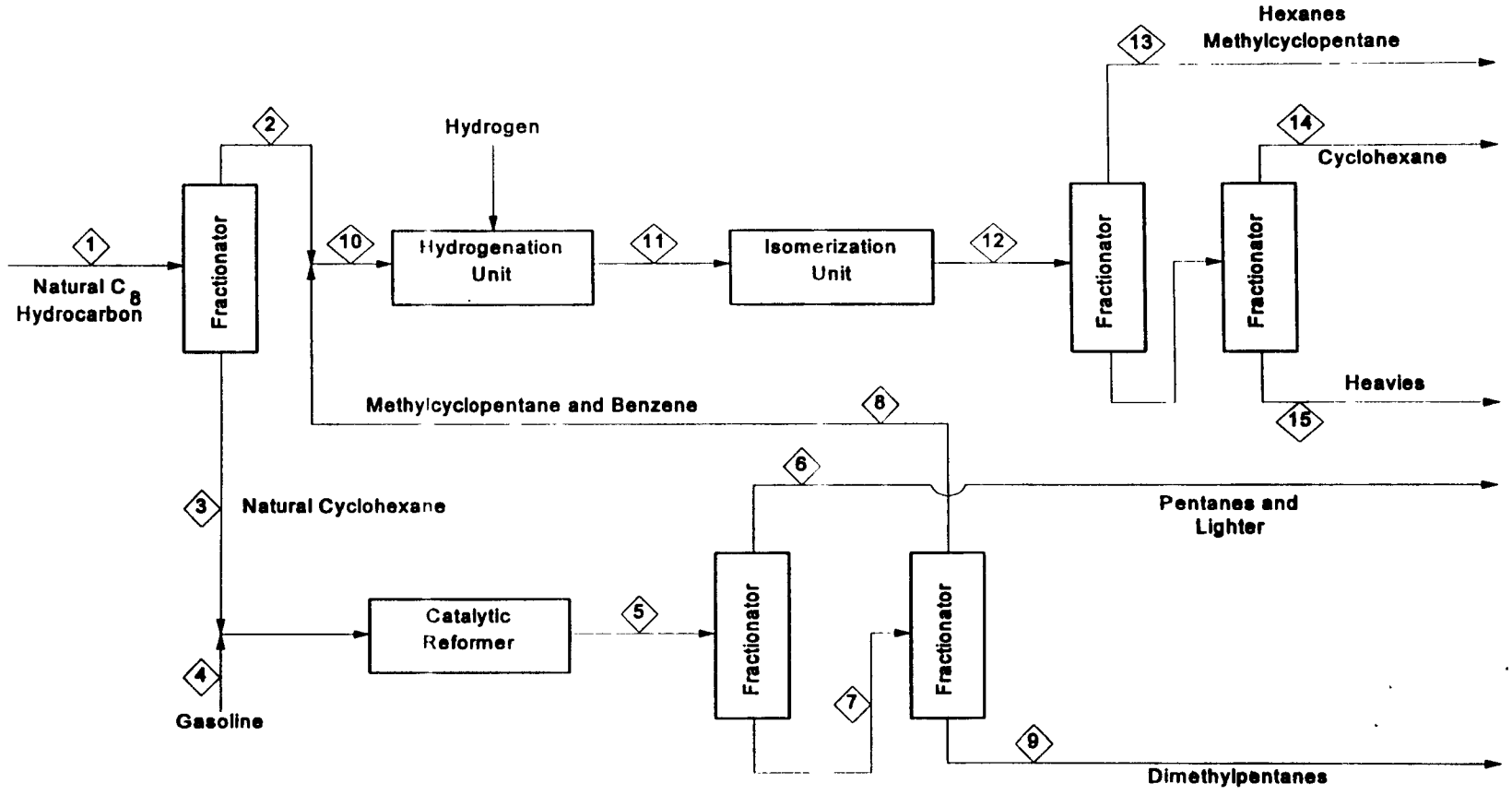
Other potential sources of emissions are catalyst handling (B) and absorber wastewater (C) (when an aqueous solution is used to purify the recycled hydrogen). Caution is taken to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[76]

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:

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(propylene)}}{CH_2CHCH_3} \xrightarrow{[\text{catalyst}]} \underset{\text{(cumene)}}{(CH_3)_2CHC_6H_5}$$

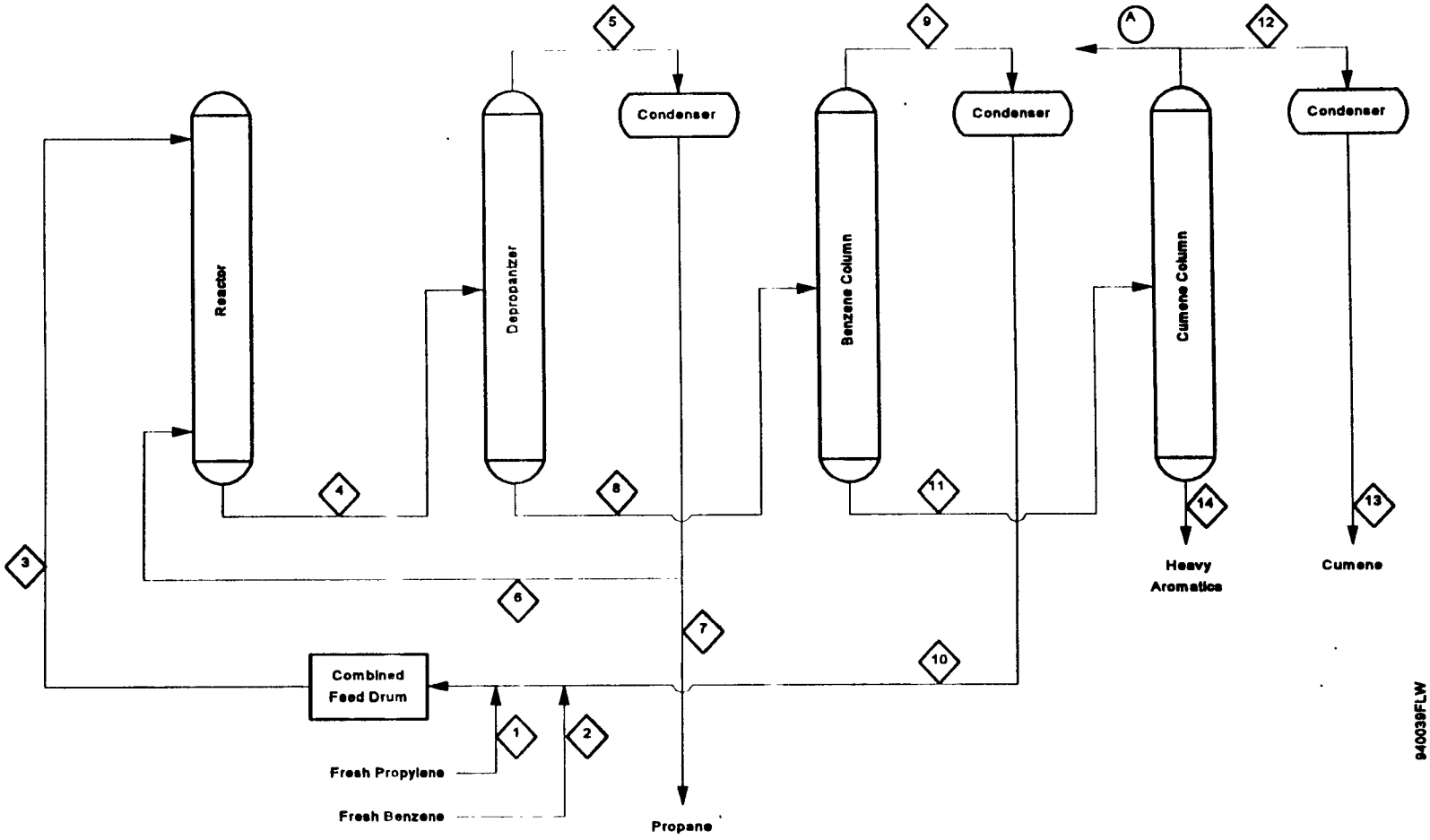
The exothermic reaction is typically conducted using solid phosphoric acid as a catalyst, but the reaction may also be conducted using aluminum chloride or sulfuric acid as the catalyst. The aluminum chloride and sulfuric acid processes are similar; therefore, the sulfuric acid process is not described 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]

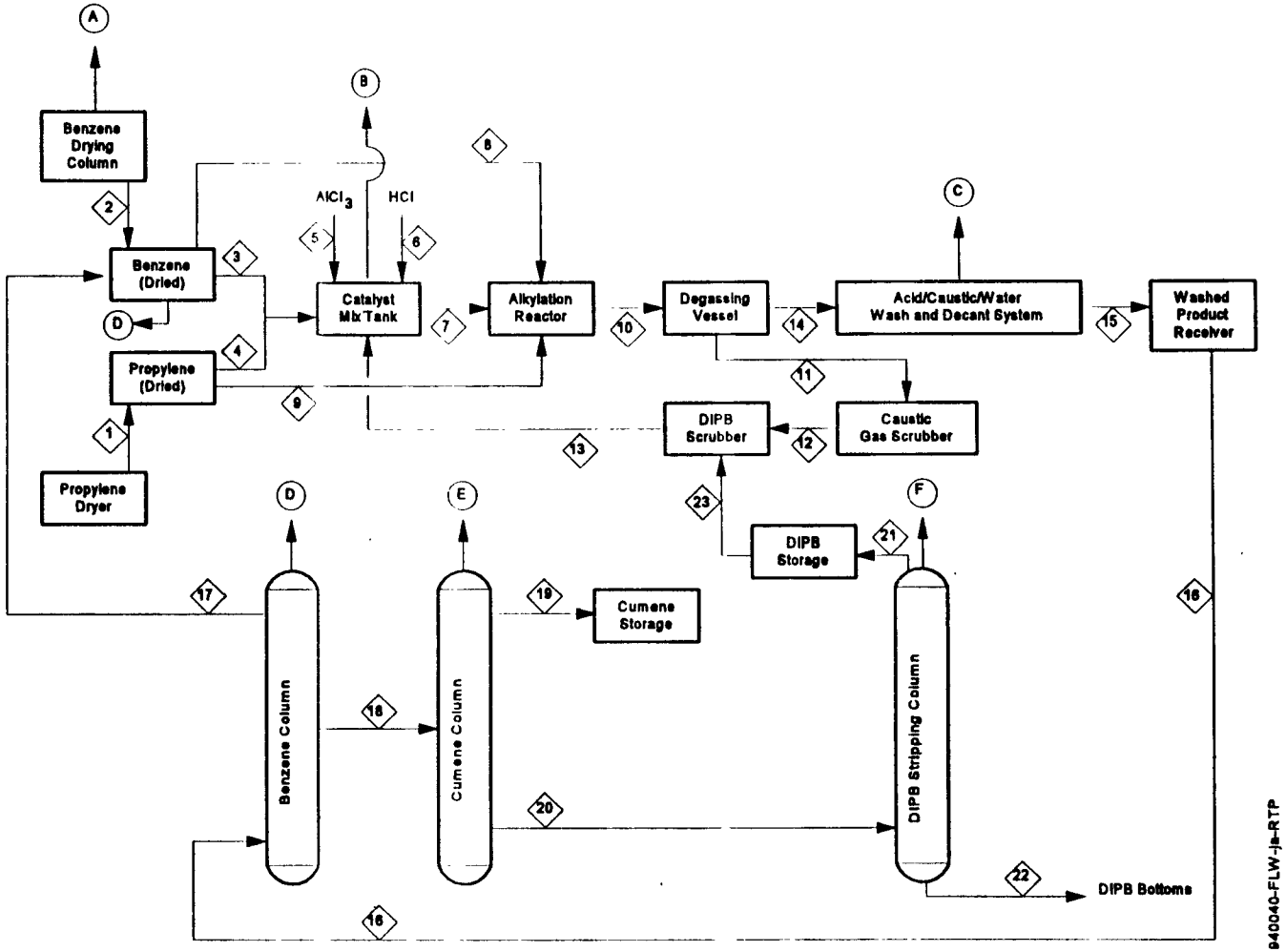
Unpurified product from the depropanizer (Stream 8) is sent to the benzene distillation column, where unreacted benzene is recovered overhead (Stream 9), sent through a condenser, and recycled to the feed drum (Stream 10). From the bottom of the benzene column (Stream 11), the crude product is sent to 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 Plaquemine, LA	160 (73) 440 (200)	Cumene peroxidation 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]

$$\underset{\text{(cumene)}}{C_6H_5CH(CH_3)_2} + \underset{\text{(air)}}{O_2} \rightarrow \underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2}$$

$$\underset{\text{(cumene hydroperoxide)}}{C_6H_5COOH(CH_3)_2} \xrightarrow[\text{(acid)}]{[H_2SO_4]} \underset{\text{(acetone)}}{CH_3COCH_3} + \underset{\text{(phenol)}}{C_6H_5OH}$$

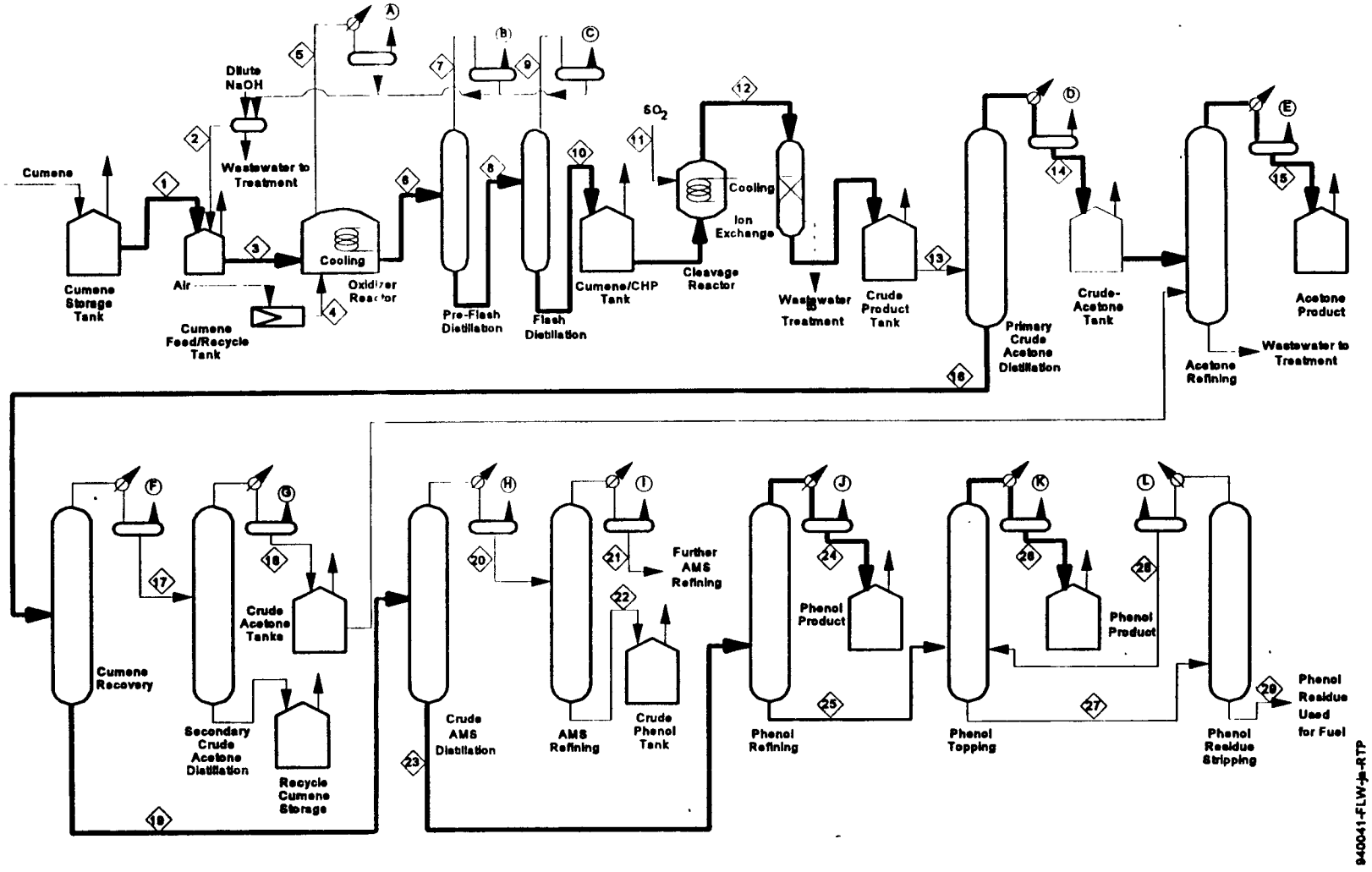
5.4.1 Phenol Production Techniques

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

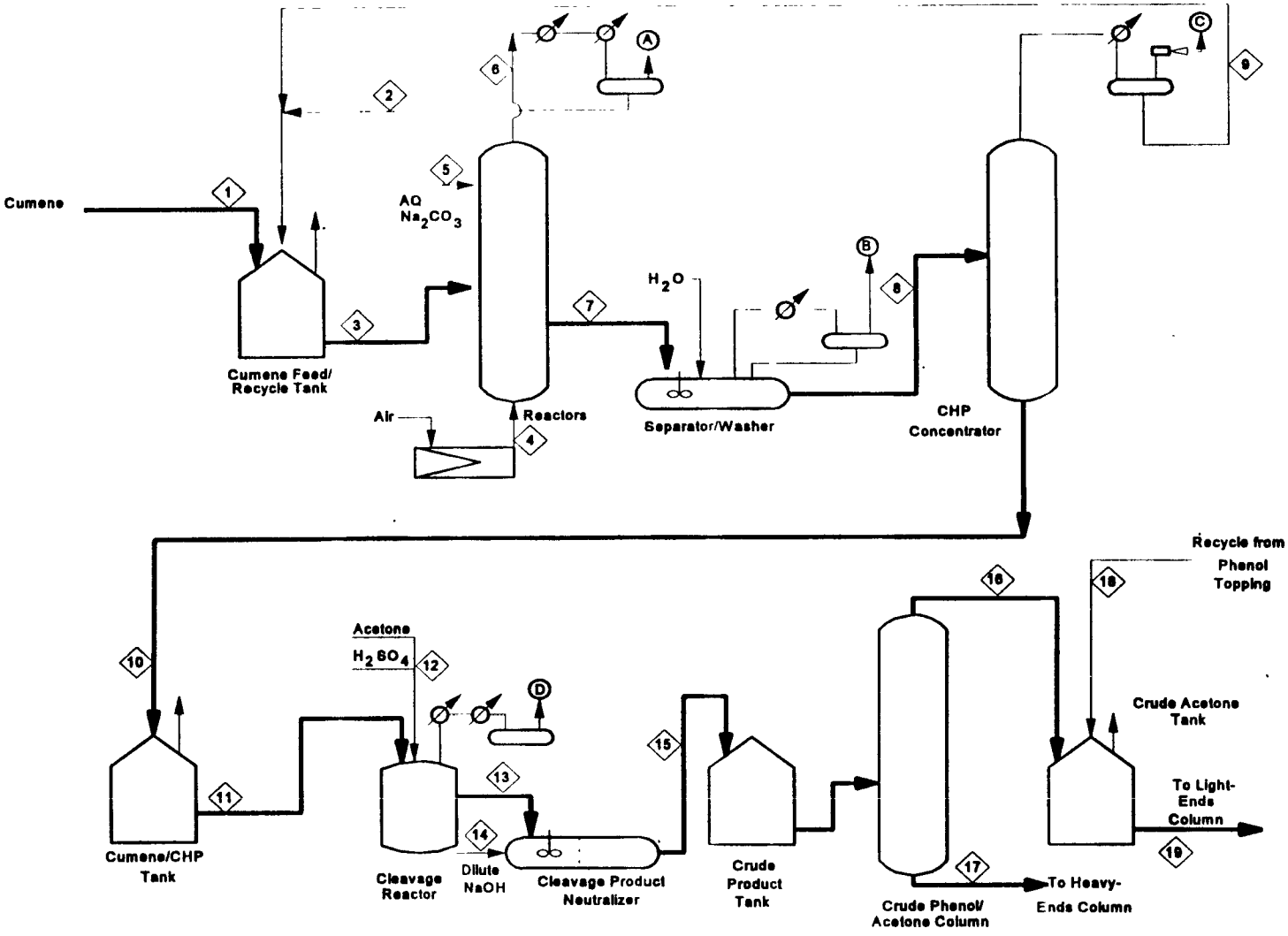
for on-site industrial boilers. The overheads from the phenol residue stripping column are condensed (Stream 28) and fed back to the phenol topping column to further recover phenol product. The uncondensed vapors from the condenser following the phenol residue stripping column are vented (Vent L).[84,85]

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]

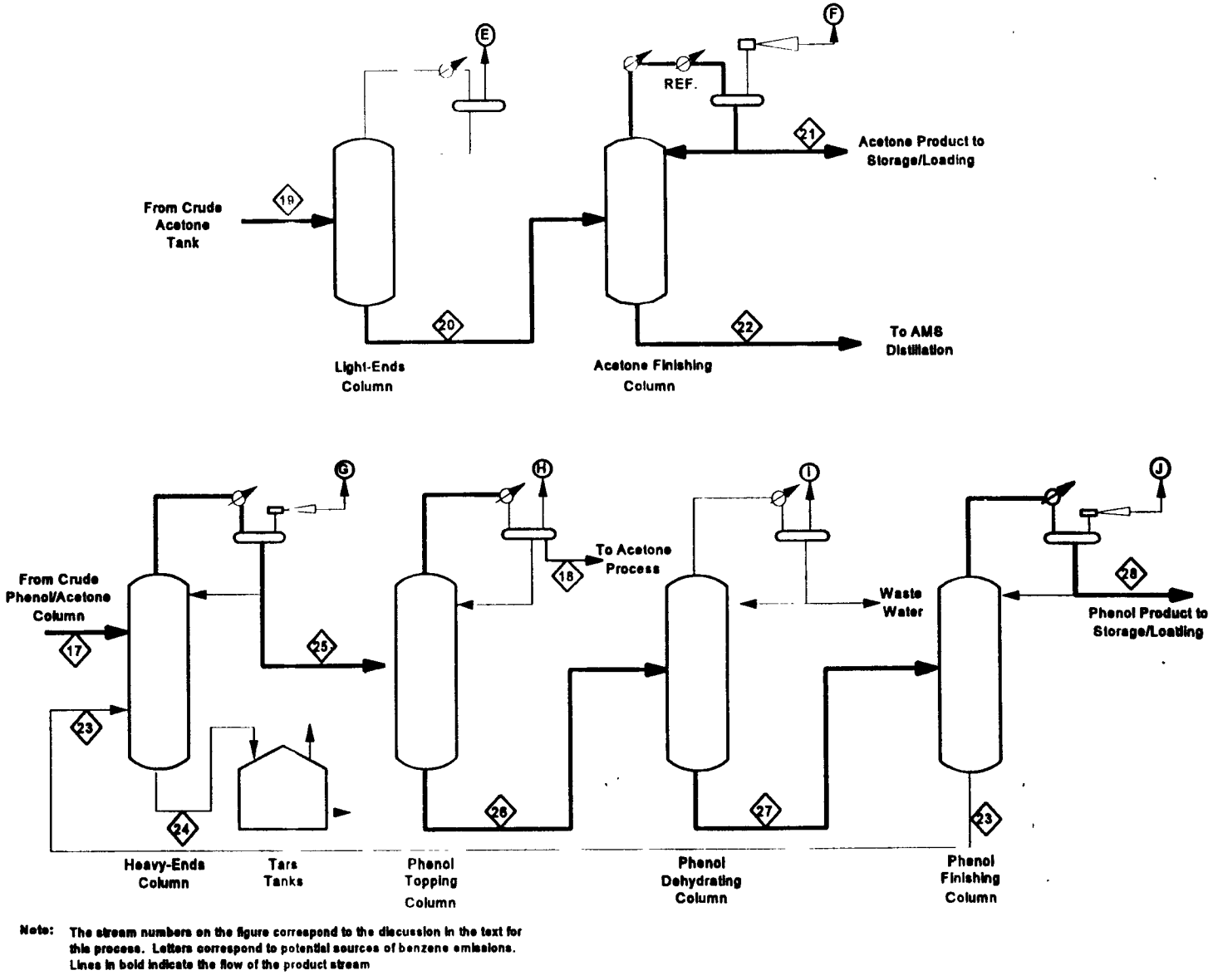
The oxidation reaction product (Stream 7) flows into a separator to remove spent carbonate solution and then is washed with water to remove remaining carbonate and other soluble components. The air stream removed is sent to a condenser from which uncondensed vapors are vented (Vent B). The washed product (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)

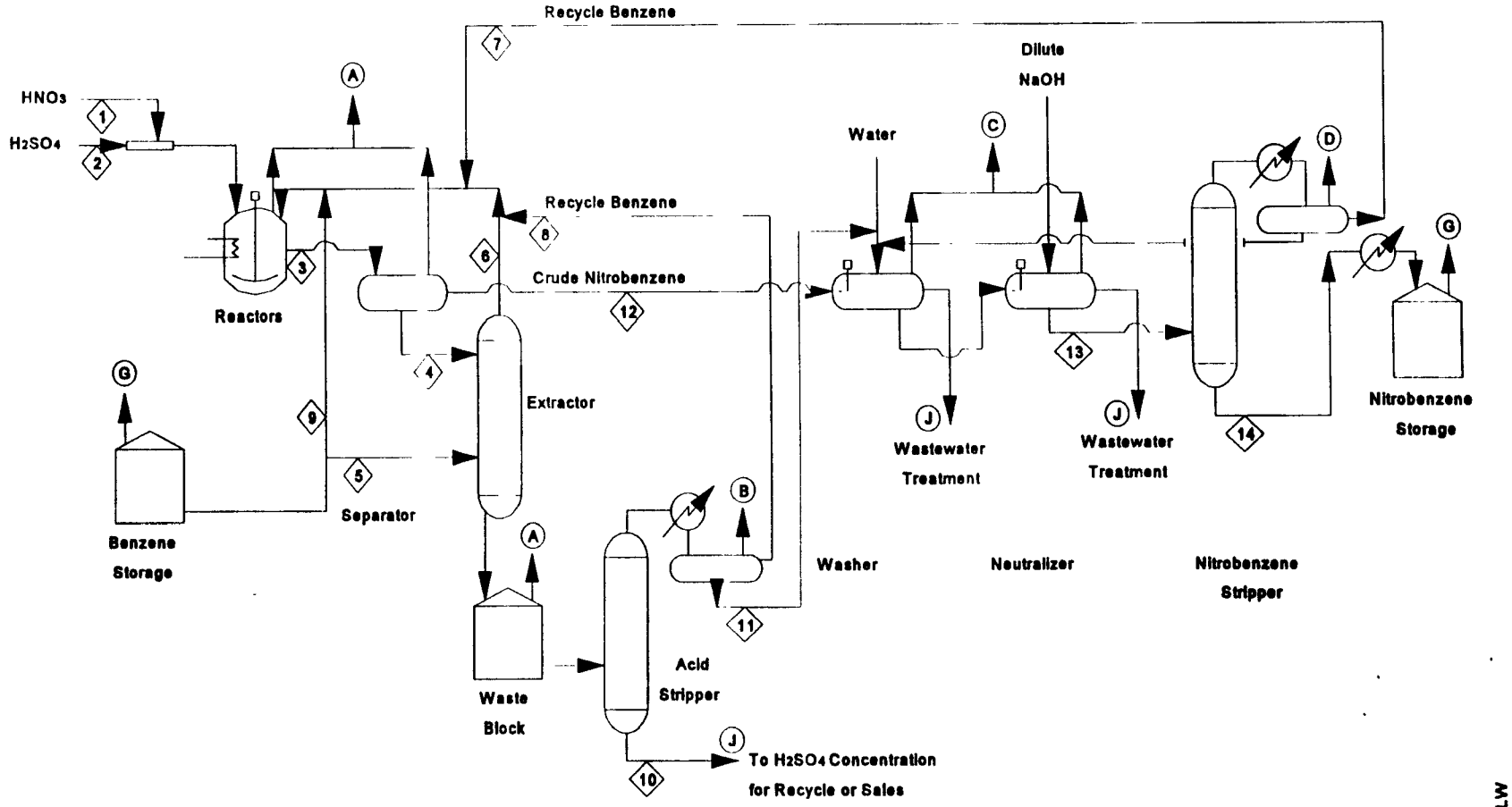
Source: Reference 11.

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.[94] A flow 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.



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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 5-11. 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 ft³ (m³)	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 ft³ (m³)	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).

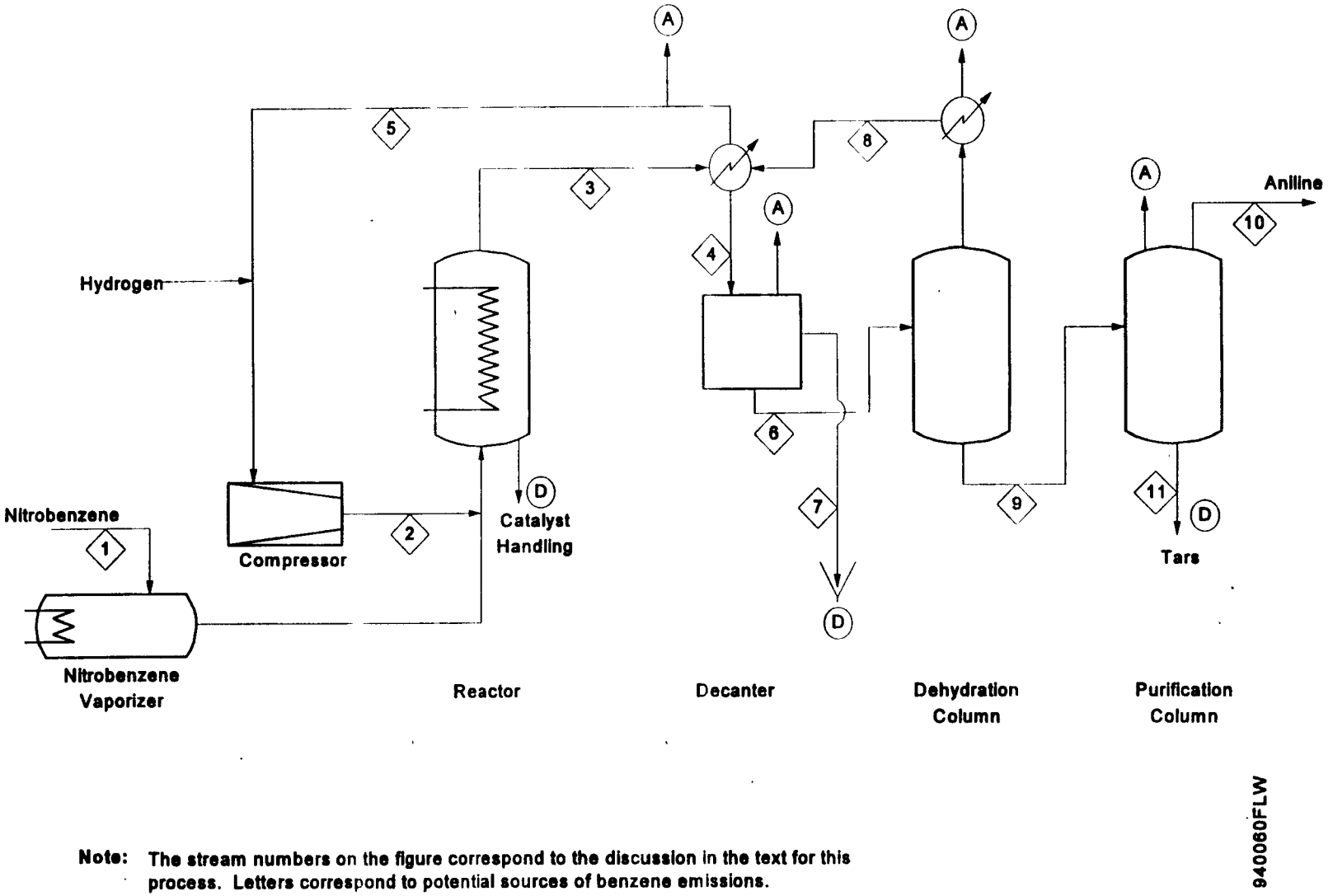
The crude aniline phase is routed to a dehydration column that operates under vacuum. Aniline is recovered from the aqueous phase by stripping or extraction with nitrobenzene. Overheads from the dehydration column (Stream 8) are condensed and recycled to the decanter. The bottoms from the dehydration 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.



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.

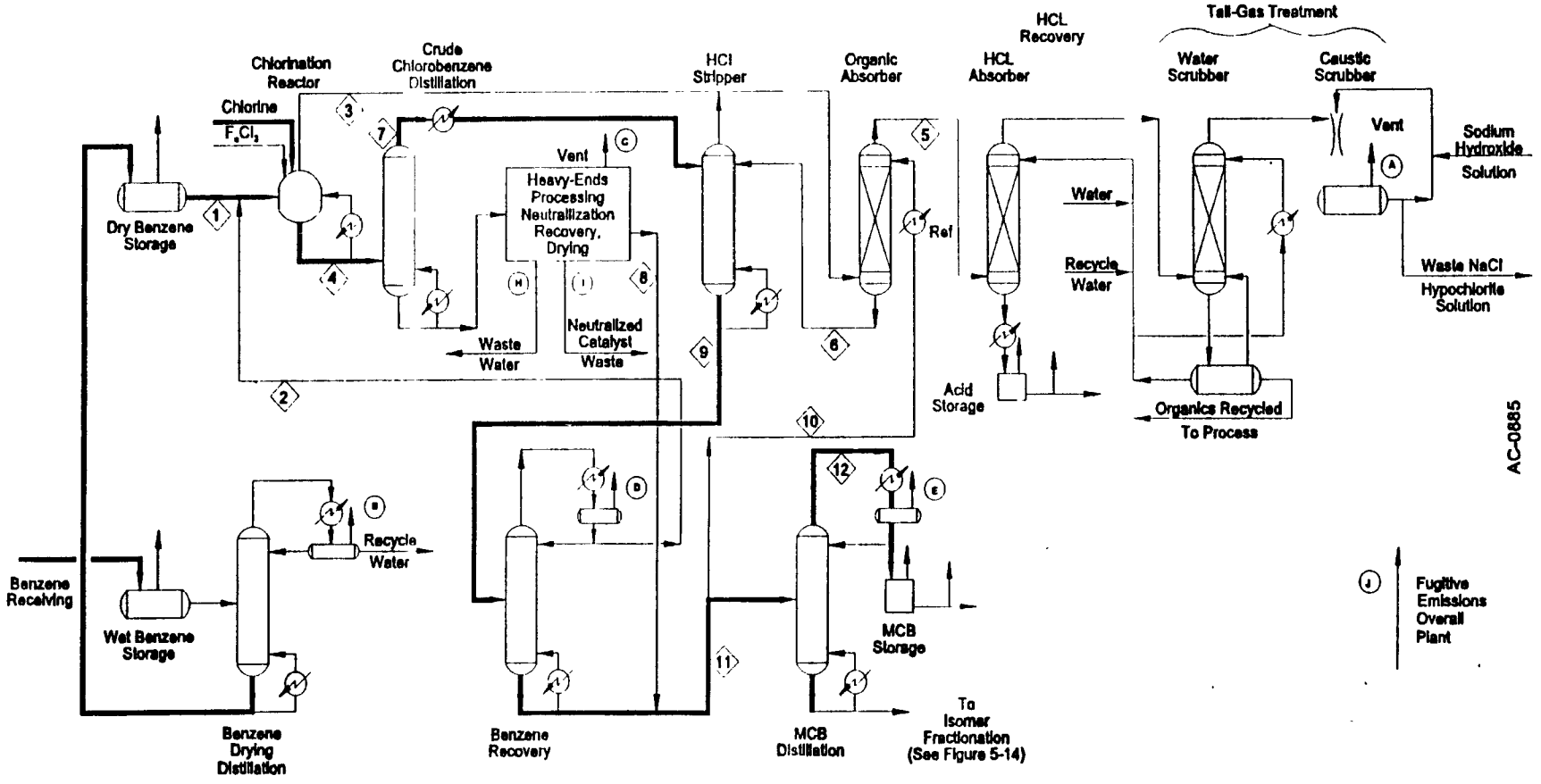


Figure 5-13. Monochlorobenzene Continuous Production Process Diagram

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]

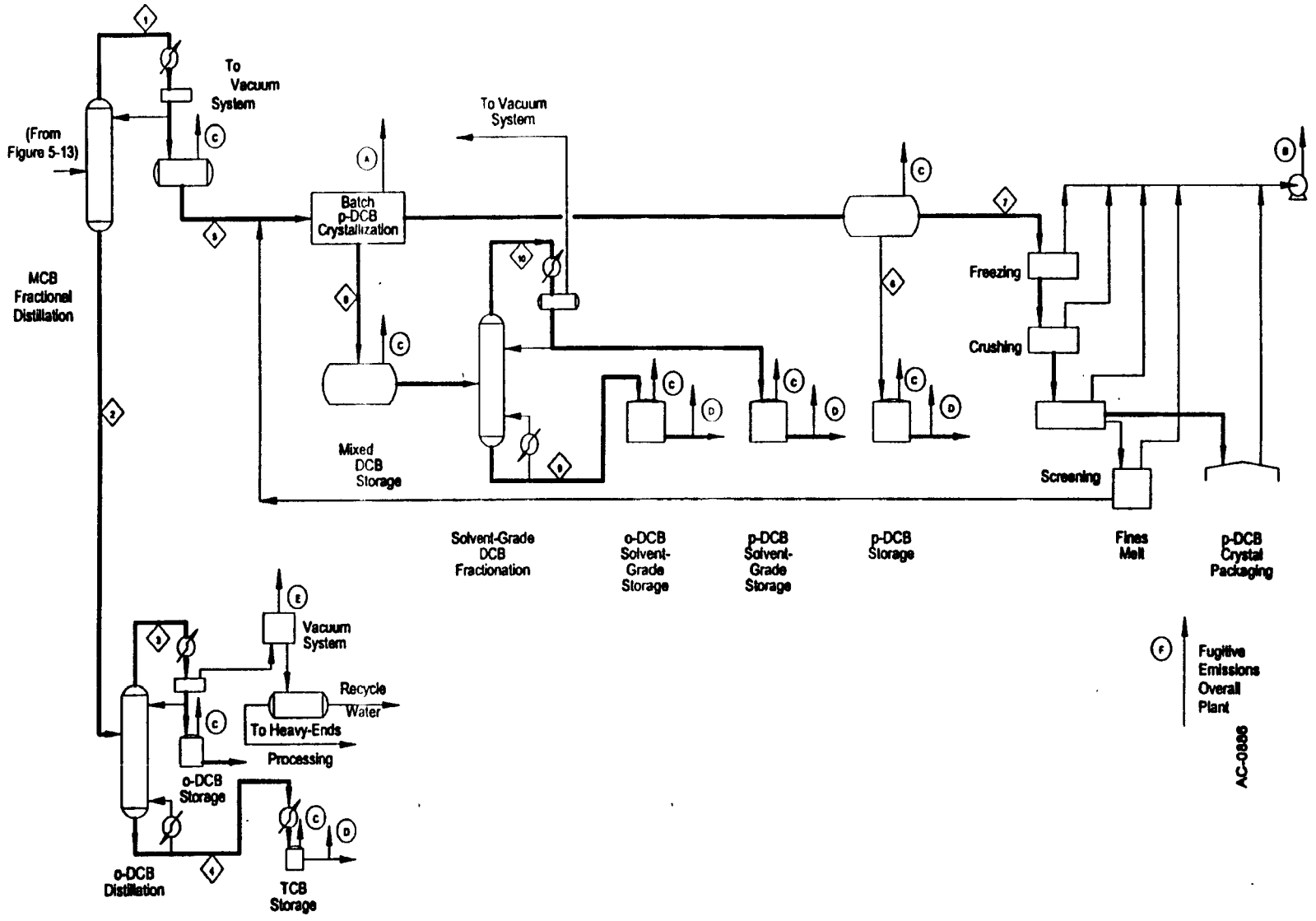


Figure 5-14. Dichlorobenzene and Trichlorobenzene Continuous Production Diagram

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.

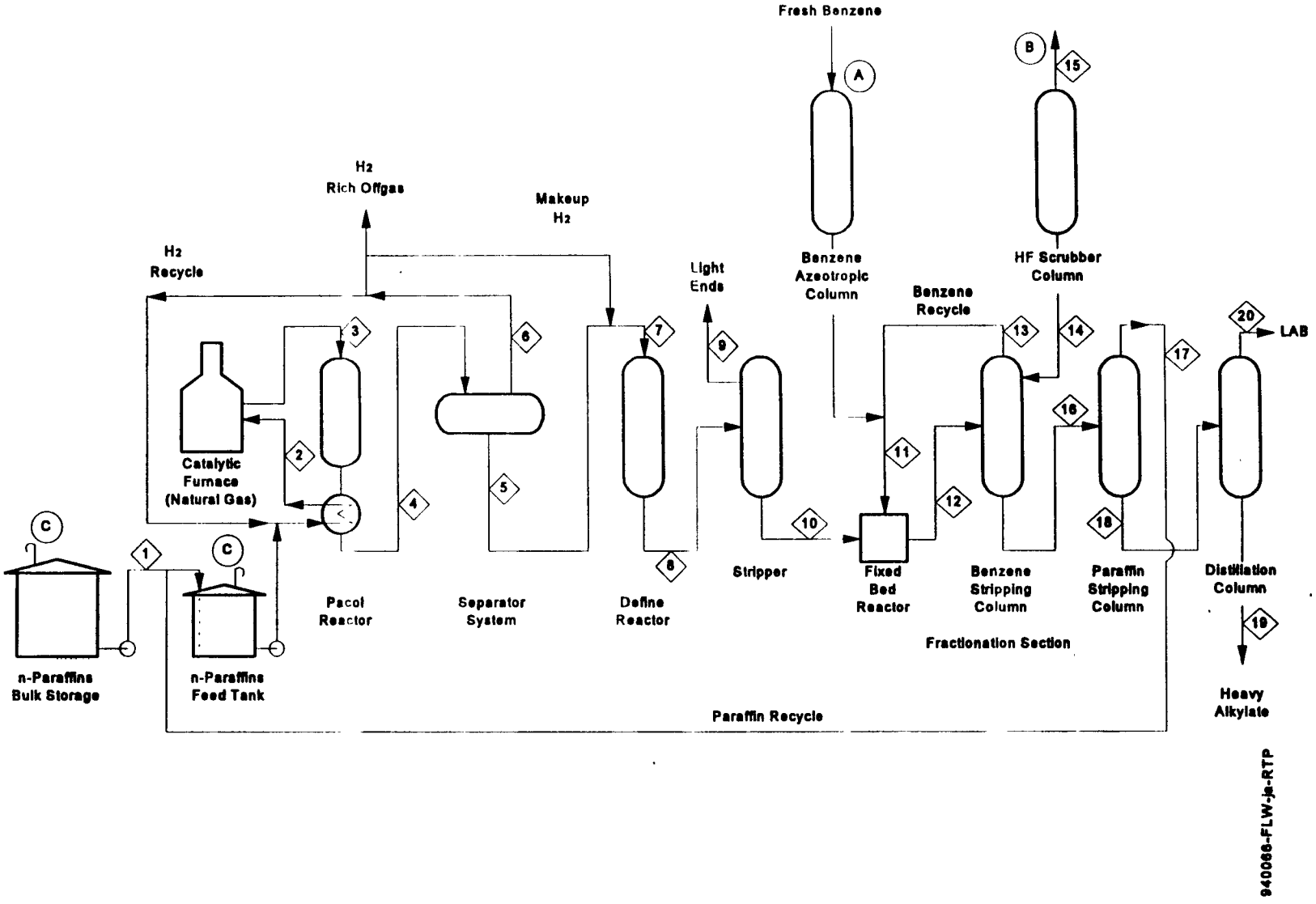


Figure 5-15. Linear Alkybenzene Production Using the Olefin Process

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.

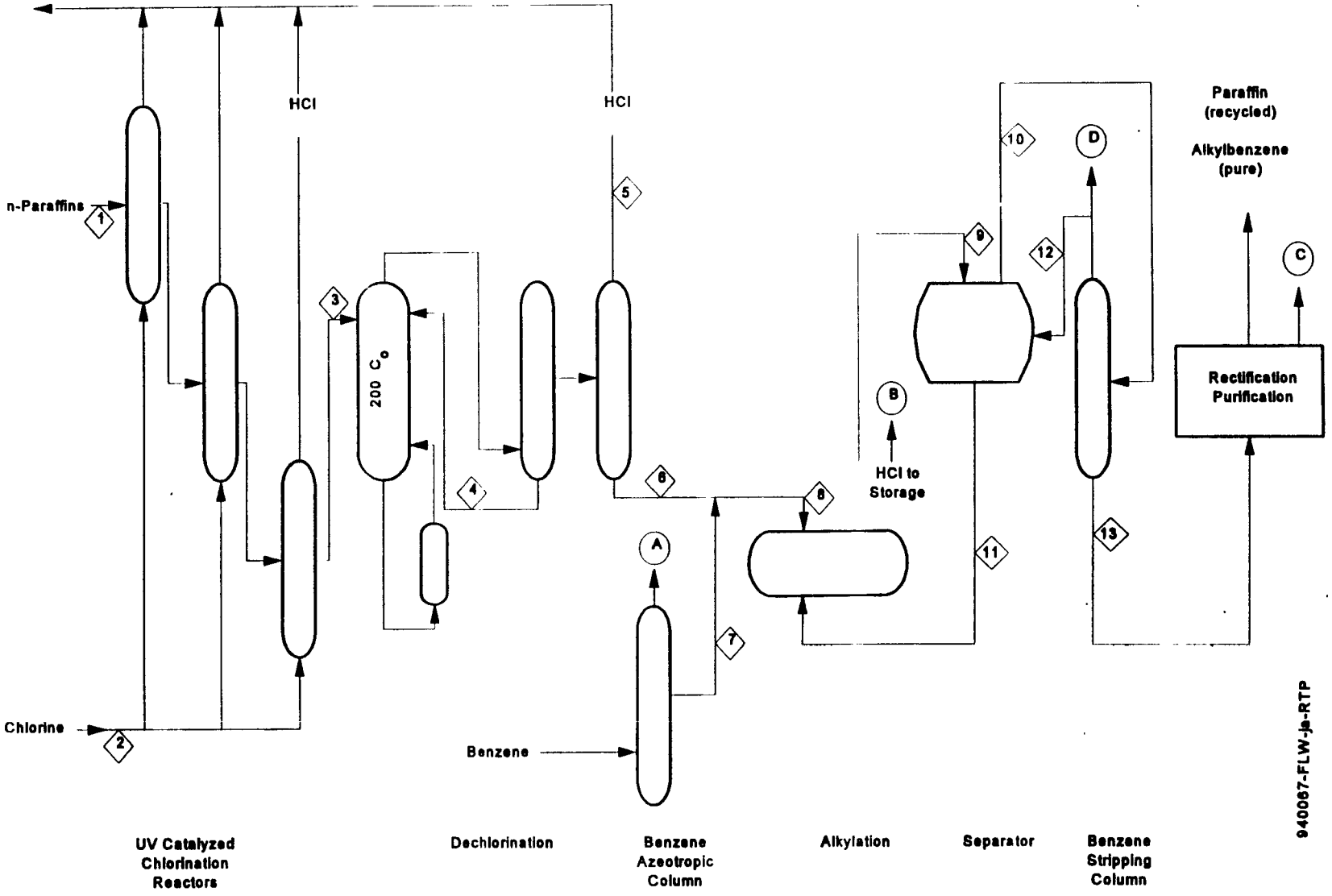


Figure 5-16. Production of Linear Alkybenzenes via Chlorination

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:

$$R_1 - CH_2 - R_2 + Cl \text{ ---> } R - \underset{\displaystyle Cl}{\underset{|}{CH}} - R_2 + HCl + \text{heat}$$

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:

$$R_1 - \underset{\displaystyle Cl}{\underset{|}{CH}} - R_2 + C_6H_6 \text{ ---> } R_1 - CH - R_2 + HCl + \text{heat, possible olefins, short-chained paraffins, etc.}$$

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 Clinton, IA Decatur, IL Peoria, IL Walhalla, ND	700 (2,650) 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 Pekin, IL	22 (83) 19 (72)
Minnesota Corn Processors	Columbus, NB Marshall, MN	NA 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 Description of Oil and Gas Wellheads

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]

SCC Number	Description	Emission Source	Emission level[b]	Emission Factor: Total Hydrocarbons lb/hr/wellhead (kg/hr/wellhead)	Emission Factor: 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.

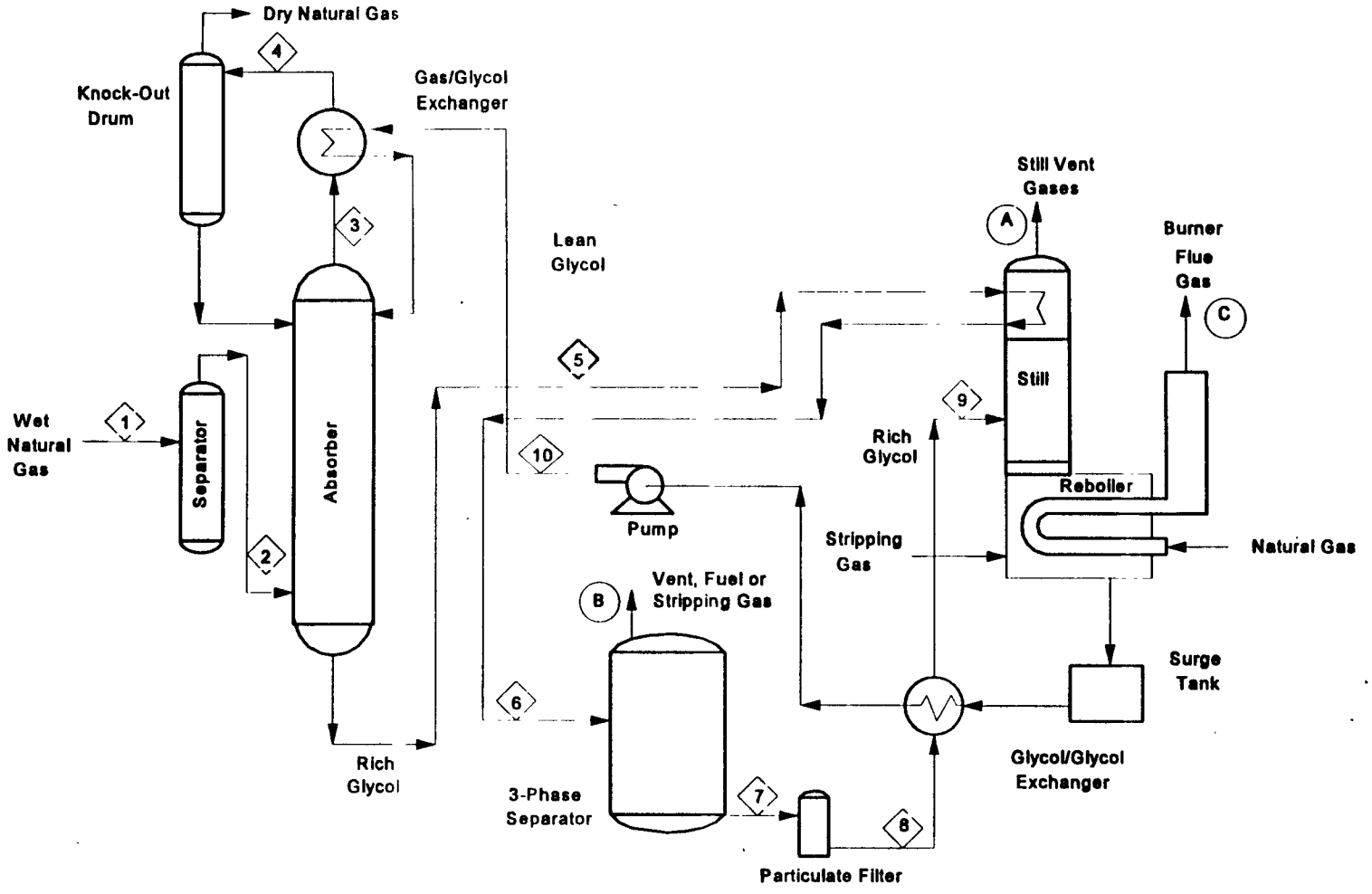


Figure 6-1. Flow Diagram for Glycol Dehydration Unit

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 one 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).

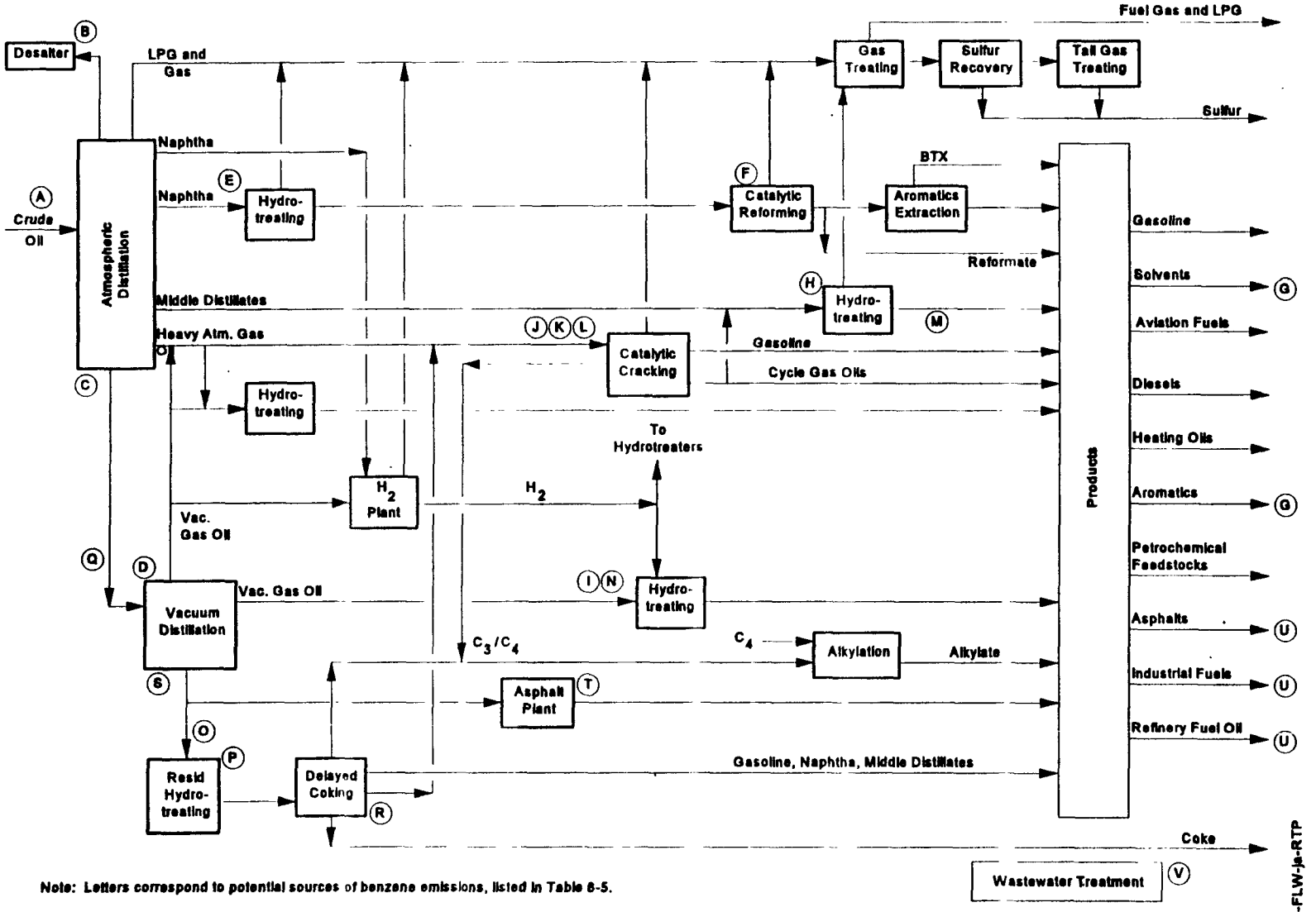


Figure 6-2. Process Flow Diagram for a Model Petroleum Refinery

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)

Process Unit	Stream Type		
	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]

Process Unit	Valves			Pumps		Compressors	Pressure Relief Valves			Flanges			Open-ended Lines	Sampling Connections
	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid		Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid		
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]

Process Unit	Valves			Pumps		Compressors	Pressure Relief Valves			Flanges			Open-ended Lines	Sampling Connections
	Gas	Light Liquid	Heavy Liquid	Light Liquid	Heavy Liquid		Gas	Light Liquid	Heavy Liquid	Gas	Light Liquid	Heavy Liquid		
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]		Average Volatile HAP Concentration[a]		Fraction Emitted[f]
		Value (ppmw)[d]	Origin[e]	Value (ppmw)[d]	Origin[e]	
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]

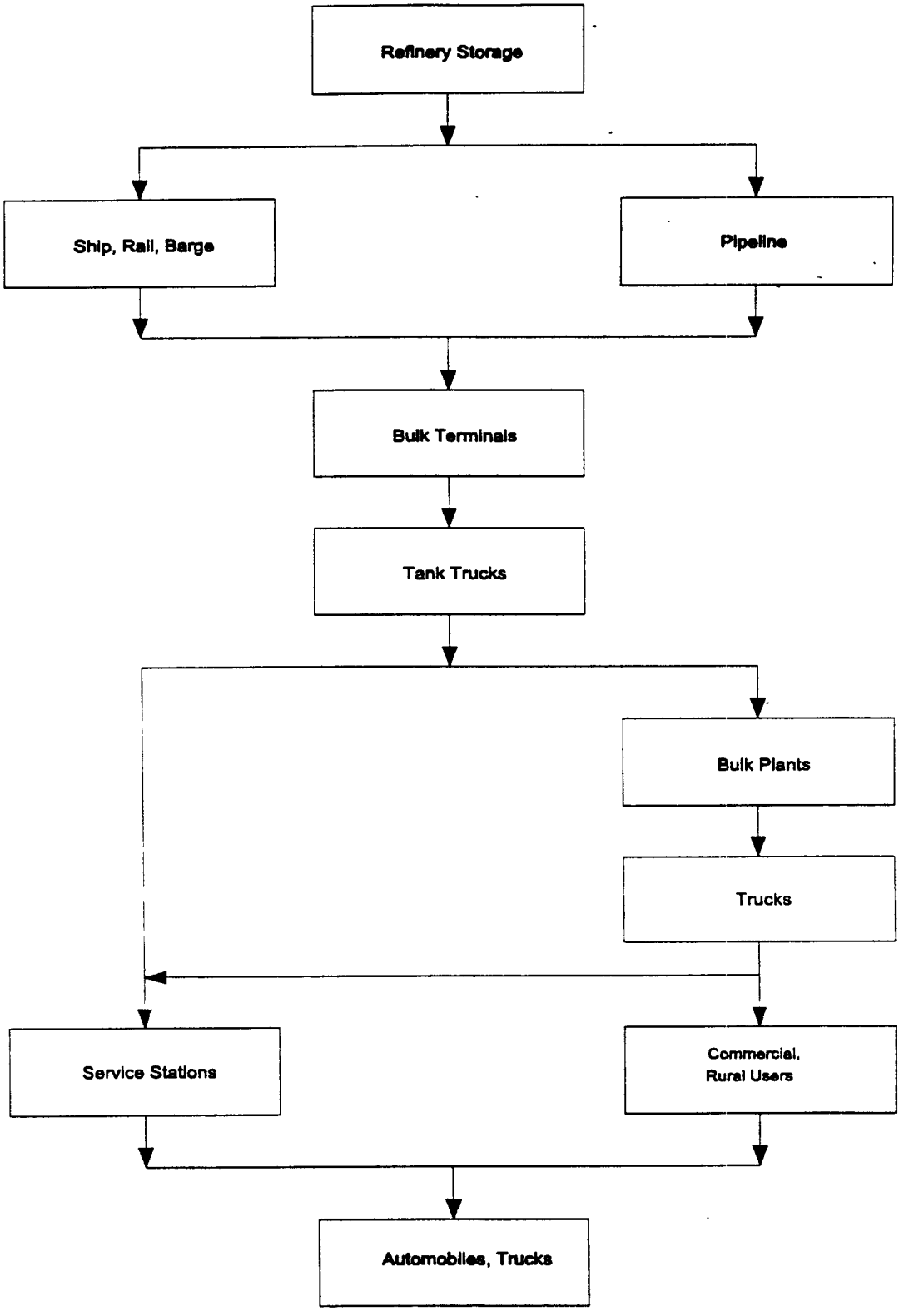


Figure 6-3. The Gasoline Marketing Distribution System in the United States

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

SCC Number	Storage Method	Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		Emission Factor Rating
		Non-Winter	Winter	Non-Winter	Winter	
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

SCC Number	Storage Method	Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		Emission Factor Rating
		Non-Winter	Winter	Non-Winter	Winter	
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 = $(5.1 \times 10^{-8} Q)$ ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(4.6 \times 10^{-10} Q)$ ton/yr.

[g] Gasoline vapor emission factor = $(4.6 \times 10^{-8} Q)$ Mg/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(4.1 \times 10^{-10} Q)$ 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 = $(8.1 \times 10^{-8} Q)$ ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(7.3 \times 10^{-10} Q)$ ton/yr.

[k] Gasoline vapor emission factor = $(7.3 \times 10^{-8} Q)$ Mg/yr, where Q is the throughput through the tank in barrels.
Benzene emission factor = $(6.6 \times 10^{-10} Q)$ 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]

SCC Number	Storage Method	Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		Emission Factor Rating
		Non-Winter	Winter	Non-Winter	Winter	
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[e]	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

SCC Number	Storage Method	Gasoline Vapor VOC Emission Factor[a,b] ton/yr/Tank (Mg/yr/Tank)		Benzene Emission Factor[c] ton/yr/Tank (Mg/yr/Tank)		Emission Factor Rating
		Non-Winter	Winter	Non-Winter	Winter	
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 = $(5.1 \times 10^{-8} Q)$ ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(4.6 \times 10^{-10} Q)$ ton/yr.

[f] Gasoline vapor emission factor = $(4.6 \times 10^{-8} Q)$ Mg/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(4.1 \times 10^{-10} Q)$ Mg/yr.

[g] Gasoline vapor emission factor = $(8.1 \times 10^{-8} Q)$ ton/yr, where Q is the throughput through the tanks in barrels.
Benzene emission factor = $(7.3 \times 10^{-10} Q)$ ton/yr.

[h] Gasoline vapor emission factor = $(7.3 \times 10^{-8} Q)$ Mg/yr, where Q is the throughput through the tank in barrels.
Benzene emission factor = $(6.6 \times 10^{-10} Q)$ 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,

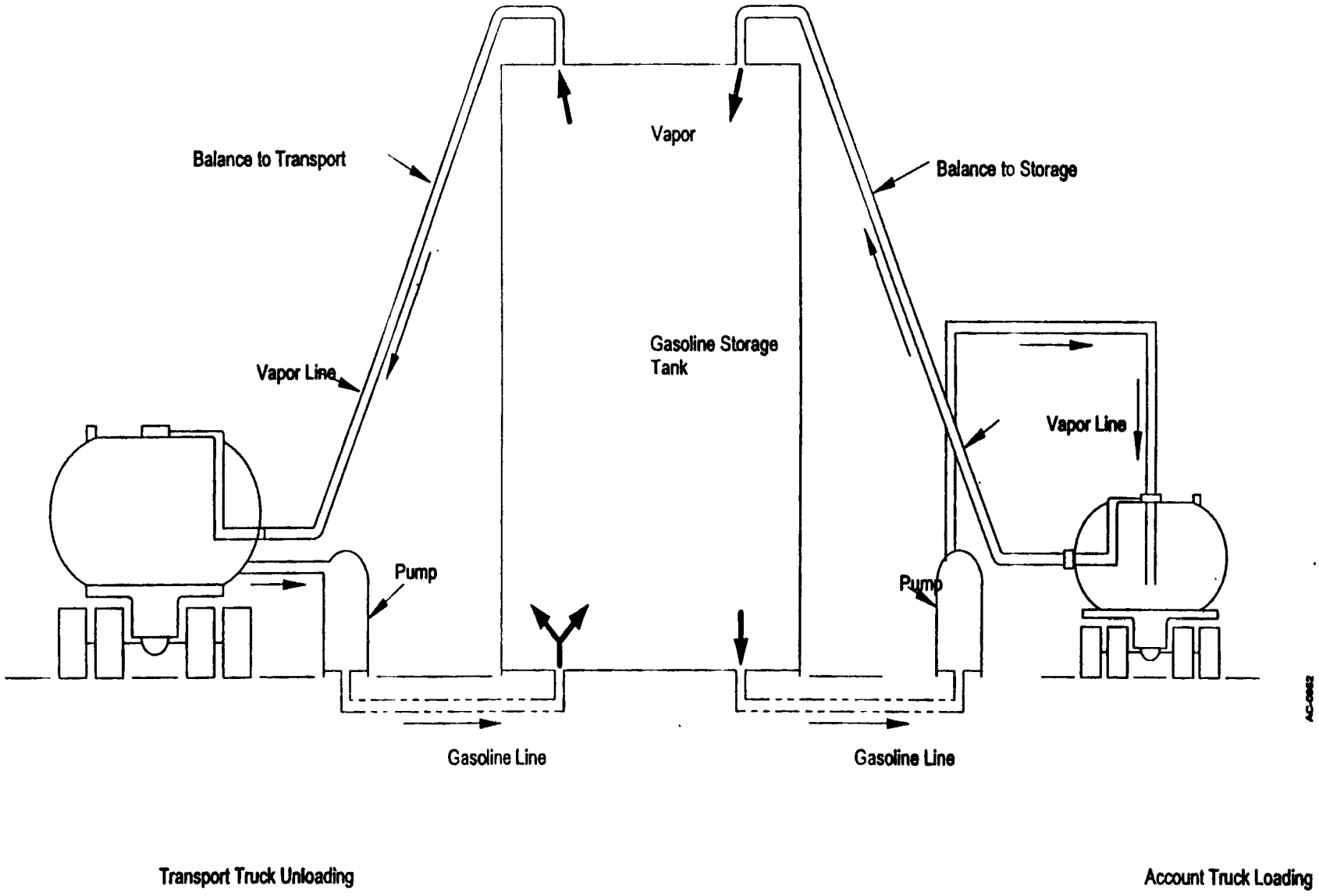


Figure 6-4. Bulk Plant Vapor Balance System (Stage I)

Source: Reference 160.

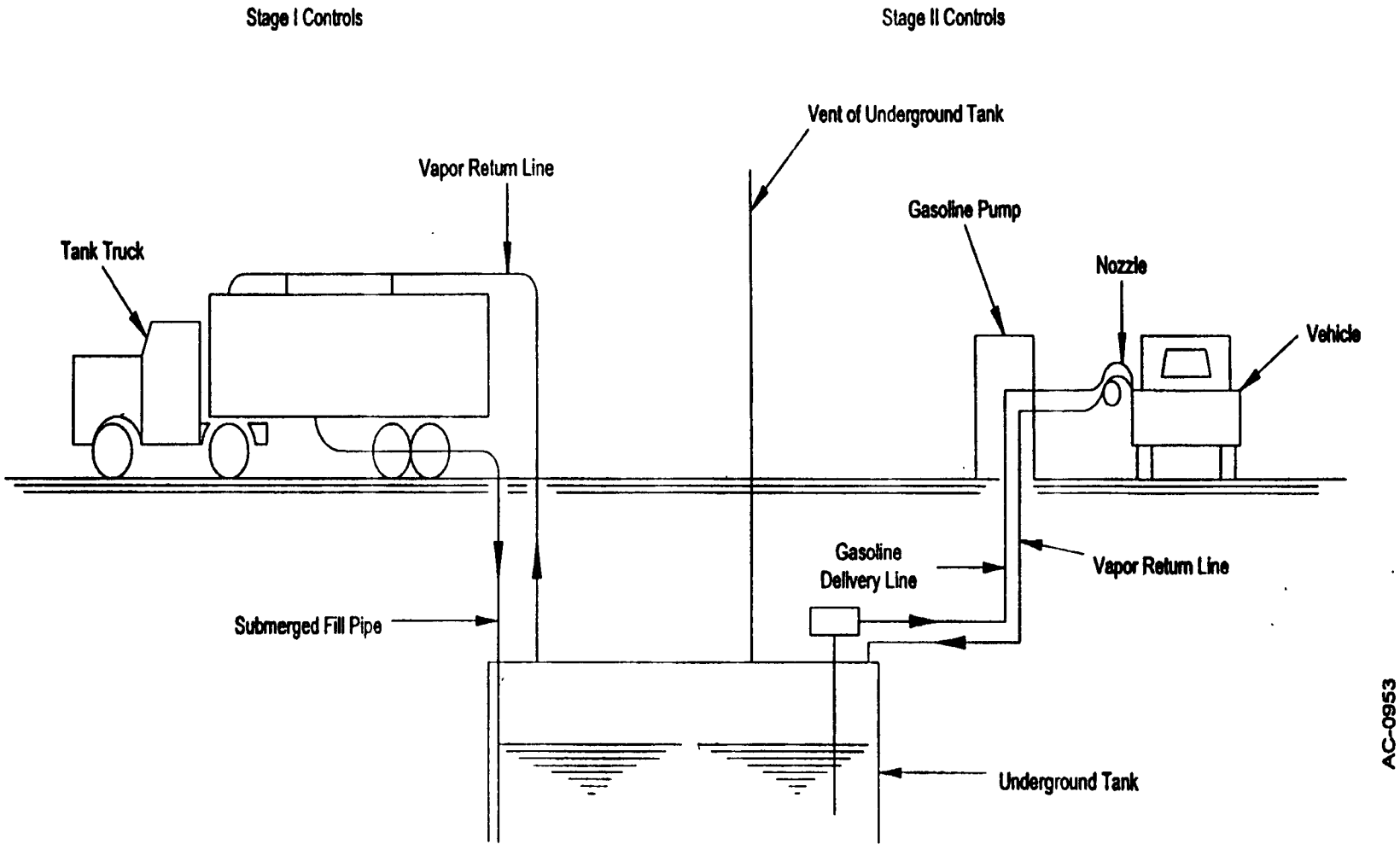


Figure 6-5. Service Station Vapor Balance System

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

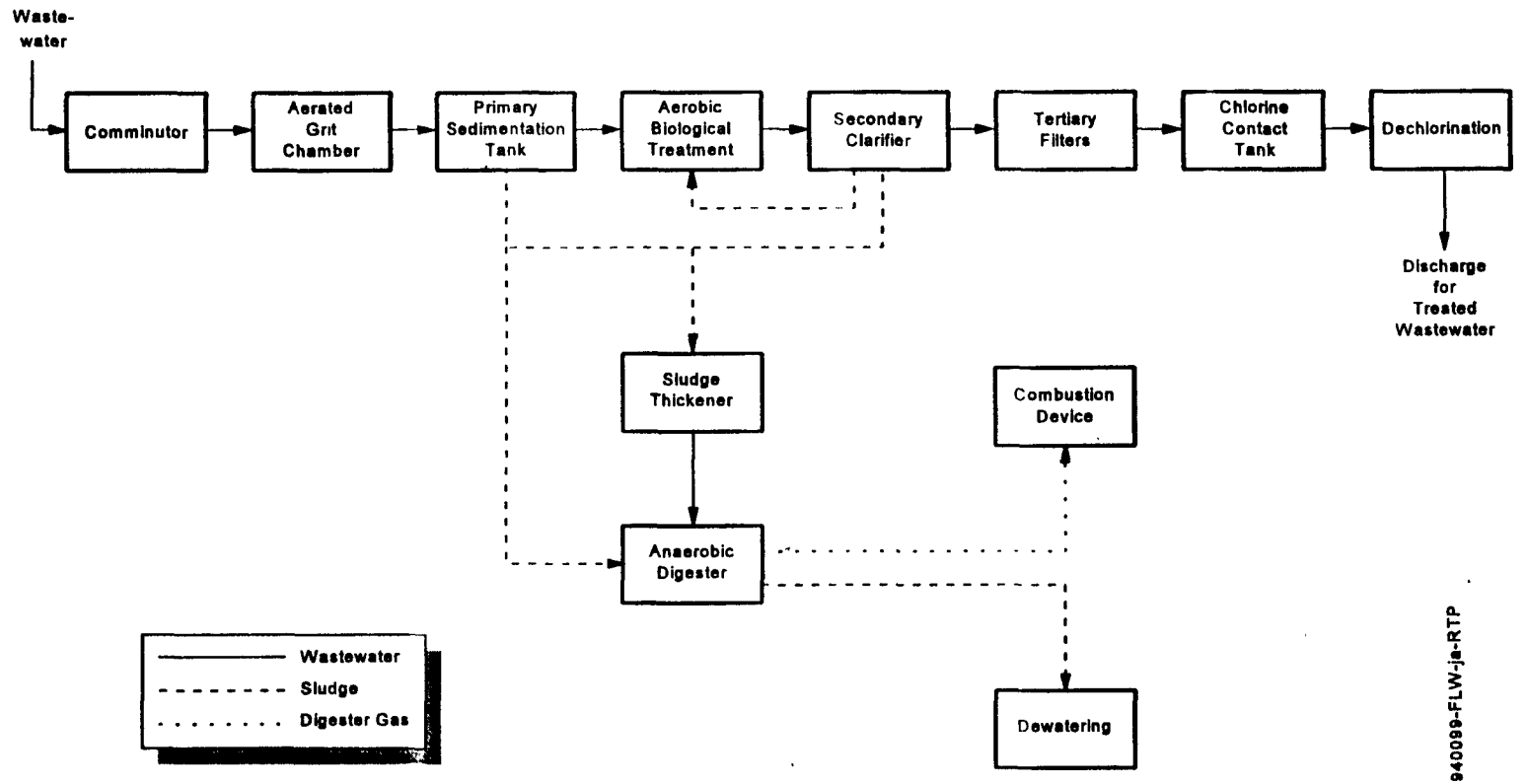


Figure 6-6. Process Flow Diagram for a Typical POTW

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]

Trickling Filter--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:

$$I_{BZ} = Q_{BZ} * \frac{78.113}{(8.205 \times 10^{-5}\ m^3\text{-atm/mol-°K})\ (1000\ g)\ (273 + T)}$$

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

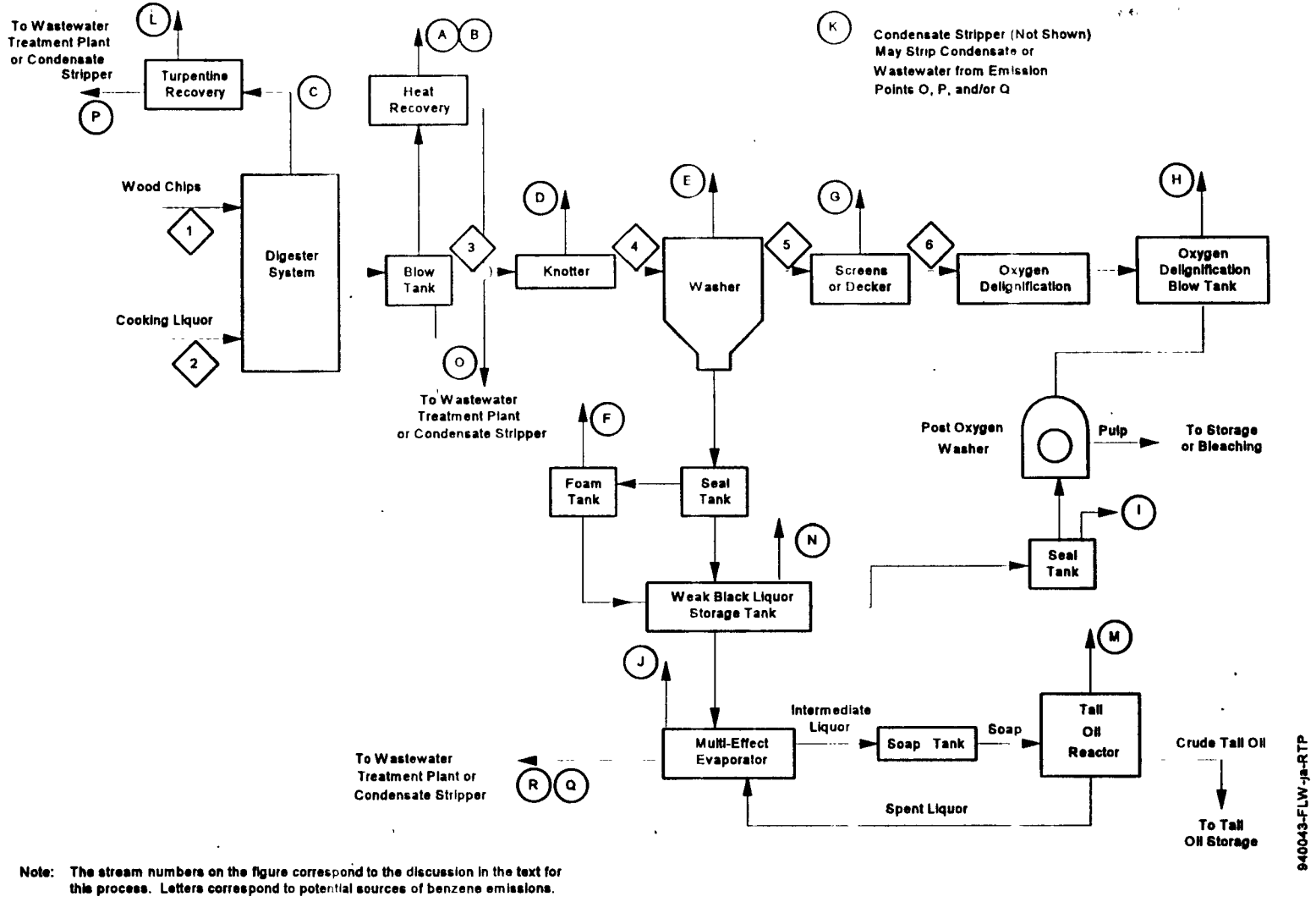
Digester relief vents	Washer filtrate tanks
Turpentine recovery system vents	Decker
Digester blow gas vents	Screen
Noncondensible gas system vents	Weak black liquor storage tank
Evaporator noncondensible gas vent	Recovery furnace stack
Evaporator hotwell gas vent	Slaker/causticizer vents
Knotter	Lime 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

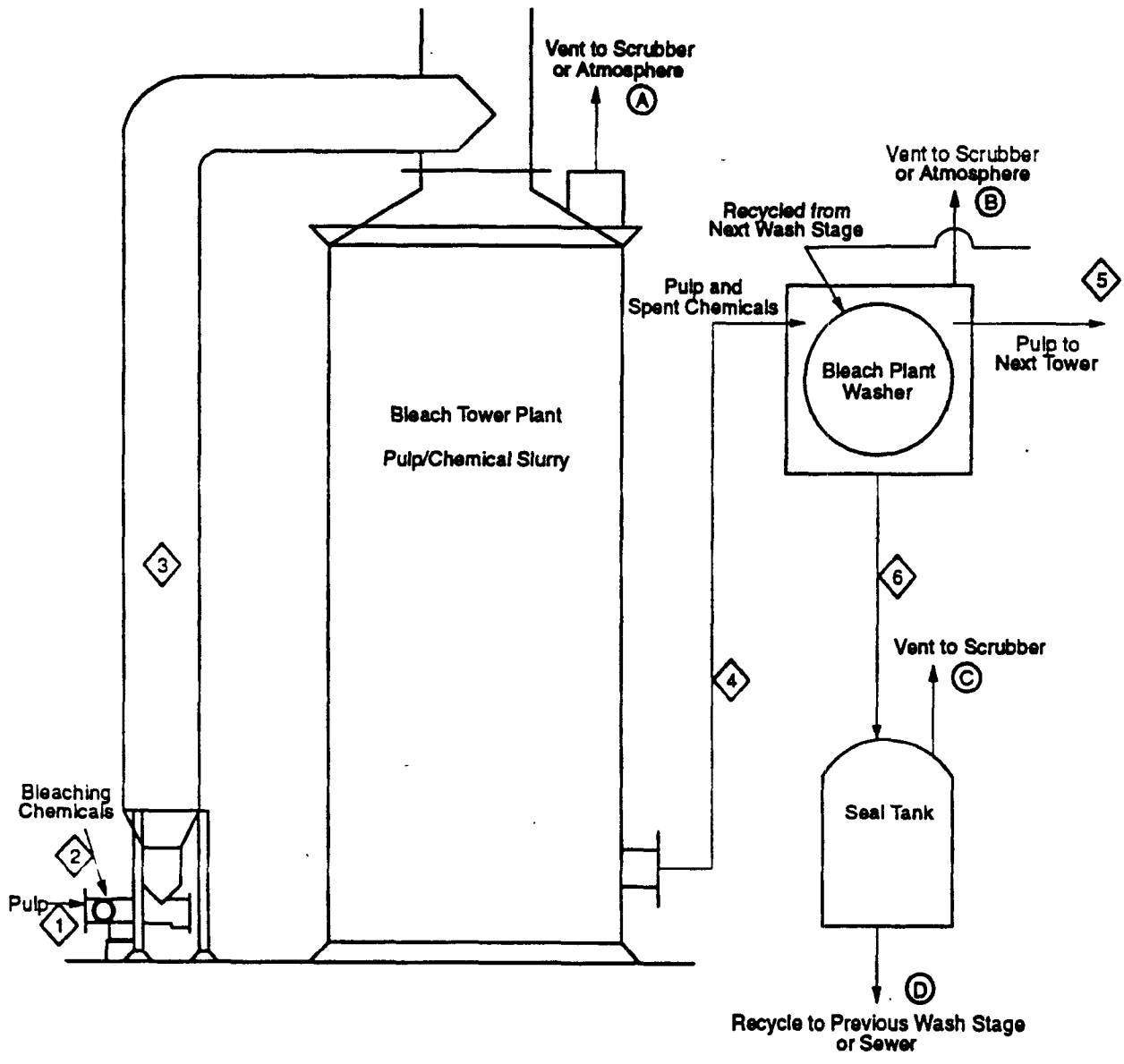


Figure 6-8. Typical Down-flow Bleach Tower and Washer

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.

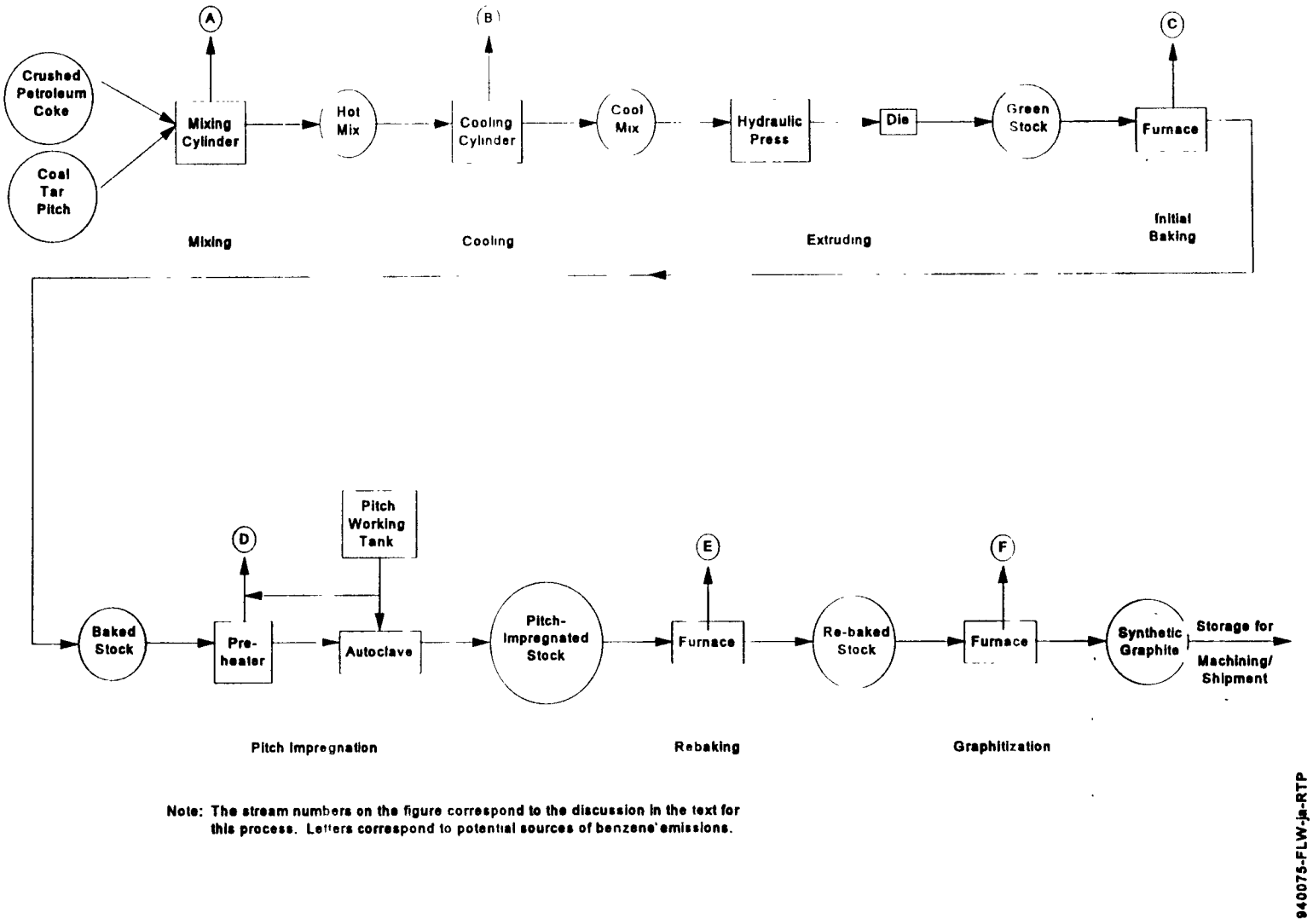
6.8.1 Process Description for Synthetic Graphite Production

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.

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

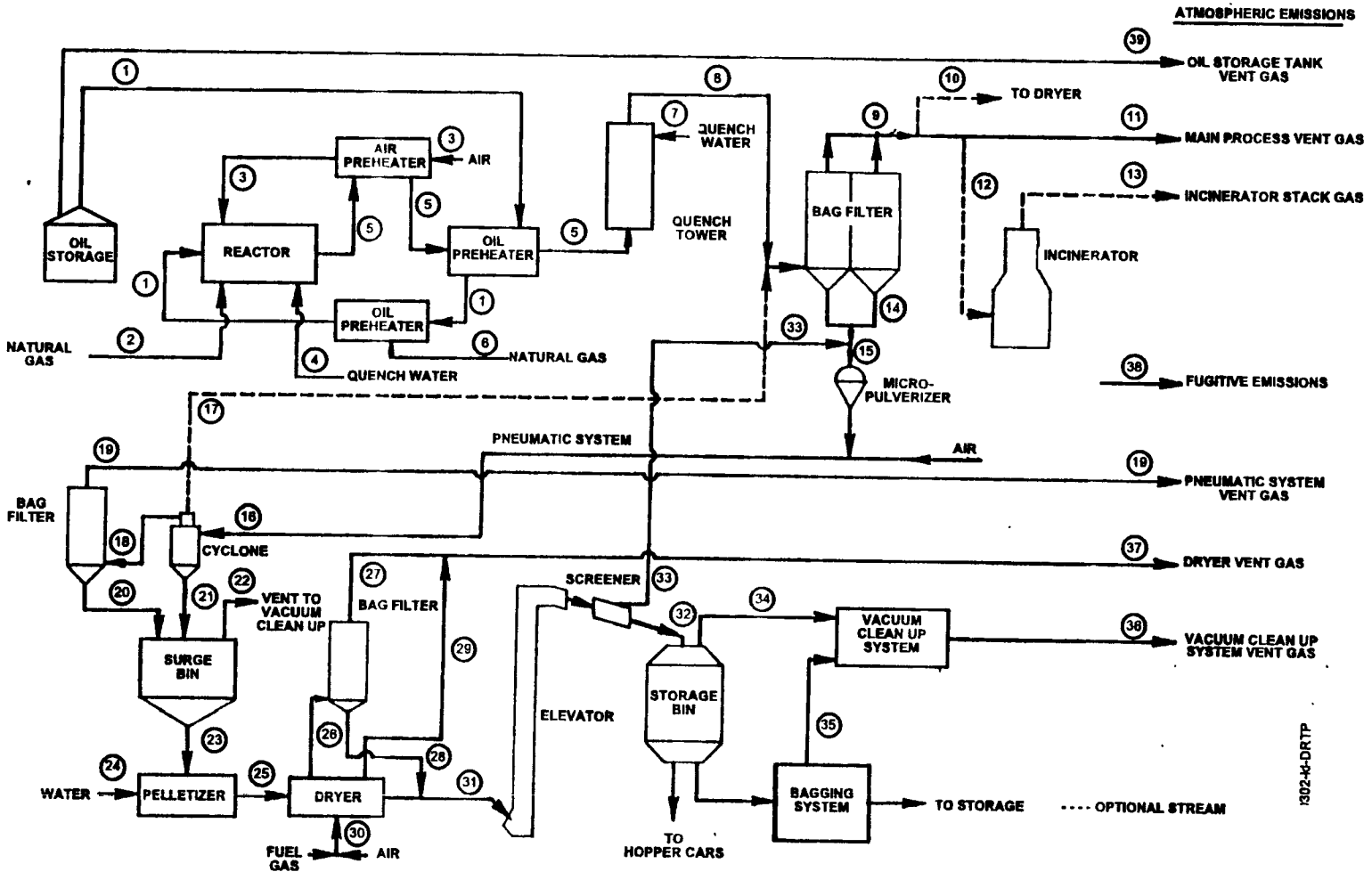


Figure 6-10. Process Diagram for an Oil-Furnace Carbon Black Plant

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 6.23×10^{-4} lb (2.83×10^{-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

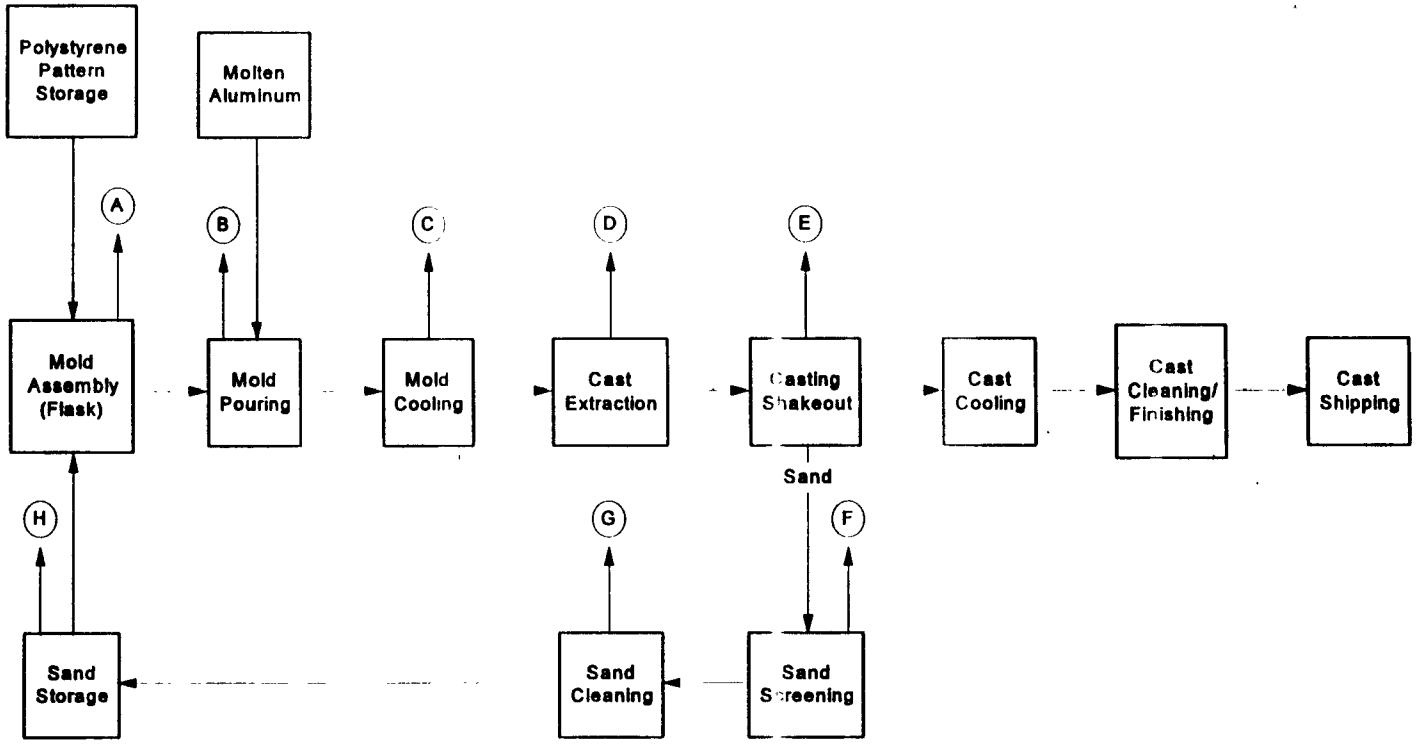
A common method for making the mold for aluminum motor parts is to utilize polystyrene foam patterns or "positives" of the desired metal part. The basic principle of the casting operation involves the replacement of the polystyrene pattern held within a sand mold with molten metal to form the metal casting. 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

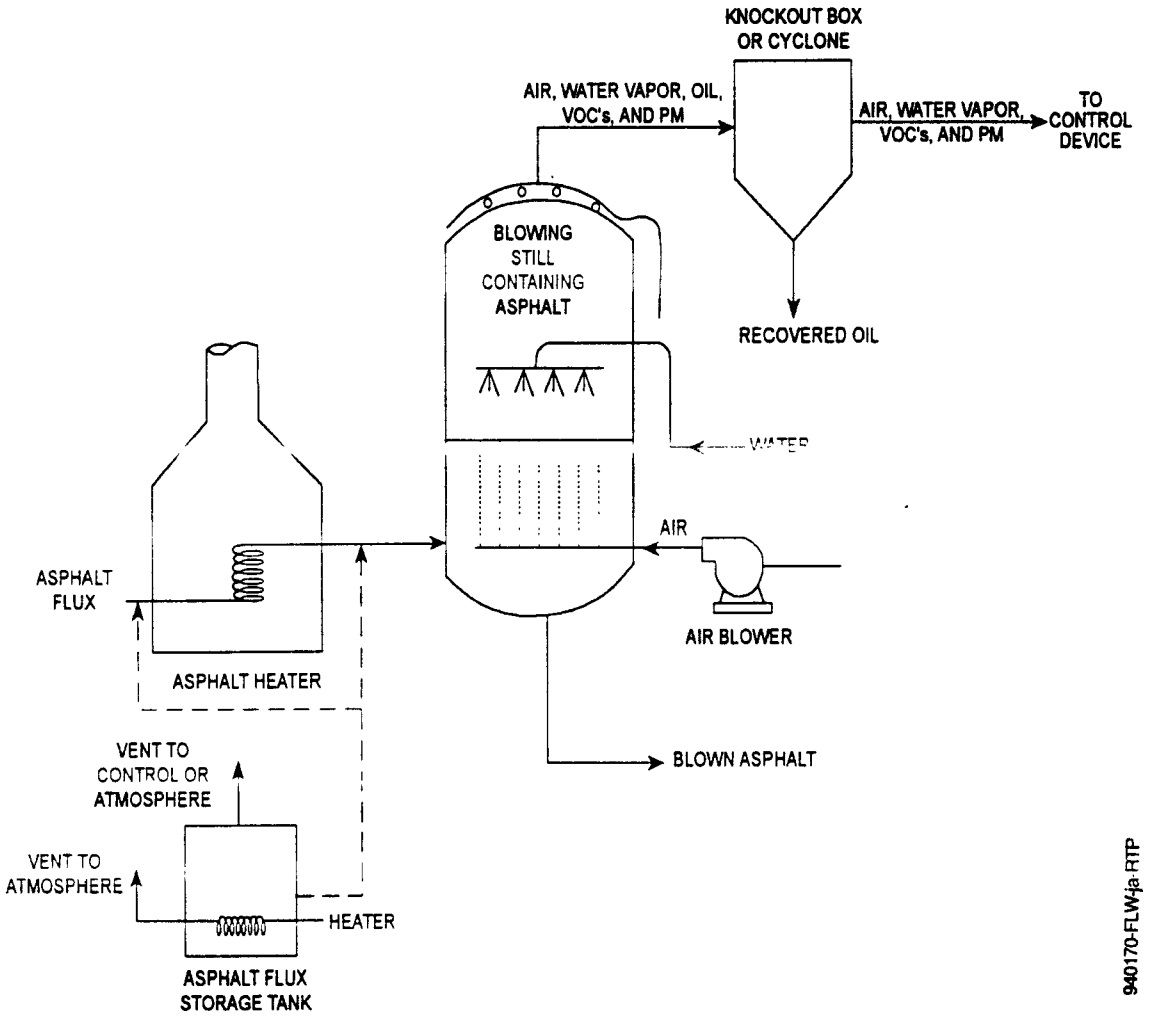


Figure 6-12. Asphalt Blowing Process Flow Diagram

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.

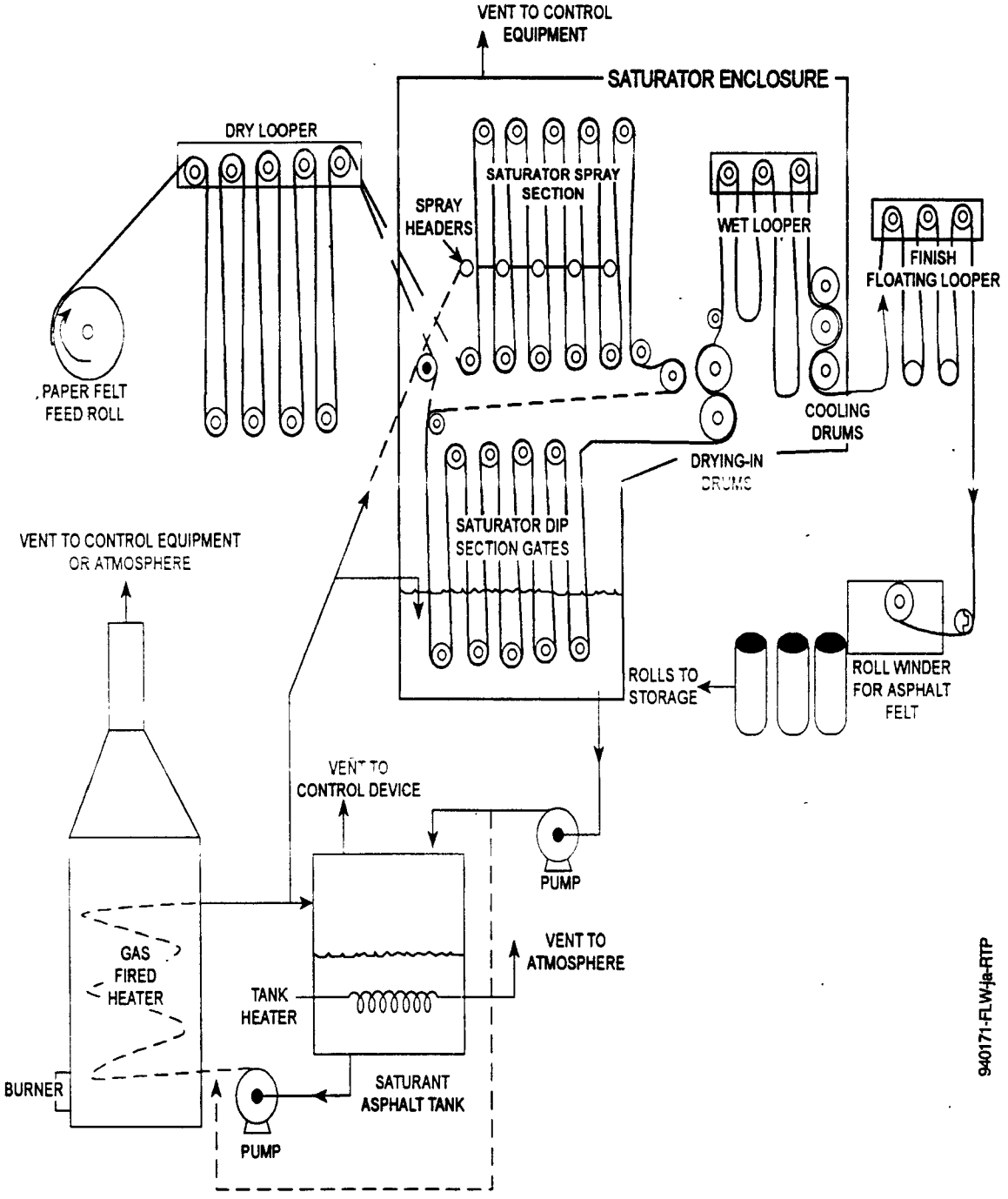


Figure 6-13. Asphalt-Saturated Felt Manufacturing Process

Source: Reference 185.

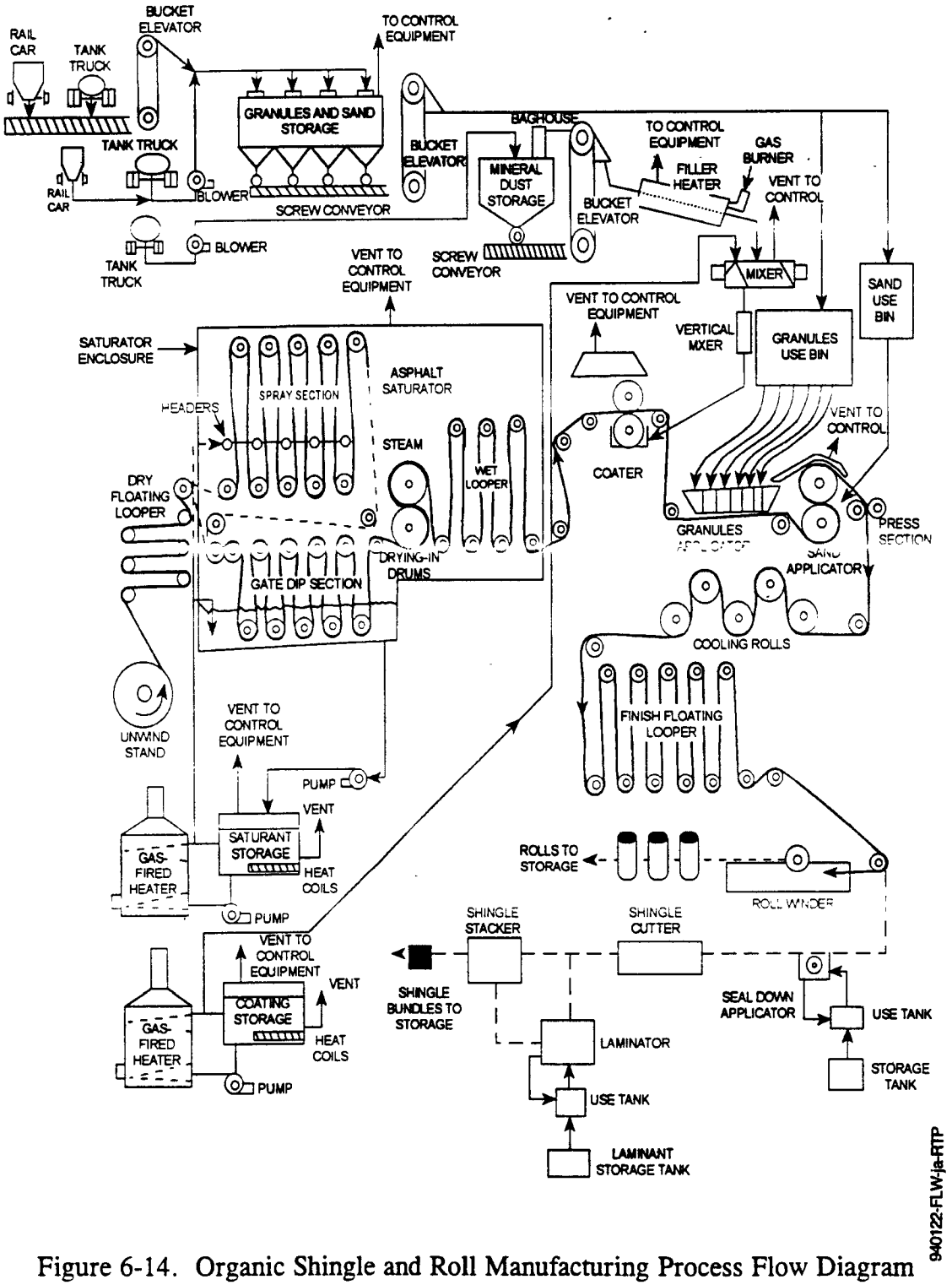


Figure 6-14. Organic Shingle and Roll Manufacturing Process Flow Diagram

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

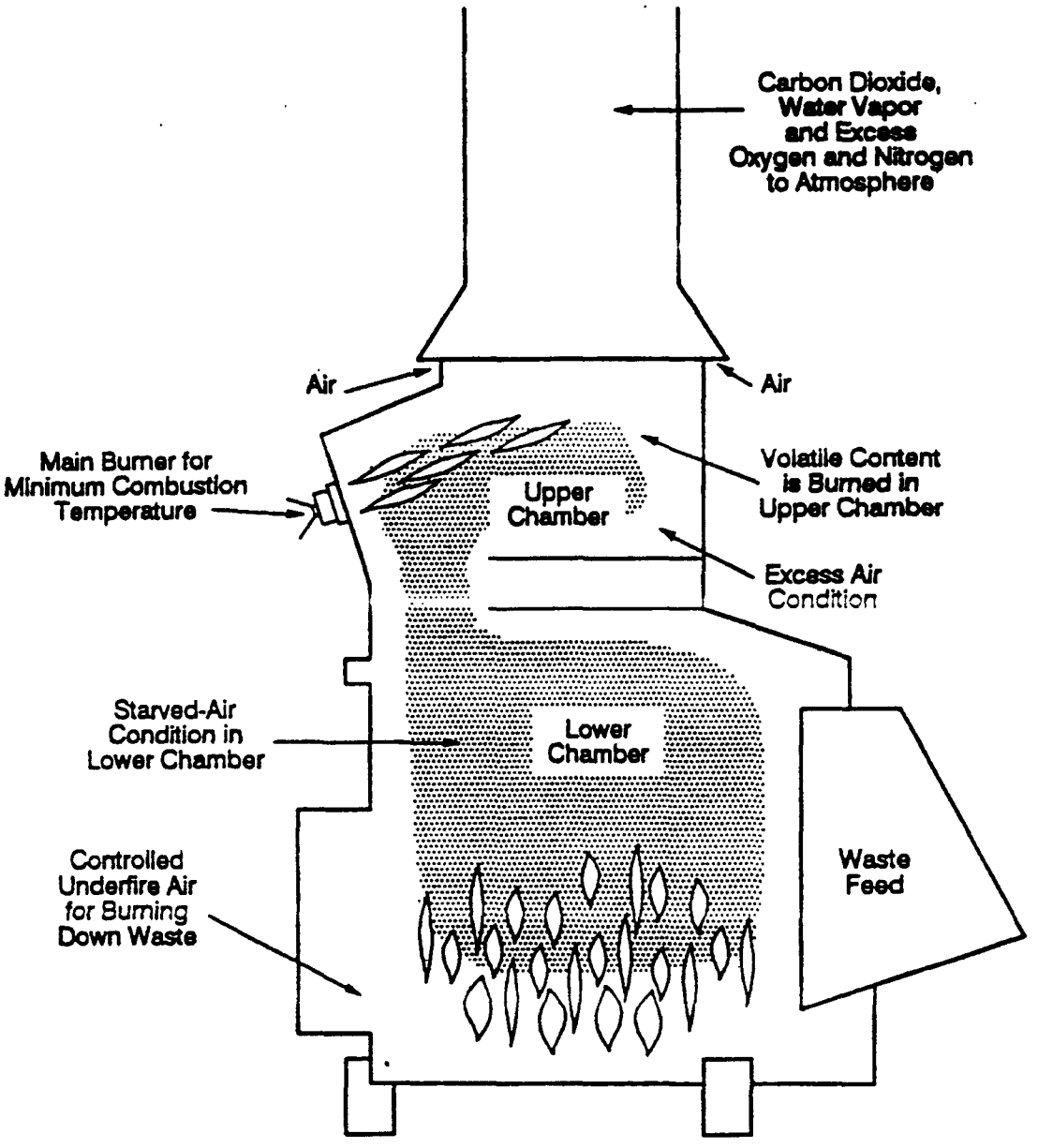


Figure 7-1. Controlled-Air Incinerator

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

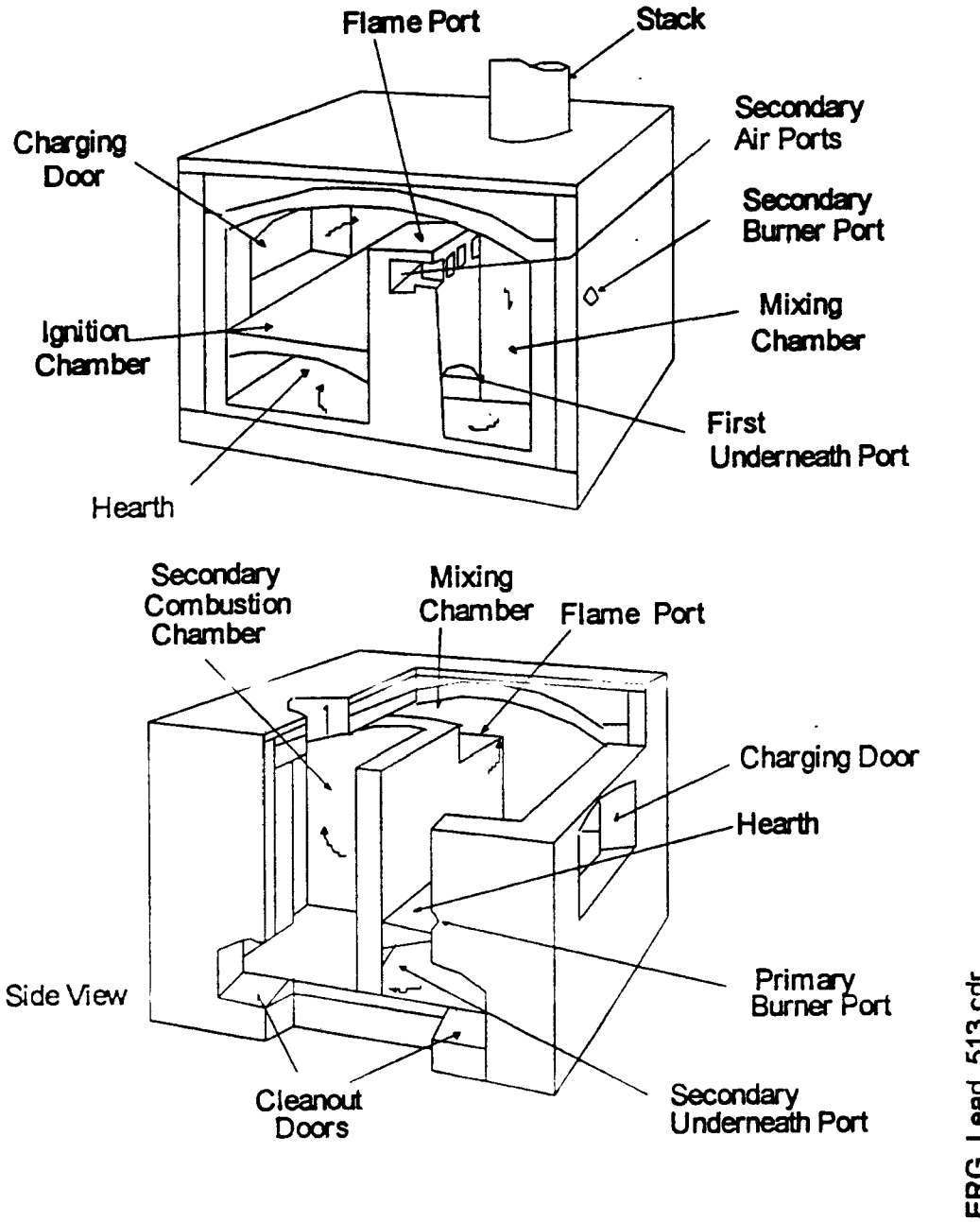


Figure 7-2. Excess-Air Incinerator

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

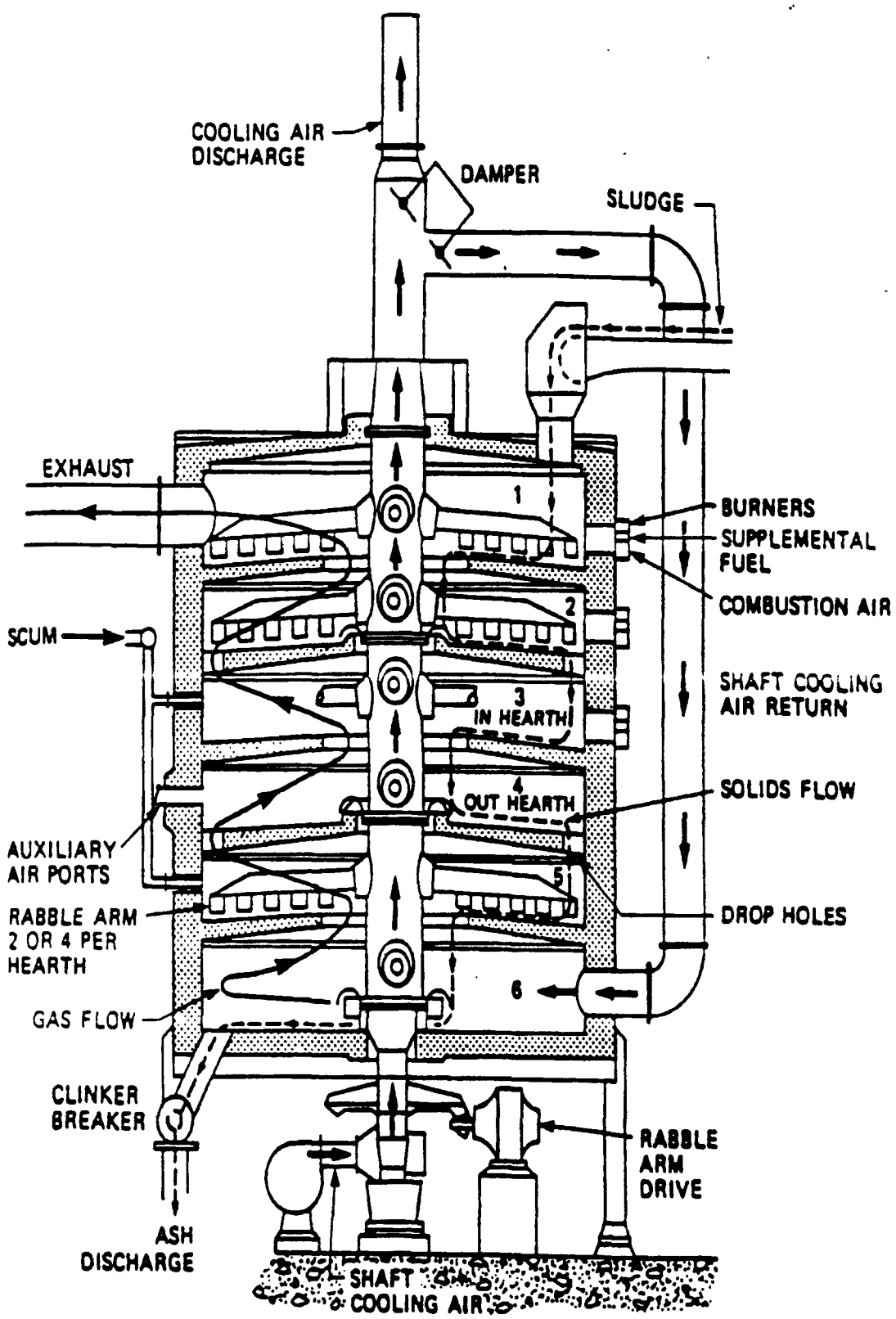


Figure 7-3. Cross Section of a Multiple Hearth Furnace

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

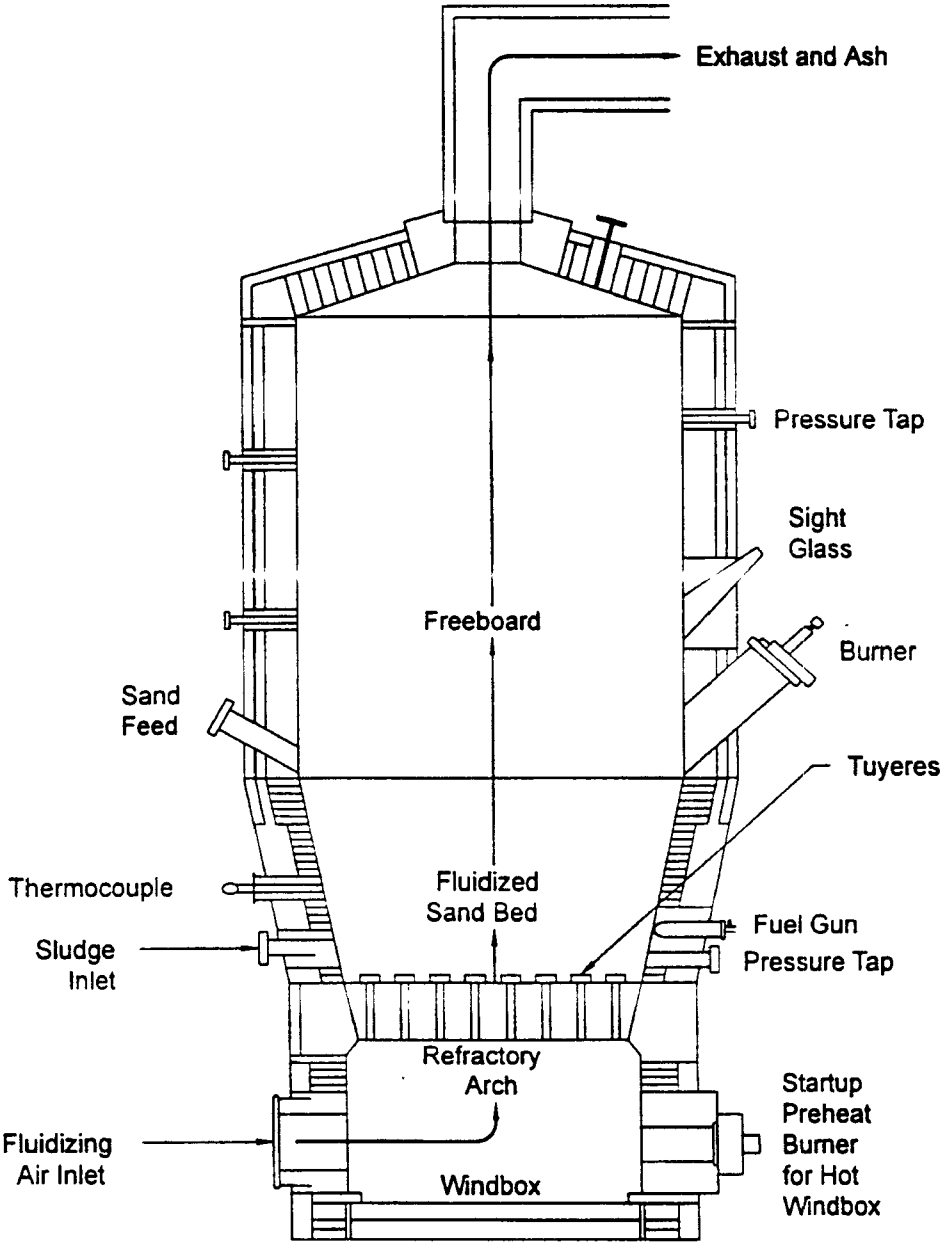


Figure 7-4. Cross Section of a Fluidized Bed Furnace

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

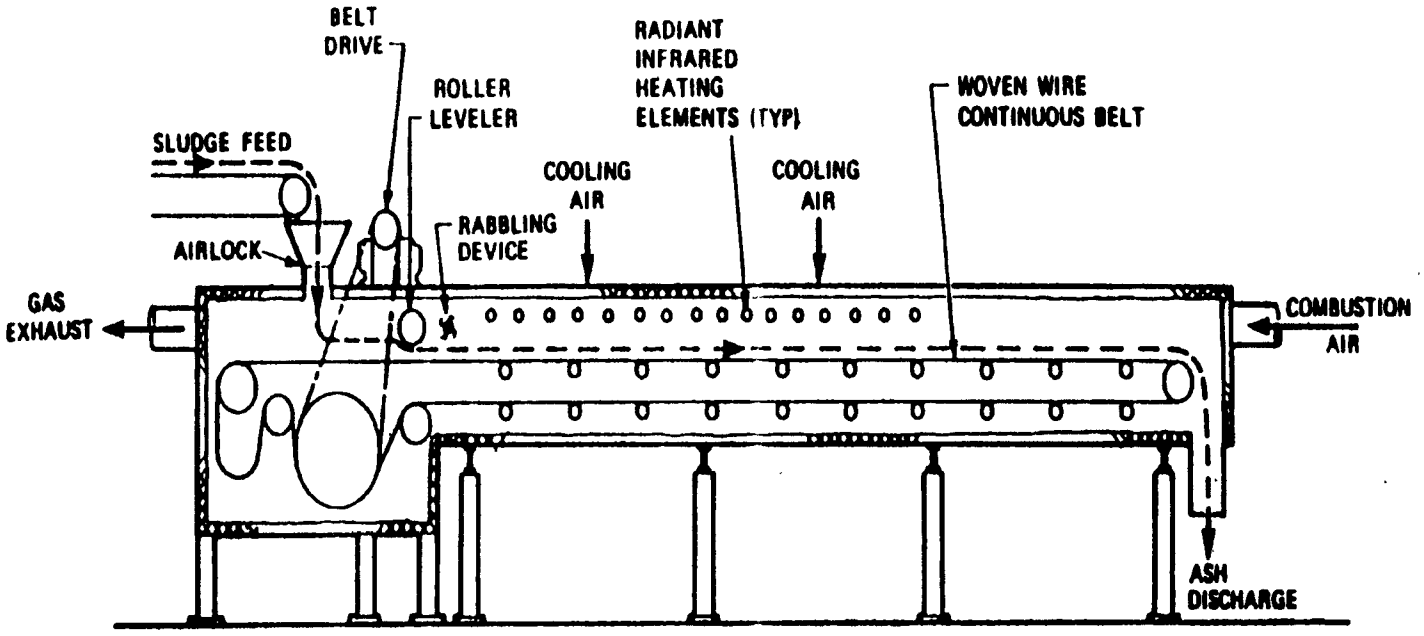


Figure 7-5. Cross Section of an Electric Infrared Furnace

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]	1.73×10^{-2} (8.61)	--	D
		Venturi/Impingement Scrubbers[b]	1.34×10^{-2} (6.66)	23	D
		Elevated Operating Temperature[c]	2.65×10^{-3} (1.32)	85	D
		Elevated Operating Temperature/Afterburner[c]	1.41×10^{-3} (7.02×10^{-1})	92	D
		Elevated Operating Temperature/ Afterburner/Venturi and Impingement Scrubbers[c]	3.35×10^{-4} (1.67×10^{-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

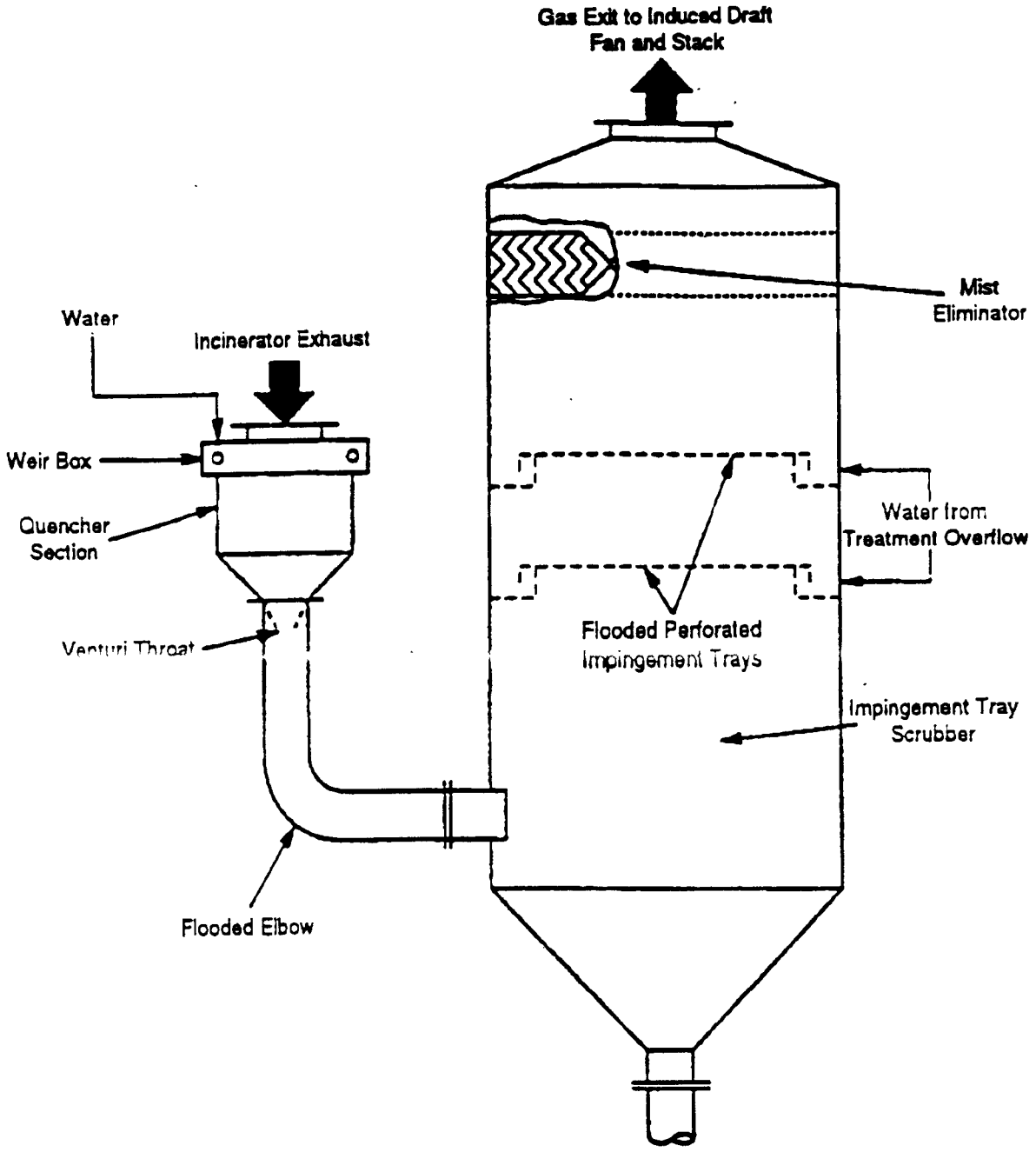


Figure 7-6. Venturi/Impingement Tray Scrubber

Source: Reference 198.

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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

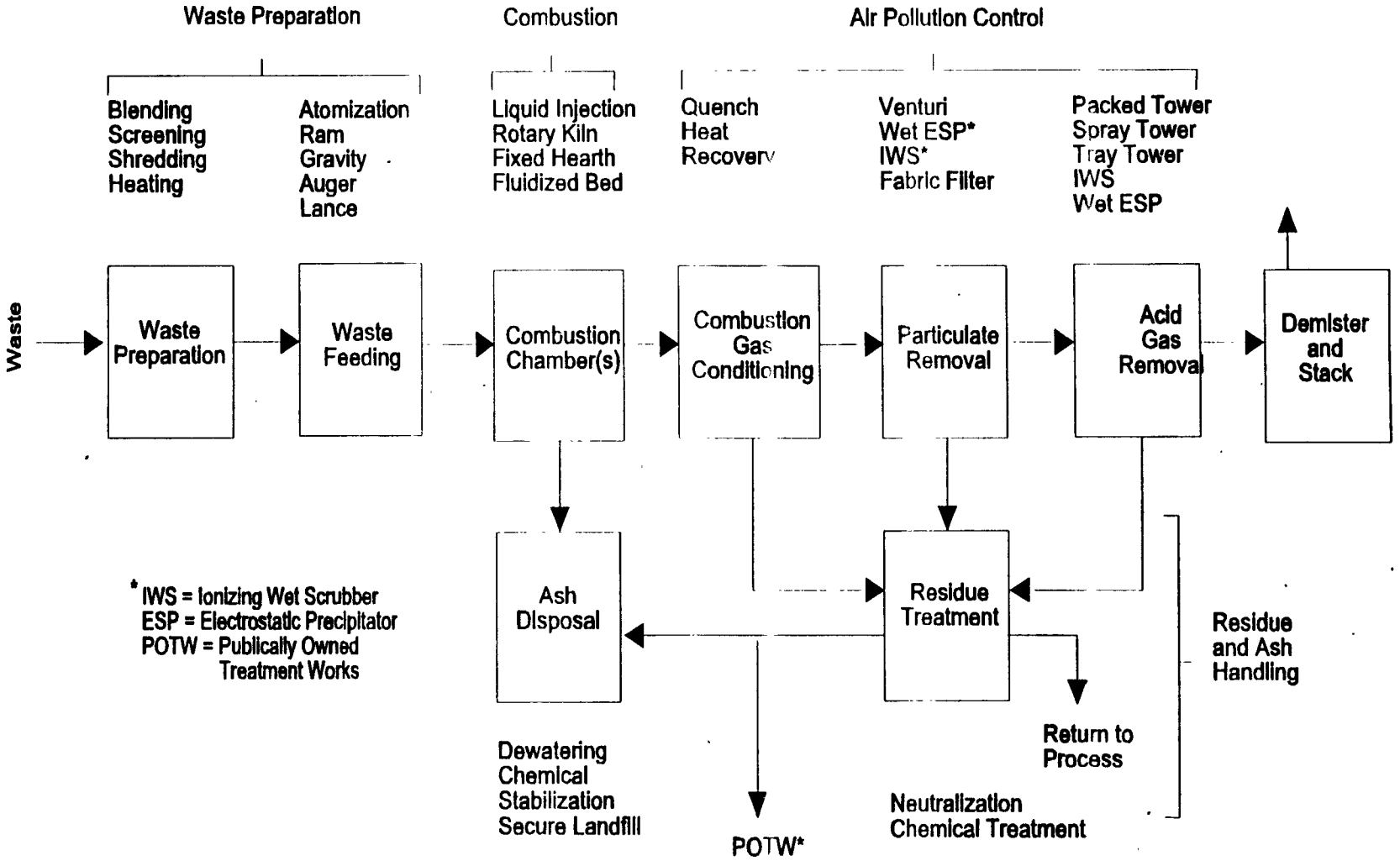

Figure 7-7. General Orientation of Hazardous Waste Incineration Subsystems and Typical Component Options

Source: Reference 201.

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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[203]

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

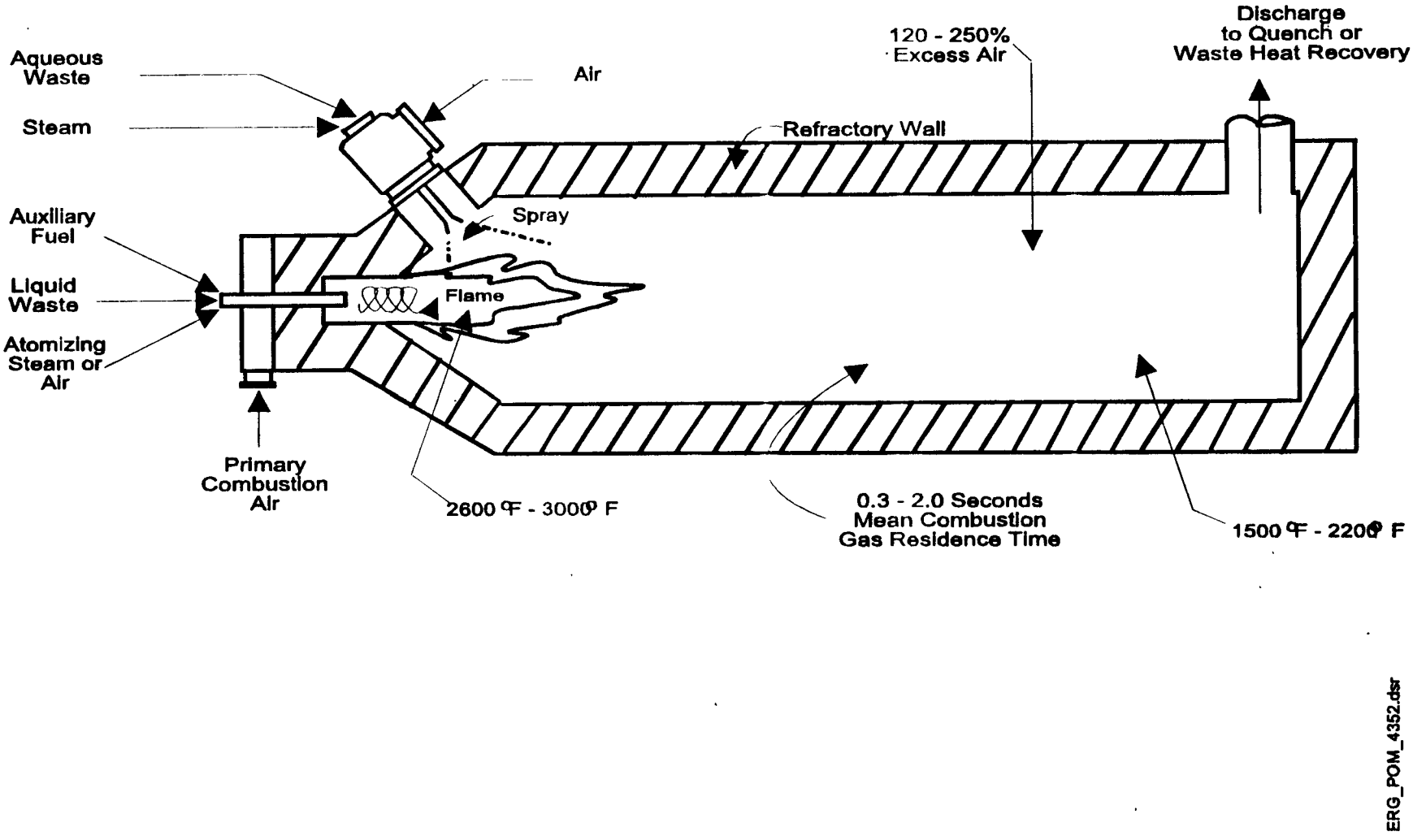

Figure 7-8. Typical Liquid Injection Combustion Chamber

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]

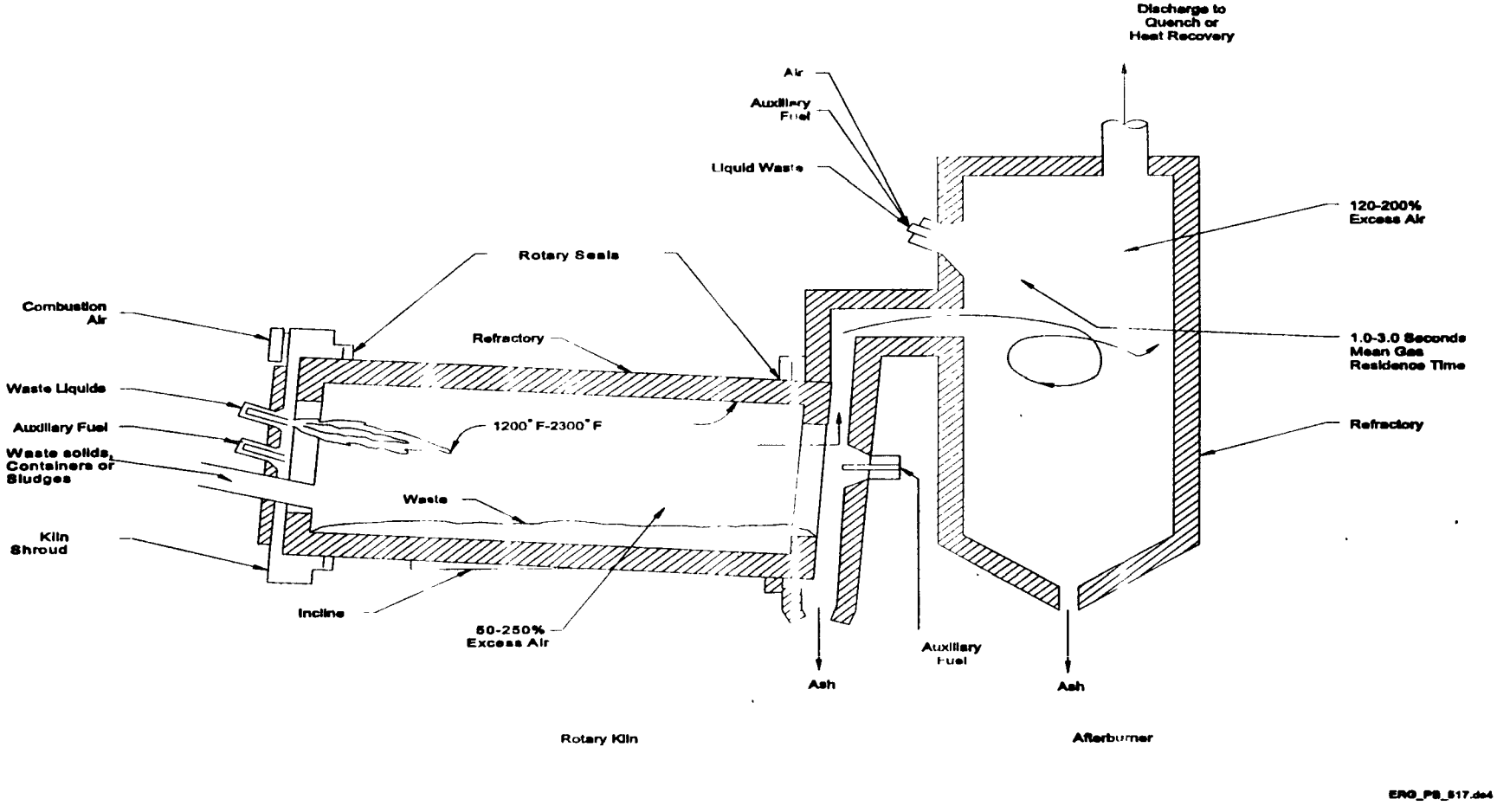

Figure 7-9 Typical Rotary Kiln/Afterburner Combustion Chamber

Source: Reference 201.

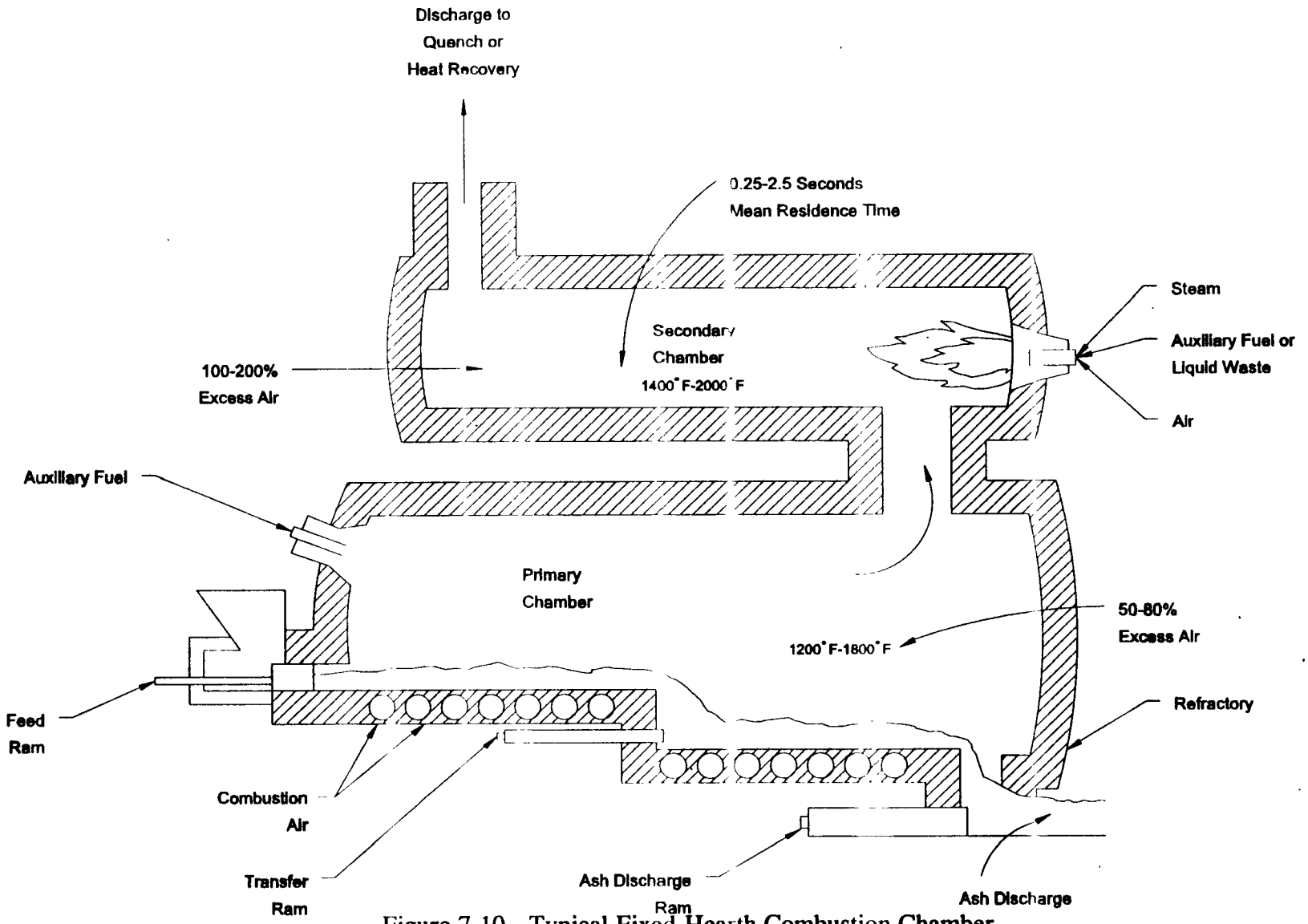

Figure 7-10. Typical Fixed-Hearth Combustion Chamber

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

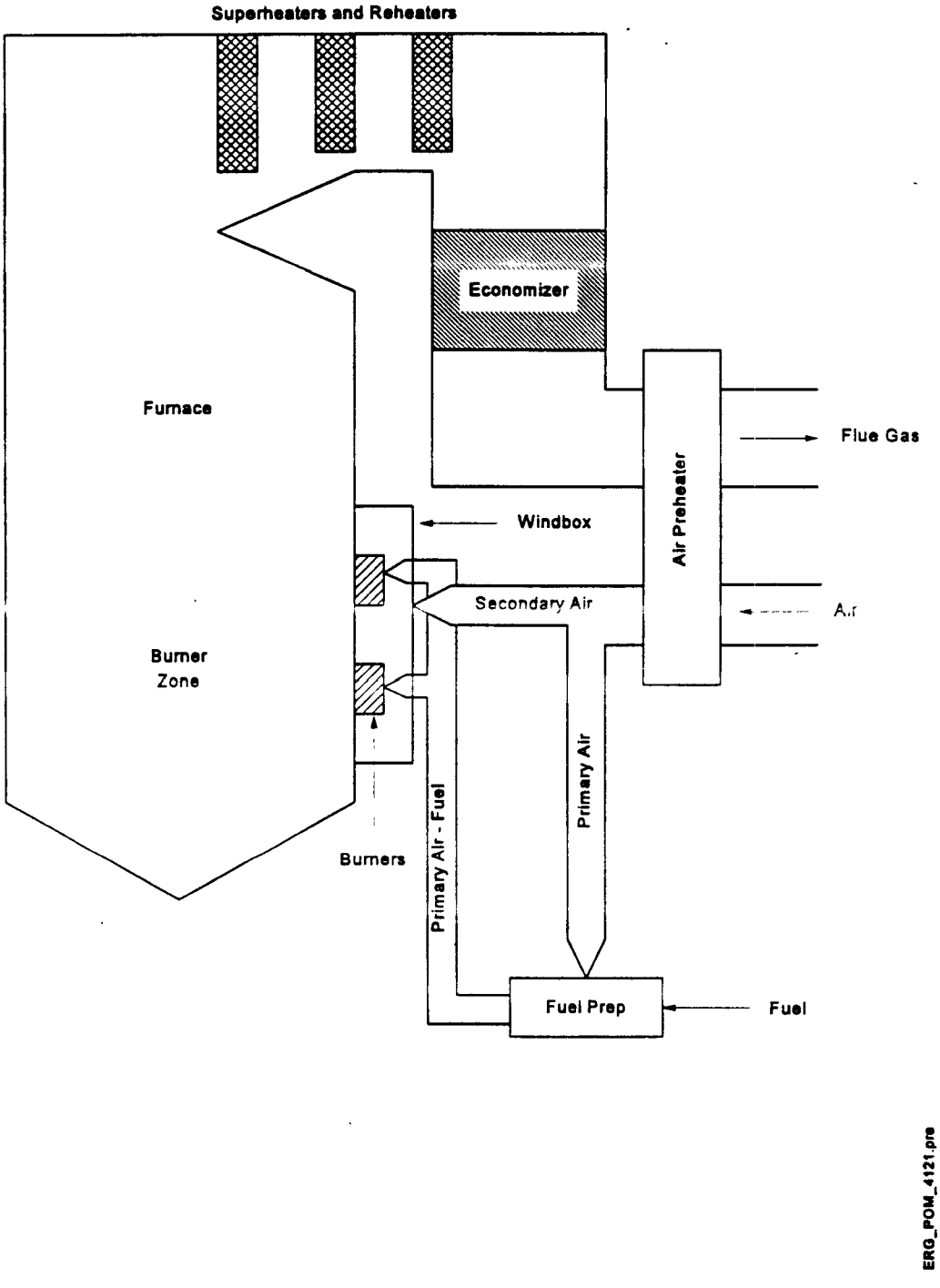

Figure 7-11. Simplified Boiler Schematic

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]

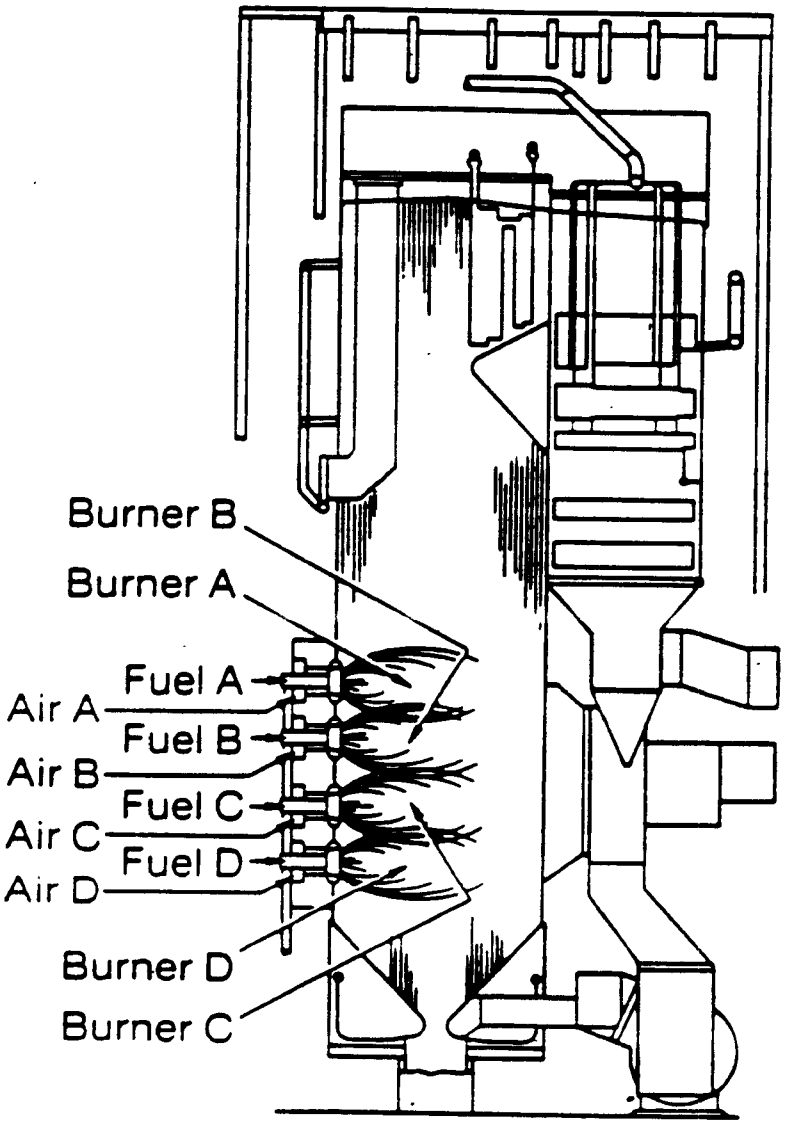

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Figure 7-12. Single Wall-fired Boiler

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.

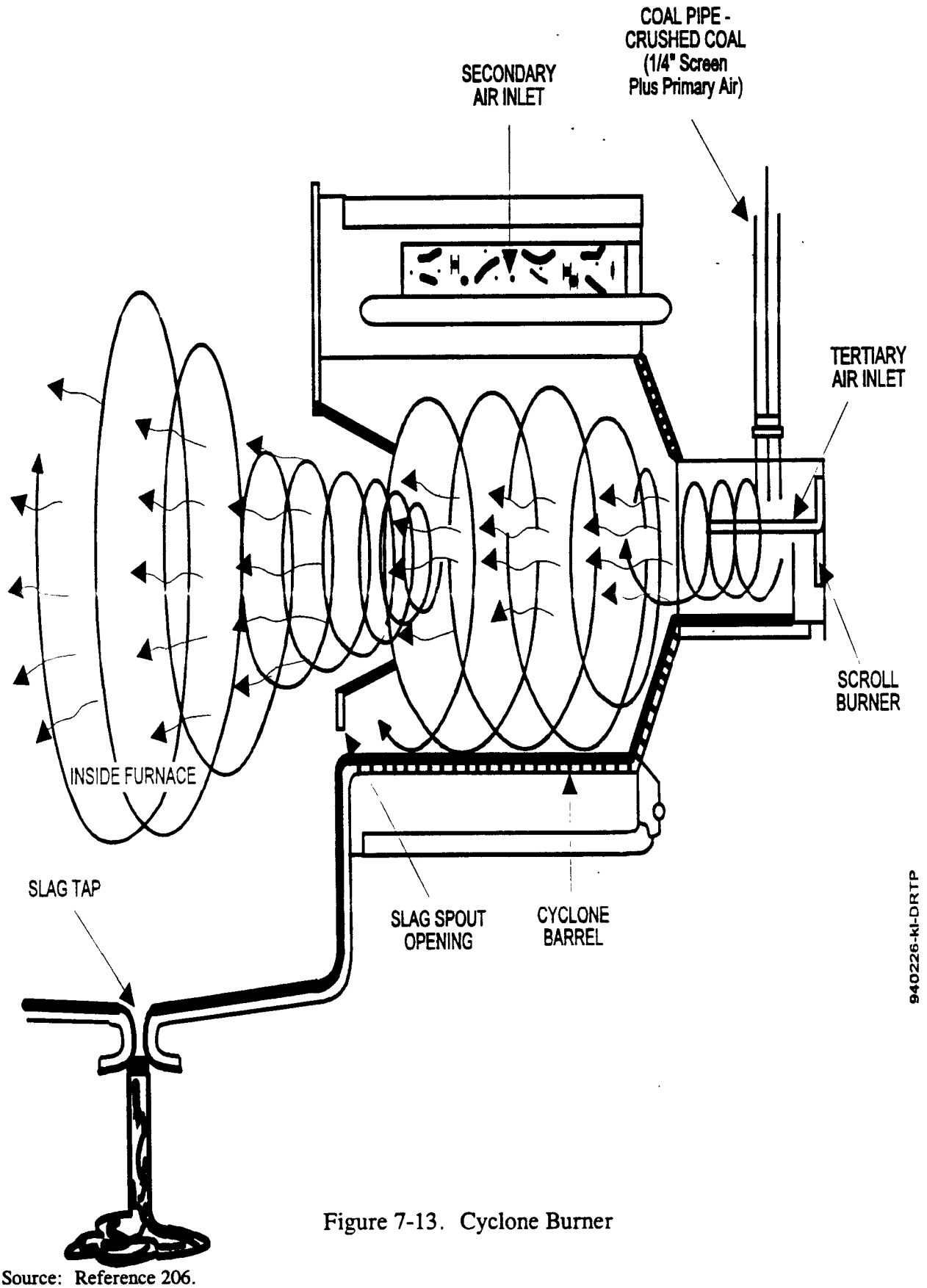

Figure 7-13. Cyclone Burner

Source: Reference 206.

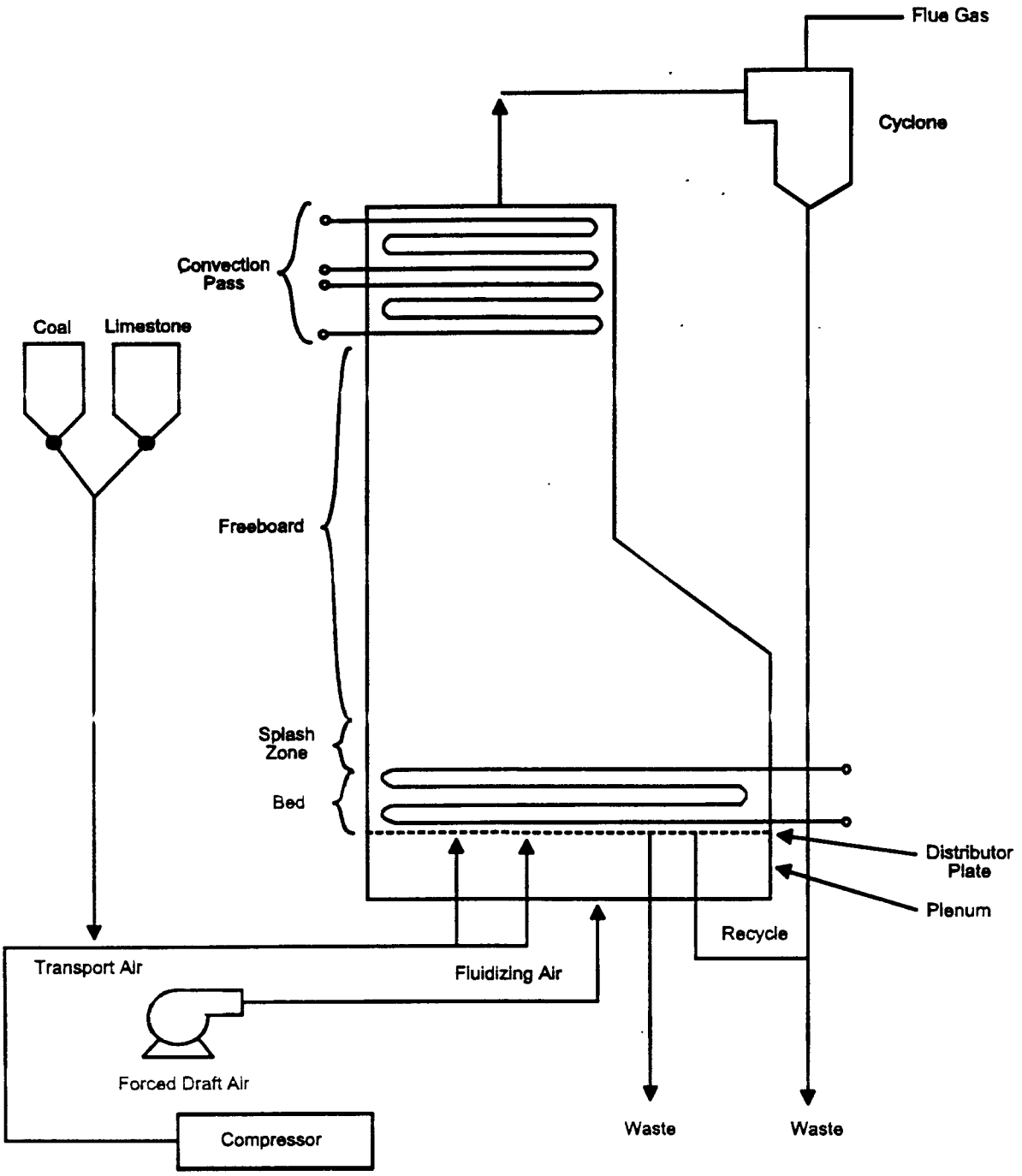

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Figure 7-14. Simplified Atmospheric Fluidized Bed Combustor Process Flow Diagram

Source: Reference 206.

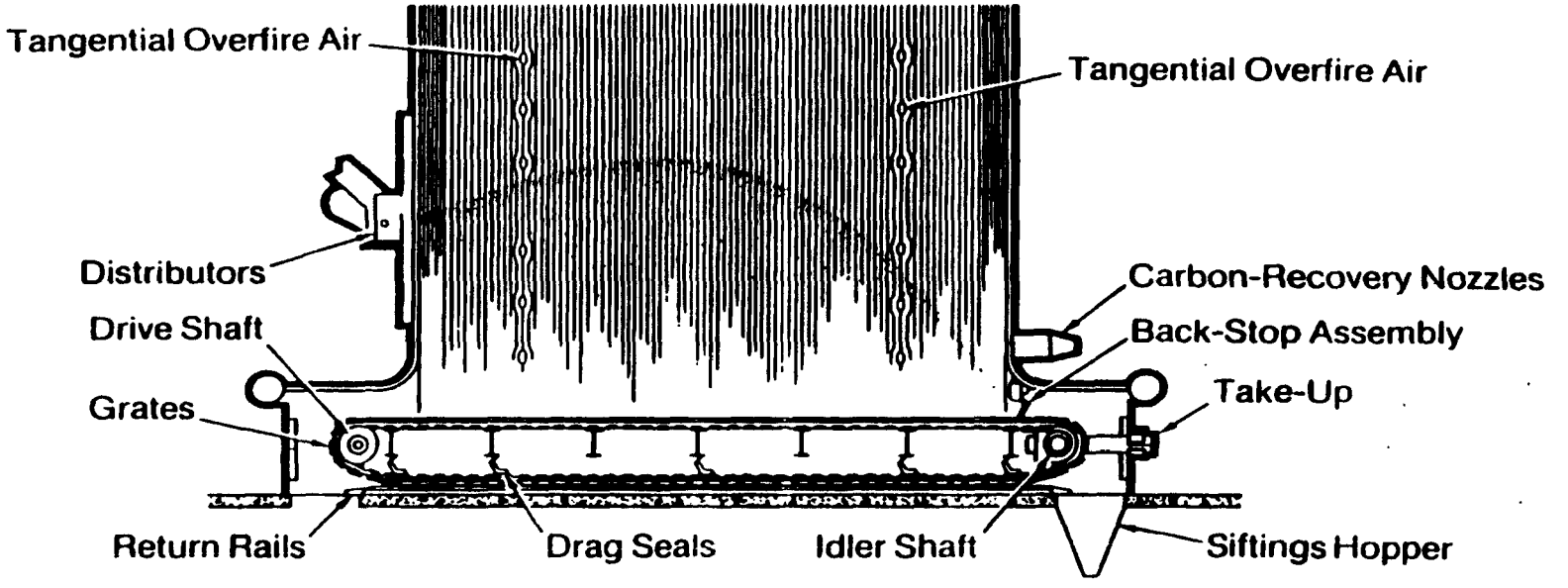


Figure 7-15. Spreader Type Stoker-fired Boiler - Continuous Ash Discharge Grate

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]	5.58×10^{-6} (2.40×10^{-6})	D	209
1-01-002-03	Cyclone boiler	Coal	Electrostatic precipitator	7.90×10^{-6} (3.40×10^{-6})	D	209
1-01-003-02	Tangentially-fired boiler	Lignite[c]	Electrostatic precipitator/ scrubber[d]	3.95×10^{-5} (1.70×10^{-5})	D	209
1-01-006-01	Opposed-wall boiler[e]	Natural gas	Flue gas recirculation	1.40×10^{-6} (6.02×10^{-7})	D	210
1-01-006-04	Tangentially-fired boiler[e]	Natural gas	Flue gas recirculation	4.00×10^{-7} (1.72×10^{-7})	D	210
1-01-009-01	Boiler	Bark[f]	Uncontrolled	3.60×10^{-3} lb/ton (1.80×10^{-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]

Wood Combustion--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]

Natural Gas Combustion--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.

Distillate Oil (Diesel)--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

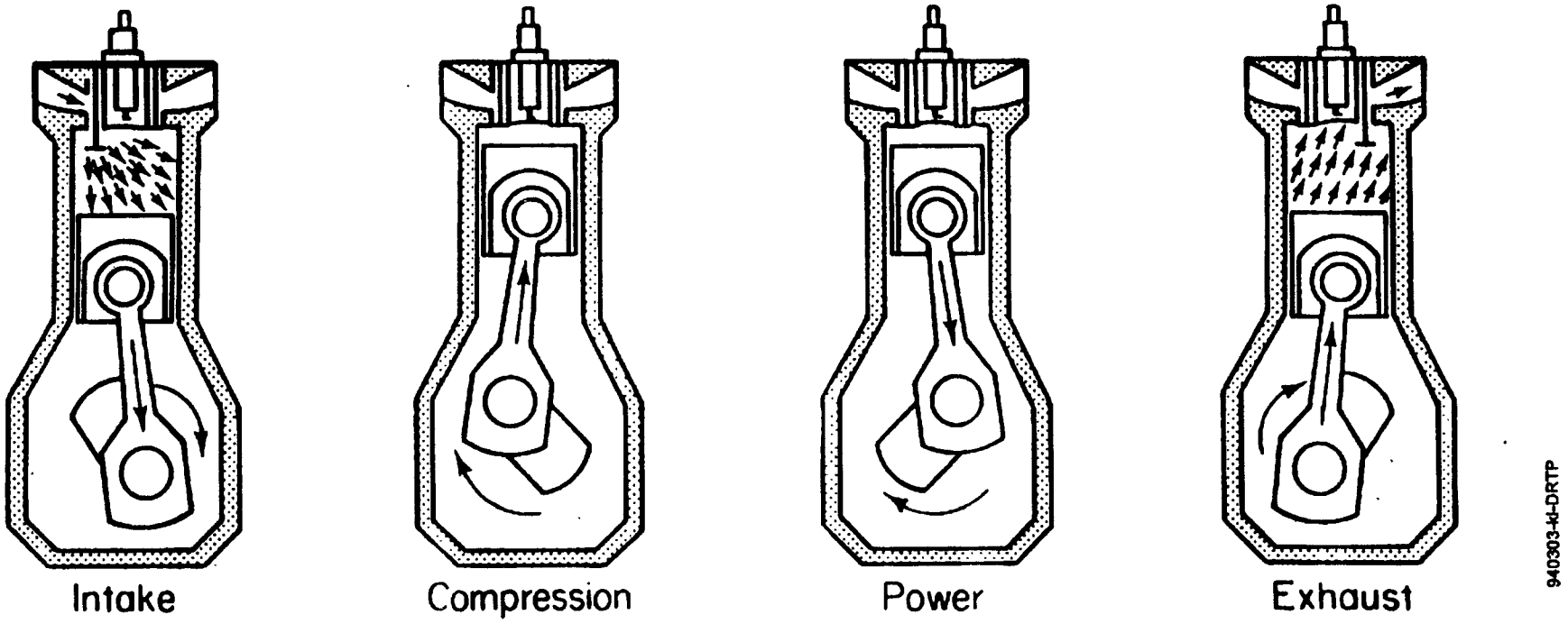


Figure 7-16. Basic Operation of Reciprocating Internal Combustion Engines

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

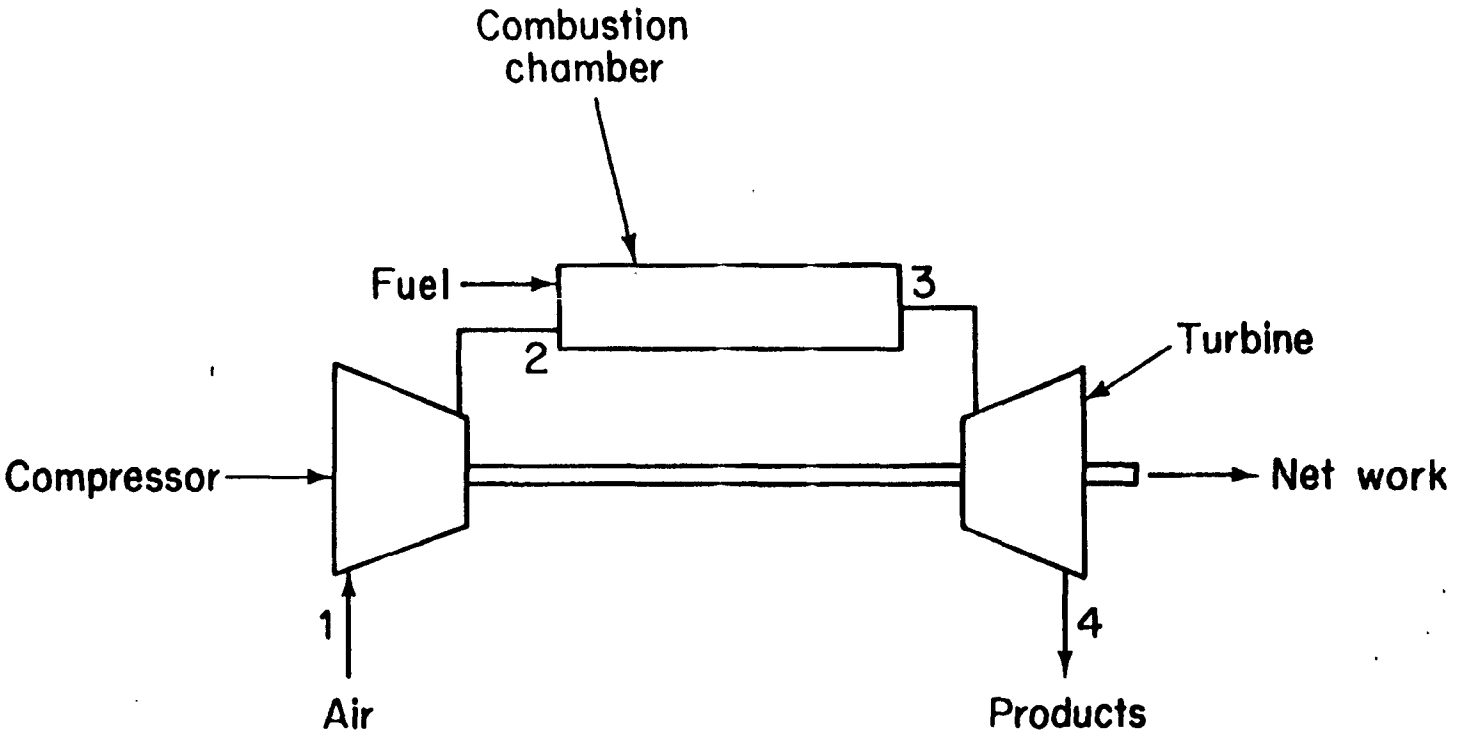


Figure 7-17. Gas Turbine Engine Configuration

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.

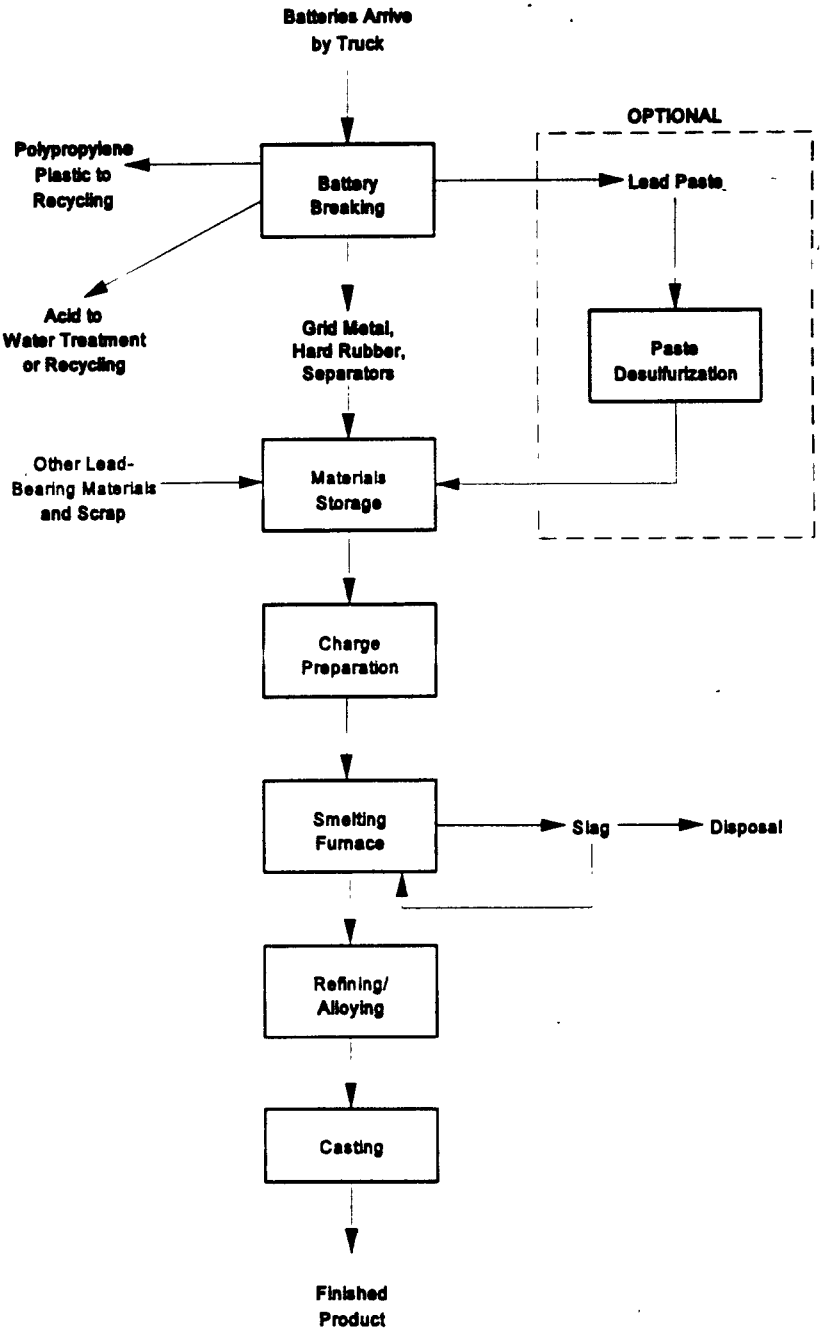


Figure 7-18. Simplified Process Flow Diagram for Secondary Lead Smelting

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

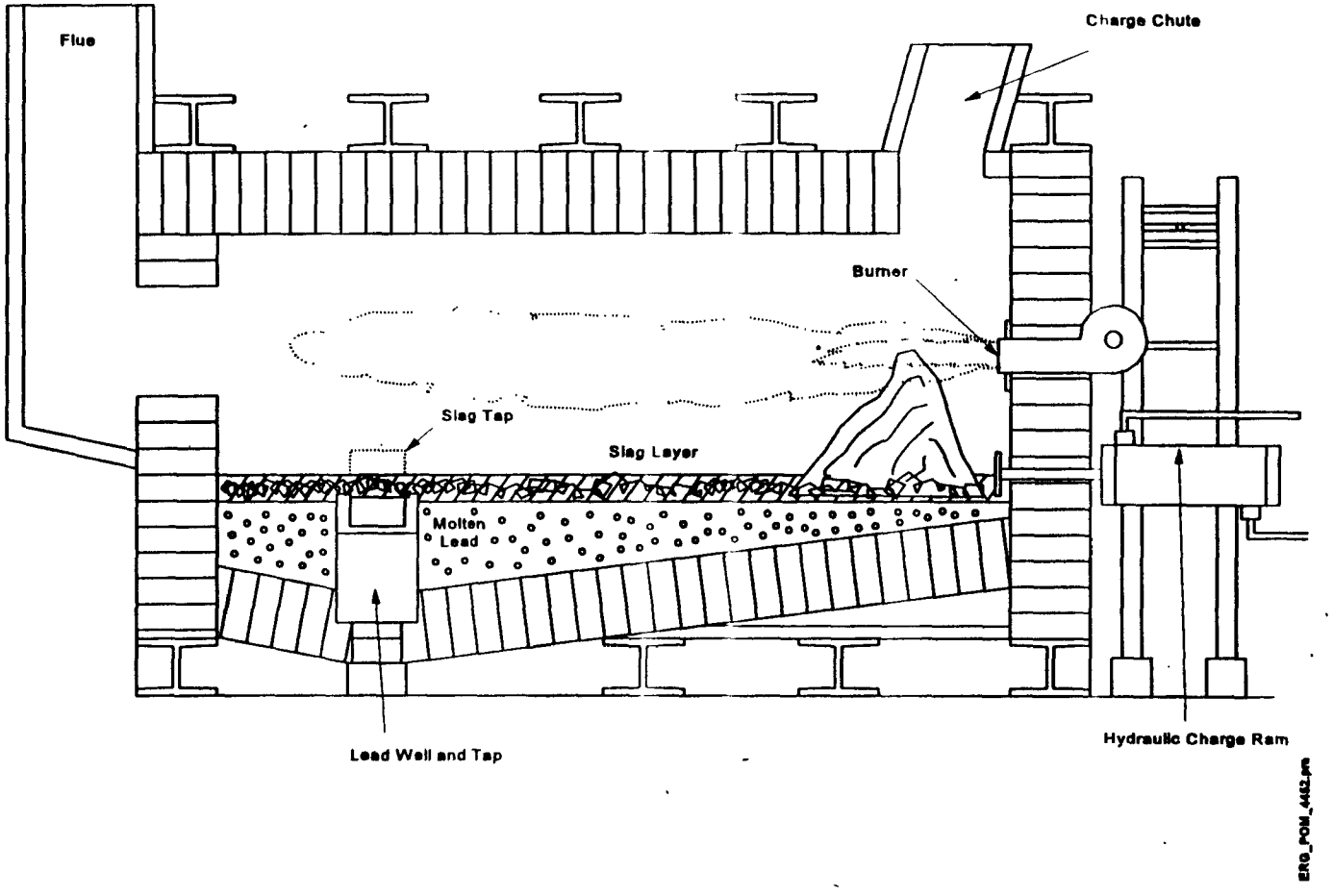


Figure 7-19. Cross-sectional View of a Typical Stationary Reverberatory Furnace

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.

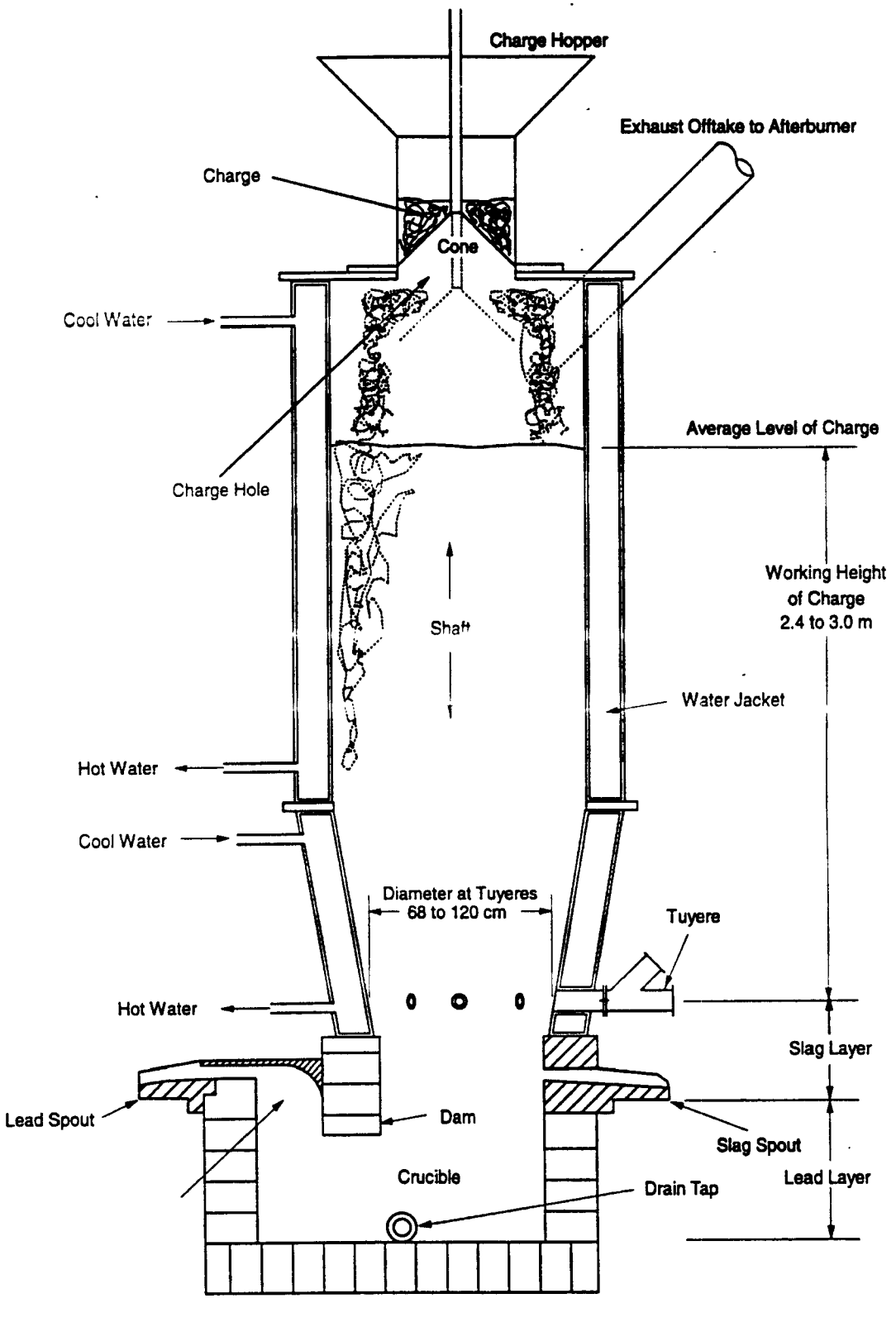


Figure 7-20. Cross Section of a Typical Blast Furnace

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.

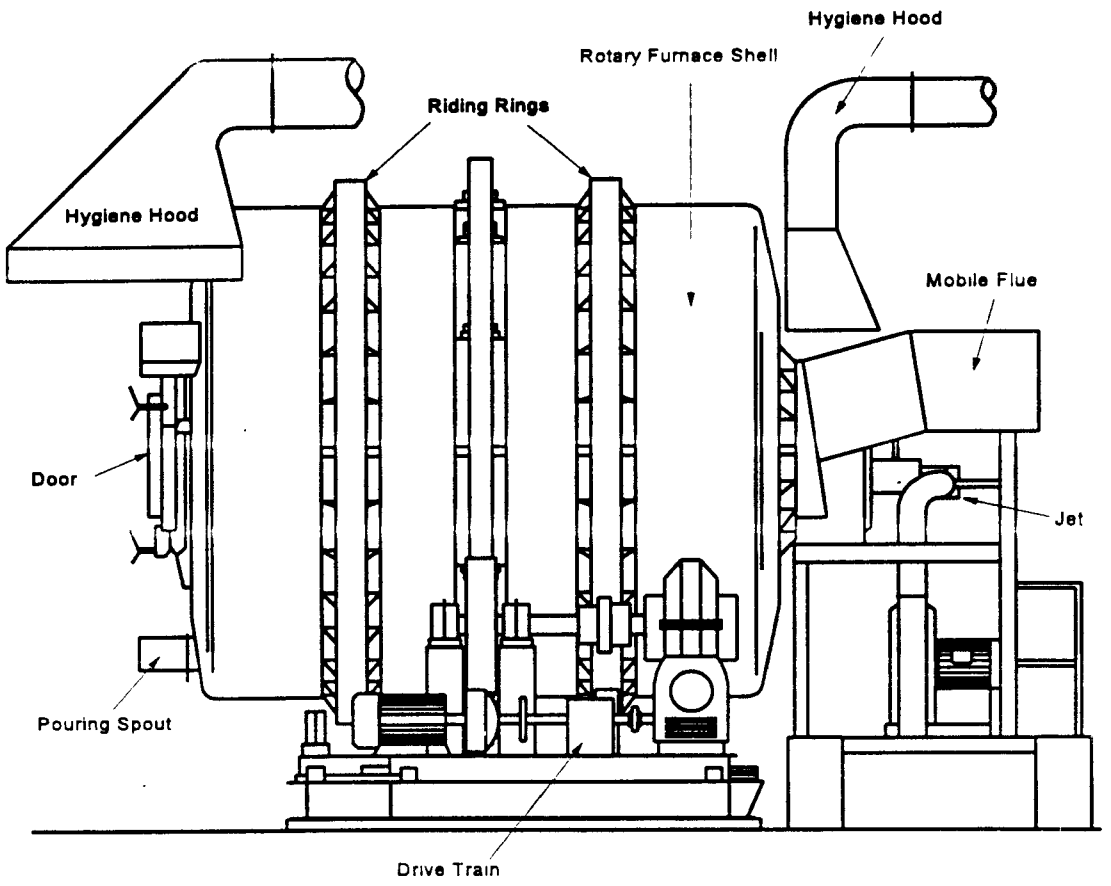


Figure 7-21. Side-view of a Typical Rotary Reverbertory Furnace

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.

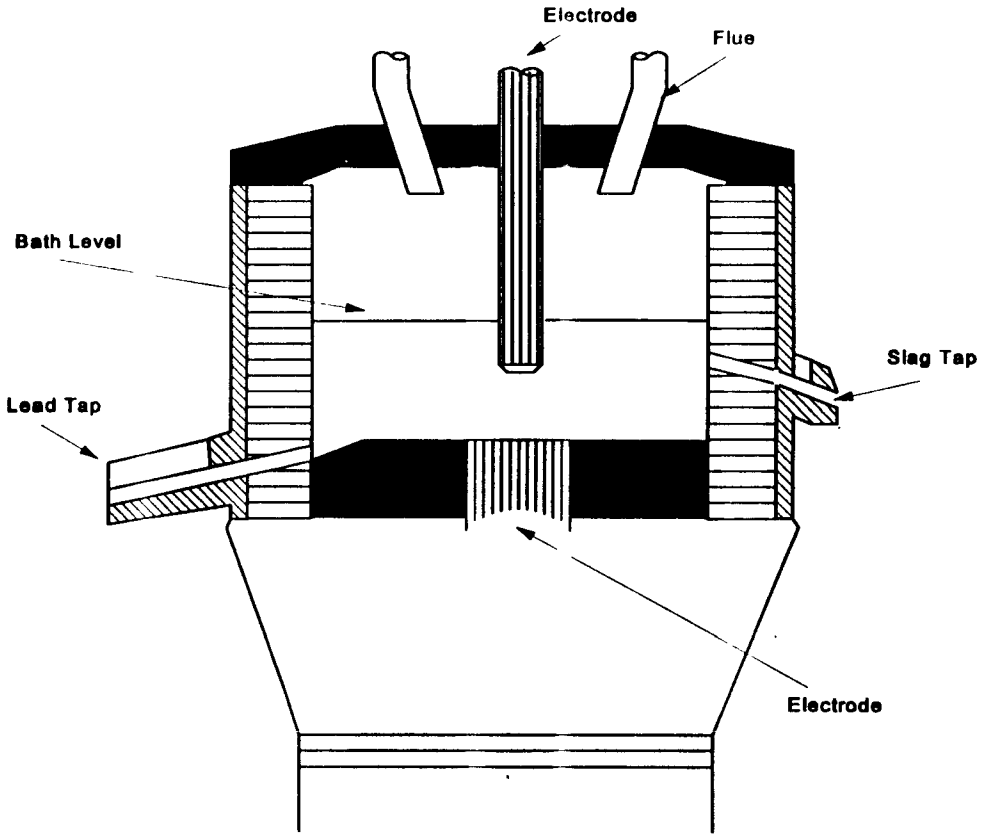


Figure 7-22. Cross-sectional View of an Electric Furnace for Processing Slag

Source: Reference 236.

ERG_Lead_46.pre

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

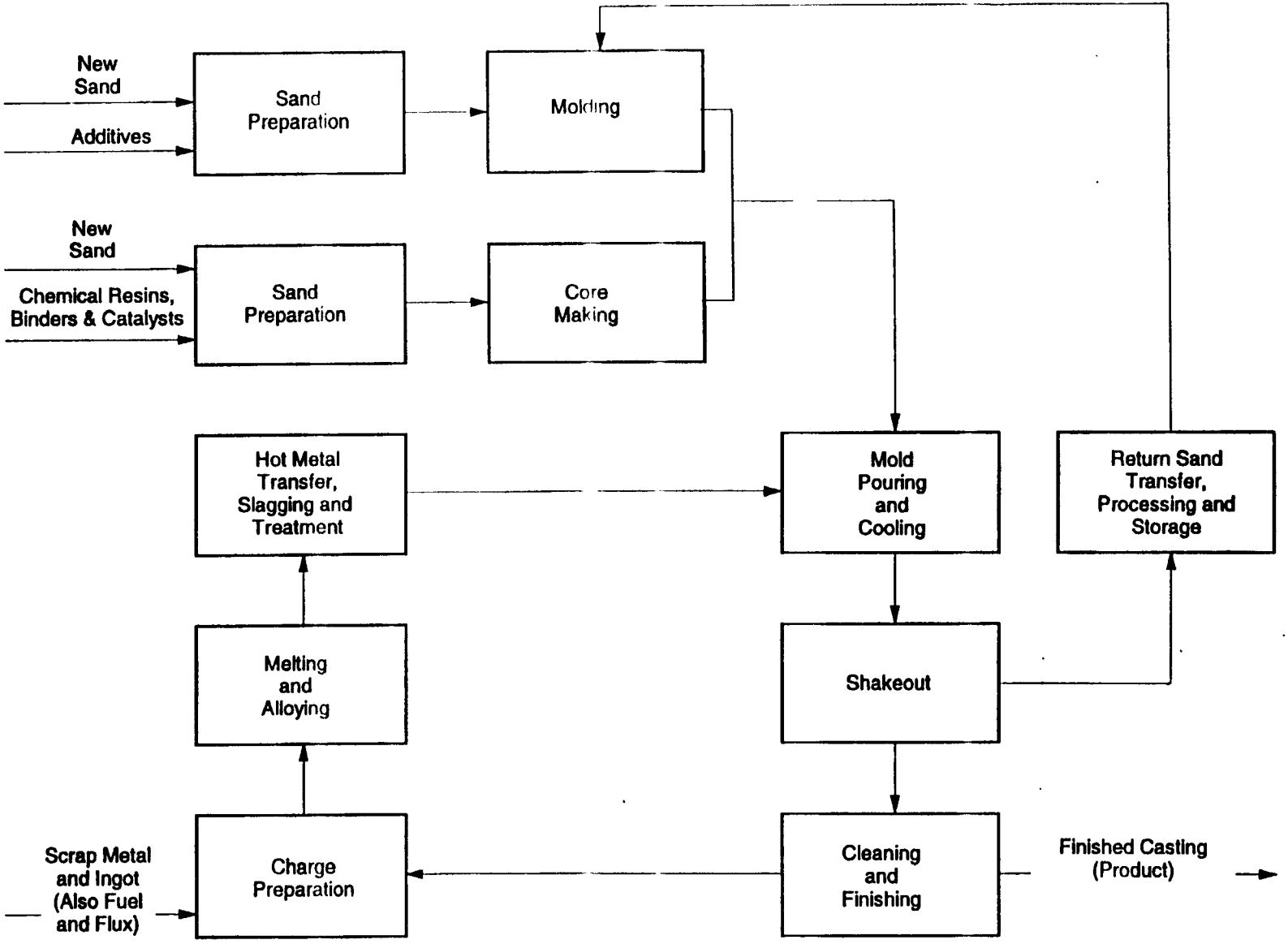


Figure 7-23. Process Flow Diagram for a Typical Sand-Cast Iron and Steel Foundry

Source: Reference 242.

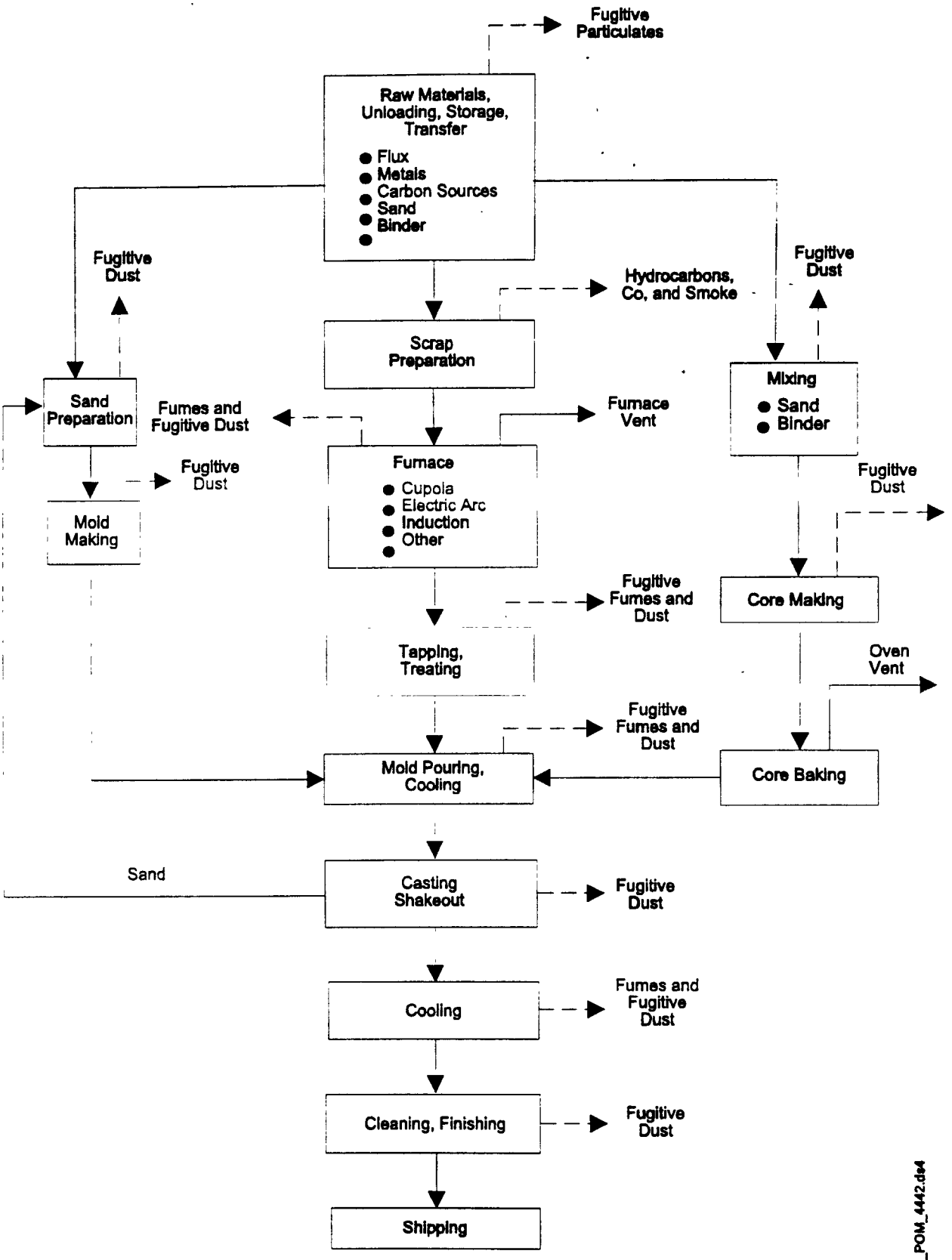


Figure 7-24. Emission Points in a Typical Iron and Steel Foundry

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

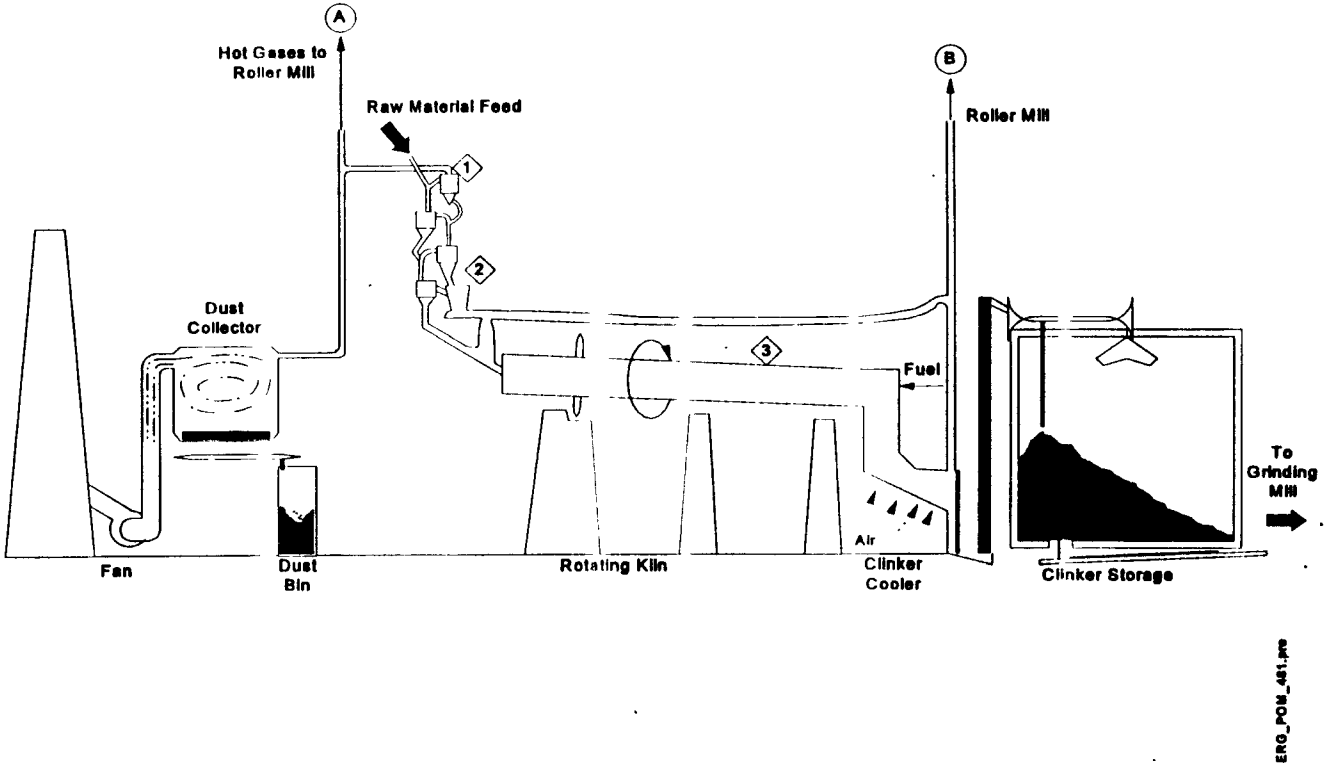


Figure 7-25. Process Diagram of Portland Cement Manufacture by Dry Process With Preheater

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	3.7×10^{-3} (1.8×10^{-3})	B	247, 251
	Kiln--Burning Hazardous Waste and Natural Gas as Fuel	EP	7.5×10^{-3} (3.7×10^{-3})	D	251
	Kiln--Burning Hazardous Waste and Coal at High Combustion Temperature	EP	3.9×10^{-6} (1.9×10^{-6})	D	251
3-05-006-06 Cement Manufacturing - Dry Process	Kiln--Burning Coal in Precalciner Process	FF	1.6×10^{-2} (8×10^{-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.

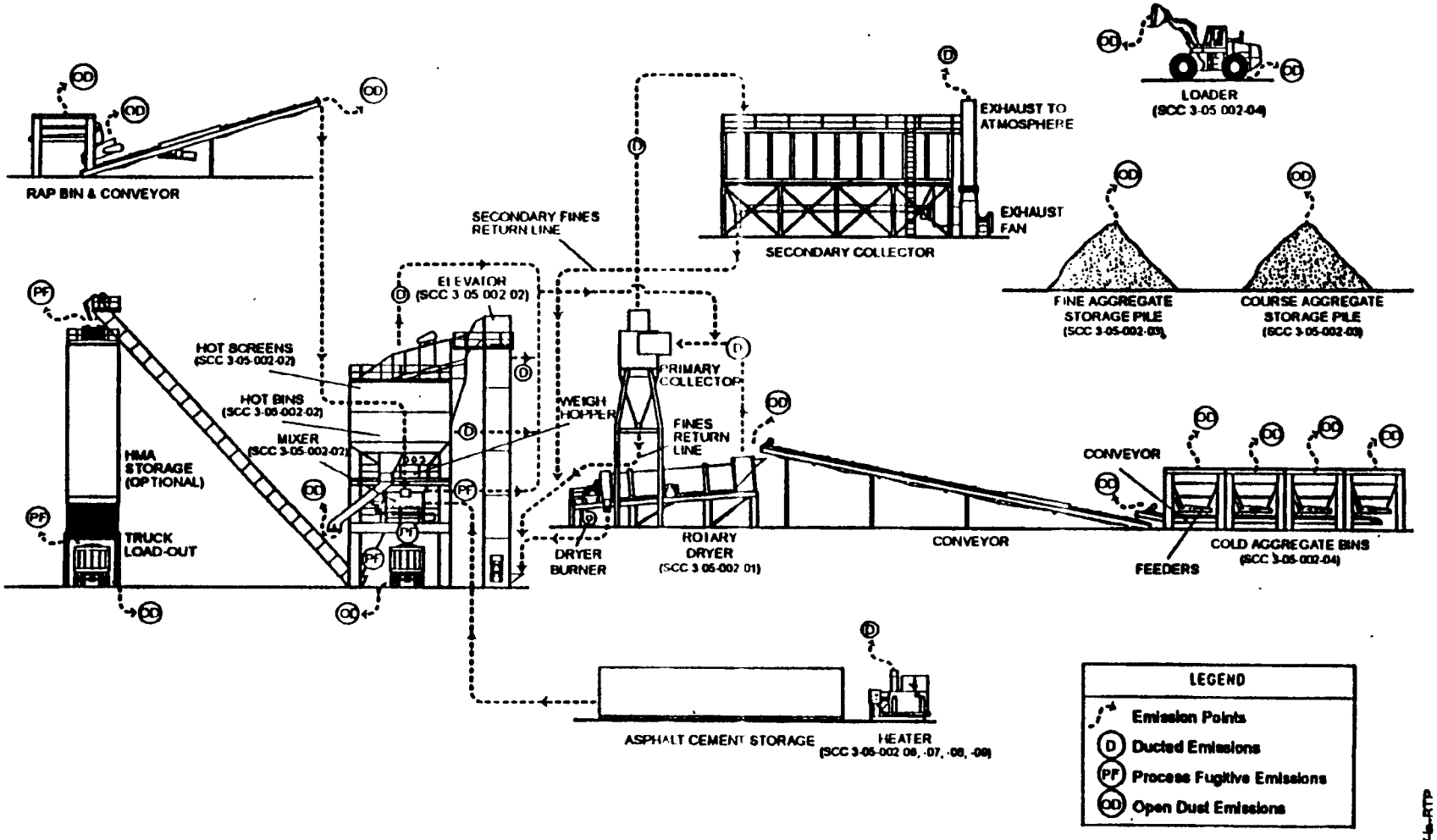


Figure 7-26. General Process Flow Diagram for Batch Mix Asphalt Paving Plants

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

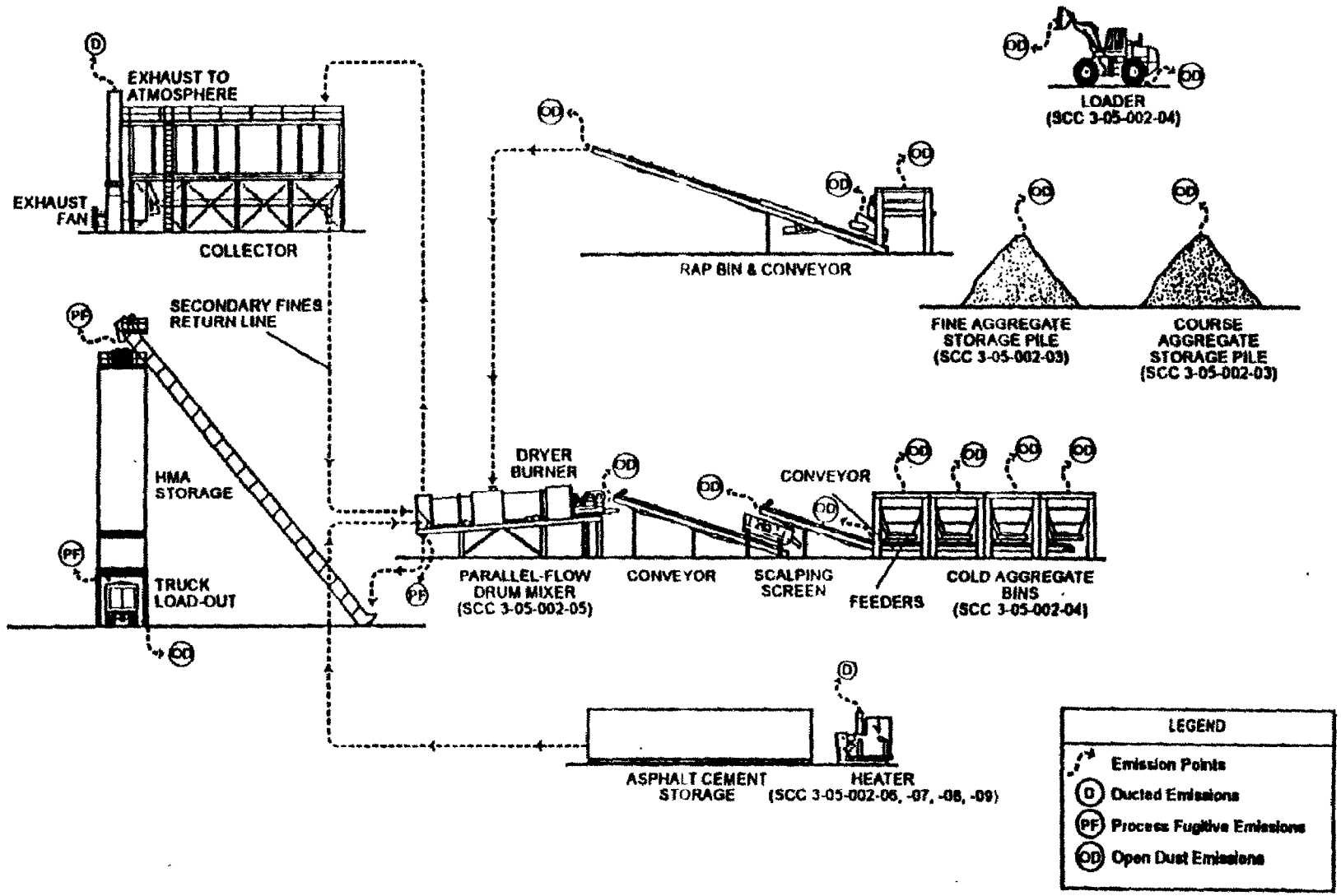


Figure 7-27. General Process Flow Diagram for Drum Mix Asphalt Paving Plants

Source: Reference 252.

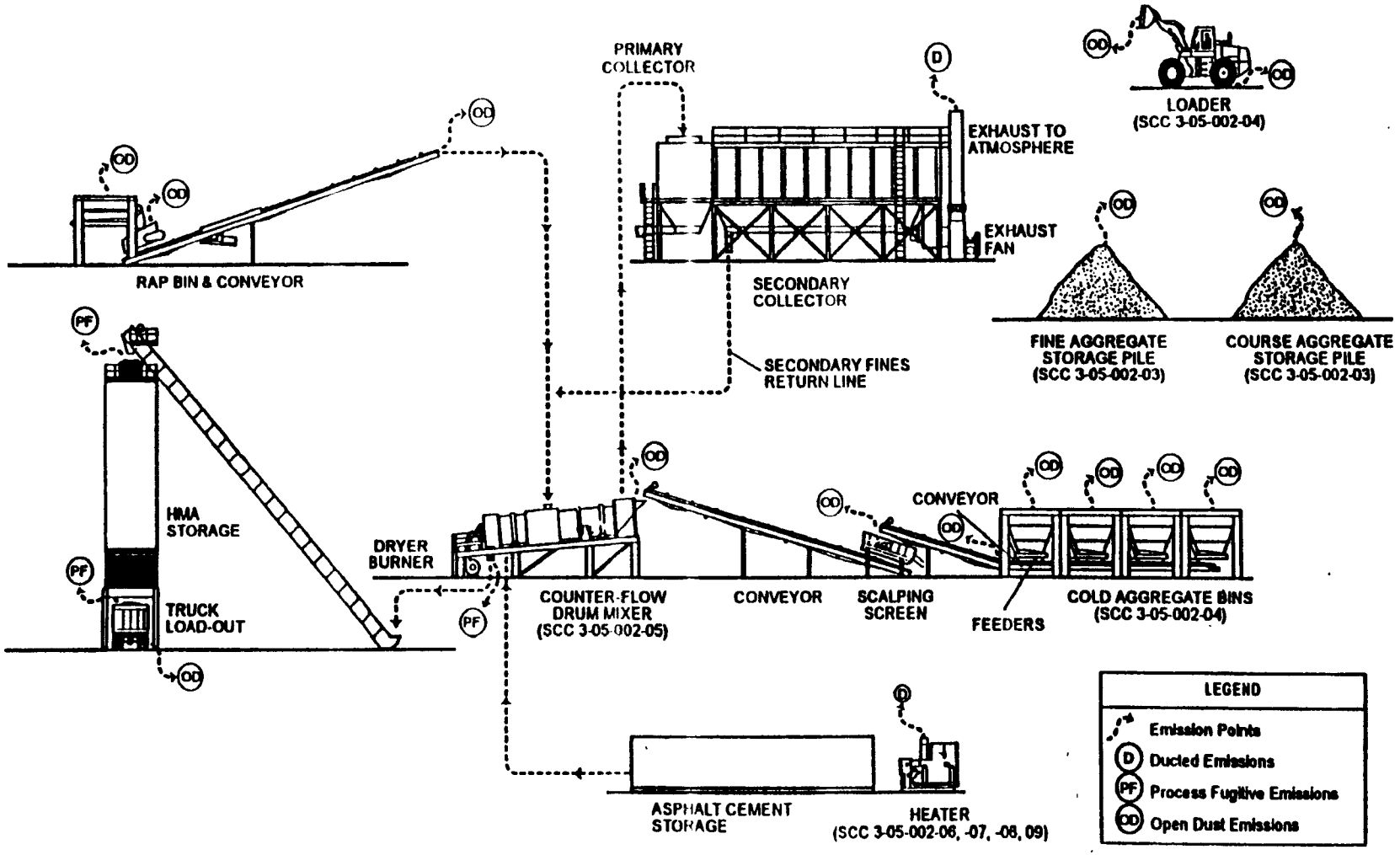


Figure 7-28. General Process Flow Diagram for Counter Flow Drum Mix Asphalt Paving Plants

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	5.35×10^{-4} (2.68×10^{-4})	C	254-256
	Rotary Dryer, oil-fired	Multiple cyclone	7.70×10^{-5} (3.85×10^{-5})	C	3, 257
	Rotary Dryer, natural gas- or oil-fired	Baghouse with single cyclone, knock-out box, or multiple cyclone	2.08×10^{-4} (1.04×10^{-4})	B	258-261
	Rotary Dryer, natural gas- or diesel-fired	Wet scrubber	1.95×10^{-5} (9.75×10^{-6})	C	262, 263
3-05-002-08 Petroleum Industry-Asphalt Concrete-Asphalt heater-Distillate oil	Asphalt Heater, diesel-fired	Uncontrolled	1.50×10^{-4} (7.50×10^{-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).[1] 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.

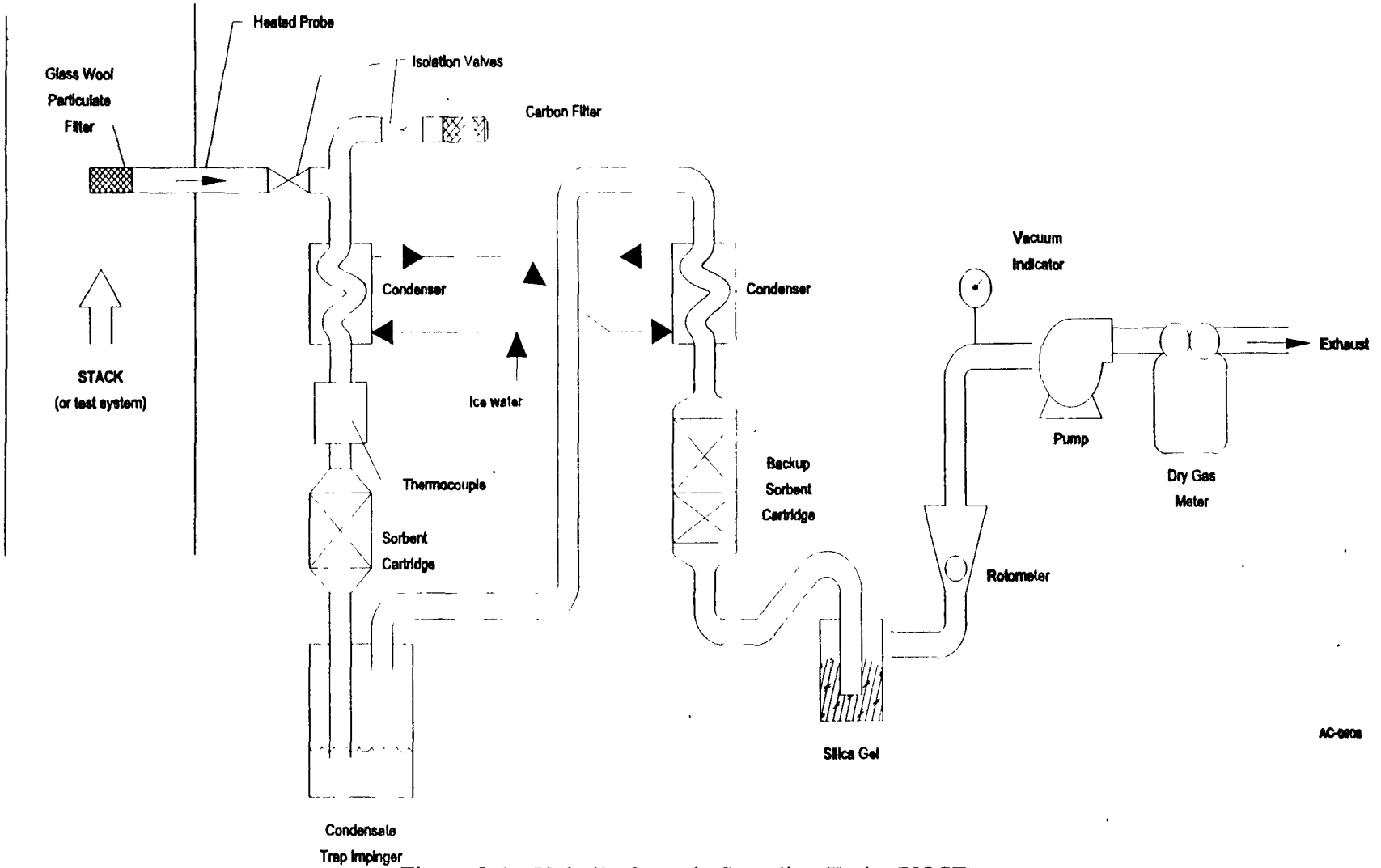


Figure 9-1. Volatile Organic Sampling Train (VOST)

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

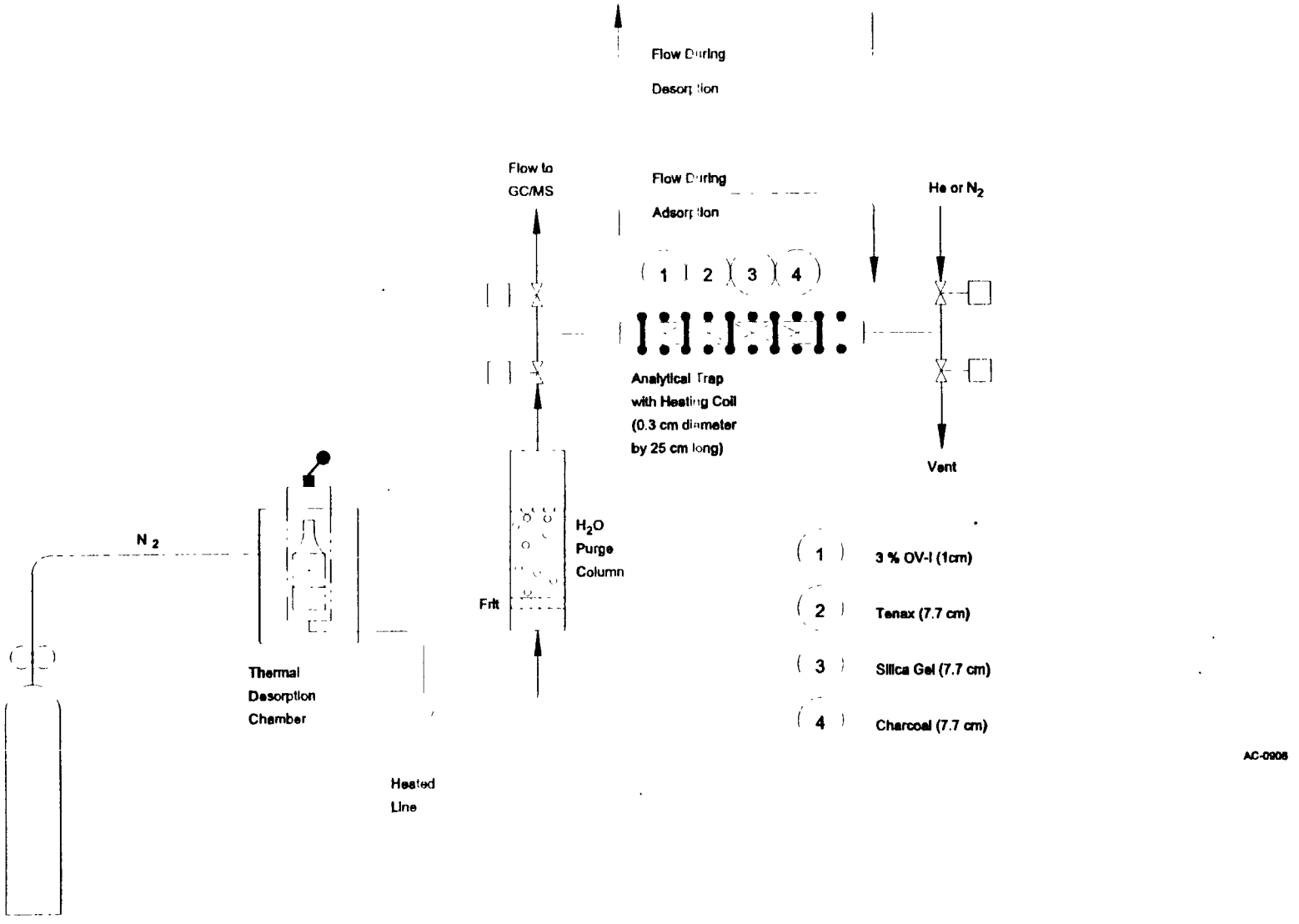


Figure 9-2. Trap Desorption/Analysis Using EPA Methods 5040/5041

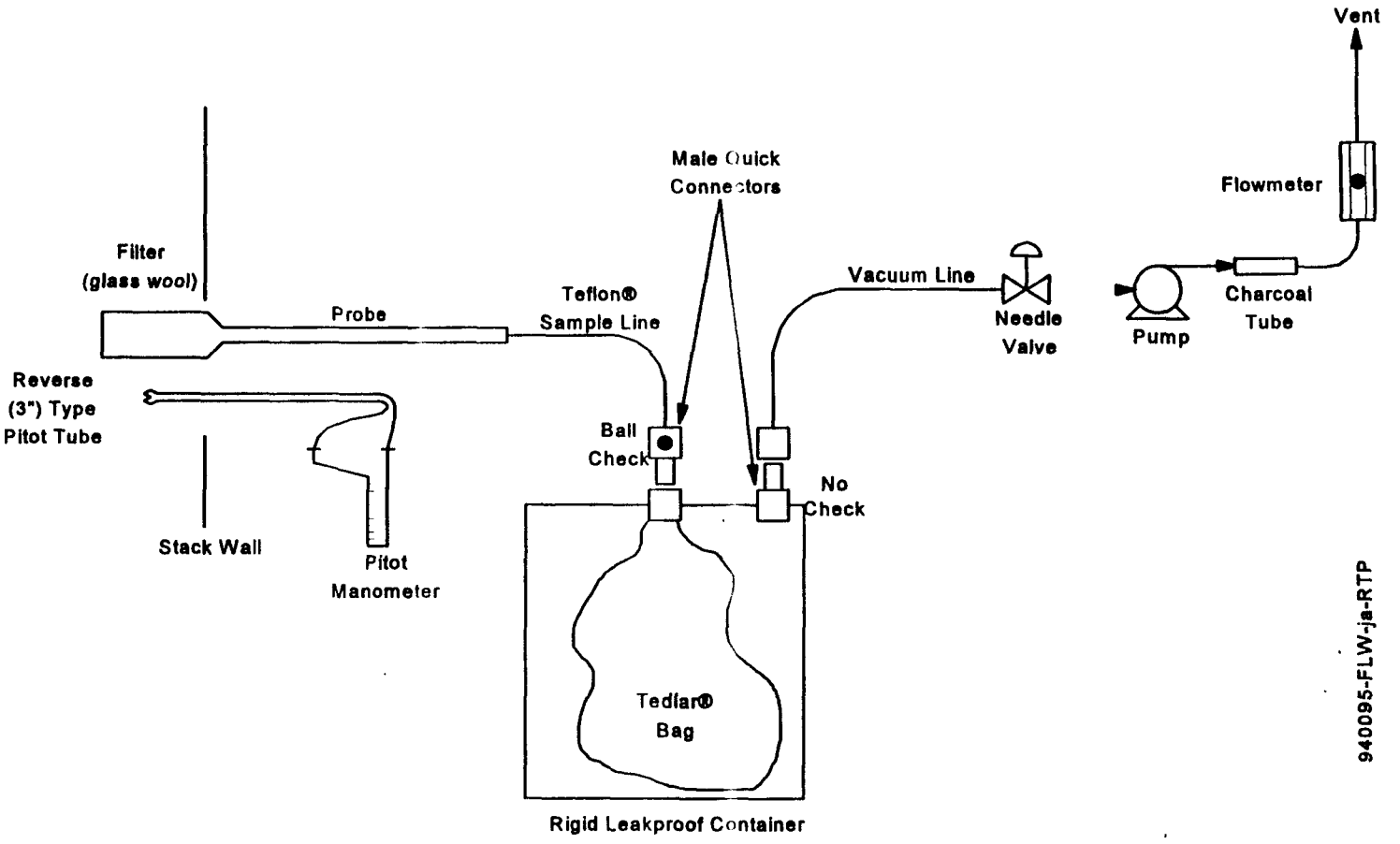


Figure 9-3. Integrated Bag Sampling Train

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

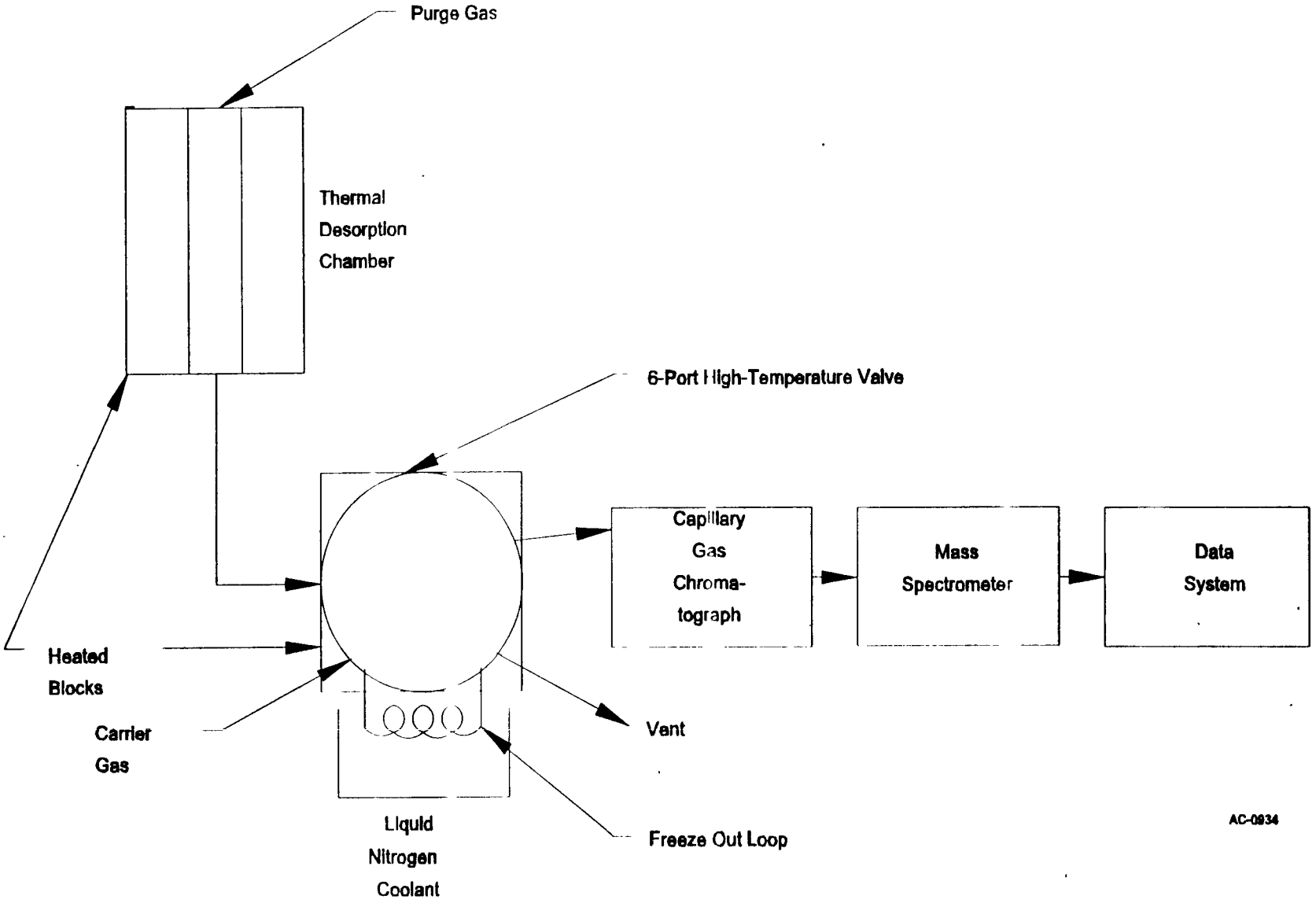
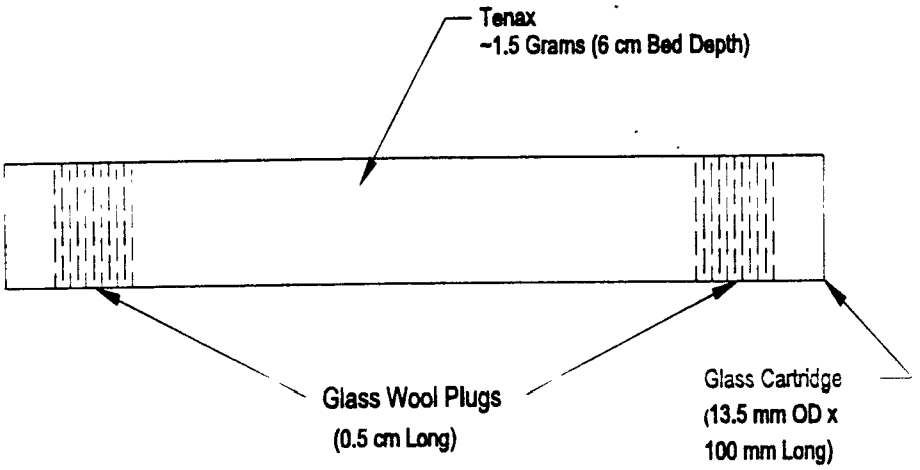
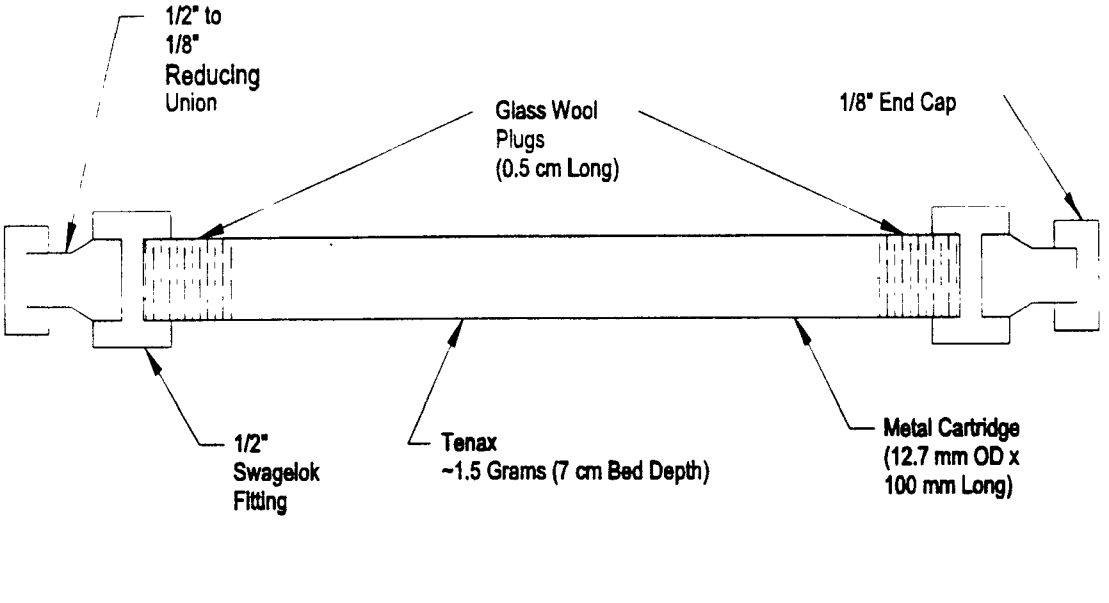


Figure 9-4. Block Diagram of Analytical System for EPA Method TO-1

Source: Reference 289.



(a) Glass Cartridge



(b) Metal Cartridge

Figure 9-5. Typical Tenax® Cartridge

Source: Reference 289.

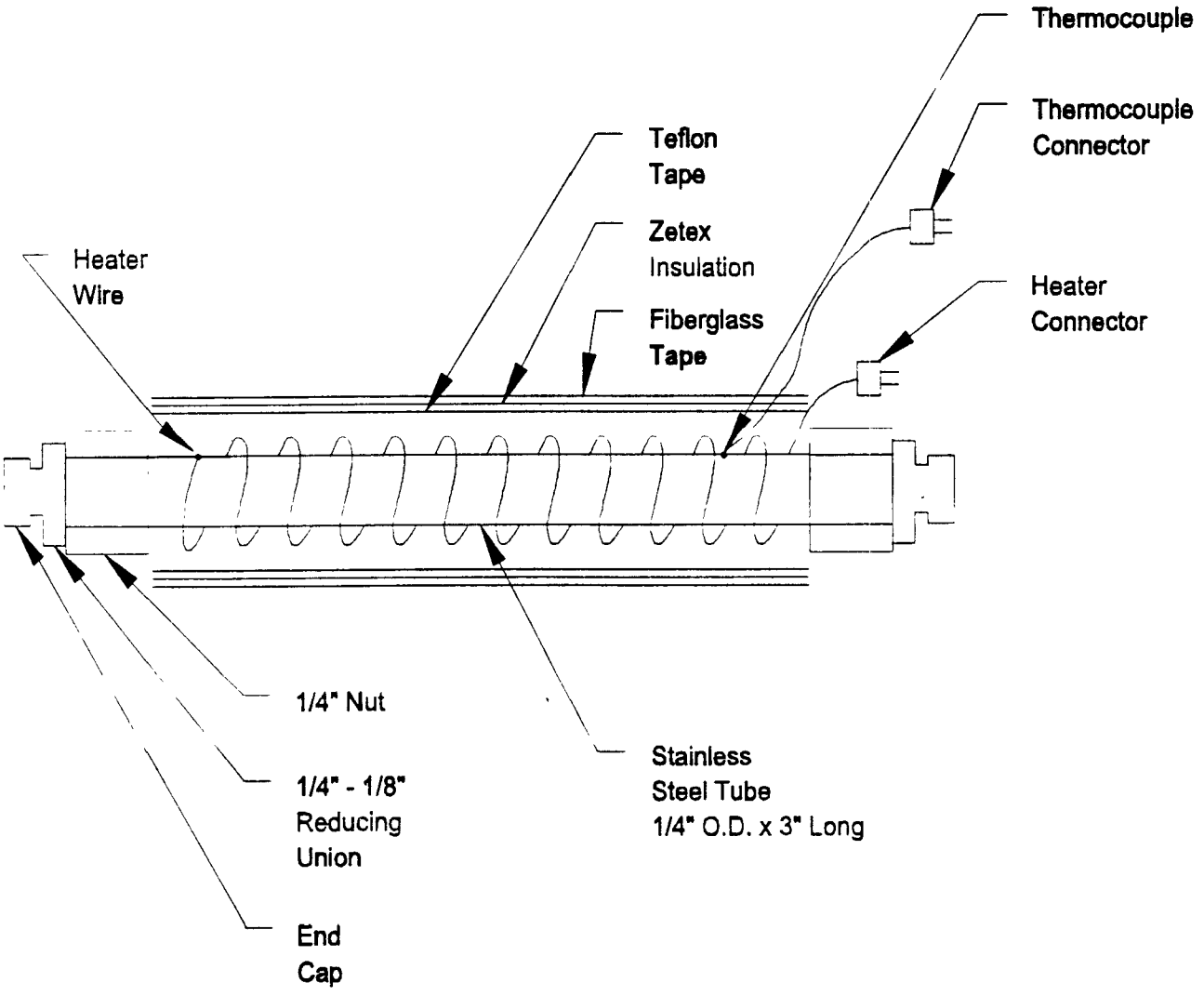


Figure 9-6. Carbon Molecular Sieve Trap (CMS) Construction

Source: Reference 289.

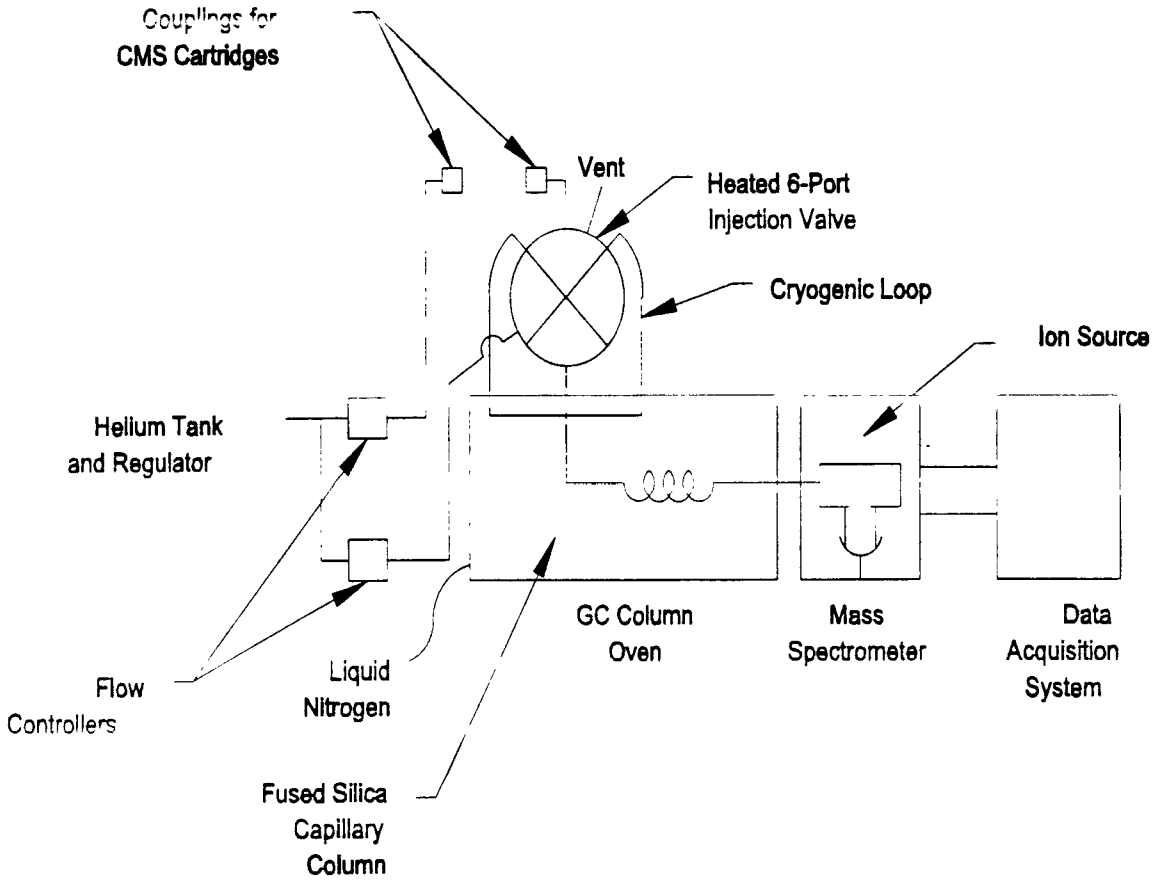


Figure 9-7. GC/MS Analysis System for CMS Cartridges

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.

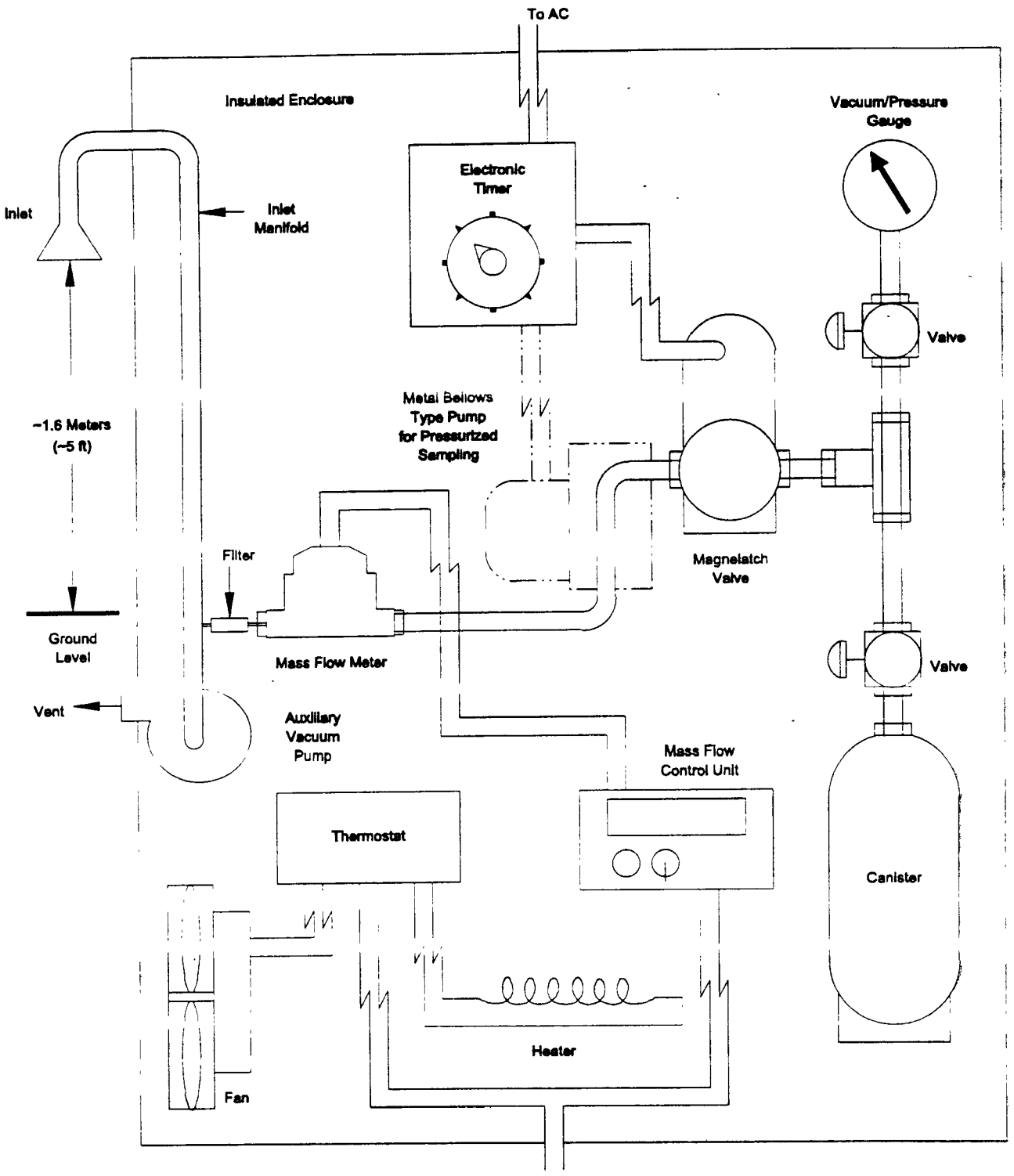


Figure 9-8. Sampler Configuration for EPA Method TO-14

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.

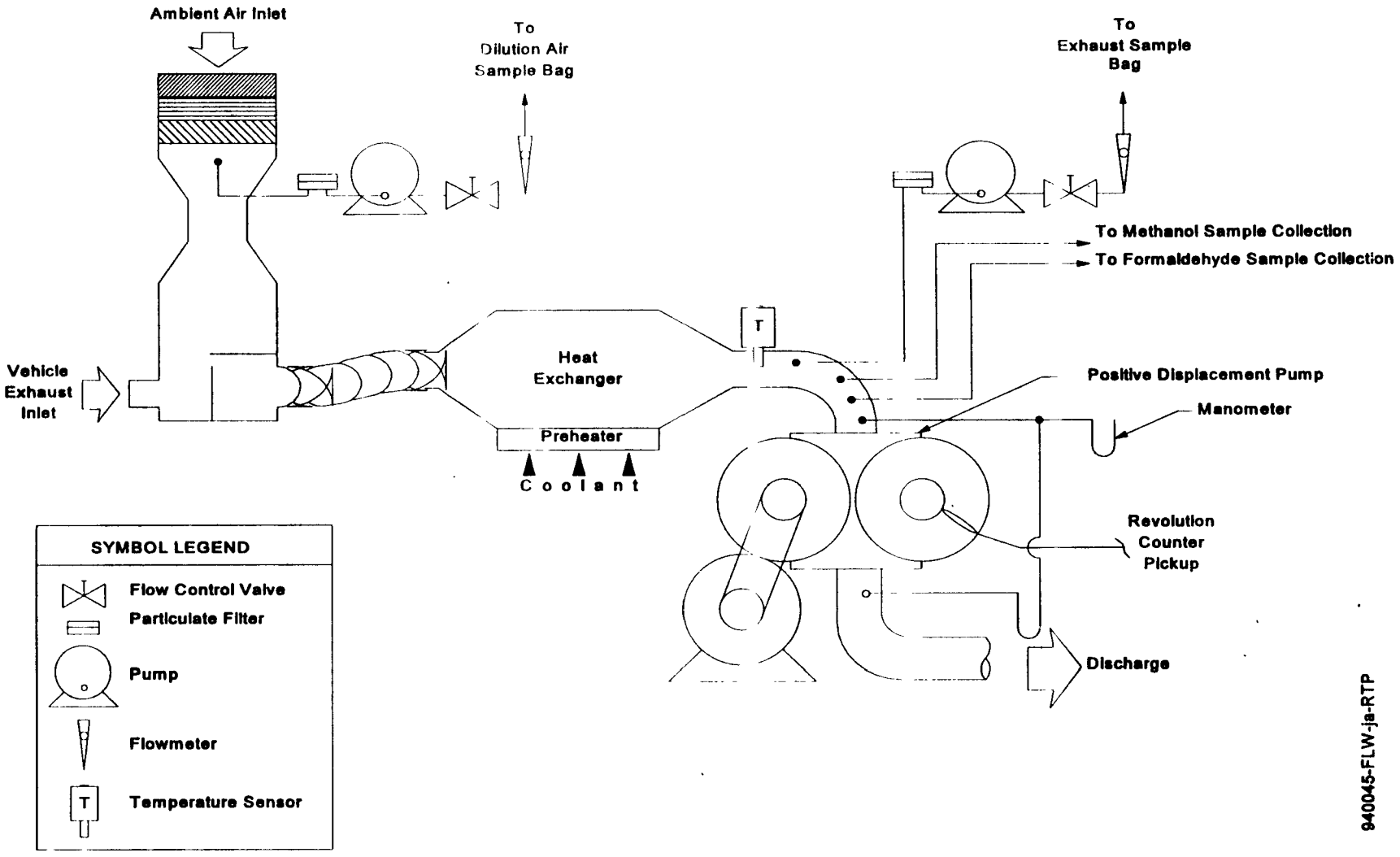


Figure 9-9. Vehicle Exhaust Gas Sampling System

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	2.4×10^{-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	2.4×10^{-4} lb/ton (0.12 g/Mg)	E
		Flushing-Liquor Circulation Tank	Uncontrolled	0.026 lb/ton (13 g/Mg)	E
			Gas Blanketing	5.2×10^{-4} lb/ton (0.26 g/Mg)	E
		Excess-Ammonia Liquor Tank	Uncontrolled	0.018 lb/ton (9 g/Mg)	E
			Gas Blanketing	5.6×10^{-4} lb/ton (0.028 g/Mg)	E
		Wash-Oil Decanter	Uncontrolled	7.6×10^{-3} lb/ton (3.8 g/Mg)	E
			Gas Blanketing	1.5×10^{-4} lb/ton (0.076 g/Mg)	E
		Wash-Oil Circulation Tank	Uncontrolled	7.6×10^{-3} lb/ton (3.8 g/Mg)	E
			Gas Blanketing	1.5×10^{-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	1.9×10^{-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 x 10^{-3} lb/ton (1.0 g/Mg)	E
			Gas Blanketing	4.0 x 10^{-5} lb/ton (0.020 g/Mg)	E
		Wash-Oil Decanter	Uncontrolled	4.2 x 10^{-3} lb/ton (2.1 g/Mg)	E
			Gas Blanketing	8.2 x 10^{-5} lb/ton (0.041 g/Mg)	E
		Wash-Oil Circulation Tank	Uncontrolled	4.2 x 10^{-3} lb/ton (2.1 g/Mg)	E
			Gas Blanketing	8.2 x 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[c]	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[e]	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[1]	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 x 10^{-4} lb/MMBtu (4.73 x 10^{-2} ng/J)	E
3-04-004-03	Secondary Metals - Secondary Lead Production	Blast Furnace (Cupola)	Uncontrolled	4.08 x 10^{-1} lb/ton (2.04 x 10^{-1} kg/Mg)	D
			Afterburner	2.47 x 10^{-2} lb/ton (1.23 x 10^{-2} kg/Mg)	D
3-04-004-04	Secondary Metals - Secondary Lead Production	Rotary Sweating Furnace	Uncontrolled	1.66 x 10^{-1} lb/ton (8.30 x 10^{-2} kg/Mg)	D
3-04-003-98	Secondary Metals - Gray Iron Foundries	Sand Cooling and Belts	Baghouse	6.99 x 10^{-4} lb/ton (3.50 x 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 x 10^{-3} lb/ton (1.8 x 10^{-3} kg/Mg)	B
		Kiln--Burning Hazardous Waste and Natural Gas as Fuel	ESP	7.5 x 10^{-3} lb/ton (3.7 x 10^{-3} kg/Mg)	D
		Kiln--Burning Hazardous Waste and Coal at High Combustion Temperature	ESP	3.9 x 10^{-6} lb/ton (1.9 x 10^{-6} kg/Mg)	D
3-05-006-06	Cement Manufacturing - Dry Process	Kiln--Burning Coal in Precalciner Process	FF	1.6 x 10^{-2} lb/ton (8 x 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

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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

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16. ABSTRACT

TO ASSIST GROUPS INTERESTED IN INVENTORYING AIR EMISSIONS OF VARIOUS POTENTIALLY TOXIC SUBSTANCES, THE U.S. ENVIRONMENTAL PROTECTION AGENCY IS PREPARING A SERIES OF DOCUMENTS, SUCH AS THIS, TO COMPILE AVAILABLE INFORMATION ON SOURCES AND EMISSIONS OF THESE SUBSTANCES. THIS DOCUMENT DEALS SPECIFICALLY WITH BENZENE. ITS INTENDED AUDIENCE INCLUDES, FEDERAL, STATE, AND LOCAL AIR POLLUTION PERSONNEL AND OTHERS INTERESTED IN LOCATING POTENTIAL EMITTERS OF BENZENE AND IN MAKING GROSS ESTIMATES OF AIR EMISSIONS THEREFROM.

THIS DOCUMENT 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 BENZENE RELEASES INTO THE AIR FROM EACH OPERATION.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI FIELD/GROUP
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