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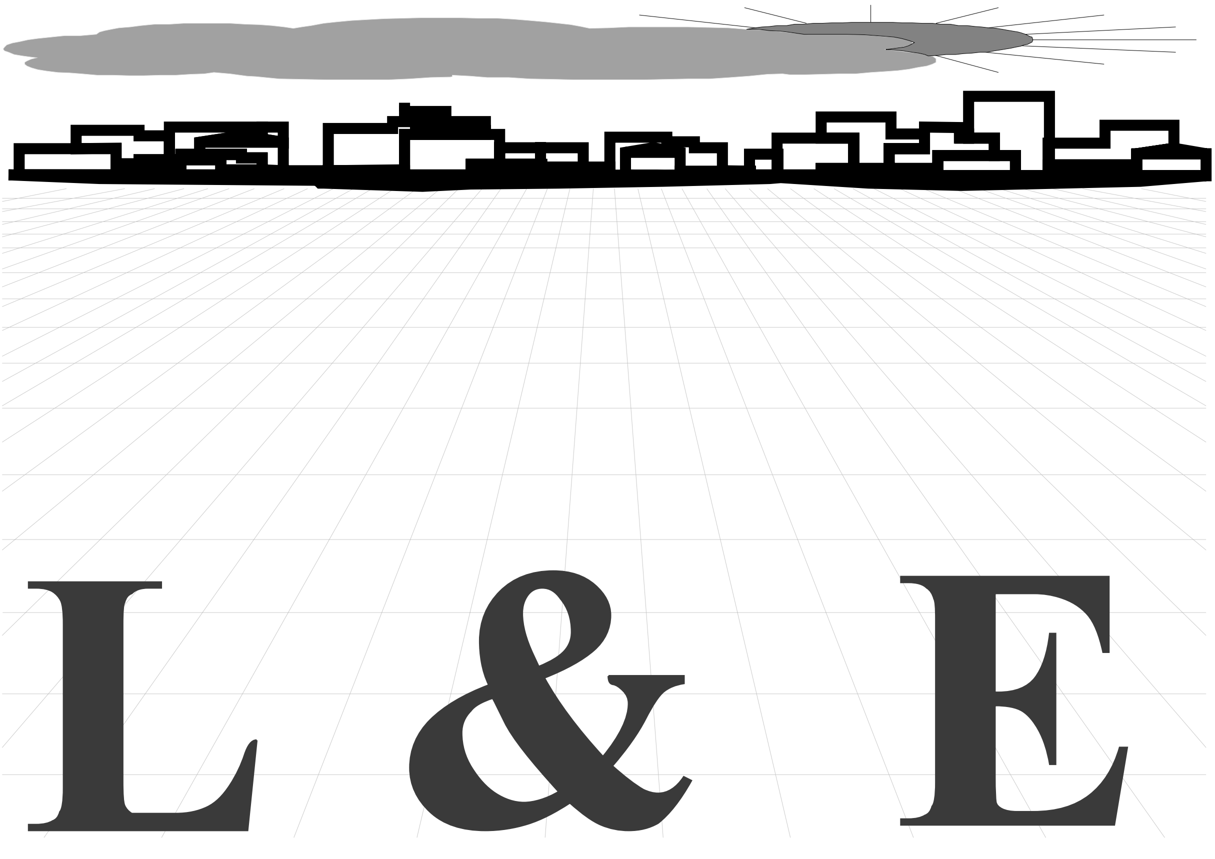
AIR

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.

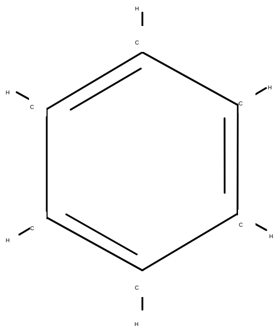


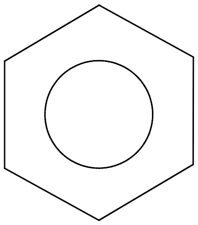
TABLE 3-1. CHEMICAL IDENTIFICATION OF BENZENE

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]

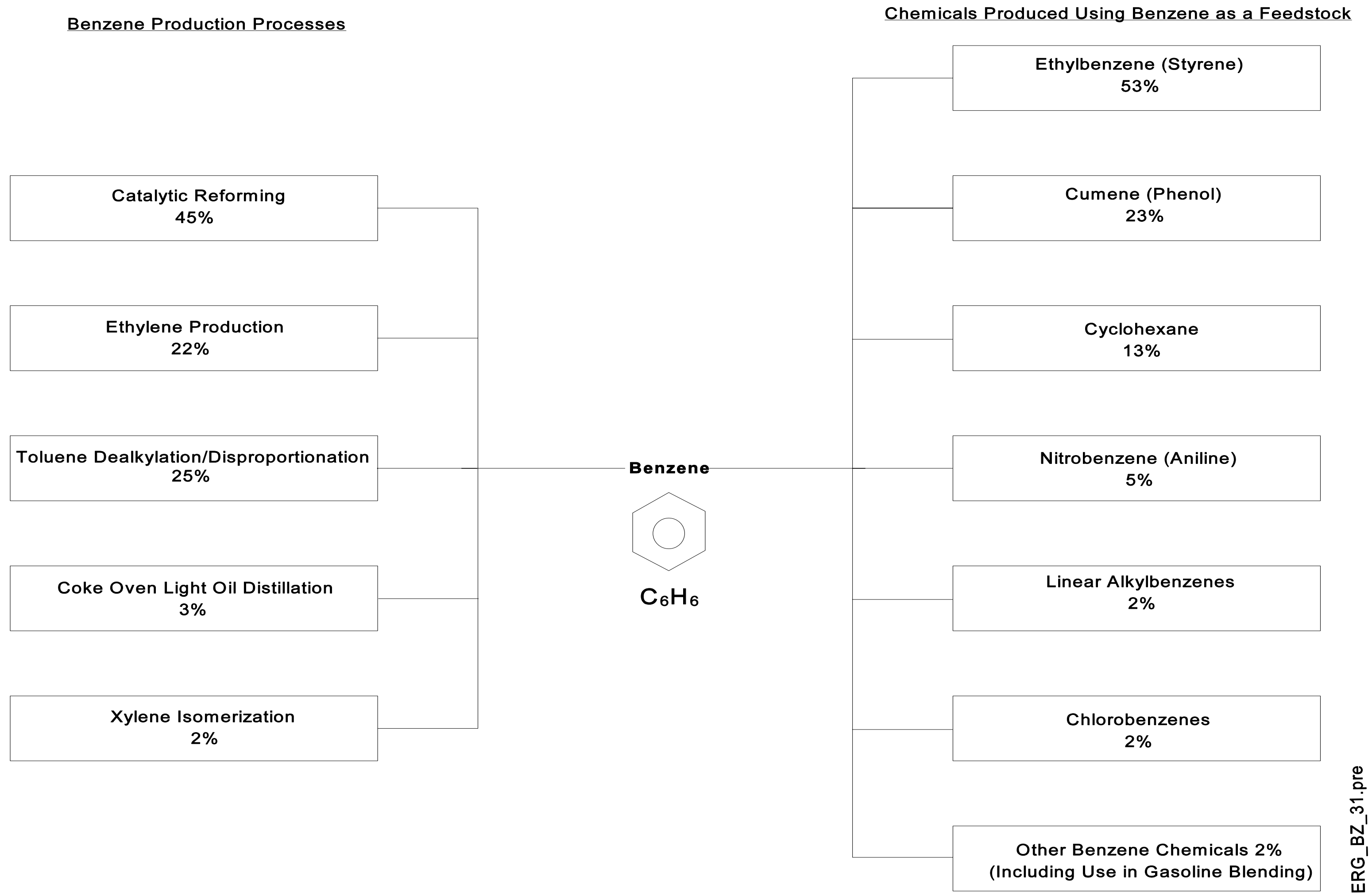


Figure 3-1. Production and Use Tree for Benzene

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	St. Croix, Virgin Islands	75 (284)	Catalytic reformate;
Hess Oil Virgin Islands Corporation, subsidiary			toluene; no captive use
American Petrofina, Incorporated	Port Arthur, Texas	33 (125)	Catalytic reformate; partly captive
Fina Oil and Chemical Company, subsidiary		31 (117)	Toluene; partly captive
Amoco Corporation	Texas City, Texas	85 (322)	Catalytic reformate; partly captive
Amoco Oil Company, subsidiary		25 (95)	Pyrolysis gasoline; partly captive
		12 (45)	Xylene isomerization
Aristech Chemical Corporation	Clairton, Pennsylvania	45 (170)	Coke-oven light oil
Ashland Oil, Incorporated	Catlettsburg, Kentucky	55 (208)	Coke-oven light oil; captive
Ashland Chemical Company, division		2 (8)	Catalytic reformate; captive
Petrochemicals Division			
Atlantic Richfield Corporation	Channelview, Texas	90 (341)	Pyrolysis gasoline; captive
Lyondell Petrochemical Company, subsidiary	Houston, Texas	35 (132)	Catalytic reformate; no captive use
		15 (57)	Toluene; no captive use

(continued)

TABLE 4-1. CONTINUED

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
BP Oil	Alliance, Louisiana	18 (68)	Catalytic reformate; no captive use
		47 (178)	Toluene
	Lima, Ohio	35 (132)	Catalytic reformate; no captive use
		80 (303)	Toluene
Chevron Corporation	Philadelphia, Pennsylvania	24 (91)	Catalytic reformate; captive
Chevron Chemical Company, subsidiary		21 (79)	Toluene; captive
Aromatics and Derivatives Division	Port Arthur, Texas	42 (159)	Catalytic reformate; partly captive
		24 (91)	Pyrolysis gasoline; partly captive
		35 (132)	Toluene; partly captive
Citgo Petroleum Corporation	Corpus Christi, Texas	55 (208)	Catalytic reformate; captive
		23 (87)	Toluene
Coastal Eagle Point Oil Co.	Westville, New Jersey	15 (57)	Catalytic reformate
Coastal Refining and Marketing, Inc.	Corpus Christi, Texas	50 (189)	Toluene; captive use
		7 (26)	Catalytic reformate
Dow Chemical U.S.A.	Freeport, Texas	25 (95)	Pyrolysis gasoline; captive
	Plaquemine, Louisiana	80 (303)	Pyrolysis gasoline; captive
		120 (454)	Toluene; captive

(continued)

TABLE 4-1. CONTINUED

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Exxon Corporation Exxon Chemical Company, division Exxon Chemical Americas	Corpus Christi, Texas	50 (189)	Pyrolysis gasoline
		30 (114)	Toluene
	Baton Rouge, Louisiana	50 (189)	Catalytic reformate
		30 (114)	Pyrolysis gasoline; no captive use
	Baytown, Texas	75 (284)	Catalytic reformate; no captive use
		20 (76)	Pyrolysis gasoline
		20 (76)	Xylene isomerization
		23 (87)	Toluene
Huntsman Chemical Corporation	Bayport, Texas	15 (57)	Toluene; captive
Kerr-McGee Corporation Southwestern Refining Company, Incorporated, subsidiary	Corpus Christi, Texas	17 (64)	Catalytic reformate; no captive use
Koch Industries, Incorporated Koch Refining Company, subsidiary	Corpus Christi, Texas	25 (95)	Catalytic reformate; captive
		55 (208)	Toluene; captive
		10 (38)	Xylene isomerization
		50 (189)	Toluene
Mobil Corporation Mobil Oil Corporation Mobil Chemical Company, division Petrochemicals Division U.S. Marketing and Refining Division	Beaumont, Texas	90 (341)	Catalytic reformate; no captive use
		10 (38)	Pyrolysis gasoline
	Chalmette, Louisiana	20 (76)	Catalytic reformate; no captive use

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Occidental Petroleum Corporation Petrochemicals Olefins and Aromatics Division	Chocolate Bayou, Texas	60 (227) 40 (151)	Pyrolysis gasoline Toluene
Phibro Energy USA, Inc.	Houston, Texas	5 (19)	Catalytic reformate; no captive use
Phillips Petroleum Company Chemicals Division Olefins and Cyclics Branch	Sweeny, Texas	11 (42)	Catalytic reformate; captive
Phillips Puerto Rico Core, Incorporated, subsidiary	Guayama, Puerto Rico	35 (132) 48 (182)	Catalytic reformate; captive Toluene; captive
Shell Oil Company Shell Chemical Company, division	Deer Park, Texas	75 (284) 80 (303)	Catalytic reformate; partly captive Pyrolysis gasoline; partly captive
	Wood River, Illinois	50 (189)	Catalytic reformate; no captive use
Sun Company, Incorporated Sun Refining and Marketing Company, Incorporated, subsidiary	Marcus Hook, PA	26 (98) 11 (42)	Catalytic reformate; no captive use Toluene; no captive use
	Toledo, Ohio	19 (72)	Catalytic reformate

(continued)

TABLE 4-1. BENZENE PRODUCTION FACILITIES

Company Name	Location	Annual Capacity million gal (million L)	Production Processes[a]
Texaco, Incorporated	El Dorado, Kansas	15 (57)	Catalytic reformate; captive
Texaco Chemical Company, subsidiary	Port Arthur, Texas	46 (174)	Catalytic reformate; captive
		20 (76)	Pyrolysis gasoline; captive
The UNO-VEN Company	Lemont, Illinois	12 (45)	Catalytic reformate
		7 (26)	Coke-oven light oil; no captive
USX Corporation	Lake Charles, Louisiana	55 (208)	Catalytic reformate; captive
Marathon Oil Company, subsidiary	Texas City, Texas	7 (26)	Toluene
Marathon Petroleum Company, subsidiary			
TOTAL		2,350(8,896)	

Source: Reference 11.

[a] Captive means used for subsequent processes on site.

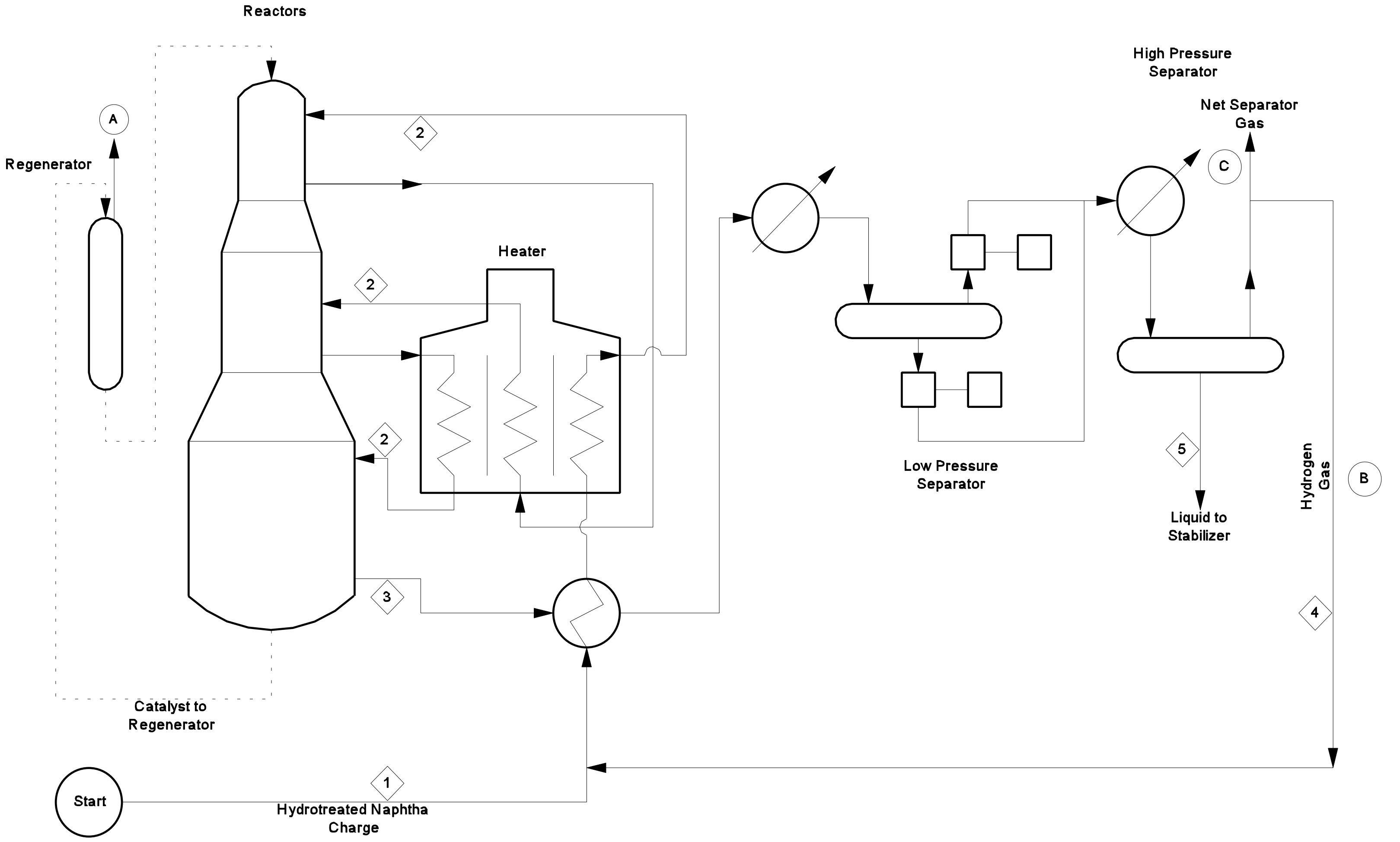
Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel. Reference SRI '93 indicates these data reflect changes made in product locations as of January 1993.

4.1 CATALYTIC REFORMING/SEPARATION PROCESS

Production of benzene by reforming/separation is associated with the production of toluene and xylene (BTX plants). Catalytic reforming is used to prepare high-octane blending stocks for gasoline production and for producing aromatics as separate chemicals. The reforming process, shown in Figure 4-1,[22] accounts for about 45 percent of all benzene produced in the United States.[12] In the following description of the reforming process, potential emission points are identified; however, not all of the emission points discussed in this section are always present at plants using this production process. Some companies have indicated that they have closed systems; others have indicated that process vent emissions are well-controlled by flares or scrubbers.[22]

4.1.1 Process Description for Catalytic Reforming/Separation

The reforming process used at BTX plants (shown in Figure 4-1) can greatly increase the aromatic content of petroleum fractions by such reactions as dehydrogenation, isomerization and dehydrogenation, or cyclization. The usual feedstock in this process is a straight-run, hydrocracked, thermally cracked, or catalytically cracked naphtha. After the naphtha is hydrotreated to remove sulfur (Stream 1), it is mixed with recycled hydrogen (Stream 4) and heated. This feed (Stream 2) is sent through catalytic reactors in which the catalyst, usually platinum or rhenium chloride, converts paraffins to aromatic compounds. The product stream (Stream 3) consists of excess hydrogen and a reformate rich in aromatics. Products from the reactor (Stream 3) are fed to the separation section, which separates the hydrogen gas from the liquid product. The hydrogen gas can be recycled to the reactor (Stream 4). The liquid product from the separator (Stream 5) is fed to a stabilizer (not shown in the figure).[22] The stabilizer is a fractionator in which more volatile, light hydrocarbons are removed from the high-octane liquid product. The liquid is then sent to a debutanizer (not shown in the figure). Aromatics (benzene, toluene, and mixed xylenes) are then extracted from the stabilized reformate.[22]



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

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

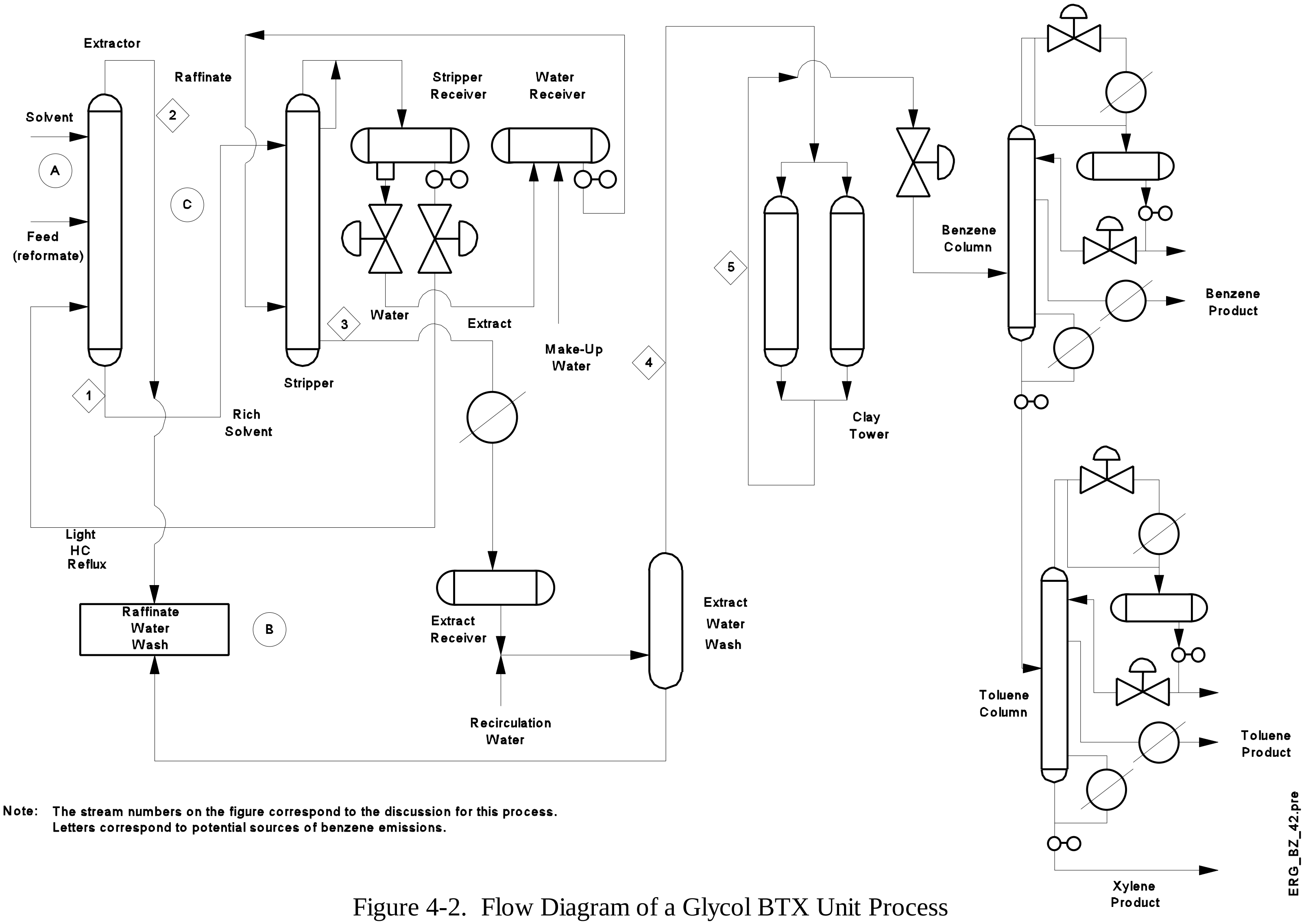
Source: Reference 22.

Numerous solvents are available for the extraction of aromatics from the stabilized reformate stream. Glycols (tetraethylene glycol) and sulfolane (1,1-tetrahydrothiophene dioxide) are most commonly used. The processes in which these solvents are used are similar, so only the glycol process is described here. In the glycol process shown in Figure 4-2, aromatics are separated from the reformate in the extractor.[22] The raffinate (stream 2) is water-washed and stored. The dissolved aromatics extract (Stream 1) is steam-stripped and the hydrocarbons separated from the solvent. The hydrocarbon stream (Stream 3) is water-washed to remove remaining solvent and is then heated and sent through clay towers to remove olefins (Stream 4). Benzene, toluene, and xylene (Stream 5) are then separated by a series of fractionation steps.[22]

4.1.2 Benzene Emissions from Catalytic Reforming/Separation

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the catalytic reforming/separation process is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points from this process, the reader is referred to Section 4.5 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

A literature search, a review of materials in the docket (A-79-27) for some National Emission Standards for Hazardous Air Pollutants (NESHAP) efforts on benzene, and information provided by the benzene production industry revealed no source-specific emission factors for benzene from catalytic reforming/separation.[22] However, information provided by the benzene production industry indicates that BTX is commonly produced in closed systems, and that any process vent emissions are well-controlled by flares and/or scrubbers. (See Section 4.5 of this chapter for a discussion of control devices.)[22] Furthermore, some descriptive data were found, indicating that benzene may be emitted from the



Note: The stream numbers on the figure correspond to the discussion for this process.
Letters correspond to potential sources of benzene emissions.

Figure 4-2. Flow Diagram of a Glycol BTX Unit Process

Source: Reference 22.

catalytic/reforming process during catalyst regeneration or replacement, during recycling of hydrogen gas to the reformer, and from the light gases taken from the separator. These potential emission points are labeled as A, B, and C, respectively, in Figure 4-1.

One general estimate of the amount of benzene emitted by catalytic reforming/separation has been reported in the literature. In this reference, it was estimated that 1 percent of total benzene produced by catalytic reforming is emitted.[23]

Benzene may be emitted from separation solvent regeneration, raffinate wash water, and raffinate in association with the separation processes following catalytic reforming. These potential sources are shown as A, B, and C, respectively, in Figure 4-2. However, no specific data were found showing emission factors or estimates for benzene emissions from these potential sources. One discussion of the Sulfolane process indicated that 99.9-percent recovery of benzene was not unusual. Therefore, the 0.1 percent unrecovered benzene may be a rough general estimate of the benzene emissions from separation processes.[23]

4.2 TOLUENE DEALKYLATION AND TOLUENE DISPROPORTIONATION PROCESS

Benzene can also be produced from toluene by hydrodealkylation (HDA) or disproportionation. The amount of benzene produced from toluene depends on the overall demand and price for benzene because benzene produced by HDA costs more than benzene produced through catalytic reforming or pyrolysis gasoline.[24] At present, benzene production directly from toluene accounts for almost 30 percent of total benzene produced.[11] Growth in demand for toluene in gasoline (as an octane-boosting component for gasoline blending) appears to be slowing because of increased air quality legislation to remove aromatics from gasoline. (At present, gasoline blending accounts for 30 percent of the end use of toluene.) If toluene is removed from the gasoline pool to any great extent, its value is expected to drop because surpluses will occur. In such a scenario, increased use of toluene to produce benzene by HDA or disproportionation would be expected.[24] At present, production of benzene by the HDA and disproportionation processes accounts for 50 percent of toluene end use.

4.2.1 Toluene Dealkylation

Process Description

Hydrodealkylation of toluene can be accomplished through thermal or catalytic processes.[25] The total dealkylation capacity is almost evenly distributed between the two methods.[10] As shown in Figure 4-3, pure toluene (92 to 99 percent) or toluene (85 to 90 percent) mixed with other heavier aromatics or paraffins from the benzene fractionation column is heated together with hydrogen- containing gas to 1,346°F (730°C) at a specified pressure (Stream 1) and is passed over a dealkylation catalyst in the reactor (Stream 2). Toluene reacts with the hydrogen to yield benzene and methane. The benzene may be separated from methane in a high-pressure separator (Stream 3) by flashing off the methane-containing gas.[25]

The product is then established (Stream 4), and benzene is recovered by distillation in the fractionalization column (Stream 5).[10] Recovered benzene is sent to storage (Stream 6). Unreacted toluene and some heavy aromatic by-products are recycled (Stream 7). About 70 to 85 percent conversion of toluene to benzene is accomplished per pass through the system, and the ultimate yield is 95 percent of the theoretical yield. Because there is a weight loss of about 23 percent, the difference in toluene and benzene prices must be high enough to justify use of the HDA process.

Benzene Emissions

The available information on benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with benzene production using the toluene dealkylation process was reviewed. No source-specific emission factors were found for benzene emissions from its production through dealkylation of toluene. The reader is referred to Section 4.5 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these emission points.

Potential sources of emissions from the dealkylation process include the separation of benzene and methane, distillation, catalyst regeneration, and stabilization.[23] These potential sources are shown as emission points A, B, C, and D respectively, in Figure 4-3.[10,15,25]

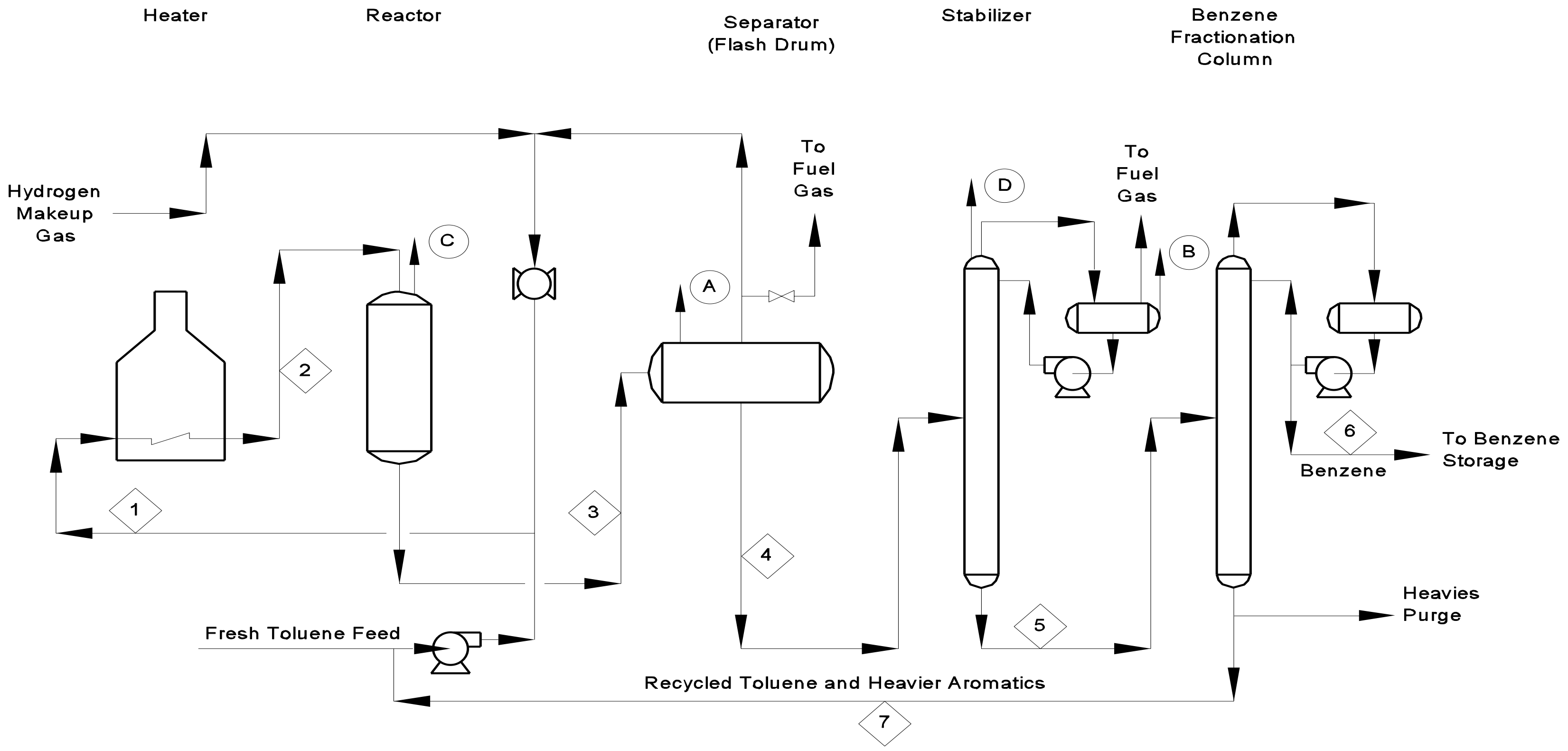
4.2.2 Toluene Disproportionation

Process Description

Toluene disproportionation (or transalkylation) catalytically converts two molecules of toluene to one molecule each of benzene and xylene.[24] As shown in Figure 4-4, the basic process is similar to toluene hydrodealkylation, but can occur under less severe conditions.[15,26] Transalkylation operates at lower temperatures, consumes little hydrogen, and no loss of carbon to methane occurs as with HDA.[24] Toluene material is sent to a separator for removal of off-gases (Stream 3). The product is then established (Stream 4) and sent through clay towers (Stream 5). Benzene, toluene, and xylene are recovered by distillation, and unreacted toluene is recycled (Stream 6). Note that if benzene is the only product required, then HDA is a more economical and feasible process.[27]

Benzene Emissions

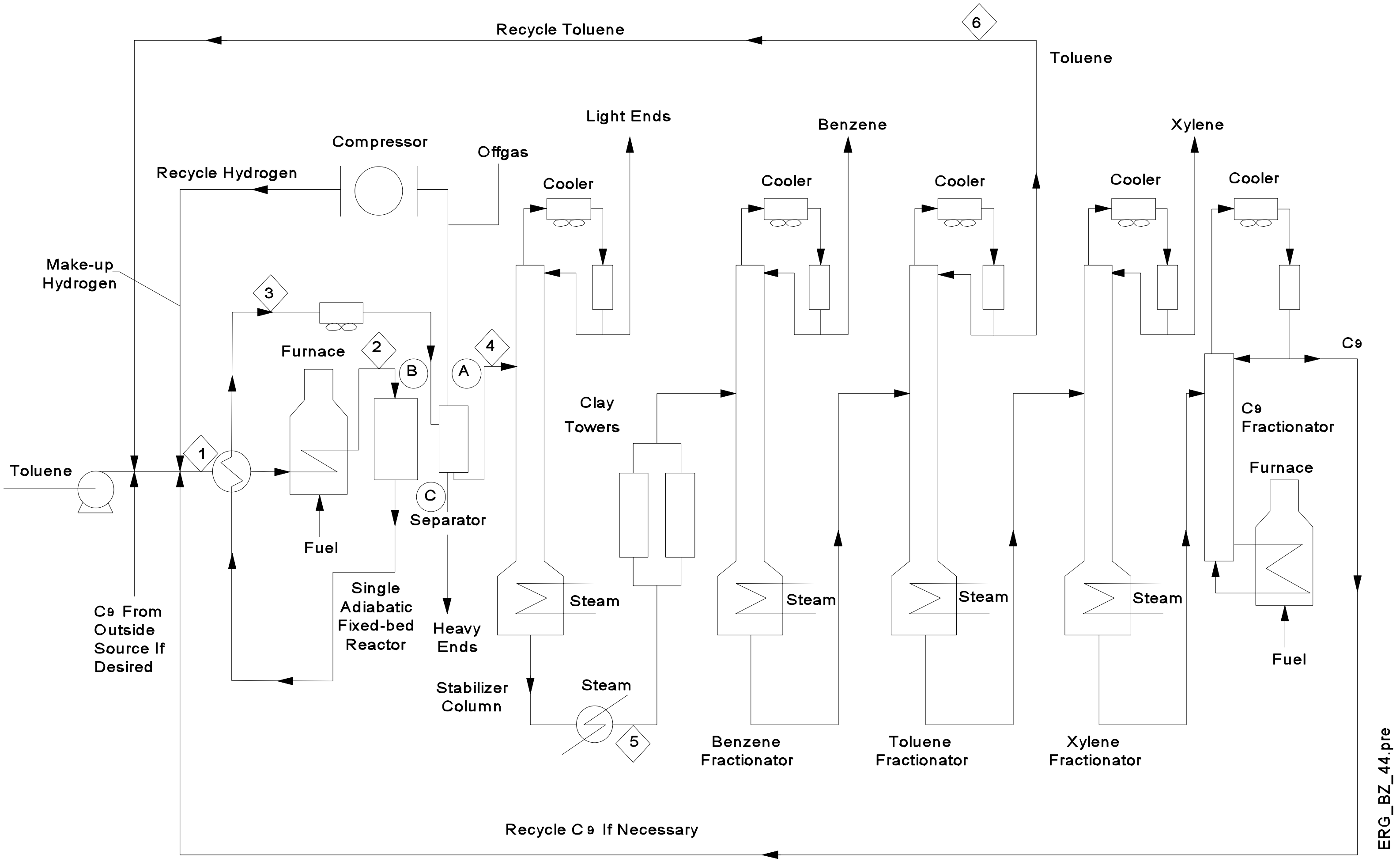
No specific emission factors were found for benzene emissions from its production via toluene disproportionation. Potential sources of benzene emissions from this process are associated with the separation of benzene and xylene, catalyst regeneration, and heavy hydrocarbons that do not break down.[23] These potential sources are shown as points A, B, and C, respectively, in Figure 4-4.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-3. Process Flow Diagram of a Toluene Dealkylation Unit

Source: References 10, 15, and 25.



Note: Stream numbers correspond to the discussion in the text for this process. Letters represent potential sources of benzene emissions.

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

Source: References 15 and 26.

4.3 ETHYLENE PRODUCTION

4.3.1 Process Description

Ethylene is produced through pyrolysis of natural gas concentrates or petroleum fractions such as naphthas and atmospheric gas oils.[28] Pyrolysis gasoline is a liquid by-product formed as part of the steam-cracking process. The liquid pyrolysis gasoline is rich in benzene. Ethylene plants of the same production capacity, but using different feedstocks (ethane/propane versus naphthas/gas oils), will produce different amounts of pyrolysis gasoline with different benzene concentrations. For example, an ethylene plant producing 1 billion pounds (453.5 gigagrams [Gg]) of ethylene per year from ethane will produce about 16,097,023 lbs (7.3 Gg) pyrolysis gasoline with about 7,497,244 lbs (3.4 Gg) benzene in the pyrolysis gasoline.[28] A plant producing the same amount of ethylene from atmospheric gas oils will produce about 754,134,509 lbs (342 Gg) of pyrolysis gasoline containing 213,450,937 lbs (96.8 Gg) benzene.[28]

Because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from the pyrolysis gasoline. Table 4-1 lists facilities reported to recover benzene from pyrolysis gasoline. However, benzene can be emitted from ethylene plants that produce pyrolysis gasoline but do not recover benzene. Table 4-2 lists ethylene producers and their locations. To locate most of the potential sources of benzene from ethylene/pyrolysis gasoline plants, information is included here on ethylene/pyrolysis gasoline production, as well as information on recovery of benzene from pyrolysis gasoline. But because ethylene plants using naphthas/gas oils as feedstocks produce more pyrolysis gasoline and more often treat the gasoline prior to storage, these types of plants are emphasized in the following discussion.

Reference 28 provides more detailed information on ethylene plants using natural gas concentrates as feedstocks. In general, natural gas-using plants are less complex than naphtha-using plants. The potential emissions sources of benzene at the two types of

TABLE 4-2. ETHYLENE PRODUCERS - LOCATION AND CAPACITY

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Atlantic Richfield Company			
Lyondell Petrochemical Company, subsidiary	Channelview, Texas	3,360 (1,524)	Partly captive
The BF Goodrich Company			
BF Goodrich Chemical Group	Calvert City, Kentucky	350 (159)	Merchant
Chemicals & Speciality Products Group	Alvin, Texas	2,384 (1,081)	Mostly merchant
Chevron Corporation			
Chevron Chemical Company, subsidiary			
Olefins and Derivatives Division	Cedar Bayou, Texas	1,450 (658)	Mostly captive
	Port Arthur, Texas	1,250 (567)	Mostly captive use at Orange, Texas
Dow Chemical U.S.A.	Freeport, Texas	2,050 (930)	Captive
	Plaquemine, Louisiana	2,300 (1,043)	Captive
Du Pont			
Du Pont Chemicals	Orange, Texas	1,050 (476)	Captive
Eastman Chemical Company			
Texas Eastman Company	Longview, Texas	1,400 (635)	Mostly Captive

(continued)

TABLE 4-2. CONTINUED

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Exxon Chemical Company			
Exxon Chemical Americas	Baton Rouge, Louisiana	1,775 (805)	Captive
	Baytown, Texas	2,100 (953)	Some captive use at Mont Belvieu, Texas
Javelina Gas Processing	Corpus Christi, Texas	180 (82)	Recovered from gas by-products of local refineries; merchant
Koch Industries, Inc.			
Koch Refining Company, subsidiary	Corpus Christi, Texas	24 (11)	Captive
Mobil Oil Corporation			
Mobil Chemical Company, division	Beaumont, Texas	1,100 (499)	Mostly captive
Petrochemicals Division	Houston, Texas	500 (227)	Mostly captive
Occidental Petroleum Corporation			
Petrochemicals			
Olefins & Aromatics Division	Chocolate Bayou, Texas	1,100 (499)	Mostly captive
	Corpus Christi, Texas	1,700 (771)	Mostly captive
	Lake Charles, Louisiana	750 (340)	Captive
Phillips Petroleum Company			
Chemicals Division	Sweeny, Texas	2,550 (1,157)	Partly captive
Olefins and Cyclics Branch			

(continued)

TABLE 4-2. CONTINUED

Producer	Location	Annual Capacity million lb (million kg)	Notes[a]
Quantum Chemical Corp.			
USI Division	Clinton, Iowa	900 (408)	Captive
	Deer Park, Texas	1,500 (680)	Captive
	Morris, Illinois	1,000 (454)	Captive
Rexene Corporation	Odessa, Texas	500 (228)	Partly captive
Shell Oil Company			
Shell Chemical Company, division	Deer Park, Texas	1,900 (862)	Partly merchant
	Noroco, Louisiana	2,560 (1,161)	Partly captive
Sun Refining and Marketing Co.	Brandenburg, Kentucky	NA	Captive
	Claymont, Delaware	250 (113)	Partly captive
Sweeny Olefins Limited Partnership	Sweeny, Texas	1,500 (680)	Merchant
Texaco Chemical Company	Port Arthur, Texas	1,150 (522)	Some captive use at Port Neches
	Port Neches, Texas	350 (159)	Captive
Union Carbide Corporation	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.

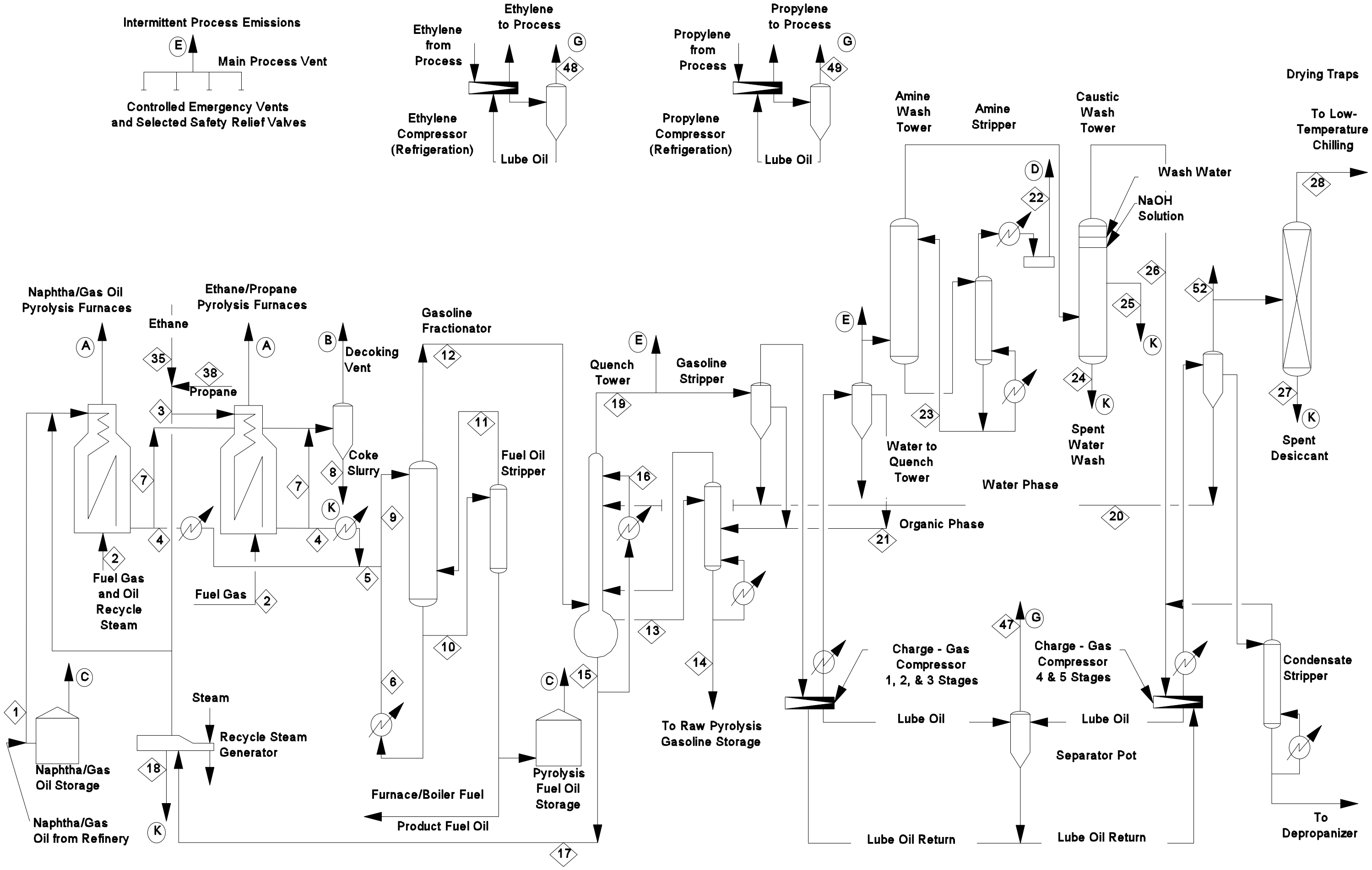
Ethylene/Pyrolysis Gasoline Production

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.

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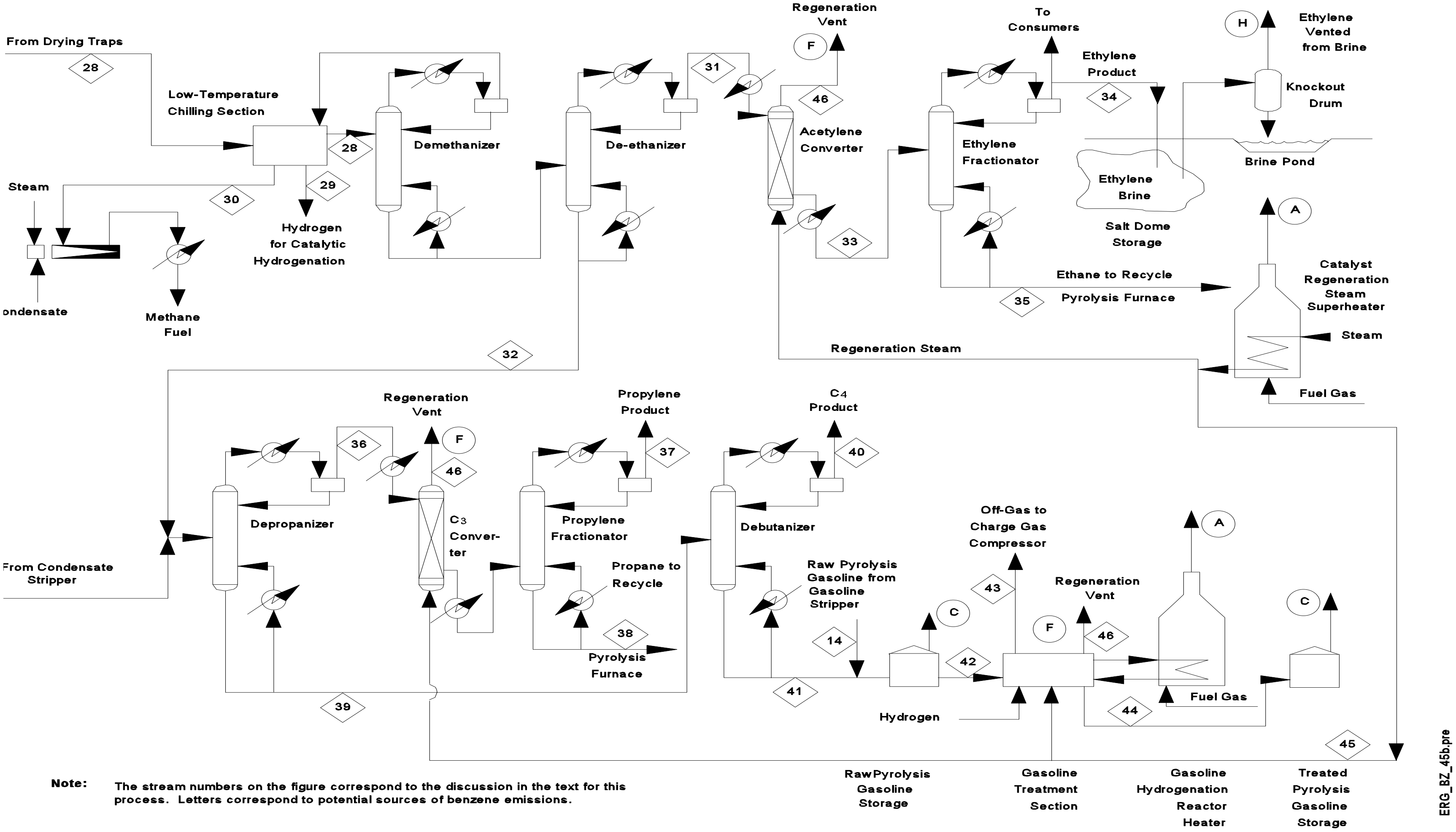
Figure 4-5. Process Flow Diagram for Ethylene Production from Naphtha and/or Gas-Oil Feeds

Source: Reference 28.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

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

Source: Reference 28.

TABLE 4-3. STREAM DESIGNATIONS FOR FIGURE 4-5, PRODUCTION OF ETHYLENE FROM NAPHTHA AND/OR GAS-OIL FEEDS

Stream Number	Stream Description
1	Naphtha or gas oil feed
2	Fuel gas and oil
3	Ethane/propane recycle stream
4	Cracked gas
5	Cracked gas
6	Recycled pyrolysis fuel oil from gasoline fractionator
7	Furnace exhaust
8	Slurry of collected furnace decoking particles
9	Quenched cracked gas
10	Surplus fuel oil
11	Light fractions
12	Overheads from gasoline fractionator
13	Condensed organic phase
14	Raw pyrolysis gasoline to intermediate storage
15	Water phase (saturated with organics) from quench tower
16	Recycled water phase from heat exchangers
17	Surplus water from quench tower
18	Wastewater blowdown from recycle steam generator
19	Overheads from quench tower
20	Water condensed during compression
21	Organic fractions condensed during compression
22	Acid gas stripped in amine stripper
23	Diethanolamine (DEA)
24	Liquid waste stream from caustic wash tower
25	Liquid waste stream from caustic wash tower
26	Process gas stream from caustic wash tower
27	Solid waste stream from drying traps

(continued)

TABLE 4-3. CONTINUED

Stream Number	Stream Description
28	Process gas
29	Hydrogen rich stream from demethanizer
30	Methane rich stream from demethanizer
31	C_2 components from de-ethanizer
32	C_3 and heavier components from de-ethanizer
33	Hydrogenated acethylene from acetylene convertor
34	Overheads from ethylene fractionator
35	Ethane to recycle pyrolysis furnace
36	Overheads from depropanizer
37	Propylene (purified)
38	Propane to ethane/propane pyrolysis furnace
39	C_4 and heavier components to debutanizer
40	Overheads from debutanizer
41	C_5 and heavier components from debutanizer
42	Combined C_5 components and gasoline stripper bottoms fractions
43	Light ends to cracked gas compressor
44	C_5 and heavier components
45	Superheated stream
46	Stream and hydrocarbons
47	Organic vapor from separator pot
48	Organic vapor from separator pot
49	Organic vapor from separator pot

which end pyrolysis and simultaneously generate steam. The streams from the transfer-line exchangers (Stream 5) are combined and further quenched by the injection of recycled pyrolysis fuel oil from the gasoline fractionator (Stream 6).

The remaining operations shown in Figure 4-5 are required for separation of the various product fractions formed in the cracking of gas oil and/or naphtha; for removal of acid gases (primarily hydrogen sulfide [H_2S]) and carbon dioxide (CO_2) and water; and for hydrogenation of acetylene compounds to olefins or paraffins.

The quenched cracked gas (Stream 9) passes to the gasoline fractionator, where pyrolysis fuel oil is separated. Most of the fuel oil passes through water-cooled heat exchangers and is recycled (Stream 6) to the preceding oil-quenching operation. The surplus fuel oil (Stream 10), equivalent to the quantity initially present in the cracked gas, passes first to the fuel oil stripper, where light fractions are removed, and then to fuel oil storage. The light fractions (Stream 11) removed in the fuel oil stripper are recycled to the gasoline fractionator. The gasoline fractionator temperatures are well above the vaporization temperature of water, and the contained water remains as superheated steam, with the overhead stream containing the lighter cracked-gas components.

The overhead stream from the gasoline fractionator (Stream 12) passes to the quench tower, where the temperature is further reduced, condensing most of the water and part of the C_5 and heavier compounds. The condensed organic phase (Stream 13) is stripped of the lighter components in the gasoline stripper and is passed to raw pyrolysis gasoline intermediate storage (Stream 14). Most of the water phase, which is saturated with organics, is separated in the quench tower (Stream 15), passed through water-cooled heat exchangers (Stream 16), and then recycled to the quench tower to provide the necessary cooling. The surplus water (Stream 17), approximately equivalent to the quantity of steam injected with the pyrolysis furnace feed, passes to the dilution steam generator, where it is vaporized and recycled as steam to the pyrolysis furnaces. Blowdown from the recycle steam generator is removed as a wastewater stream (Stream 18).

On leaving the quench tower, the pyrolysis gas is compressed to about 3.5 mPa in five stages.[29] The overhead stream from the quench tower (Stream 19) passes to a centrifugal charge-gas compressor (first three stages), where it is compressed. Water (Stream 20) and organic fractions (Stream 21) condensed during compression and cooling are recycled to the quench tower and gasoline stripper.

Lubricating oil (seal oil) discharged from the charge-gas compressor is stripped of volatile organics in a separator pot before the oil is recirculated. The organic vapor is vented to the atmosphere (Vent G). Similar separator pots separate volatile organics from lubricating oil from both the ethylene and propylene refrigeration compressors (Streams 48 and 49).

Following compression, acid gas (H_2S and CO_2) is removed by absorption in diethanolamine (DEA) or other similar solvents in the amine wash tower followed by a caustic wash step. The amine stripper strips the acid gas (Stream 22) from the saturated DEA and the DEA (Stream 23) is recycled to the amine wash tower. Very little blowdown from the DEA cycle is required.

The waste caustic solution, blowdown from the DEA cycle, and wastewater from the caustic wash tower are neutralized, stripped of acid gas, and removed as liquid waste streams (Streams 24 and 25). The acid gas stripped from the DEA and caustic waste (Stream 22) passes to an emission control device (Vent D), primarily to control H_2S emissions.

Following acid gas removal, the remaining process gas stream (Stream 26) is further compressed and passed through drying traps containing a desiccant, where the water content is reduced to the low level necessary to prevent ice or hydrate formation in the low-temperature distillation operations. The drying traps are operated on a cyclic basis, with periodic regeneration necessary to remove accumulated water from the desiccant. The desiccant is regenerated with heated fuel gas and the effluent gas is routed to the fuel system. Fouling of the desiccant by polymer formation necessitates periodic desiccant replacement, which results in the generation of a solid waste (Stream 27). However, with a normal desiccant service life of possibly several years, this waste source is relatively minor.

With the exception of three catalytic hydrogenation operations, the remaining process steps involve a series of fractionations in which the various product fractions are successively separated.

The demethanizer separates a mixture of hydrogen and methane from the C_2 and heavier components of the process gas (Stream 28). The demethanizer overhead stream (hydrogen and methane) is further separated into hydrogen-rich and methane-rich streams (Streams 29 and 30) in the low-temperature chilling section. The methane-rich stream is used primarily for furnace fuel. Hydrogen is required in the catalytic hydrogenation operations.

The de-ethanizer separates the C_2 components (ethylene, ethane, and acetylene) (Stream 31) from the C_3 and heavier components (Stream 32). Following catalytic hydrogenation of acetylene to ethylene by the acetylene converter (Stream 33), the ethylene-ethane split is made by the ethylene fractionator. The overhead from the ethylene fractionator (Stream 34) is removed as the purified ethylene product, and the ethane fraction (Stream 35) is recycled to the ethane/propane cracking furnace. For the separation of binary mixtures with close boiling points, such as in the ethylene-ethane fractions, open heat pumps are thermodynamically the most attractive. Both heating and cooling duties have to be incorporated into the cascade refrigeration system for optimum energy utilization.[29]

The de-ethanizer bottoms (C_3 and heavier compounds) (Stream 32) pass to the depropanizer, where a C_3-C_4 split is made. The depropanizer overhead stream (primarily propylene and propane) (Stream 36) passes to a catalytic hydrogenation reactor (C_3 converter), where traces of propadiene and methyl acetylene are hydrogenated. Following hydrogenation, the C_3 fraction passes to the propylene fractionator, where propylene is removed overhead as a purified product (Stream 37). The propane (Stream 38) is recycled to the ethane/propane pyrolysis furnace.

The C_4 and heavier components (Stream 39) from the depropanizer pass to the debutanizer, where a C_4-C_5 split is made. The overhead C_4 stream (Stream 40) is removed as feed to a separate butadiene process.

The stream containing C_5 and heavier compounds from the debutanizer (Stream 41) is combined with the bottoms fraction from the gasoline stripper as raw pyrolysis gasoline. The combined stream (Stream 42) is hydrogenated in the gasoline treatment section. Following the stripping of lights (Stream 43), which are recycled to the cracked-gas compressor, the C_5 and heavier compounds (Stream 44) are transferred to storage as treated pyrolysis gasoline. This stream contains benzene and other aromatics formed by pyrolysis.

The three catalytic hydrogenation reactors for acetylene, C_3 compounds, and pyrolysis gasoline all require periodic regeneration of the catalyst to remove contaminants. The catalyst is generally regenerated every four to six months. At the start of regeneration, as superheated steam (Stream 45) is passed through a reactor, a mixture of steam and hydrocarbons leaving the reactor (Stream 46) is passed to the quench tower. After sufficient time has elapsed for stripping of organics (approximately 48 hours), the exhaust is directed to an atmospheric vent (Vent F) and a steam-air mixture is passed through the catalyst to remove residual carbon. This operation continues for an additional 24 to 48 hours. The presence of air during this phase of the regeneration prevents the vented vapor from being returned to the process.

Because the olefins and di-olefins present in pyrolysis gasoline are unstable in motor gasoline and interfere with extraction of aromatics, they are hydrogenated prior to extraction of aromatics.[10] Also, as mentioned before, because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from the pyrolysis gasoline.

Recovery of Benzene from Pyrolysis Gasoline

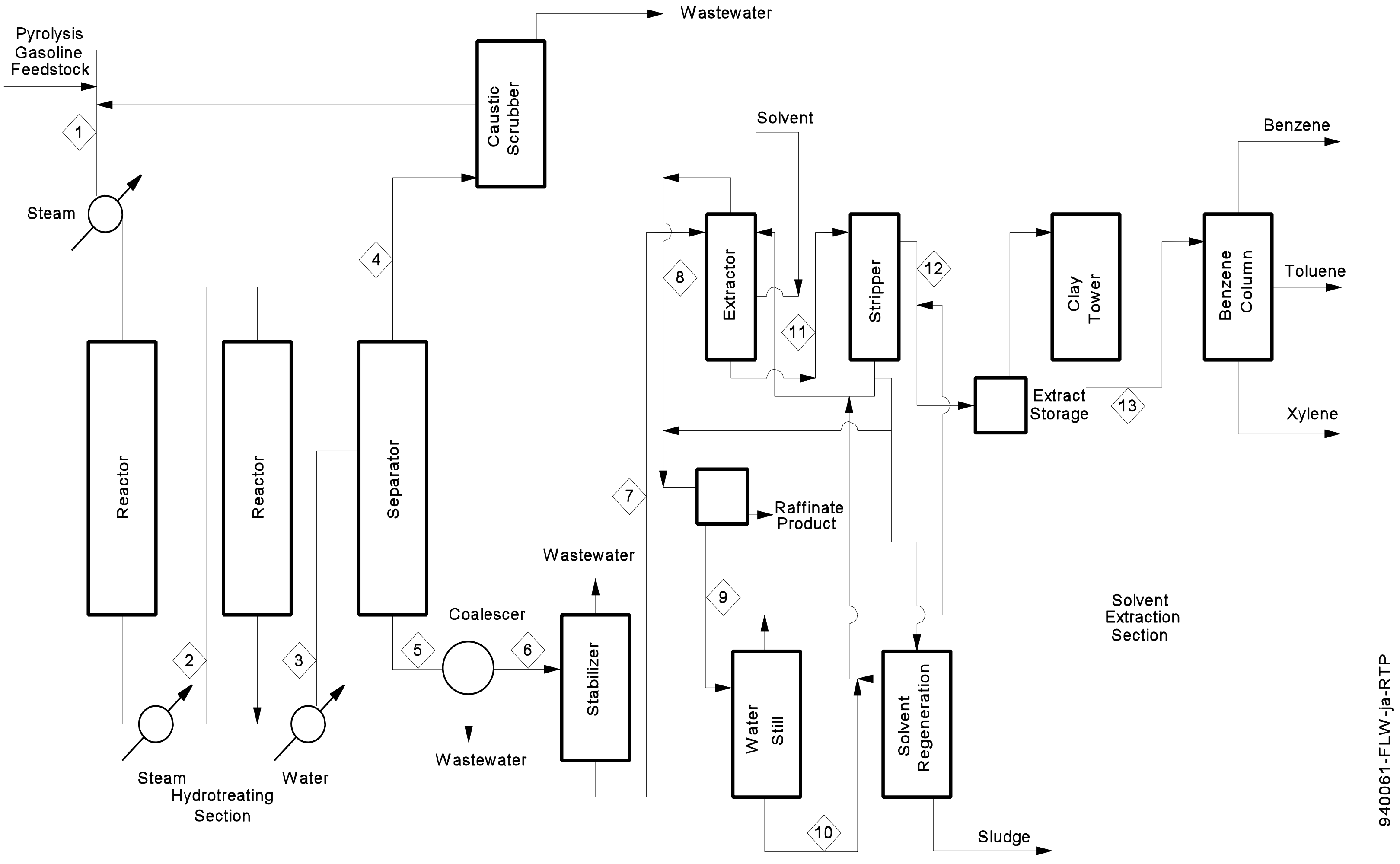
A process flow diagram for a plant producing benzene, toluene, and xylenes by hydrogenation of pyrolysis gasoline is presented in Figure 4-6. Pyrolysis gasoline is fed with make-up hydrogen into the first stage hydrogenation reactor (Stream 1), where olefins are hydrogenated. The reaction conditions are mild (104 to 203°F [40 to 95°C] and 147 to 588 lb/in^2 [10 to 40 atmospheres pressure]).[10]

The catalyst in the first stage reactor (nickel or palladium) requires more frequent regeneration than most refinery catalysts because of the formation of gums. Catalyst may be regenerated about every 4 months and coke is burned off every 9 to 12 months.[10,30]

From the first reactor, the hydrogenated di-olefins and olefins are sent to a second reactor (Stream 2). Reactor effluent is then cooled and discharged into a separator (Stream 3). Part of the gas stream from the separator is recycled back to the reactor (Stream 4) after being scrubbed with caustic solution. The liquid phase from the separator is sent to a coalescer (Stream 5), where water is used to trap particles of coke formed in the reactor.[30] Next, the light hydrocarbons are removed from the liquid in the stabilizer (Stream 6). At this point, the process becomes similar to the solvent extraction of reformate in the catalytic reforming of naphtha. The stabilized liquid is extracted with a solvent, usually Sulfolane or tetraethylene glycol (Stream 7).

The raffinate (Stream 8) contains paraffins and may be sent to a cracking furnace to produce olefins.[30] The solvent may be regenerated (Streams 9 and 10). Dissolved aromatics (benzene, toluene, and xylene) are separated from the solvent by distillation (Stream 11) and sent through clay towers (Stream 12). Individual components (benzene, toluene, and xylene) are finally separated (Stream 13) and sent to storage.

The above process may vary among facilities. For example, Stream 1 may be passed over additional catalyst, such as cobalt molybdenum, after being passed over a nickel or



Note: No data were available concerning benzene emission points. Likely emission points include reactor vents, compressors, and any vents on the benzene column.

Figure 4-6. Production of BTX by Hydrogenation of Pyrolysis Gasoline

Source: Reference 30.

palladium catalyst. Also, the olefins produced from the raffinate stream (Stream 8) may be added to a gasoline process or sold as a reformer stock.[31]

4.3.2 Benzene Emissions from Ethylene Plants and Benzene Recovery from Pyrolysis Gasoline

Production of ethylene from naphtha/gas oil does not produce large quantities of volatile organic compounds (VOC) or benzene emissions from process vents during normal operations.[28] Emission factors for benzene from sources at ethylene plants are shown in Table 4-4. The chief source of benzene emissions during normal operations is the charge gas compressor lubricating oil vent (Stream 47, Vent G in Figure 4-5). The emission factors in Table 4-4 were developed from data supplied by ethylene manufacturers.

Most benzene emissions from ethylene plants are intermittent and occur during plant startup and shutdown, process upsets, and emergencies (Vent E). For example, benzene may be emitted from pressure relief devices, during intentional venting of off-specification materials, or during depressurizing and purging of equipment for maintenance.[28] Charge gas compressor and refrigeration compressor outages are also potential sources. Emissions from these compressors are generally short term in duration, but pollutants may be emitted at a high rate.

In general, intermittent emissions and emissions from all pressure relief devices and emergency vents are routed through the main process vent (Vent E in Figure 4-5). The vent usually is controlled. The relief valve from the demethanizer is usually not routed to the main vent, but the valve is operated infrequently and emits mainly hydrogen and methane.[28]

Potential sources of benzene such as flue gas from the cracking furnace (Vent A), pyrolysis furnace decoking (Vent B), acid gas removal (Vent D), and hydrogenation catalyst regeneration (Vent F) generally are not significant sources.[28] Flue gas normally contains products of hydrogen and methane combustion. Emissions from pyrolysis furnace decoking consist of air, steam, CO_2, CO, and particles of unburned carbon.[28] Emissions from

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[a]

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)	Factor Rating
3-01-197-45 Ethylene Manufacturing-Compressor Lube Oil Vent	Compressor Lube Oil Vents	Uncontrolled	0.0006 (0.0003)	U
	Single Compressor Train	Uncontrolled	0.0004 (0.0002)	U
	Dual Compressor Train	Uncontrolled	0.0008 (0.0004)	U
3-01-197-42 Ethylene Manufacturing - Pyrolysis Furnace Decoking	Pyrolysis Furnace Decoking		No benzene emissions	
3-01-197-43 Ethylene Manufacturing-Acid Gas Removal	Acid Gas Removal		No benzene emissions	
3-01-197-44 Ethylene Manufacturing - Catalyst Regeneration	Catalyst Regeneration		No benzene emissions	
3-01-197-XX Ethylene Manufacturing - Secondary Sources	Secondary Wastewater Treatment	Uncontrolled	0.0434 (0.0217)	U
3-01-197-49 Ethylene Manufacturing - Equipment Leak Emissions	Equipment Leak Emissions	Detection/ Correction of leaks	See Section 4.5.2	
		Uncontrolled	See Section 4.5.2	

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT[a]

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)	Factor Rating
3-01-197-XX Ethylene Manufacturing-Intermittent Emissions	Intermittent Emissions[c]			
	Single Compressor Train	Flare	0.1584-0.0316 (0.0792-0.0158)	U
		Uncontrolled	1.584 (0.7919)	U
	Dual Compressor Train	Flare	0.0202-0.004 (0.0101-0.002)	U
		Uncontrolled	0.2022 (0.1011)	U

[a] Data are for a hypothetical plant using 50 percent naphtha/50 percent gas oil as feed and having an ethylene capacity of 1,199,743 lb/yr (544.2 Gg/yr).

[b] Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylene produced.

[c] Intermittent emissions have been reported from the activation of pressure relief devices and the depressurization and purging of equipment for maintenance purposes.

acid gas removal are H_2S, SO_2, and CO_2; these emissions are generally controlled to recover H_2S as sulfur or convert H_2S to SO_2. As discussed earlier, catalyst regeneration is infrequent and no significant concentrations of benzene have been reported as present in the emissions.[28]

Equipment leak benzene emissions at ethylene plants may originate from pumps, valves, process sampling, and continuous process analysis. Refer to Section 4.5.2 of this document, for information on emission estimates procedures, and available emission factors. Regarding equipment leak component counts, totals of 377 and 719 valves for benzene vapor and benzene liquid service respectively had been reported for ethylene plants.[32] Storage of ethylene in salt domes is not a potential source of benzene emissions because the ethylene generally does not contain benzene.

The emission factor for benzene from storage vessels shown in Table 4-4 was derived from AP-42 equations.[33] No supporting data showing how the equations were applied were provided by the emission factor reference.

Secondary emissions include those associated with handling and disposal of process wastewater. The emission factor in Table 4-4 was derived from estimates of wastewater produced and the estimated percent of the volatile organic compounds (VOC) emitted from the wastewater that is benzene.

No data were available concerning benzene emissions from recovering benzene from pyrolysis gasoline. Likely sources include reactor vents, compressors, and any vents on the benzene column (Figure 4-6).

The primary control techniques available for intermittent emissions of benzene (pressure relief valves, emergency vents) are flaring and combustion within industrial waste boilers. Other control methods are not as attractive because the emissions are infrequent and of short duration. The estimated control efficiency of flares is 98 percent or greater[34] while control efficiencies for industrial waste boilers vary depending upon design and operation.[28]

For additional discussion on flares and industrial waste boilers as control methods, see Section 4.5.1. One ethylene producer that provided a process description stated that all process vents are connected to flares. However, it was not possible to determine how prevalent such systems are for ethylene production.[35]

Equipment leak emissions may be controlled by inspection/maintenance plans or use of equipment such as tandem seal pumps. For additional discussion on equipment leak emissions, see Section 4.5.2. Emissions from sampling lines can be controlled by piping sample line purge gas to the charge gas compressor or to a combustion chamber. Streams from process analyzers may be controlled in the same manner.[28]

The primary means of controlling emissions from pyrolysis gasoline or naphtha feedstock storage is floating roof tanks. Emissions can be reduced by 85 percent when internal floating roof devices are used.[28] For additional discussion on storage tank emissions, see Section 4.5.3.

4.4 COKE OVEN AND COKE BY-PRODUCT RECOVERY PLANTS

Most coke is produced in the U.S. using the by-product recovery process. In 1994, there was one plant that used a “nonrecovery” process. This section will focus on the by-product recovery process because there are so few nonrecovery facilities in operation.[296]

4.4.1 Process Description

Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil at coke by-product recovery plants. Light oil is a clear yellow-brown oil that contains coke oven gas components with boiling points between 32 and 392°F (0 and 200°C).[26] Most by-product recovery plants recover light oil, but not all plants refine it. About 3.4 to 4.8 gal (13 to 18 liters [L]) of light oil can be recovered from the coke oven gas evolved in coke ovens producing 0.91 ton (1 megagram [Mg]) of furnace coke (3 to 4 gal/ton [10.3 to 13.7 L/Mg]). Light oil itself is 60 to 85 percent benzene.[37]

The coke by-product industry recovers various components of coke oven gas including:

- Coal tar, a feedstock for producing electrode binder pitch, roofing pitch, road tar, and numerous basic chemicals;
- Light oil, a source of benzene and other light aromatic chemicals;
- Ammonia or ammonium sulfate, for agriculture and as chemical feedstocks;
- Sulfur, a basic chemical commodity;
- Naphthalene, used primarily as an intermediate in the production of organic chemicals; and
- Coke oven gas, a high-quality fuel similar to natural gas.[38]

Because it is contained in the coke oven gas, benzene may be emitted from processes at by-product recovery plants that do not specifically recover or refine benzene. Table 4-5 lists coke oven batteries with by-product recovery plants in the United States.[36] Figure 4-7 shows a process flow diagram for a representative coke by-product recovery plant.[37,39] The figure does not necessarily reflect any given plant, nor does it include all possible operations that could be found at a given facility. The number of units and the types of processes used varies among specific plants. For example, naphthalene recovery is not practiced at all plants, and some plants do not separate benzene from the light oil. Therefore, it is advisable to contact a specific facility to determine which processes are used before estimating emissions based on data in this document.

Coal is converted to coke in coke ovens. About 99 percent of the U.S. production of coke uses the slot oven process, also referred to as the Kopper-Becker by-product coking process; the other 1 percent is produced in the original beehive ovens.

TABLE 4-5. COKE OVEN BATTERIES CURRENTLY OPERATING IN THE UNITED STATES

Plant (Location)	Battery Identification Number
ABC Coke (Tarrant, AL)	A
	5
	6
Acme Steel (Chicago, IL)	1
	2
Armco, Inc. (Middletown, OH)	1
	2
	3
Armco, Inc. (Ashland, KY)	3
	4
Bethlehem Steel (Bethlehem, PA)	A
	2
	3
Bethlehem Steel (Burns Harbor, IN)	1
	2
Bethlehem Steel (Lackawanna, NY)	7
	8
Citizens Gas (Indianapolis, IN)	E
	H
	1
Empire Coke (Holt, AL)	1
	2
Erie Coke (Erie, PA)	A
	B
Geneva Steel (Provo, UT)	1
	2
	3
	4
Gulf States Steel (Gadsden, AL)	2
	3

(continued)

TABLE 4-5. CONTINUED

Plant (Location)	Battery Identification Number
Inland Steel (East Chicago, IN)	6 7 9 10 11
Koppers (Woodward, AL)	1 2A 2B 4A 4B 5
LTV Steel (Cleveland, OH)	6 7
LTV Steel (Pittsburgh, PA)	P1 P2 P3N P3S P4
LTV Steel (Chicago, IL)	2
LTV Steel (Warren, OH)	4
National Steel (Ecorse, MI)	5
National Steel (Granite City, IL)	A B
New Boston Coke (Portsmouth, OH)	1
Sharon Steel (Monessen, PA)	1B 2
Shenango (Pittsburgh, PA)	1 4
Sloss Industries (Birmingham, AL)	3 4 5
Toledo Coke (Toledo, OH)	C
Tonawanda Coke (Buffalo, NY)	1

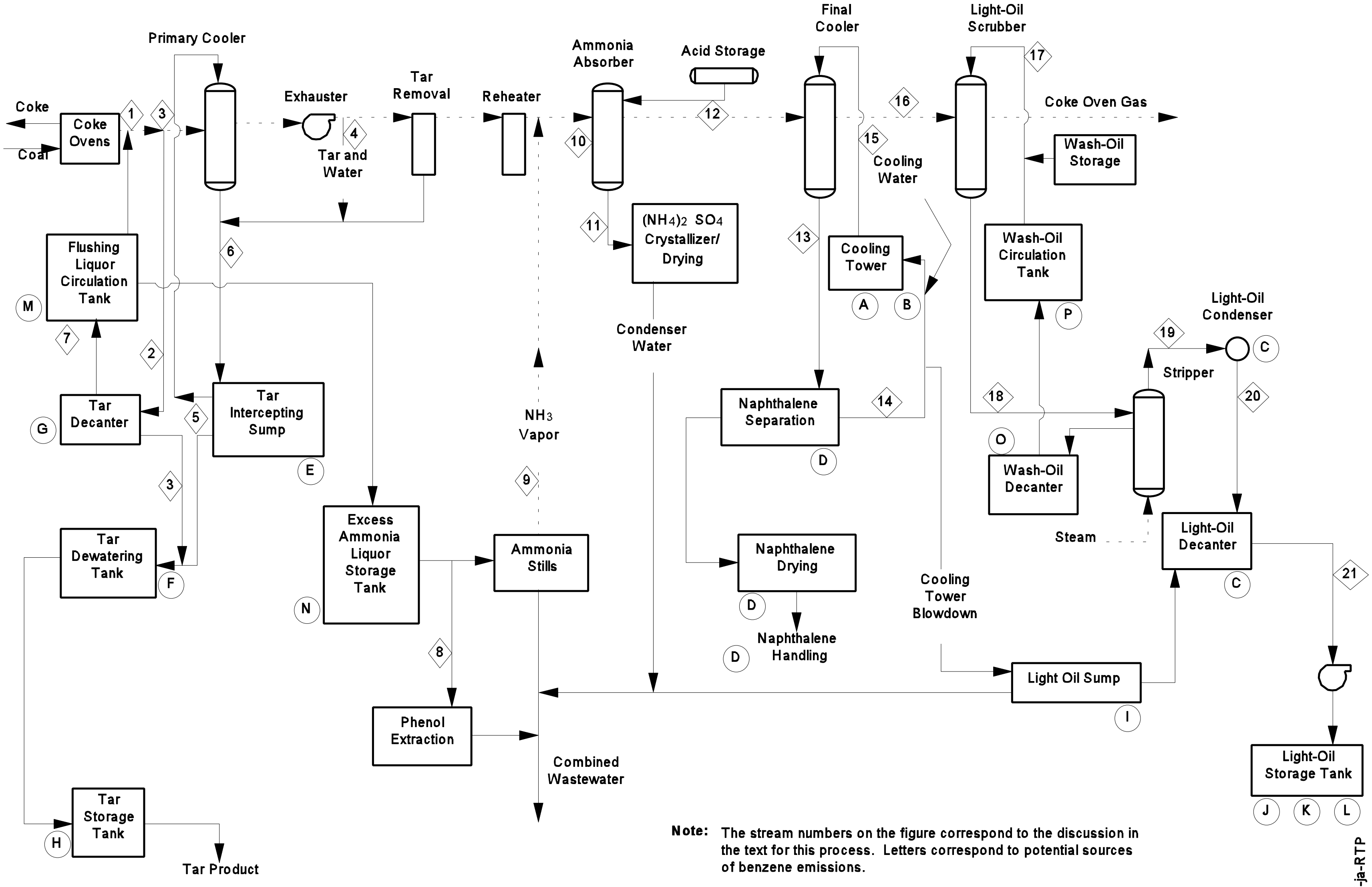
(continued)

TABLE 4-5. CONTINUED

Plant (Location)	Battery Identification Number
USX (Clairton, PA)	1
	2
	3
	7
	8
	9
	13
	14
	15
	19
	20
	B
USX (Gary, IN)	23
	5
	7
Wheeling-Pittsburgh (East Steubenville, WV)	1
	2
	3
	8

Source: Reference 36.

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These operating plants and locations were current as of April 1, 1992.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

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

Source: Reference 37 and 39.

Each oven has 3 main parts: coking chambers, heating chambers, and regenerative chambers. All of the chambers are lined with refractory (silica) brick. The coking chamber has ports in the top for charging of the coal.[22]

Each oven is typically capable of producing batches of 10 to 55 tons (9.1 to 49.9 Mg) of coke product. A coke oven battery is a series of 20 to 100 coke ovens operated together, with offtake flues on either end of the ovens to remove gases produced. The individual ovens are charged and discharged at approximately equal time intervals during the coke cycle. The resulting constant flow of evolved gas from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. Process heat comes from the combustion of gases between the coke chambers. Approximately 40 percent of cleaned oven gas (after the removal of its byproducts) is used to heat the coke ovens. The rest is either used in other production processes related to steel production or sold. Coke oven gas is the most common fuel for underfiring coke ovens.[22] The coking time affects the type of coke produced. Furnace coke results when coal is coked for about 15 to 18 hours. Foundry coke, which is less common and is of higher quality (because it is harder and less readily ignited), results when coal is coked for about 25 to 30 hours.[37]

The coking process is actually thermal distillation of coal to separate volatile and nonvolatile components. Pulverized coal is charged into the top of an empty, but hot, coke oven. Peaks of coal form under the charging ports and a leveling bar smoothes them out. After the leveling bar is withdrawn, the topside charging ports are closed and the coking process begins.

Heat for the coke ovens is supplied by a combustion system under the coke oven. The gases evolved during the thermal distillation are removed through the offtake main and sent to the by-product recovery plant for further processing.

After coking is completed (no volatiles remain), the coke in the chamber is ready to be removed. Doors on both sides of the chamber are opened and a ram is inserted into the chamber. The coke is pushed out of the oven in less than 1 minute, through the coke guide and into a quench car. After the coke is pushed from the oven, the doors are cleaned and repositioned. The oven is then ready to receive another charge of coal.

The quench car carrying the hot coke moves along the battery tracks to a quench tower where approximately 270 gallons of water per ton of coke (1,130 L of water per Mg) are sprayed onto the coke mass to cool it from about 2000 to 180°F (1100 to 80°C) and to prevent it from igniting. The quench car may rely on a movable hood to collect particulate emissions, or it may have a scrubber car attached. The car then discharges the coke onto a wharf to drain and continue cooling. Gates on the wharf are opened to allow the coke to fall onto a conveyor that carries it to the crushing and screening station. After sizing, coke is sent to the blast furnace or to storage.

As shown in Figure 4-7, coke oven gas leaves the oven at about 1292°F (700°C) and is immediately contacted with flushing liquor (Stream 1). The flushing liquor reduces the temperature of the gas and acts as a collecting medium for condensed tar. The gas then passes into the suction main. About 80 percent of the tar is separated from the gas in the mains as “heavy” tar and is flushed to the tar decanter (Stream 2).[37] Another 20 percent of the tar is “light” tar, which is cleaner and less viscous, and is condensed and collected in the primary cooler.[39] Smaller amounts of “tar fog” are removed from the gas by collectors (electrostatic precipitators or gas scrubbers) (Stream 4).[37] Light tar and tar fog is collected in the tar intercept sump (stream 6) and is routed to the tar decanter (Stream 5).

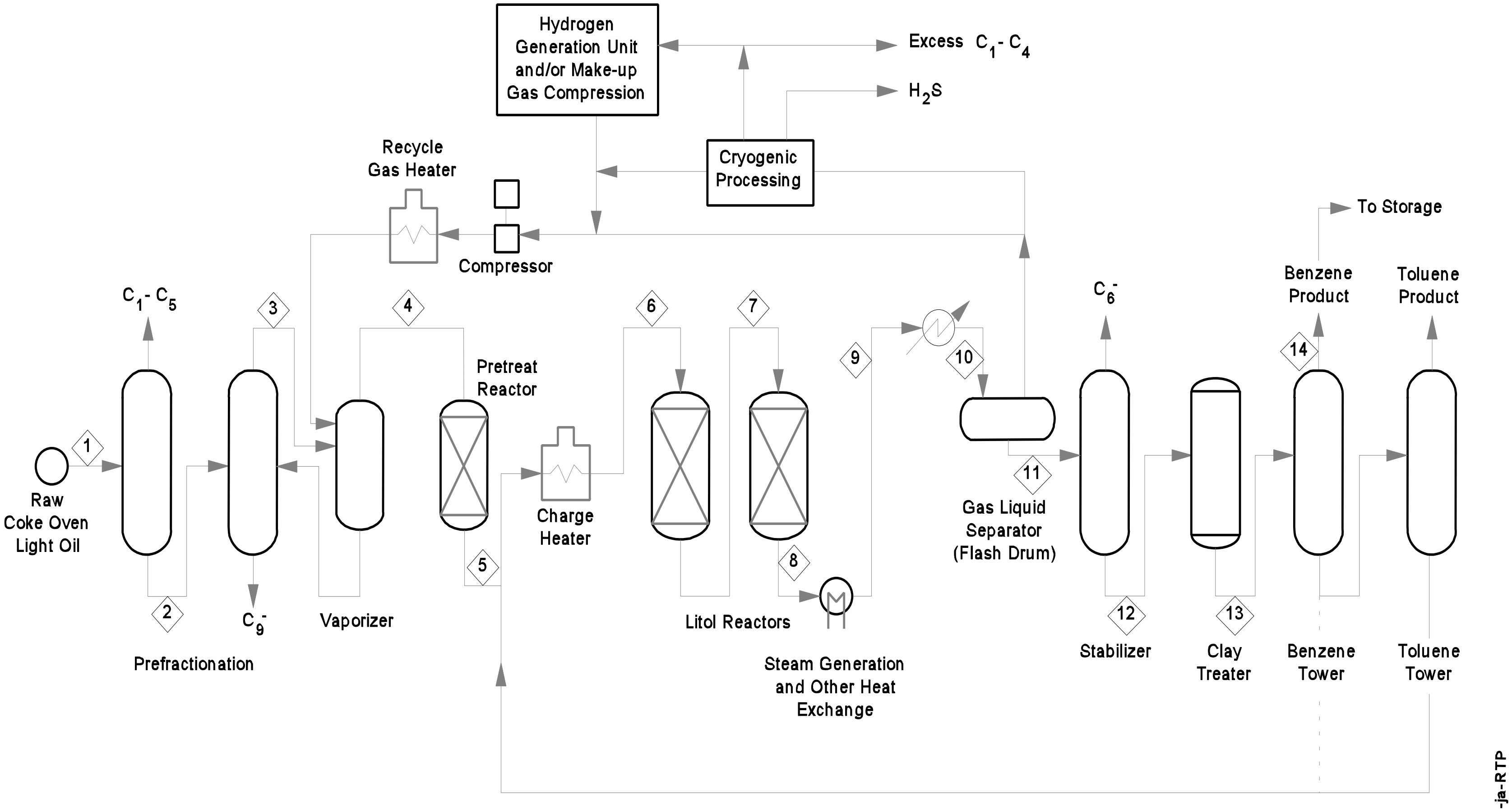
Depending on plant design, the heavy and light tar streams (Streams 2 and 5) may be merged or separated. The tar is separated from the flushing liquor by gravity in the tar decanter. Recovered flushing liquor is returned to the Flushing Liquor Circulation Tank (Stream7) and re-used. Tar from the decanter is further refined in the tar dewater tank

(Stream 3). Tar may be sold to coal tar refiners or it may be refined further on site. Tar and tar products are stored on site in tanks.

Wastewater processing can recover phenol (Stream 8) and ammonia, with the ammonia routinely being reinjected into the gas stream (Stream 9). Ammonia salts or ammonia can be recovered by several processes. Traditionally, the ammonia-containing coke oven gas is contacted with sulfuric acid (Stream 10), and ammonium sulfate crystals are recovered (Stream 11). The coke oven gas from which tar and ammonia have been recovered is sent to the final cooler (Stream 12). The final cooler is generally a spray tower, with water serving as the cooling medium.[37]

Three types of final coolers and naphthalene recovery technologies are currently used: (1) direct cooling with water and naphthalene recovery by physical separation, (2) direct cooling with water and naphthalene recovery in the tar bottom of the final cooler, and (3) direct cooling with wash oil and naphthalene recovery in the wash oil.[37] Most plants use direct water final coolers and recover naphthalene by physical separation.[37] In this method, naphthalene in the coke oven gas is condensed in the cooling medium and separated by gravity (Stream 13). After the naphthalene is separated, the water is sent to a cooling tower (Stream 14) and recirculated to the final cooler (Stream 15). The coke oven gas that leaves the final cooler is sent to the light oil processing segment of the plant (Stream 16).

As shown in Figure 4-7, light oil is primarily recovered from coke oven gas by continuous countercurrent absorption in a high-boiling liquid from which it is stripped by steam distillation.[10] Coke oven gas is introduced into a light oil scrubber (Stream 16). Packed or tray towers have been used in this phase of the process, but spray towers are now commonly used.[10] Wash oil is introduced into the top of the tower (Stream 17) and is circulated through the contacting stages of the tower at around 0.11 to .019 gal/ft^3 (1.5 to 2.5 liters per cubic meter [L/m3]) of coke oven gas.[39] At a temperature of about 86°F (30°C), a light oil scrubber will remove 95 percent of the light oil from coke oven gas. The



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-8. Litol Process Flow Diagram

Source: References 40 and 41.

benzene-containing wash oil is steam-stripped (Stream 18) to recover the light oil.[39] Steam and stripped vapors are condensed and separated (Streams 19 and 20). The light oil is sent to storage (Stream 21).[37,39]

To recover the benzene present in the light oil, processes such as Litol (licensed by Houdry) or Hydeal (licensed by UOP) are used. Figure 4-8 shows a process diagram of the Litol process. The following discussion of the Litol process is drawn from two published descriptions of the process.[40,41]

The light oil is prefractionated (Stream 1) to remove the C_5 and lighter fractions, and the C_9 and heavier fractions (Stream 2). The remaining “heart cut” is sent to a vaporizer, where it contacts gas with a high hydrogen content (Stream 3). The light oil and hydrogen then flow to a pretreat reactor (Stream 4), where styrene, di-olefins, and some sulfur compounds are hydrogenated (at about 572°F [300°C]). The partially hydrogenated stream is heated by the charge heater to the temperature required for the main reactor (Stream 5).

The stream is then sent through a set of fixed-bed (Litol) reactors (Streams 6 and 7), where all remaining sulfur compounds are converted to H_2S and organics are dehydrogenated or dealkylated. The reactor effluent is cooled by post-reactor exchangers (Streams 8 and 9). At the flash drum, aromatics are condensed and separated from the gas stream (Stream 10). At the stabilizer, additional gas is removed, resulting in a hot liquid fuel for clay treatment (Stream 11). The clay treater removes the last trace of unsaturates from the aromatics (Stream 12). Conventional distillation yields pure benzene followed by pure toluene (Stream 13). Benzene product may then be sent to storage (Stream 14).[40,41]

4.4.2 Benzene Emissions

Benzene may be emitted from many points in a coke and coke by-product plant; emissions are not limited to the benzene recovery section of the process. The coke ovens themselves are potential sources of benzene emissions from the charging operation, leaking coke oven doors, topside port lids and offtake systems on the topside of the battery, collecting mains, and bypass/bleeder stacks.[36]

During charging, moist coal contacts the hot oven floor and walls and, as a result, the release of volatile components begins immediately. Control of charging emissions is more dependent on operating procedures than on equipment. Control options include staged charging, sequential charging, and use of wet scrubbers on larry cars (the mobile hoppers that discharge the coal).

Staged charging involves pouring coal into the coke ovens so that an exit space for the generated gases is constantly maintained.[42] The hoppers delivering the coal are discharged such that emissions are contained in the ovens and collecting mains by steam aspiration. Generally, a maximum of two hoppers are discharging at the same time.

In sequential charging, the first hoppers are still discharging when subsequent hoppers begin discharging coal. As with staged charging, the coke ovens are under aspiration in sequential charging. The sequential charging procedure is designed to shorten the charging time.

In the use of wet scrubbers on larry cars, the scrubber emissions are contained by hoods or shrouds that are lowered over the charging ports.

Another potential source of benzene emissions at coke ovens is leaking doors. The doors are sealed before the coking process begins. Some doors have a flexible metal band or rigid knife edge as a seal. The seal is formed by condensation of escaping tars on the door's metal edge. Other doors are sealed by hand by troweling a mixture into the opening between the coke oven door and door frame. After the coking process is complete, the doors are opened to push the coked coal out into special railroad cars called quench cars for transport to the quench tower. Quenched coke is then discharged onto a “coke wharf” to allow quench water to drain and to let the coke cool. Control techniques for leaking doors include oven door seal technology, pressure differential devices, hoods/shrouds over the doors, and the use of more efficient operating/maintenance procedures.[42]

Oven door seal technology relies on the principle of producing a resistance to the flow of gases out of the coke oven. This resistance may be produced by a metal-to-metal seal, a resilient soft seal, or a luted seal (applying a slurry mixture of clay, coal, and other materials). Small cracks and defects in the seal allow pollutants to escape from the coke oven early in the cycle. The magnitude of the leak is determined by the size of the opening, the pressure drop between the oven and the atmosphere, and the composition of the emissions.

The effectiveness of a pressure differential control device depends on the ability of the device to reduce or reverse the pressure differential across any defects in the door seal. These systems either provide a channel to permit gases that evolve at the bottom of the oven to escape to the collecting main, or the systems provide external pressure on the seal through the use of steam or inert gases.

Oven door emissions also can be reduced by collecting the leaking gases and particulates and subsequently removing these pollutants from the air stream. A suction hood above each door with a wet electrostatic precipitator for fume removal is an example of this type of system.

Other control techniques rely on operating and maintenance procedures rather than only hardware. Operating procedures for emission reduction could include changes in the oven cycle times and temperatures, the amount and placement of each charge, and any adjustments of the end-door while the oven is on line. Maintenance procedures include routine inspection, replacement, and repair of control devices and doors.

Topside leaks are those occurring from rims of charging ports and standpipe leaks on the top of the coke oven. These leaks are primarily controlled by proper maintenance and operating procedures that include:[42]

- Replacement of warped lids;
- Cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seats;
- Patching or replacing cracked standpipes;
- Sealing lids after a charge or whenever necessary with lute; and
- Sealing cracks at the base of a standpipe with lute.

Luting mixtures are generally prepared by plant personnel according to formulas developed by each plant. The consistency (thickness) of the mixture is adjusted to suit different applications.

There are few emission factors specifically for benzene emissions at coke ovens. One test that examined emissions of door leaks detected benzene in the emissions.[42] The coke oven doors being tested were controlled with a collecting device, which then fed the collected emissions to a wet electrostatic precipitator. Tests at the precipitator inlet showed benzene concentrations of 1.9×10^{-7} to 6.2×10^{-7} lb/ft^3 (1 to 3 parts per million [ppm] or about 3 to 10 milligrams per cubic meter [Mg/m3]). These data translated into an estimated benzene emission factor of 1.3 lb to 5.3 lb (0.6 to 2.4 kilograms [kg]) benzene per hour of operation for coke oven doors. In addition to coke oven door emissions, benzene may also be emitted from the coke oven bypass stack at a rate of 22 lbs/ton of coal charged (11,000 g/Mg) uncontrolled, 0.22 lbs/ton of coal charged (110 g/Mg) controlled with flare.[296] No additional emission factors for benzene and coke ovens were found in the literature. However, an analysis of coke oven gas indicated a benzene content of 1.3×10^{-3} to 2.2×10^{-3} lb/ft^3 (21.4 to 35.8 grams per cubic meter [g/m^3]).

Other potential sources of benzene emissions associated with the by-product recovery plant are given in Table 4-6, along with emission factors.[37,43]

Equipment leaks may also contribute to benzene emissions. Emission factors for pumps, valves, etc., at furnace coke and foundry coke by-product recovery plants are shown in Tables 4-7 and 4-8, respectively.[37,43] The following paragraphs describe the potential sources of benzene emissions listed in Tables 4-6, 4-7, and 4-8. Emission sources and control technologies are described in groups of related processes, beginning with the final cooling unit.

The final cooling unit itself is not a source of benzene because coolers are closed systems. However, the induced-draft cooling towers used in conjunction with direct-water and tar-bottom final coolers are potential sources of benzene. Benzene can be condensed in the direct-contact cooling water, and in the cooling tower, lighter components (such as benzene) will be stripped from the recirculating cooling water. The emission factor of 0.54 pound per ton (lb/ton) (270 g/Mg) coke shown in Table 4-6 was based on actual measurements of benzene concentrations and volumetric gas flow rates taken from source testing reports.[37]

Use of a wash oil final cooler effectively eliminates the benzene emissions associated with direct water or tar bottom coolers because the wash oil is cooled by an indirect heat exchanger, thereby eliminating the need for a cooling tower.[37] Wash oil is separated after it leaves the heat exchanger and recirculates back through the circulation tank to the final cooler.

Coke by-product recovery plants may recover naphthalene by condensing it from the coke oven gas and separating it from the cooling water by flotation. Benzene may be emitted from most naphthalene separation and processing operations.[37] Vapors from naphthalene separation tanks have been reported to contain benzene, benzene homologs, and other aromatic hydrocarbons.[37] The emission factors for naphthalene separation and

TABLE 4-6. SUMMARY OF BENZENE EMISSION FACTORS FOR FURNACE AND FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

			Emission Factor lb/ton (g/Mg)[b]		
SCC and Description	Emissions Source[a]	Control Device	Furnace Coke	Foundry Coke	Factor Rating
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 x 10^{-3} (1.8)	1.9 x 10^{-3} (0.97)	E
	Naphthalene Separation and Processing (D)	Uncontrolled	0.22 (110)	0.16 (80)	E
		Activated Carbon	7.0 x 10^{-4} (0.35)	5.0 x 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 x 10^{-4} (0.45)	4 x 10^{-4} (0.2)	E

(continued)

TABLE 4-6. CONTINUED

SCC and Description	Emissions Source[a]	Control Device	Emission Factor lb/ton (g/Mg)[b]		Factor Rating
			Furnace Coke	Foundry Coke	
	Tar Decanter (G)	Uncontrolled	0.11 (54)	0.05 (25)	E
		Gas Blanketing	22 x 10^{-3} (1.1)	1.0 x 10^{-3} (0.5)	E
	Tar Storage (H)	Uncontrolled	0.013 (6.6)	6.2 x 10^{-3}	E
		Gas Blanketing	7.6 x 10^{-4} (0.38)	3.6 x 10^{-4} (0.18)	E
	Light-Oil Sump (I)	Uncontrolled	0.03 (15)	0.016 (8.1)	E
		Gas Blanketing	6 x 10^{-4} (0.3)	3.2 x 10^{-4} (0.16)	E
	Light-Oil Storage (J)	Uncontrolled	0.012 (5.8)	6.2 x 10^{-3} (3.1)	E
		Gas Blanketing	2.4 x 10^{-4} (0.12)	1.2 x 10^{-4} (0.06)	E
	BTX Storage (K)[d]	Uncontrolled	0.012 (5.8)	6.2 x 10^{-3} (3.1)	E
		Gas Blanketing	2.4 x 10^{-4} (0.12)	1.2 x 10^{-4} (0.06)	E
	Benzene Storage (L)[d]	Uncontrolled	0.0116 (5.8)	6.2 x 10^{-3} (3.1)	E
		Gas Blanketing	2.4 x 10^{-4} (0.12)	1.2 x 10^{-4} (0.06)	E

(continued)

TABLE 4-6. CONTINUED

			Emission Factor lb/ton (g/Mg)[b]		
SCC and Description	Emissions Source[a]	Control Device	Furnace Coke	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)	$8 .2 \times 10^{-5}$ (0.041)	E

Source: Reference 296.

[a] Source identification letters correspond to locations identified in Figure 4-7.
[b] Emission factors are expressed as g benzene emitted per Mg coke produced.
[c] Usually only smaller plants use direct-water final cooler; all final coolers are shown as one unit in Figure 4-7.
[d] Not all plants separate BTX or benzene. Therefore, all product storage is indicated in one box on the diagram in Figure 4-7.

TABLE 4-7. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FURNACE COKE BY-PRODUCT RECOVERY PLANTS

				Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)		Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
3-03-003-15 By-Product Coke - Gas By-Product Recovery	Valves	Uncontrolled		0.4 (0.18)	0.49 (0.22)	U
		Quarterly inspection	(63)	0.15 (0.07)	0.18 (0.08)	U
		Monthly inspection	(72)	0.11 (0.05)	0.13 (0.06)	U
		Use sealed bellows valves	(100)	--	--	
	Pumps	Uncontrolled		4.2 (1.9)	5.1 (2.3)	U
		Quarterly inspection	(71)	1.2 (0.55)	1.5 (0.67)	U
		Monthly inspection	(83)	0.71 (0.32)	0.86 (0.39)	U
		Use dual mechanical seals	(100)	--	--	
	Exhausters	Uncontrolled		0.62 (0.28[c])	0.62 (0.28[c])	U
		Quarterly inspection	(55)	0.29 (0.13)	0.29 (0.13)	U
		Monthly inspection	(64)	0.22 (0.10)	0.22 (0.10)	U
		Use degassing reservoir vents	(100)	--	--	
	Pressure Relief Devices	Uncontrolled		6.0 (2.7)	7.5 (3.4)	U
		Quarterly inspection	(44)	3.3 (1.5)	4.2 (1.9)	U
		Monthly inspection	(52)	2.9 (1.3)	3.5 (1.6)	U
		Use rupture disk system	(100)	--	--	
	Sampling Connections	Uncontrolled		0.55 (0.25)	0.68 (0.31)	U
		Closed-purge sampling	(100)	--	--	

(continued)

TABLE 4-7. CONTINUED

SCC and Description	Emissions Source	Control (% efficiency)	Emission Factor lb/source day (kg/source day)[a,b]		Factor Rating
			Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	
	Open-ended Lines	Uncontrolled	0.084 (0.038)	0.104 (0.047)	U
		Plug or cap (100)	--	--	

Source: Reference 37.

[a] Factors are based on the total VOC emissions from petroleum refineries and the percent of benzene in light oil and refined benzene.

[b] Factors are expressed as lb emitted per source day (kg benzene emitted per source day).

[c] Emission factors are presented for two different types of coke by-product recovery plants, but are not representative of any particular plant.

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

				Emission Factor lb/source day (kg/source day)[a,b]		
SCC and Description	Emissions Source	Control (% efficiency)		Light Oil BTX Recovery[c]	Light Oil Recovery, Benzene Refining[c]	Factor Rating
3-03-003-15 By-Product Coke - Gas By-Product Recovery	Valves	Uncontrolled		0.35 (0.16)	0.44 (0.20)	U
		Quarterly inspection	(63)	0.13 (0.06)	0.15 (0.07)	U
		Monthly inspection	(72)	0.09 (0.04)	0.13 (0.06)	U
		Use sealed bellows valves	(100)	--	--	
	Pumps	Uncontrolled		3.7 (1.7)	4.6 (2.1)	U
		Quarterly inspection	(71)	1.1 (0.5)	1.3 (0.6)	U
		Monthly inspection	(83)	0.66 (0.3)	0.88 (0.4)	U
		Use dual mechanical seals	(100)	--	--	
	Exhausters	Uncontrolled		0.55 (0.25)	0.55 (0.25)	U
		Quarterly inspection	(55)	0.24 (0.11)	0.24 (0.11)	U
		Monthly inspection	(64)	0.20 (0.09)	0.20 (0.09)	U
		Use degassing reservoir vents	(100)	--	--	
	Pressure Relief Devices	Uncontrolled		5.5 (2.5)	6.8 (3.1)	U
		Quarterly inspection	(44)	3.1 (1.4)	3.7 (1.7)	U
		Monthly inspection	(52)	2.6 (1.2)	3.3 (1.5)	U
		Use rupture disk system	(100)	--	--	
	Sampling Connections	Uncontrolled		0.51 (0.23)	0.62 (0.28)	U
		Plug or cap	(100)	--	--	

(continued)

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

SCC and Description	Emissions Source	Control (% efficiency)		Emission Factor lb/source day (kg/source day)[a,b] Light Oil BTX Recovery[c]	Emission Factor lb/source day (kg/source day)[a,b] Light Oil Recovery, Benzene Refining[c]	Factor Rating
	Open-ended Lines	Uncontrolled		0.077 (0.035)	0.95 (0.043)	U
		Closed-purge sampling	(100)	--	--	

Source: Reference 37.

[a] Factors for foundry coke are drawn from Reference 43.
[b] Factors are expressed in terms of lb (kg) of benzene emitted per source day.
[c] Emission factors are presented for two different types of foundry coke by-product recovery plants, but are not representative of any particular plant.

"--" = Data not available.

processing shown in Table 4-6 are based on source testing data from a flotation unit, drying tank, and melt pit at a coke by-product recovery plant.[37]

Benzene may also be emitted from the light oil plant, which includes the light-oil condenser vent, light oil decanter, storage tank, intercepting sumps, the wash-oil decanter, wash-oil circulation tank(s), and BTX storage. A control technique required by the benzene NESHAP is the use of gas blanketing with clean coke oven gas from the gas holder (or battery underfire system).[44] With this technology, a positive (or negative) pressure blanket of clean coke oven gas is piped to the light oil plant and the enclosed sources are connected to the blanketing line. Using a series of piping connections and flow inducing devices (if necessary), vapor emissions from the enclosed sources are transported back into the clean gas system (the coke-oven battery holder, the collecting main, or another point in the by-product recovery process).

Ultimate control of the vapors is accomplished by the combustion of the coke oven gas.[37] Such systems are currently in use at some by-product recovery plants and reportedly have operated without difficulty. Examples of gases that may be used as the gas blanket include dirty or clean coke gas, nitrogen, or natural gas.[37] The control efficiency is estimated to be 98 percent.[37,44] The control technique required by the benzene NESHAP for the light oil sump is a tightly fitting, gasketed cover with an estimated 96-percent efficiency.[44] The emission factors for benzene sources in the light oil plant shown in Table 4-6 are based on source tests.[37]

Sources of benzene emissions from tar processing include the tar decanter, the tar-intercepting sump, tar dewatering and storage, and the flushing-liquor circulation tank. Emission factors for these sources are shown in Table 4-6.

Benzene emissions from the tar decanter are sensitive to two operating practices: residence time in the separator and optimal heating of the decanter.[37] These two variables should be kept in mind when using the emission factors presented in Table 4-6.

Benzene is emitted from tar decanters through vents. Coke oven gas can be mechanically entrained with the tar and liquor that are fed into the decanter. Because tar is fed into the decanter at a slightly higher pressure, the coke oven gas will build up in the decanter if it is not vented.[37] Emissions were measured at tar decanters at several locations in the United States and the emission factor shown in Table 4-6 is the average of the test values.[37]

The water that separates from the tar in the decanter is flushing liquor, which is used to cool the gas leaving the coke oven. Excess flushing liquor is stored in the excess ammonia liquor tank. Benzene may be emitted from the flushing liquor circulation tank and the excess ammonia liquor tank. The emission factor of 0.026 lb benzene/ton (13 g benzene/Mg) coke produced was derived from a source test of fugitive emissions from a primary cooler condensate tank. It was assumed that the condensate tank was similar in design and in liquids stored as the ammonia liquor and the flushing liquor circulation tanks.[296] The actual benzene emission rate from the flushing liquor circulation tank and excess ammonia liquor tank depends on the number of tanks, the number of vents, and the geometry of the tanks.[37]

The tar-intercepting sump is a type of decanter that accepts light tar and condensate from the primary cooler. Some of this condensate may be used to make up flushing liquor and some may be forwarded to ammonia recovery.[37] No significant benzene emissions have been identified from the recovery of ammonia, but benzene can be emitted from the intercepting sump. An emission factor of 0.019 lb/ton (9.5 g benzene/Mg) coke was reported in the literature.[296]

Tar dewatering may be accomplished by steam heating or centrifugal separation or a combination of the two methods. Use of centrifugal separation will probably not be a source of benzene emissions directly, but benzene may be emitted as a fugitive emission if storage vessels are used.[39] In steam heating, benzene could be driven off in the vapors. The emission factor for tar dewatering in Table 4-6 was derived by averaging three factors (0.082, 0.019, and 0.0258 lb benzene/ton coke [41, 9.5, and 12.9 g benzene/Mg coke]) based on source tests at tar dewatering tanks.[37] Gas blanketing is the control technology required by the benzene NESHAP for tar processing.

The final source of benzene emissions at coke by-product recovery plants is leaks from equipment such as pumps, valves, exhausters, pressure relief devices, sampling connection systems, and open-ended lines. Emission factors are shown in Tables 4-7 and 4-8 and are based on emission factors from a comprehensive survey of petroleum refineries and the percent of benzene in the liquid associated with each type of equipment.[37] Two different sets of emission factors are presented, one set for a plant practicing light oil and BTX recovery and one set for a plant producing refined benzene in addition to light oil. Emission factors for exhausters were derived by multiplying the VOC emission factor for compressors in hydrogen service and refineries by 0.235, the measured ratio of benzene to nonmethane hydrocarbons present in the coke oven gas at the exhausters.[37]

To control benzene emissions from process vessels, storage tanks, and tar-interrupting sumps as required by the benzene NESHAP, all openings must be enclosed or sealed. All gases must be routed to a gas collection system (or similar configuration) where the benzene in the gas will be removed or destroyed. Alternately, the gases may be routed through a closed vent system to a carbon absorber or vapor incinerator that is at least 98 percent efficient. See Section 4.5 for a discussion of these types of process control devices.[44] The control techniques required by the benzene NESHAP to control benzene emissions from equipment leaks are presented in Table 4-9.

For the nonrecovery process, benzene emissions for coal charging are 3.6×10^{-5} lb/ton of coal charged (1.8×10^{-2} g/Mg). Emissions from pushing and quenching are expected to be similar to those from the by-product recovery process. Additional benzene emissions occur from the combustion stack of nonrecovery batteries at the rate of 5.1×10^{-4} lb/ton of coal charged (0.26 g/Mg).[296]

TABLE 4-9. TECHNIQUES TO CONTROL BENZENE EMISSIONS FROM EQUIPMENT LEAKS REQUIRED BY THE BENZENE NESHAP FOR COKE BY-PRODUCT RECOVERY PLANTS

Emission Points	Control Technique (% efficiency)
Pumps	Monthly Inspection[a] (83)
	Dual Mechanical Seals (100)
Valves	Monthly Inspection[a] (73)
	Sealed-Bellows Valves (100)
Exhausters	Quarterly Inspections[a] (55)
	Degassing Reservoir Vents (100)
Pressure-Relief Devices	Rupture Disc System (100)
Sampling Connection Systems	Closed-Purge Sampling (100)
Open-Ended Lines	Cap or Plug (100)

Source: Reference 44.

[a] Inspection and maintenance programs include tightening seals, replacing manufacturing equipment, etc.

4.5 METHODS FOR ESTIMATING BENZENE EMISSIONS FROM EMISSION SOURCES

In this section, the sources of benzene emissions from process vents, equipment leaks, storage tanks, wastewater, and transfer operations are summarized, along with the types of controls currently available for use in the industry. In addition, an overview of methods for estimating uncontrolled and controlled emissions of benzene is presented where available. Current Federal regulations applicable to these benzene emission sources are identified. The information provided in this section is applicable to benzene production facilities (discussed earlier in this chapter) as well as to facilities that use benzene as a feedstock to produce cyclic intermediates (discussed in Chapter 5.0).

4.5.1 Process Vent Emissions, Controls, and Regulations

Benzene emissions can occur from any process vent in any chemical production operation that manufactures or uses benzene. Section 4.0 of this document contains a discussion of chemical operations that manufacture benzene, whereas Section 5.0 contains a discussion of chemical operations that use benzene as feedstock. Chemical operations that emit benzene include air oxidation processes, reactor processes, and distillation operations. In air oxidation processes, one or more chemicals are reacted with oxygen supplied as air or air enriched with oxygen to create a product. With reactor processes, one or more chemicals are reacted with another chemical (besides oxygen) and chemically altered to create one or more new products. In distillation, one or more inlet feed streams is separated into two or more outlet product streams, each product stream having component concentrations different from those in the feed streams. During separation, the more volatile components are concentrated in the vapor phase and the less volatile components in the liquid phase.[45]

Calculations for estimating emissions from any of these three processes are specific to the type of vent stream and the type of control in place.

Two general types of methods are used for controlling benzene emissions from process vents: recovery devices and combustion devices. Examples of each type of control device that can be used to comply with air pollution control standards, along with its estimated control efficiency, are summarized in Tables 4-10 and 4-11 and discussed briefly below.[45] The reader should keep in mind that the most appropriate recovery control device, as well as its effectiveness, is highly dependent upon flow rate, concentration, chemical and physical properties of the vent stream, contaminants present, and stream temperature. To achieve optimal control efficiency with recovery devices, several stream characteristics must remain within a certain range. Combustion control devices are less dependent upon these process and vent stream characteristics; however, combustion temperature and stream flow must remain within a certain range to ensure complete combustion.[46]

TABLE 4-10. CONTROL TECHNOLOGIES THAT FORM THE BASIS OF AIR POLLUTION CONTROL STANDARDS

Type	Control Levels Achievable	Design Conditions to Meet Control Level	Comments
Flares	≥ 98%	• Flame present at all times - monitor pilot • Non-assisted Flares - >200 Btu/scf heating value, and 60 ft/sec (18 m/sec) maximum exit velocity • Air and Steam Assisted Flares - >300 Btu/scf heating value, and maximum exit velocity based on Btu content formula	• Destroys rather than recovers organics • Smoking allowed for 5 min/2 hr • Not used on corrosive streams
Industrial Boilers/Process Heaters	≥ 98%	• Vent stream directly into flame	• Destroys rather than recovers organics
Thermal Oxidation	≥ 98%, or 20 ppm	• 1600°F (871°C) Combustion temperature • 0.75 sec. residence • For halogenated streams 2000°F (1093°C), 1.0 sec. and use a scrubber on outlet • Proper mixing	• Destroys rather than recovers organics • May need vapor holder on intermittent streams
Adsorption	≥ 95%	• Adequate quantity and appropriate quality of carbon • Gas stream receives appropriate conditioning (cooling, filtering) • Appropriate regeneration and cooling of carbon beds before breakthrough occurs	• Most efficient on streams with low relative humidity (<50 percent). • Recovers organics

Source: Reference 45.

TABLE 4-11. OTHER CONTROL TECHNOLOGIES THAT CAN BE USED TO MEET STANDARDS

Type	Estimated Control Level	Critical Variables That Affect Control Level	Comments
Catalytic Oxidation	up to 98%	• Dependent on compounds, temp. and catalyst bed size	• Destroys rather than recovers organics • Technical limitations include particulate or compounds that poison catalysts
Absorption	50 to 95%	• Solubility of gas stream in the absorbent • Good contact between absorbent and gas stream	• Appropriate absorbent needed may not be readily available • Disposal of spent absorbent may require special treatment procedures, and recovery of organic from absorbent may be time consuming • Preferable on concentrated streams
Condensation	50 to 95%	• Proper design of the heat exchanger • Proper flow and temperature of coolant	• Preferable on concentrated streams • Recovers organics

Source: Reference 45.

Three types of recovery devices have been identified for controlling benzene emissions: condensation, absorption, and adsorption. With a condensation-type recovery device, all or part of the condensible components of the vapor phase are converted to a liquid phase. Condensation occurs as heat from the vapor phase is transferred to a cooling medium. The most common type of condensation device is a surface condenser, where the coolant and vapor phases are separated by a tube wall and never come in direct contact with each other. Efficiency is dependent upon the type of vapor stream entering the condenser and the flow rate and temperature of the cooling medium. Condenser efficiency varies from 50 to 95 percent. Stream temperature and the organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.[46]

In absorption, one or more components of a gas stream are selectively transferred to a solvent liquid. Control devices in this category include spray towers, venturi scrubbers, packed columns, and plate columns. Absorption efficiency is dependent upon the type of solvent liquid used, as well as design and operating conditions. Absorption is desirable if there is a high concentration of compound in the vent stream that can be recovered for reuse. For example, in the manufacture of monochlorobenzene, absorbers are used to recover benzene for reuse as a feedstock.[46] Stream temperature, specific gravity (the degree of adsorbing liquid saturation), and the organic concentration level must remain within a certain range to ensure optimal control efficiency.[46] Absorbers are generally not used on streams with VOC concentrations below 300 ppmv.[45] Control efficiencies vary from 50 to 95 percent.[45]

In adsorption, the process vent gas stream contains a component (adsorbate) that is captured on a solid-phase surface (adsorbent) by either physical or chemical adsorption mechanisms. Carbon adsorbers are the most commonly used adsorption method. With carbon adsorption, the organic vapors are attracted to and physically held on granular activated carbon through intermolecular (van der Waals) forces. The two adsorber designs are fixed-bed and fluidized-bed. Fixed-bed adsorbers must be regenerated periodically to desorb the collected organics. Fluidized-bed adsorbers are continually regenerated.[46]

Adsorption efficiency can be 95 percent for a modern, well-designed system. Removal efficiency depends upon the physical properties of the compounds in the offgas, the gas stream characteristics, and the physical properties of the adsorbent. Stream mass flow during regeneration, the temperature of the carbon bed, and organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.[46] Adsorbers are not recommended for vent streams with high VOC concentrations.[45]

Four types of combustion devices are identified for control of benzene emissions from process vents: flares, thermal oxidizers, boilers and process heaters, and catalytic oxidizers. A combustion device chemically converts benzene and other organics to CO_2 and water. If combustion is not complete, the organic may remain unaltered or be converted to another organic chemical, called a product of incomplete combustion. Combustion temperature and stream flow must remain within a certain range to ensure complete combustion.[46]

A flare is an open combustion process that destroys organic emissions with a high-temperature oxidation flame. The oxygen required for combustion is provided by the air around the flame. Good combustion is governed by flame temperature, residence time of the organics in the combustion zone, and turbulent mixing of the components to complete the oxidation reaction. There are two main types of flares: elevated and ground flares. A combustion efficiency of at least 98 percent can be achieved with such control.[46]

A thermal oxidizer is usually a refractory-lined chamber containing a burner (or set of burners) at one end. The thermal oxidation process is influenced by residence time, mixing, and temperature. Unlike a flare, a thermal oxidizder operates continuously and is not suited for intermittent streams. Because it operates continuously, auxiliary fuel must be used to maintain combustion during episodes in which the organic concentration in the process vent stream is below design conditions. Based on new technology, it has been determined that all new thermal oxidizers are capable of achieving at least 98 percent destruction efficiency or a 20 parts per million by volume (ppmv) outlet concentration, based on operation at 870°C (1,600°F) with a 0.75-second residence time.[46]

Industrial boilers and process heaters can be designed to control organics by combining the vent stream with the inlet fuel or by feeding the stream into the boiler or stream through a separate burner. An industrial boiler produces steam at high temperatures. A process heater raises the temperature of the process stream as well as the superheating steam at temperatures usually lower than those of an industrial boiler. Greater than 99 percent control efficiency is achievable with these combustion devices.[46]

By using catalysts, combustion can occur at temperatures lower than those used in thermal incineration. A catalytic oxidizer is similar to a thermal incinerator except that it incorporates the use of a catalyst. Combustion catalysts include platinum, platinum alloys, copper oxide, chromium, and cobalt. Catalytic oxidizers can achieve destruction efficiencies of 98 percent or greater.[46]

Biofiltration is another type of VOC control. In biofiltration, process exhaust gases are passed through soil on compost beds containing micro organisms, which convert VOC to carbon dioxide, water, and mineral salts.[47]

Table 4-12 presents a comparison of the VOC control technologies (excluding combustion) that are discussed in this section.[47]

Process vents emitting benzene and other VOC that are discussed in Sections 4.1 through 4.4 and in Section 5.0 are affected by one or more of the following six Federal regulations:

1. “National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry,” promulgated April 22, 1994.[48]
2. “National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries,” promulgated August 18, 1995.[49]

TABLE 4-12. COMPARISON OF VOC CONTROL TECHNOLOGIES

Control Technology	Applicable Concentration Range, ppm	Capacity Range, cfm	Removal Efficiency	Secondary Wastes	Advantages	Limitations and Contradictions
Thermal Oxidation	100-2,000	1,000-500,000	95-99+%	Combustion products	Up to 94% energy recovery is possible.	Halogenated compounds may require additional control equipment downstream. Not recommended for batch operations.
Catalytic Oxidation	100-2,000	1,000-100,000	90-95%	Combustion products	Up to 70% energy recovery is possible.	Thermal efficiency suffers with swings in operating conditions. Halogenated compounds may require additional control equipment downstream. Certain compounds can poison the catalyst (lead, arsenic, phosphorous, chlorine, sulfur, particulate matter).
Condensation	>5,000	100-20,000	50-90%	Condensate	Product recovery can offset annual operating costs.	Not recommended for materials with boiling point <100°F. Condensers are subject to scale buildup which can cause fouling.
Carbon Adsorption	20-5,000	100-60,000	90-98%	Spent carbon; collected organic	Product recovery can offset annual operating costs. Can be used as a concentrator in conjunction with another type of control device. Works well with cyclic processes.	Not recommended for streams with relative humidity <50%. Ketones, aldehydes, and esters clog the pores of the carbon, decreasing system efficiency.

(continued)

TABLE 4-12. CONTINUED

Control Technology	Applicable Concentration Range, ppm	Capacity Range, cfm	Removal Efficiency	Secondary Wastes	Advantages	Limitations and Contradictions
Absorption	500-5,000	2,000-100,000	95-98%	Wastewater; Captured particulate	Product recovery can offset annual operating costs.	Might require exotic scrubbing media. Design could be difficult in the event of lack of equilibrium data. Packing is subject to plugging and fouling if particulates are in the gas stream. Scale formation from adsorbent/adsorber interaction can occur.
Biofiltration	0-1,000	<90,000	80-99%	Disposal of spent compost beds.	Efficient for low concentration streams. Low operating costs.	Large amount of space may be required. Microorganisms are effective only in the 50 to 100°F temperature range and may be killed if proper bed moisture content and pH is not maintained.

Source: Reference 47.

3. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Air Oxidation," promulgated July 1, 1994.[50]

4. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Distillation Operations," promulgated July 1, 1994.[51]

5. "Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Reactor Processes," promulgated July 1, 1994.[52]

6. "National Emission Standards for Benzene Emissions from Coke By-Product Recovery Plants, promulgated October 27, 1993."[53]

In general, for the affected facilities subject to these six regulations, use of the recovery devices and combustion devices discussed above is required. Tables 4-10 and 4-11 present a summary of those controls and the required operating parameters and monitoring ranges needed to ensure that the required control efficiency is being achieved.

4.5.2 Equipment Leak Emissions, Controls, and Regulations

Equipment leak emissions occur from process equipment components whenever the liquid or gas streams leak from the equipment. Equipment leaks can occur from the following components: pump seals, process valves, compressor seals and safety relief valves, flanges, open-ended lines, and sampling connections. The following approaches for estimating equipment leak emissions are presented in the EPA publication *Protocol for Equipment Leak Emission Estimates*:[54]

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches differ in complexity; however, greater complexity usually yields more accurate emissions estimates.

The simplest method, the average emission factor approach, requires that the number of each component type be known. For each component, the benzene content of the stream and the time the component is in service are needed. This information is then multiplied by the EPA's average emission factors for the SOCMI shown in Table 4-13.[54] Refinery average emission factors are shown in Table 4-14; marketing terminal average emission factors are shown in Table 4-15; and oil and gas production average emission factors are shown in Table 4-16.[54] This method is an improvement on using generic emissions developed from source test data, inventory data, and/or engineering judgement. However, this method should only be used if no other data are available because it may result in an overestimation or underestimation of actual equipment leak emissions. For each component, estimated emissions are calculated as follows:

$$\begin{bmatrix} \text{No. of} \\ \text{equipment} \\ \text{components} \end{bmatrix} \text{ x } \begin{bmatrix} \text{Weight \%} \\ \text{benzene} \\ \text{in the stream} \end{bmatrix} \text{ x } \begin{bmatrix} \text{Component-} \\ \text{specific} \\ \text{emission factor} \end{bmatrix} \text{ x } \begin{bmatrix} \text{No. hr/yr in} \\ \text{benzene service} \end{bmatrix}$$

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]

		≥10,000 ppmv Emission Factor[b]	<10,000 ppmv Emission Factor[b]
Equipment Type	Service	lb/hr/source(kg/hr/source)	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	$9.8x10^{-2}$	$2.5x10^{-5}$
	Heavy Oil	NA	$8.4x10^{-6}$
	Light Oil	$8.7x10^{-2}$	$1.9x10^{-5}$
	Water/Oil	$6.4x10^{-2}$	$9.7x10^{-6}$
Pump seals	Gas	$7.4x10^{-2}$	$3.5x10^{-4}$
	Heavy Oil	NA	NA
	Light Oil	$1.0x10^{-1}$	$5.1x10^{-4}$
	Water/Oil	NA	$2.4x10^{-5}$
Others[c]	Gas	$8.9x10^{-2}$	$1.2x10^{-4}$
	Heavy Oil	NA	$3.2x10^{-5}$
	Light Oil	$8.3x10^{-2}$	$1.1x10^{-4}$
	Water/Oil	$6.9x10^{-2}$	$5.9x10^{-5}$
Connectors	Gas	$2.6x10^{-2}$	$1.0x10^{-5}$
	Heavy Oil	NA	$7.5x10^{-6}$
	Light Oil	$2.6x10^{-2}$	$9.7x10^{-6}$
	Water/Oil	$2.8x10^{-2}$	$1.0x10^{-5}$
Flanges	Gas	$8.2x10^{-2}$	$5.7x10^{-6}$
	Heavy Oil	NA	$3.9x10^{-7}$
	Light Oil	$7.3x10^{-2}$	$2.4x10^{-6}$
	Water/Oil	NA	$2.9x10^{-6}$
Open-ended lines	Gas	$5.5x10^{-2}$	$1.5x10^{-5}$
	Heavy Oil	$3.0x10^{-2}$	$7.2x10^{-6}$
	Light Oil	$4.4x10^{-2}$	$1.4x10^{-5}$
	Water/Oil	$3.0x10^{-2}$	$3.5x10^{-6}$

Source: Reference 54.

[a] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50 percent, from the point of origin to the point where the water content reaches 99 percent. For water streams with a water content greater than 99 percent, the emission rate is considered negligible.

[b] These factors are for total organic compound emission rates (including non-VOC such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[c] The "other" equipment type was derived from compressors, diaphrams, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

TABLE 4-21. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

Equipment Component (Emission Source)	Control Technique	Percent Reduction[a]
Pump Seals:		
Packed and Mechanical	Seal area enclosure vented to a combustion device	100
	Monthly LDAR[b]	69
	Quarterly LDAR	45
Double Mechanical[c]	N/A[d]	--
Compressors	Vent degassing reservoir to combustion device	100
Flanges	None available	0
Valves:		
Gas	Monthly LDAR	87
	Quarterly LDAR	67
Liquid	Monthly LDAR	84
	Quarterly LDAR	61
Pressure Relief Devices		
Gas	Monthly LDAR	50
	Quarterly LDAR	44
	Rupture Disk	100
Sample Connections	Closed-purge sampling	100
Open-Ended Lines	Caps on open ends	100

Source: Reference 55.

[a] If a negative reduction for a control technique was indicated, zero was used.
[b] LDAR = Leak detection and repair, at a leak definition of 10,000 ppmv.
[c] Assumes the seal barrier fluid is maintained at a pressure above the pump stuffing box pressure and the system is equipped with a sensor that detects failure of the seal and/or barrier fluid system.
[d] N/A - Not applicable. There are no VOC emissions from this component.

practices that reduce organic emissions include keeping manholes and other access doors gasketed and bolted unless in use.

The control efficiencies achieved by the various types of control equipment vary. Storage tanks with internal or external floating roofs will have varying emission control efficiencies depending on the type of floating deck and seal mechanism used, as well as various other factors. The control efficiency achieved by closed-vent systems and control devices also varies, depending on the type and specific design of the control device used. For information on the control efficiencies associated with specific control devices, refer to Tables 4-10 and 4-11. The control devices applicable to reducing process vent emissions listed in these tables are also applicable to storage tanks.

Storage tanks containing benzene and other organic compounds are regulated by the four following Federal rules:

1. "National Emission Standard for Benzene Emissions from Benzene Storage Vessels;"[61]
2. "Standards of Performance for Volatile Organic Liquid Storage Vessels for which Construction, Reconstruction, or Modification Commenced after July 23, 1984;"[62]
3. "National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater;"[63] and
4. "National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries."[49]

In combination, these four regulations generally require new and existing facilities subject to the rules to store benzene in an internal-floating-roof storage tank, an external-floating-roof storage tank, or a fixed-roof storage tank with a closed-vent system and control device that reduces emissions by 95 percent for a new facility, or 90 percent for an existing facility. Additionally, the four regulations include requirements for specific seal mechanisms and gaskets to be utilized on a floating roof, as well as certain work practices.

4.5.4 Wastewater Collection and Treatment System Emissions, Controls, and Regulations

A possible source of benzene emissions from chemical production operations that use benzene are wastewater collection and treatment systems that handle wastewater containing benzene. Benzene emissions from wastewater collection systems can originate from various types of equipment including wastewater tanks, surface impoundments, containers, drain systems, and oil-water separators. Emissions also originate from wastewater treatment systems. Equations for estimating emissions of organic compounds from wastewater collection and treatment systems are provided in the EPA document *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 4.[64]

Two control strategies can be applied to benzene emissions from wastewater. The first control strategy is waste minimization through process modifications, modification of operating practices, preventive maintenance, recycling, or segregation of waste streams. The second control strategy is to reduce the benzene content of the wastewater through treatment before the stream contacts ambient air. A complete strategy for reducing the benzene content of the wastewater includes: (1) suppression of emissions from collection and treatment system components by hard piping or enclosing the existing wastewater collection system up to the point of treatment, (2) treatment of the wastewater to remove benzene, and (3) treatment of residuals. Residuals include oil phases, condensates, and sludges from nondestructive treatment units.[65] This section will discuss the second control strategy of reducing benzene emissions by suppression and treatment.

The benzene emissions from wastewater collection and treatment systems can be controlled either by hard piping or by enclosing the transport and handling system from the point of wastewater generation until the wastewater is treated to remove or destroy the organic compounds. Suppression techniques can be broken down into four categories: collection system controls, roofs, floating membranes, and air-supported structures. These techniques can be applied to drain systems, tanks, containers, surface impoundments, and oil-water separators. Suppression of benzene emissions merely keeps the organic compounds in the wastewater until they reach the next potential benzene emission source. Therefore, these techniques are not effective unless the benzene emissions are suppressed until the wastewater reaches a treatment device where the organic compounds are either removed or destroyed. Also, work practices, such as leak detection and repair, must be used to maintain equipment effectiveness.[65]

Treatment techniques that can be used to remove or destroy benzene are steam stripping and air stripping (removal) and biological treatment (destruction). Steam and air stripping accomplish removal by stripping benzene out of the wastewater into a gas stream, which must then be controlled and vented to the atmosphere. Biological treatment destroys benzene by using microorganisms to biodegrade the benzene in the process of energy and biomass production.

Add-on controls serve to reduce benzene emissions by destroying or extracting benzene from gas phase vent streams before it is discharged to the atmosphere. Add-on controls are applicable to vents associated with collection and treatment covers, such as drain covers, fixed roofs, and air-supported structures, and with organic compound removal devices, such as air strippers and steam strippers. Add-on controls for benzene emissions are classified into four broad categories: adsorption, combustion, condensation, and absorption. The type of add-on control best suited for a particular wastewater emission source depends on the size of the source and the characteristics of the wastewater in the source.[65]

The control efficiencies associated with the various types of suppression, treatment, and add-on control equipment vary. Estimating the control efficiency of emissions suppression techniques for wastewater collection systems (e.g., water seals, covers, floating roofs, and submerged fill pipes) is complex, and equations for estimating emissions from these sources are not readily available. The control efficiency associated with use of a fixed-roof or gasketed cover and a closed-vent system routed to a control device would be equivalent to the efficiency achieved by the control device. Refer to Tables 4-10 and 4-11 for a listing of control devices applicable to wastewater systems. Additionally, the control efficiencies associated with steam and air strippers and biological treatment units vary, depending on the design of the systems. Refer to the discussion below for the specific control efficiencies associated with steam strippers and biological treatment units that would be designed to comply with existing Federal regulations.

Wastewater streams containing benzene are Federally regulated by the following rules:

1. "National Emission Standard for Benzene Waste Operations;"[66]
2. "National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater" (HON);[63] and
3. "National Emission Standards for Hazardous Air Pollutants at Petroleum Refineries."[49]

The rules regulate benzene emissions from wastewater collection and treatment systems, and apply to new and existing facilities. Chemical production processes subject to the regulations would be required to apply many of the controls specified above for both wastewater collection and waste water treatment systems.

The rules require specific suppression equipment (e.g., roofs) and work practices (e.g., leak detection and repair) rather than specifying a suppression control efficiency that must be achieved. For add-on control devices (e.g., incinerators, adsorbers) to destroy organics vented from collection and treatment equipment, both rules require 95 percent efficiency.

For treatment, the National Emission Standard for Benzene Waste Operations[66] and the National Petroleum Refinery NESHAP[49] do not require specific treatment equipment. Instead, the rule requires the treatment process to achieve either removal or destruction of benzene in the waste system by 99 percent, or removal of benzene to less than 10 parts per million by weight (ppmw). However, the technology basis for the 99 percent efficiency standard is steam stripping.

The HON offers several different wastewater treatment compliance options. These options include concentration-based limits, pollutant reduction percentages, and an equipment standard. The equipment standard is a steam stripper with specific design criteria that would result in a 99 percent reduction in benzene emissions. The HON also allows facilities to comply with the treatment standard by using biological treatment units that achieve a 95 percent reduction of total organic hazardous air pollutants in the wastewater. (Benzene is one of the hazardous air pollutants).

4.5.5 Product Loading and Transport Operations Emissions, Controls, and Regulations

Although pipeline transfer of raw materials and products is widely used in the different industries, shipment by tank cars, tank trucks, ships, and barges is also common. The product loading and transportation of chemicals and petroleum liquids represent potential sources of evaporation losses.

Emissions from the above sources are due to loading losses, ballasting losses, and transit losses. Refer to Section 6.3 (Gasoline Marketing) of this document for information on emission factors and equations to estimate emissions from loading and transport operations, as well as information on control technology.

The HON regulates organic hazardous air pollutants (HAP) emissions from product loading and transport operations.[59,63] The National Emission Standard for Benzene Emissions from Benzene Transfer Operations also regulates benzene transfer emissions.[67]

SECTION 5.0

EMISSIONS FROM MAJOR USES OF BENZENE

The largest portion of benzene produced is used in the production of ethylbenzene/styrene. Other major chemicals for which benzene is used as a feedstock include cyclohexane, cumene, phenol, nitrobenzene, and linear alkylbenzene. For each of these emission sources, the following information is provided in the sections below: (1) a brief characterization of the national activity in the United States, (2) a process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed.

Emission factors are presented, as available. The reader is advised to contact the specific source in question to verify the nature of the process, production volume, and control techniques used before applying any of the emission factors presented in this report.

Other minor chemicals where benzene is used as a feedstock include resorcinol, benzophenone, hydroquinone, anthraquinone, biphenyl, and benzene sulfonic acid.[68] These chemical processes are discussed briefly in this section. Although benzene has been used in the past as a feedstock in the production of maleic anhydride, all capacity for producing maleic anhydride in the United States is now n-butane based; therefore, the process for producing maleic anhydride from benzene is not included in this section.

5.1 ETHYLBENZENE AND STYRENE PRODUCTION

Ethylbenzene is a liquid at standard conditions, with a boiling point of 277 °F (136°C) and a vapor pressure of 1,284 Pa (0.0126 atm).[69] About 50 percent of the U.S. production of benzene is used to produce ethylbenzene. The ethylbenzene industry is closely tied to the styrene industry because styrene is produced exclusively from ethylbenzene. There can be approximately a 0.3 percent by weight carry-over of benzene into ethylbenzene and styrene.[9] Additionally, some benzene is reformed in the production of styrene. Ethylbenzene production processes and uses thereby constitute a major potential source of benzene emissions, particularly because styrene production is anticipated to experience continued growth. Ethylbenzene demand is expected to show growth of only 2.5 to 3.5 percent per year over the next several years.[70]

Ethylbenzene is used almost exclusively to produce styrene. Some ethylbenzene is used as a solvent (often replacing xylene) and in the production of some dyes.[71] Total ethylbenzene production capacity is currently 13,874 million pounds per year (lb/yr) (6,293 kg/yr).[11] Approximately 95 percent of this capacity is based on benzene alkylation, with the remainder based on extraction from mixed xylene streams. Most styrene is produced by two methods: hydrogenation of ethylbenzene (89 percent) and peroxidation of ethylbenzene with subsequent hydration (11 percent). The latter process can also co-produce propylene oxide. A third process, converting ethylbenzene isothermally to styrene, was developed in Europe. To date, no U.S. facilities report using this method.

Another method that co-produces both ethylbenzene and styrene has been patented.[72] In this process, toluene and light alkanes other than ethane are reacted at 1,832 to 2,192 °F (1,000 to 1,200°C) and then gradually cooled to produce an 80 percent ethylbenzene/12 percent styrene product with a mass of about 25 percent by weight of the toluene reactant. These products can be separated by distillation, and the ethylbenzene either recycled, sold, or converted to styrene by another process--dehydrogenation or peroxidation. This process is not reported to be in use at this time.

Table 5-1 lists U.S. producers of ethylbenzene and styrene.[11,69,73] Most facilities produce both ethylbenzene and styrene on site, thus reducing shipping and storage. Only one styrene production site does not have ethylbenzene production capacity. Four ethylbenzene production sites do not have styrene production capacity. Ethylbenzene from mixed xylene separation is generally shipped or supplemented with another ethylbenzene source for styrene production. Only one site uses the peroxidation process to produce styrene. Table 5-1 also gives the latest facility capacity.

5.1.1 Process Description for Ethylbenzene and Styrene Production Using Benzene Alkylation and Ethylbenzene Dehydrogenation

Most ethylbenzene production is integrated with the dehydrogenation process to produce styrene; therefore, these processes are described together. The primary reactions are (1) catalytic alkylation of benzene with ethylene to produce ethylbenzene, and (2) catalytic dehydrogenation of ethylbenzene to produce styrene.

A process flow diagram including the basic operations that may be used in the production of ethylbenzene by benzene alkylation with ethylene is shown in Figure 5-1.[14,74]

The first step in the process is the drying of benzene to remove water from both feed and recycled benzene. An emission source in this process is the vent from the benzene drying column (Vent B).[69]

The dry benzene (Stream 1) is fed to the alkylation reactor along with ethylene, aluminum chloride catalyst, and recycled polyethylbenzenes. The reactor effluent (Stream 2) goes to a settler, where crude ethylbenzene is decanted and the heavy catalyst-complex layer is recycled to the reactor. Any inert gases fed with the ethylene or produced in the alkylation reactor, along with some unreacted benzene, other organics, and hydrogen chloride, are exhausted from the reactor or from the treating section (Vent A). Reactor vent gas is generally routed through a condenser and scrubbers in the alkylation reaction section (not shown on the

TABLE 5-1. U.S. PRODUCERS OF ETHYLBENZENE AND STYRENE

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,e] (315)	---	---
Dow Chemical U.S.A.	Freeport, TX	A[c]	1750[a] (794)	C[b]	1420[a] (644)
Huntsman Chemical Corporation	Bayport, TX	NA	1240[a] (562)	C[b]	1250[a] (567)
Koch Refining Company	Corpus Christi, TX	65% A[c] 35% B[c]	100[a] (45)	---	---
Phibro Energy USA, Inc.	Houston, TX	NA	25[a] (11)	---	---
Rexene Corporation	Odessa, TX	NA	350[a] (159)	C[b]	320[a] (145)
Sterling Chemicals, Inc.	Texas City, TX	NA	1750[a] (794)	C[b]	1600[a] (726)
Westlake Styrene Corporation	Lake Charles, LA	NA	368[a] (167)	---	---
	Sulphur, LA	---	---	C[b]	353[a] (160)

(continued)

TABLE 5-1. CONTINUED

Source: References 11, 69, and 73.

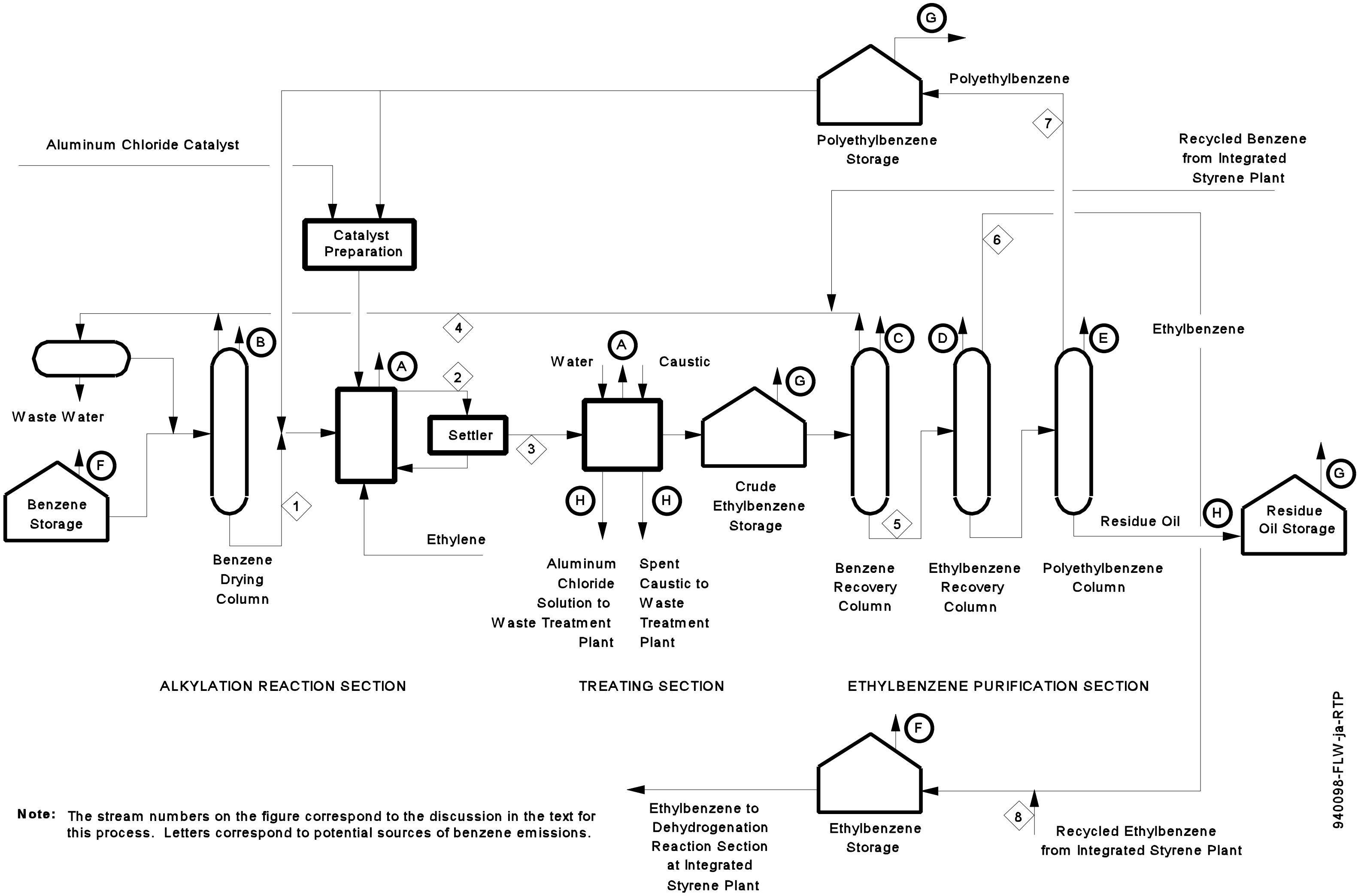
[a] Reference 11.
[b] Reference 73.
[c] Reference 69.
[d] Capacity does not include an excess capacity of 500 million pounds (227 million kg) of capacity on standby.
[e] Plant is on standby.

NA = Not available.

A = Benzene Alkylation (ethylbenzene production)
B = Xylene Separation (ethylbenzene production)
C = EB Hydrogenation (styrene production)
D = EB Peroxidation and Dehydration (styrene production)

“--” = means that the plant does not make this product.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contact with plant personnel. These data for producers and locations were current as of January 1993.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

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

Source: References 14 and 74.

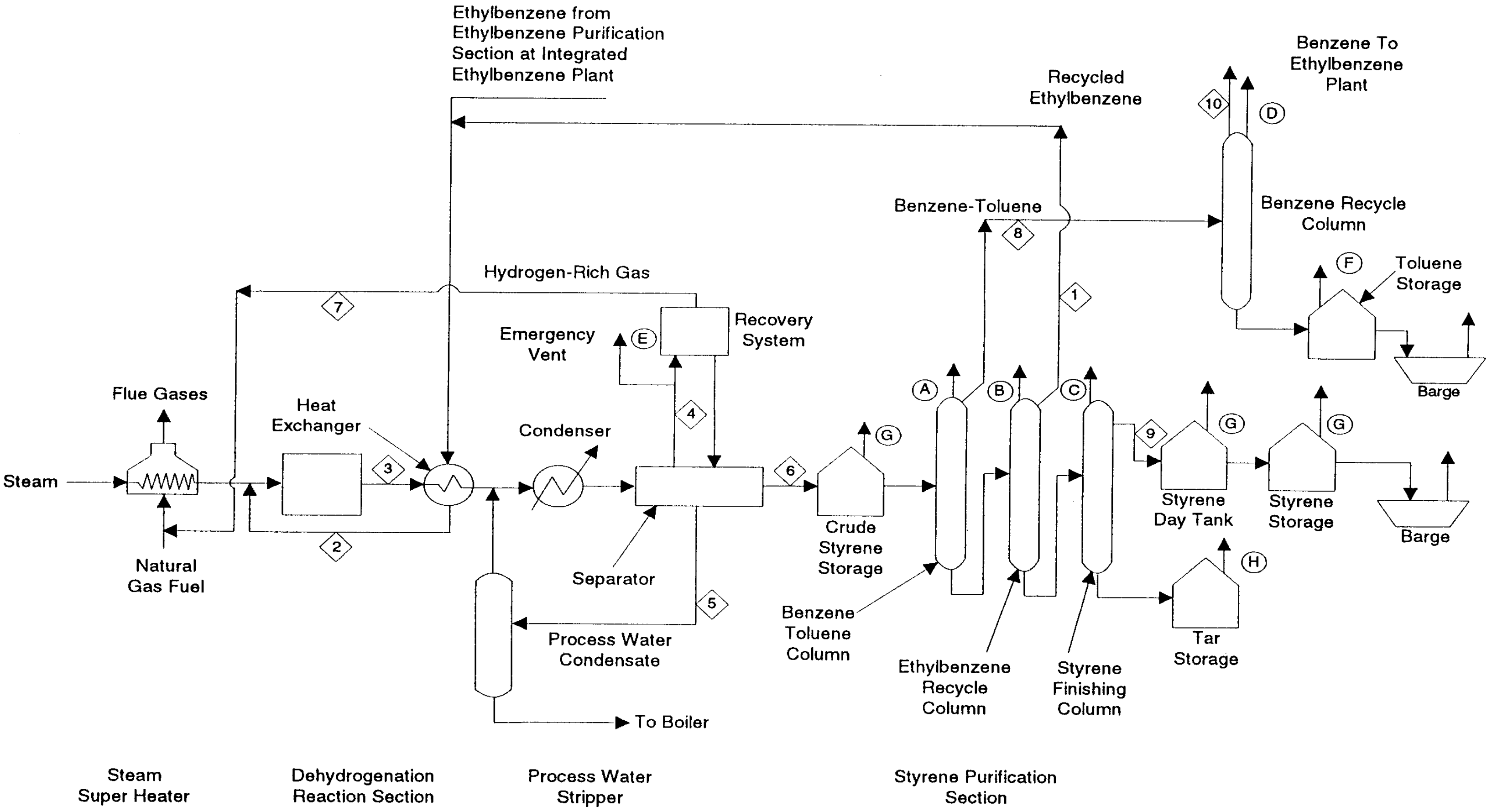
figure) to recover aromatics and to remove hydrogen chloride (HCl) before the remaining inert gases are vented.[69]

The crude ethylbenzene (Stream 3) from the settler is washed with water and caustic to remove traces of chlorides and then fed to the ethylbenzene purification section. The crude ethylbenzene contains 40 to 55 percent benzene, 10 to 20 percent polyethylbenzene (PEB), and high-boiling point materials. The first step in purification is separation of recycled benzene (Stream 4) from the crude ethylbenzene in the benzene recovery column. In the second step, the product ethylbenzene (Stream 5) is separated from the heavier hydrocarbons in the ethylbenzene recovery column. The heavier hydrocarbons are distilled in the polyethylbenzene column to separate the polyethylbenzenes, which are recycled (Stream 7), from the residue oil.[69] Emission points in the purification section include vents from the benzene and ethylbenzene recovery columns (Vent C and D, respectively) and the polyethylbenzene column (Vent E).[69]

Fresh ethylbenzene (Stream 6) from the ethylbenzene purification section is combined with recycled ethylbenzene (Stream 8) from the styrene purification section at the integrated styrene plant and is stored for use as an intermediate for making styrene.[69] Other emission points from the process including storage tanks, are shown in Figure 5-1.

A process flow diagram including the basic operations that may be used in the production of styrene by ethylbenzene dehydrogenation is shown in Figure 5-2.[69,74]

Fresh ethylbenzene from the ethylbenzene purification section (ethylbenzene plant) is combined with recycled ethylbenzene (Stream 1) from the styrene purification section. The purified ethylbenzene is preheated in a heat exchanger. The resultant vapor (Stream 2) is then mixed continuously with steam at 1,310°F (710°C) in the dehydrogenation reactor, which contains one of several catalysts. The reaction product (Stream 3) then exits through the heat exchanger and is further cooled in a condenser, where water and crude styrene vapors are condensed.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

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

Source: References 14 and 74.

The hydrogen-rich process gas is recovered and used as a fuel (Stream 7) and the process water is purified in a stripper and recycled to the boiler. The remaining crude styrene liquid (Stream 6) goes to a storage tank. Benzene and toluene (Stream 8) are removed from the crude styrene in the benzene/toluene column. They are then typically separated by distillation. The toluene is sold and the benzene is returned to ethylbenzene production section (Stream 10), or it may also be sold. Next, the ethylbenzene column removes ethylbenzene, which is directly recycled (Stream 1). Tars are removed and the product styrene (Stream 9) emerges from the styrene finishing column. In some facilities, an ethylbenzene/benzene/toluene stream is separated from the crude styrene initially and then processed separately.

Emission points in this process include vents from the columns for the styrene purification section between the separator and the recovery sections. These include the benzene toluene column (Vent A), the ethylbenzene recycle column (Vent B) and the emergency vent in the styrene finishing column (Vent C). Other emission points from the process including storage tanks and barge loading are shown in Figure 5-2.

5.1.2 Process Description for Ethylbenzene Production from Mixed Xylenes

Ethylbenzene can also be extracted from mixed xylene streams. Proportionately, however, very little ethylbenzene is produced in this fashion. The two major sources of ethylbenzene containing xylenes are catalytic reformate from refineries, and pyrolysis gasoline from ethylene production (see process description for ethylene production in Section 4.3). The amount of ethylbenzene available is dependent on upstream production variables. The ethylene separation occurs downstream of the benzene production. For this reason, the ethylbenzene produced by this process is not considered a source of benzene emissions. Instead, benzene emissions from the entire process train are considered to be emissions from benzene production and are included elsewhere in this document (Section 4.0).

When combined with the dehydrogenation process previously described to produce styrene (Figure 5-2), the process is similar except that the benzene recycling (Stream 10 in Figure 5-2) cannot be reused directly.

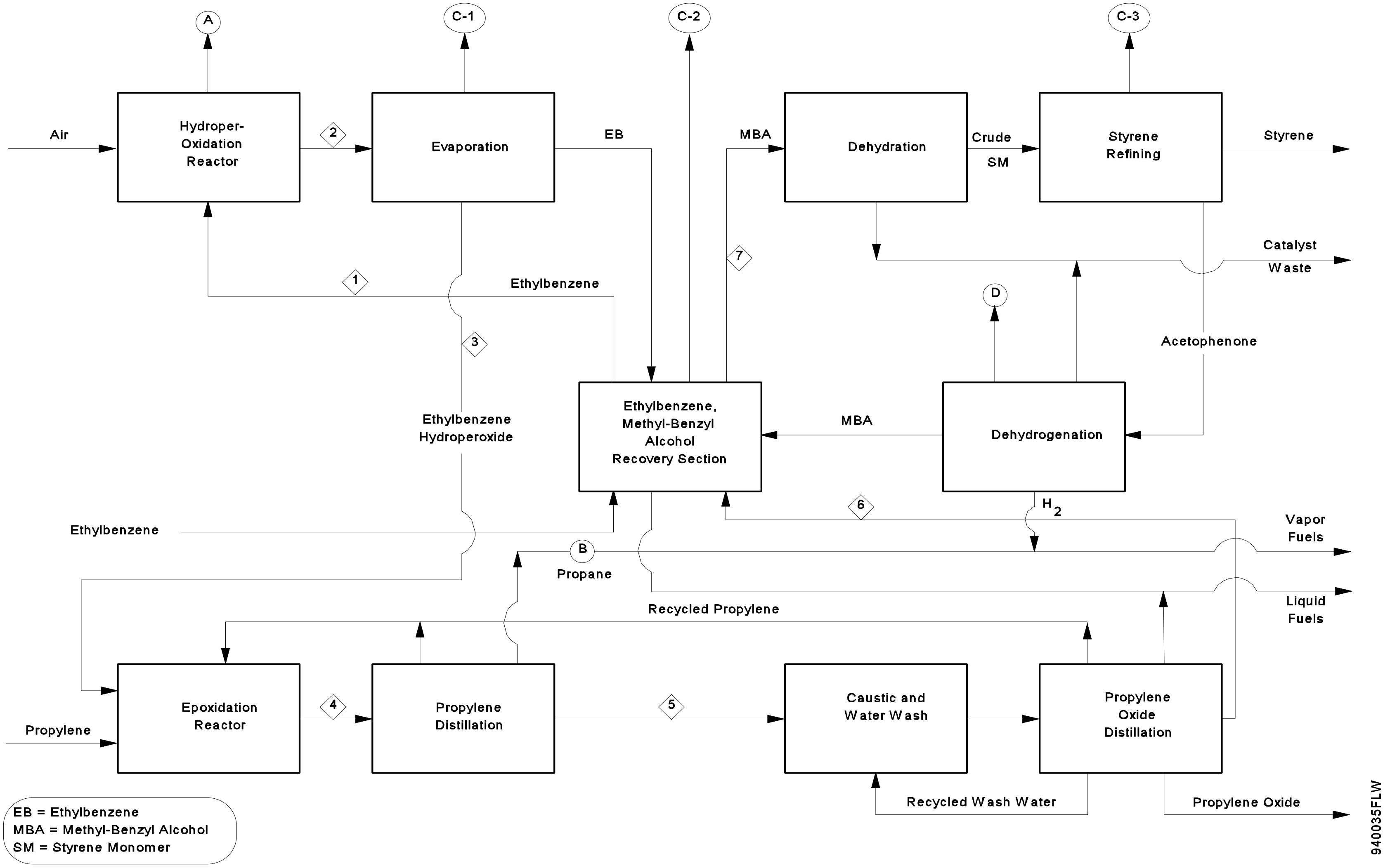
5.1.3 Process Description for Styrene Production from Ethylbenzene Hydroperoxidation

Presently, only one U.S. facility uses the hydroperoxidation process to produce styrene. Figure 5-3 shows a process flow diagram. The four major steps are described below.

Ethylbenzene (Stream 1) is oxidized with air to produce ethylene hydroperoxide (Stream 2) and small amounts of α-methyl-benzyl alcohol and acetophenone. The exit gas (principally nitrogen) is cooled and scrubbed to recover aromatics before venting. Unreacted ethylbenzene and low-boiling contaminants are removed in an evaporator. Ethylbenzene is then sent to the recovery section to be treated before reuse.

Ethylbenzene hydroperoxide (Stream 3) is combined with propylene over a catalyst mixture and high pressures to produce propylene oxide and acetophenone. Pressure is then reduced and residual propylene and other low-boiling compounds (Stream 4) are separated by distillation. The vent stream containing propane and some propylene can be used as a fuel. Propylene is recycled to the epoxidation reactor. The crude epoxidate (Stream 5) is treated to remove acidic impurities and residual catalyst material and the resultant epoxidate stream is distilled to separate the propylene oxide product for storage.

Residual water and propylene are recycled to the process train and liquid distillate is recovered as a fuel. The organic layer is routed (Stream 6) to the ethylbenzene and α-methyl-benzyl alcohol recovery section. Distillation removes any remaining ethylbenzene. Organic waste streams are separated from the α-methyl-benzyl alcohol and acetophenone organic waste liquids are used as fuel.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-3. Ethylbenzene Hydroperoxidation Process Block Diagram

Source: Reference 74.

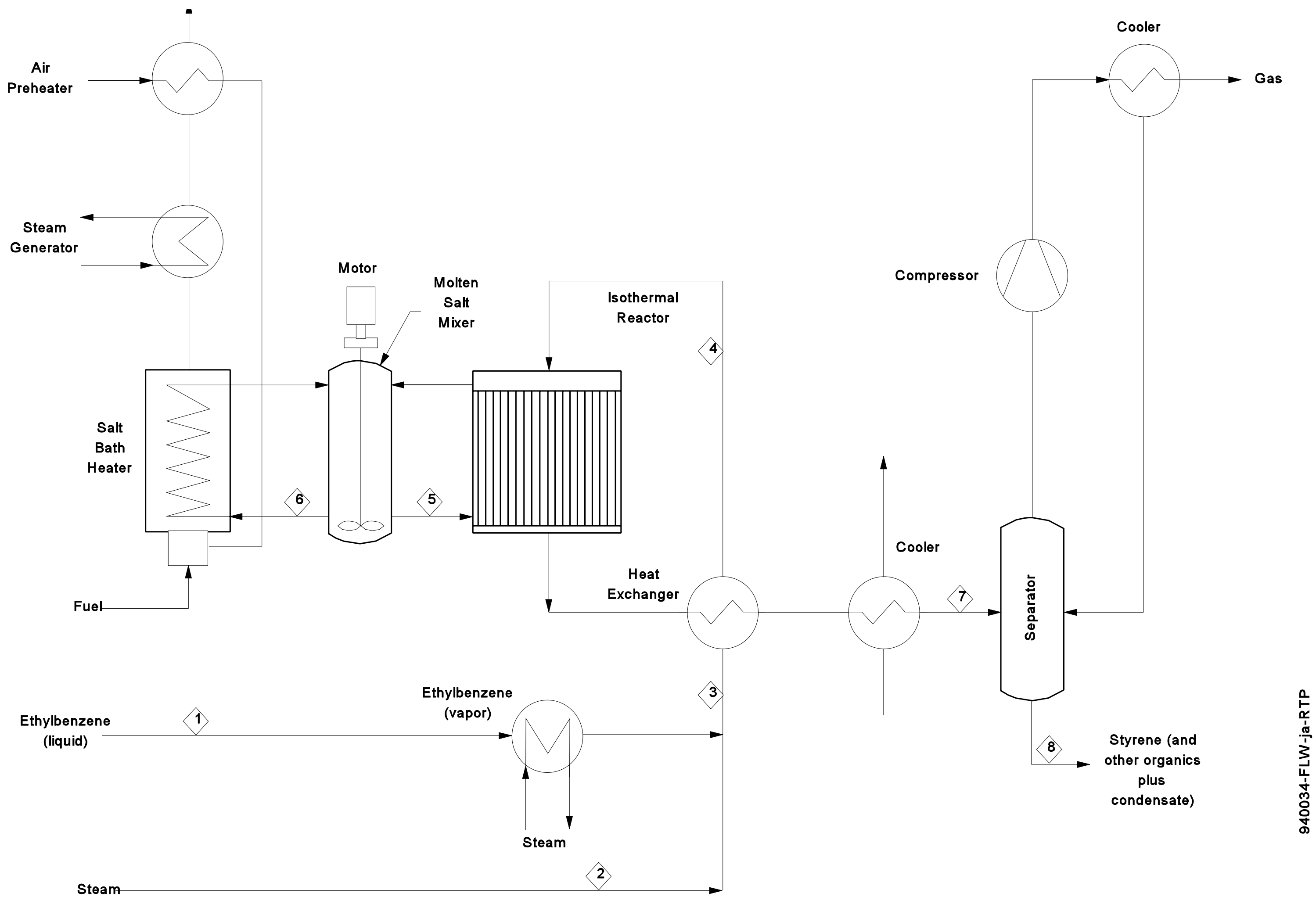
The mixed stream of α-methyl-benzyl alcohol and acetophenone (Stream 7) is then dehydrated over a solid catalyst to produce styrene. Residual catalyst solids and high-boiling impurities are separated and collected for disposal. The crude styrene goes to a series of distillation columns, where the pure styrene monomer product is recovered. The residual organic stream contains crude acetophenone, catalyst residue, and various impurities. This mixture is treated under pressure with hydrogen gas to convert the acetophenone to α-methyl-benzyl alcohol. Catalyst waste is separated from the α-methyl-benzyl alcohol, which is returned to the recovery section for processing and reuse. Hydrogen and organic vapors are recovered for use as fuel.

5.1.4 Process Description for Styrene Production by an Isothermal Process

Ethylbenzene may also be converted to styrene by an isothermal process (Figure 5-4). Liquid ethylbenzene is vaporized by condensing steam in a heat exchanger (Stream 1). Process steam (Stream 2) is then introduced into the ethylbenzene stream and the feed mixture is superheated (Stream 3) before it enters the molten-salt reactor (Stream 4) (see Figure 5-4).[75]

In the reactor, the ethylbenzene/steam mixture passes through the tubes, where it comes into contact with the catalyst and is dehydrogenated. Heat for the dehydrogenation reaction is supplied by molten salt (preferably a mixture of sodium carbonate, lithium carbonate, and potassium carbonate) surrounding the tubes (Stream 5). The reactor is maintained at a uniform wall temperature by circulating the molten-salt mixture through the heat exchanger of a fired heater (Stream 6).[75]

The reaction products are cooled and condensed in a separator (Stream 7). The liquid phase is a mixture of organic products: styrene, unreacted ethylbenzene, and small quantities of benzene, toluene, and high-boiling compounds. Styrene (Stream 8) is separated from the other liquid constituents, which then are recovered and recycled.[75]



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-4. Isothermal Processing of Styrene

Source: Reference 75.

The gas phase from the condensation step in the separator consists mainly of hydrogen, with small quantities of CO_2, CO, and methane. After these gases are compressed, they are cooled. Condensible products from this final cooling stage are then recovered and recycled to the separator. When hydrogen-rich offgas is used as fuel for the heater of the molten-salt reactor, the fuel requirement for this stage of the process is zero.[75]

5.1.5 Benzene Emissions from Ethylbenzene and Styrene Production via Alkylation and Dehydrogenation

Emission Estimates from Ethylbenzene Production and Dehydrogenation to Styrene

Emission factors have been developed based on an uncontrolled 300-million-kg/yr capacity integrated ethylbenzene/styrene production plant. Major process emission sources are the alkylation reactor area vents (Vent A in Figure 5-1), atmospheric and pressure column vents (Vents B, C, and D in Figure 5-1), vacuum column vents (Vent B in Figure 5-2), and the hydrogen separation vent (Stream 7 in Figure 5-2). Emission factors from these sources are given in Table 5-2.[69,74] The first four process vent streams in Table 5-2 are low-flow, high-concentration streams. The hydrogen separation stream (Stream 7 in Figure 5-2) is high-flow, low-concentration. Other emission sources listed in Table 5-2 include storage losses and shipment losses (Vent G). Fugitive emissions from valves and other equipment leaks are not indicated in Figure 5-1 or 5-2.

Reactor area vents remove various inerts plus entrained aromatics (benzene). Inerts include nitrogen or methane used in pressure control, unreacted ethylene, reaction byproducts, and ethylene feed impurities. In typical plants using liquid-phase aluminum chloride catalyst with high-purity ethylene, vent streams are usually cooled and scrubbed to recover aromatics. In plants using the newer solid support catalysts of the UOP or Mobil/Badger process, reactor vent flow rates are very high because of the low-purity ethylene feed. Process economics requires that these vent gases be burned as fuel.

TABLE 5-2. EMISSION FACTORS FOR ETHYLBENZENE/STYRENE PRODUCTION VIA ALKYLATION AND DEHYDROGENATION

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating
3-01-169-02 Ethylbenzene Manufacturing - Alkylation Reactor Vent	Alkylation Reactor Vent	Process Heater	0.0006 (0.0003)	U
		Uncontrolled	0.6[b] (0.3)	U
3-01-169-03 Ethylbenzene Manufacturing - Benzene Drying Column	Atmospheric/Pressure Column Vents[d]	Flare	0.024[b] - 0.96[d] (0.012 - 0.48)	U
		Uncontrolled	2.4[b] (1.2)	U
3-01-169-04 Ethylbenzene Manufacturing - Benzene Recovery Column				
3-01-169-05 Ethylbenzene Manufacturing - Ethylbenzene Recovery Column				
3-01-169-06 Ethylbenzene Manufacturing - Polyethylbenzene Recovery Column	Other Vacuum Vents[e]	Flare	0.0010[b] - 0.004[d] (0.005 - 0.002)	U
		Uncontrolled	0.10[b] (0.05)	U
3-01-206-02 Styrene Manufacturing - Benzene Recycle Column				
3-01-206-03 Styrene Manufacturing - Styrene Purification Vents				
3-01-206-XX Styrene Manufacturing -Benzene - Toluene Vacuum Vent	Benzene-Toluene Vacuum Vent	Flare	0.06[b] - 2.4[d] (0.03 - 1.2)	U
		Uncontrolled	6.0[b] (3.0)	U

(continued)

TABLE 5-2. CONTINUED

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating
3-01-206-XX Styrene Manufacturing - Hydrogen Separation Vent	Hydrogen Separation Vent	Flare	0.00006[b] - 0.0024[d] (0.00003 -0.0012)	U
		Uncontrolled	0.006[d] (0.003)	U
3-01-169-80/3-01-206-80	Equipment Leaks	Detection and Correction	See Section 4.5.2	
Ethylbenzene/Styrene Manufacturing - Equipment Leaks		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 $4.2\text{x}10^{-3}$ lb hydrocarbons/lb styrene ($4.2\text{x}10^{-3}$ kg hydrocarbons/kg styrene) in one plant where the hydrocarbons are benzene and toluene. Another condenser controlled vent emits $0.4\text{x}10^{-3}$ lb benzene/lb styrene ($0.4\text{x}10^{-3}$ 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 $9.6\text{x}10^{-6}$ lb benzene/lb styrene ($9.6\text{x}10^{-3}$ 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

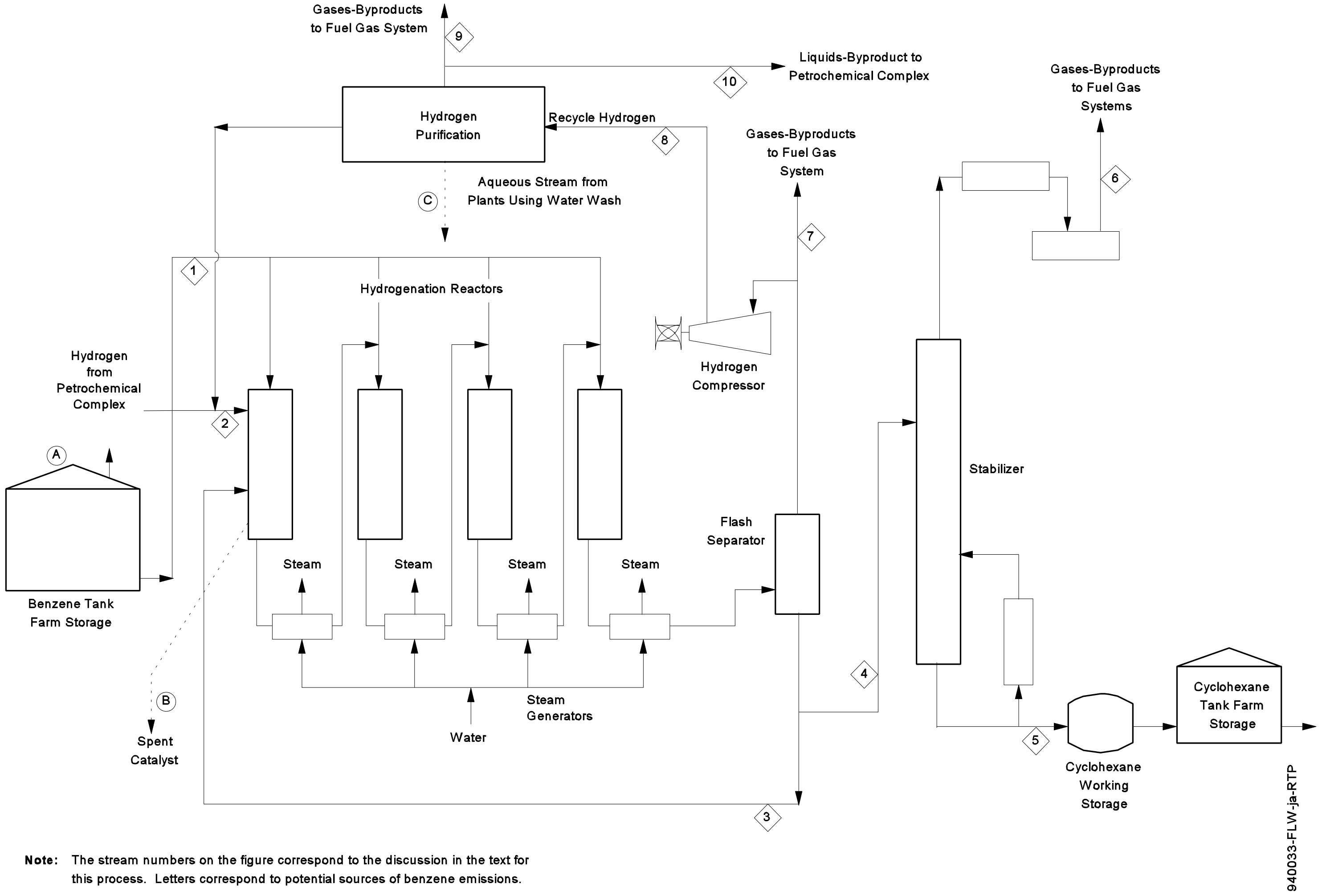
Company	Location	Annual Capacity millions of gal (l)
Chevron Chemical Company	Port Arthur, TX	38 (144)
Phillips Petroleum Company		
Specialty Chemicals Branch	Borger, TX	35 (132)
Olefins and Cyclics Branch	Sweeny, TX	90 (341)
Phillips Puerto Rico Core, Inc.	Guayama, PR	100 (379)
Texaco Chemical Company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

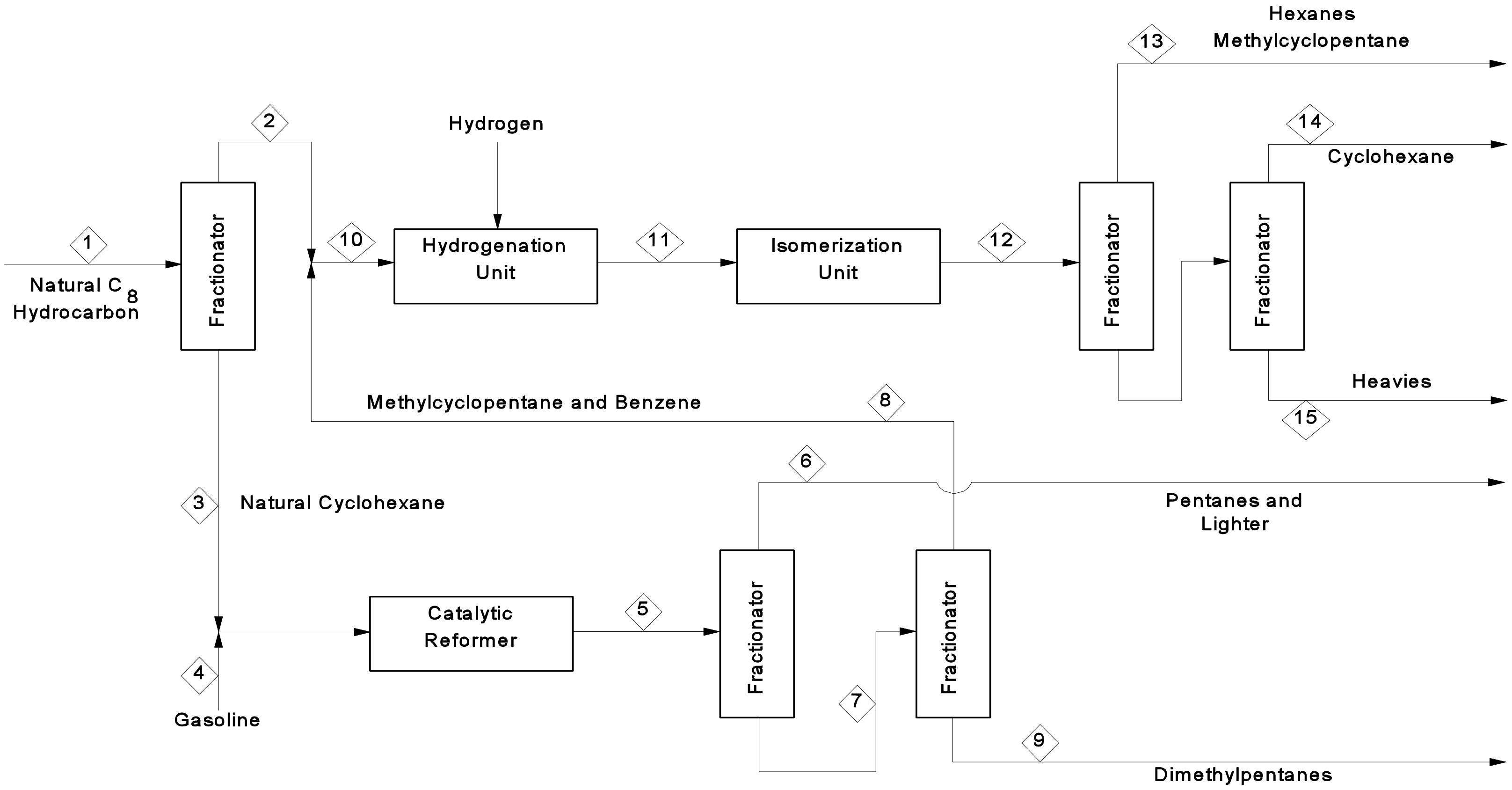
Other potential sources of emissions are catalyst handling (B) and absorber wastewater (C) (when an aqueous solution is used to purify the recycled hydrogen). Caution is taken to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.[76]

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:

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

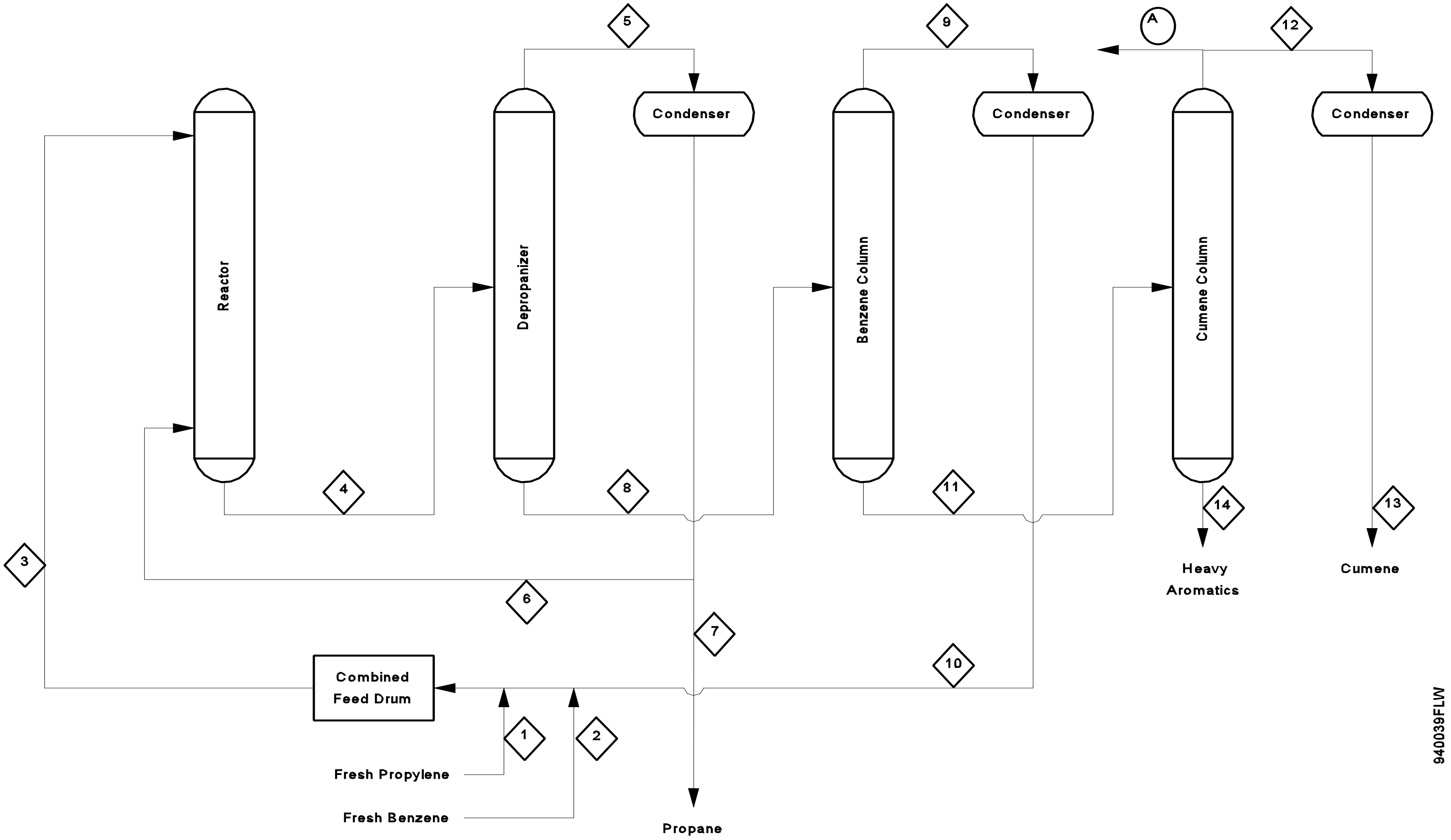
The exothermic reaction is typically conducted using solid phosphoric acid as a catalyst, but the reaction may also be conducted using aluminum chloride or sulfuric acid as the catalyst. The aluminum chloride and sulfuric acid processes are similar; therefore, the sulfuric acid process is not described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

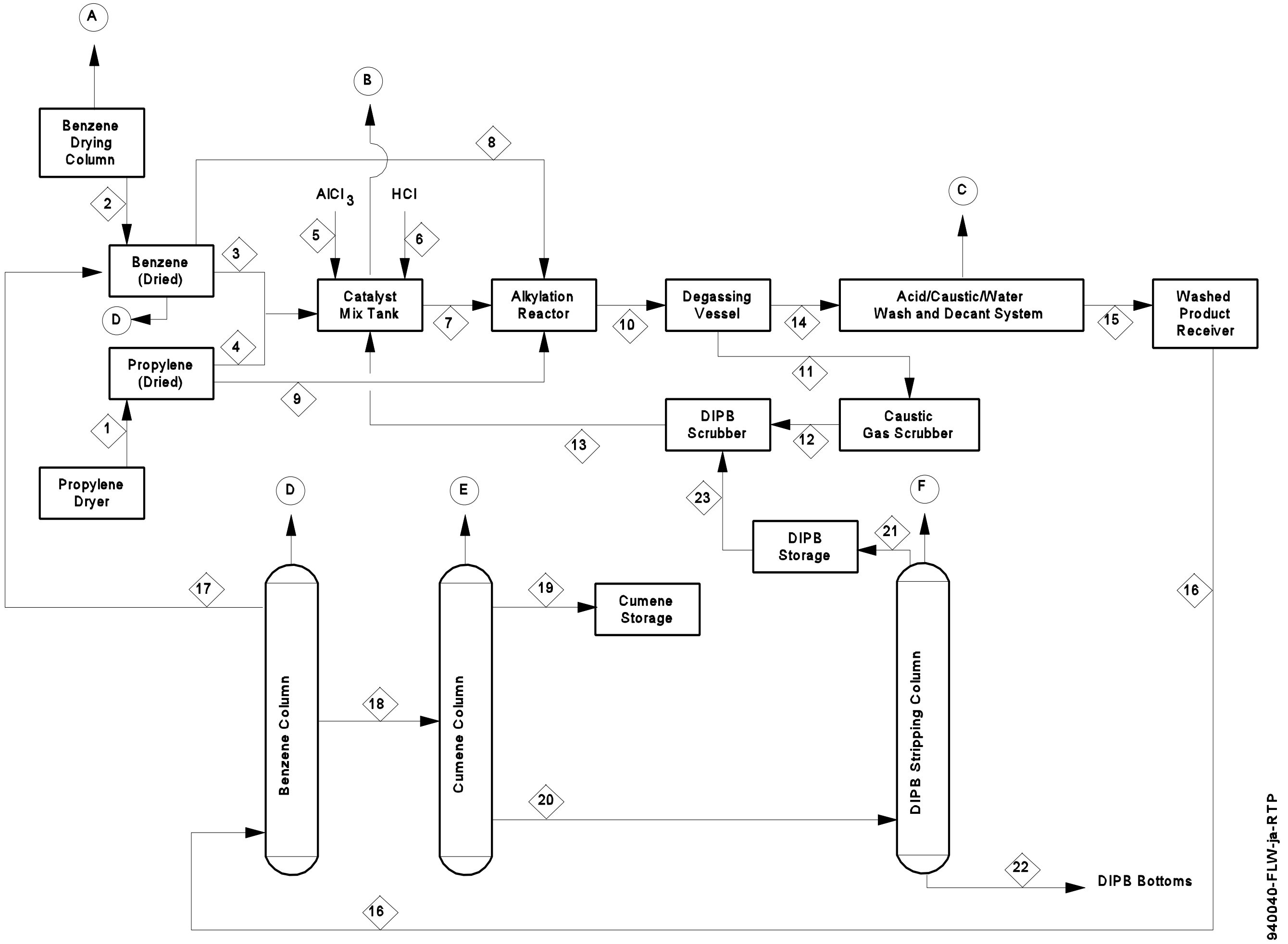
Unpurified product from the depropanizer (Stream 8) is sent to the benzene distillation column, where unreacted benzene is recovered overhead (Stream 9), sent through a condenser, and recycled to the feed drum (Stream 10). From the bottom of the benzene column (Stream 11), the crude product is sent to 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 x 10^{-2} (2.00 x 10^{-2})	U
		Flare	2.00 x 10^{-3} (1.00 x 10^{-3})	U
3-01-156-03 Cumene Manufacturing - Catalyst Mix Tank Scrubber Vent	Process Vent	Uncontrolled	3.18 x 10^{-1} (1.59 x 10^{-1})	U
		Flare	1.59 x 10^{-2} (7.95 x 10^{-3})	U
3-01-156-04 Cumene Manufacturing - Wash-Decant System Vent	Process Vent	Uncontrolled	1.57 x 10^{-2} (7.85 x 10^{-3})	U
		Flare	7.84 x 10^{-4} (3.92 x 10^{-4})	U
3-01-156-05 Cumene Manufacturing - Benzene Recovery Column	Process Vent	Uncontrolled	3.40 x 10^{-2} (1.70 x 10^{-2})	U
		Flare	1.70 x 10^{-3} (8.50 x 10^{-4})	U

Source: References 3 and 80.

[a] Factors are expressed as lb (kg) benzene emitted per ton (Mg) cumene produced.
[b] Derived by multiplying the total VOC emission factor by percent of benzene in the stream.

TABLE 5-6. U.S PRODUCERS OF PHENOL

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Allied-Signal, Inc. Engineering Materials Sector	Philadelphia, PA	810 (367)	Cumene peroxidation
Aristech Chemical Corporation	Haverhill, OH	630 (286)	Cumene peroxidation
BTL Specialty Resins Corporation	Blue Island, IL	90 (41)	Cumene peroxidation
Dakota Gasification Company	Beulah, ND	50 (23)	Petroleum and coal tar
Dow Chemical U.S.A.	Oyster Creek, TX	550 (249)	Cumene peroxidation
General Electric Company GE Plastics	Mount Vernon, IN	640 (290)	Cumene peroxidation
Georgia Gulf Corporation	Pasadena, TX	160 (73)	Cumene peroxidation
	Plaquemine, LA	440 (200)	Cumene peroxidation
Kalama Chemical, Inc.	Kalama, WA	70 (32)	Toluene oxidation
Merichem Company	Houston, TX	35 (16)	Petroleum and coal tar
PMC, Inc.	Santa Fe Springs, CA	8 (3.6)	Petroleum and coal tar
Shell Chemical Company Shell Chemical Company, Division	Deer Park, TX	600 (272)	Cumene peroxidation
Stimson Lumber Company Northwest Petrochemical Corporation, Division	Anacortes, WA	<5 (<2.3)	Petroleum

(continued)

TABLE 5-6. CONTINUED

Facility	Location	Annual Capacity million lb (million kg)	Process and Raw Material
Texaco, Inc. Texaco Chemical Company, Subsidiary	El Dorado, KS	95 (43)	Cumene peroxidation
TOTAL		<3,398 (<1,541)	

Source: References 11, 81, and 83.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of November 1993.

In the process involving peroxidation of cumene, acetone and phenol are produced by the peroxidation of cumene followed by cleavage of the resulting CHP. The two basic reactions for this process are as follows:[80]

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

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

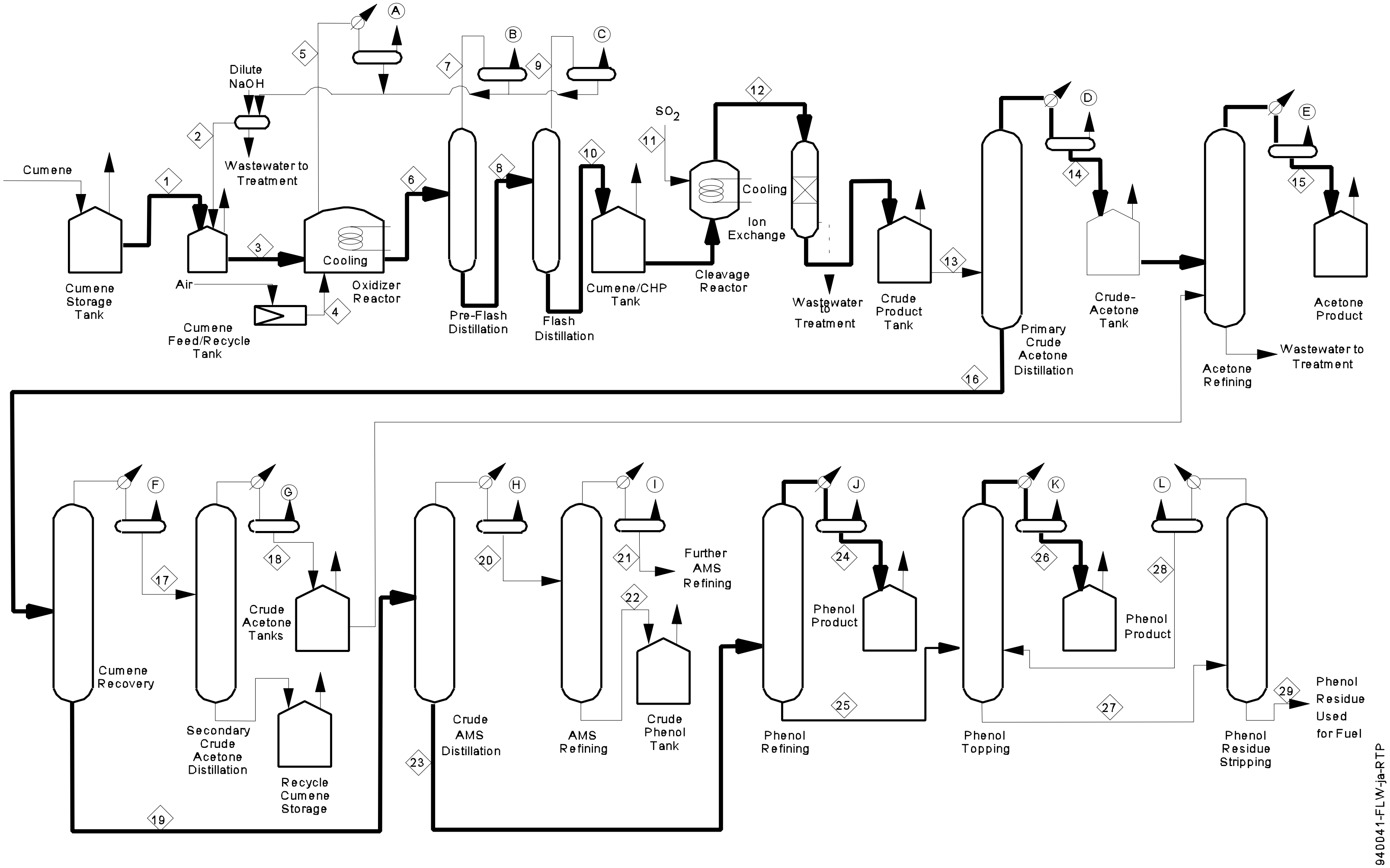
5.4.1 Phenol Production Techniques

There are two technologies for producing phenol by the peroxidation of cumene--one licensed by Allied Chemical and the other licensed by Hercules. The major differences between the Allied and Hercules processes involve the operating conditions of the peroxidation reaction and the method of neutralization of the acid in the cleavage product. These differences affect plant design primarily in the peroxidation and cleavage-product neutralization steps, in the location of process emission points, and in the potential quantity of process emissions. These two process types are discussed below.[80]

In addition to the two cumene peroxidation processes, phenol is produced by the oxidation of toluene. This process is described below; however, the description is brief because of limited available information on the process.

Allied Process

Figure 5-9 shows a typical flow diagram for the manufacture of phenol by the Allied process.[79] Cumene (Stream 1), manufactured on site or shipped to the site, and recycle cumene (Stream 2) are combined (Stream 3) and fed with air (Stream 4) to the multiple-reactor system, where cumene is oxidized to form CHP. Substantial quantities of cumene (Stream 5) are carried out of the reactors with the spent air to a refrigerated vent system, where part of the



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-9. Flow Diagram for Phenol Production from Cumene Using the Allied Process

Source: Reference 79.

cumene is recovered and recycled.[80] Uncondensed vapors, including organic compounds, are vented (Vent A).

The reaction product (Stream 6), containing primarily cumene and CHP, is vacuum flashed first in the pre-flash distillation column and then (Stream 8) in the flash distillation column to remove most of the cumene, which is recycled (Streams 7 and 9). Uncondensed vapors, including organic compounds, are vented (Vents B and C). The concentrated CHP (Stream 10) flows through the CHP concentrate tank to the cleavage reactor, where the CHP is cleaved to acetone and phenol by the addition of SO_2 (Stream 11). The cleavage product (Stream 12) is neutralized in ion-exchange columns and fed through the crude-product surge tank (Stream 13) to a multi-column distillation system.[80,84,85]

In the primary crude acetone distillation column, acetone and lower-boiling impurities such as acetaldehyde and formaldehyde are distilled overhead. This product (Stream 14) is condensed and flows through the crude acetone surge tank to the acetone refining column, where the acetone is distilled overhead. Acetone product is condensed (Stream 15) and sent to storage. Uncondensed vapors, including organic compounds, are vented from the condensers after both the primary crude acetone and acetone refining columns (Vents D and E).[80,84]

The compounds of relatively lower volatility (bottoms) from the primary crude acetone column (Stream 16) are distilled in the cumene recovery column to remove residual cumene. The overheads from the cumene recovery column are sent through a condenser (Stream 17) and into a secondary crude acetone distillation column to further remove acetone from the residual cumene. The residual cumene (i.e., the bottoms from the secondary crude acetone column) is stored for recycling.[80] The uncondensed vapors from the condensers, following both the cumene recovery column and secondary crude acetone column are vented (Vents F and G). The condensed overheads from the secondary crude acetone column (Stream 18) are fed through a crude acetone surge tank back to the acetone refining column.

Some facilities using this process may not incorporate the secondary crude acetone distillation column, which is utilized both to further recover acetone product and to reduce organic emissions from the storage tanks containing the recycle cumene. Some processes store the condensed product from the overhead of the cumene recovery column as the recycle cumene (Stream 17).

The bottoms from the cumene recovery column (Stream 19) contain primarily phenol, AMS, acetophenone, and other organics with higher boiling points than phenol. This stream is fed to the crude AMS distillation column. The crude AMS distillation column overhead stream (Stream 20) is condensed and sent to the AMS refining column. Uncondensed vapors from the condenser after the crude AMS distillation column are vented (Vent H). The stream entering the AMS refining column undergoes distillation to refine out AMS. The refined overhead stream is condensed (Stream 21) and sent to additional columns (not shown) for further refining.

The uncondensed vapors from the condenser following the AMS refining column are vented (Vent I). The bottoms from the AMS refining column (Stream 22) are stored in a crude phenol tank. The phenol in this storage tank is either sold as crude product or is fed to the phenol refining column for further refining. Crude phenol from the bottom of the crude AMS column (Stream 23) flows to the phenol refining column, where phenol is distilled overhead, condensed, (Stream 24), and fed to phenol product storage tanks. The uncondensed vapors from the condenser following the phenol refining column are vented (Vent J).[80,84,85]

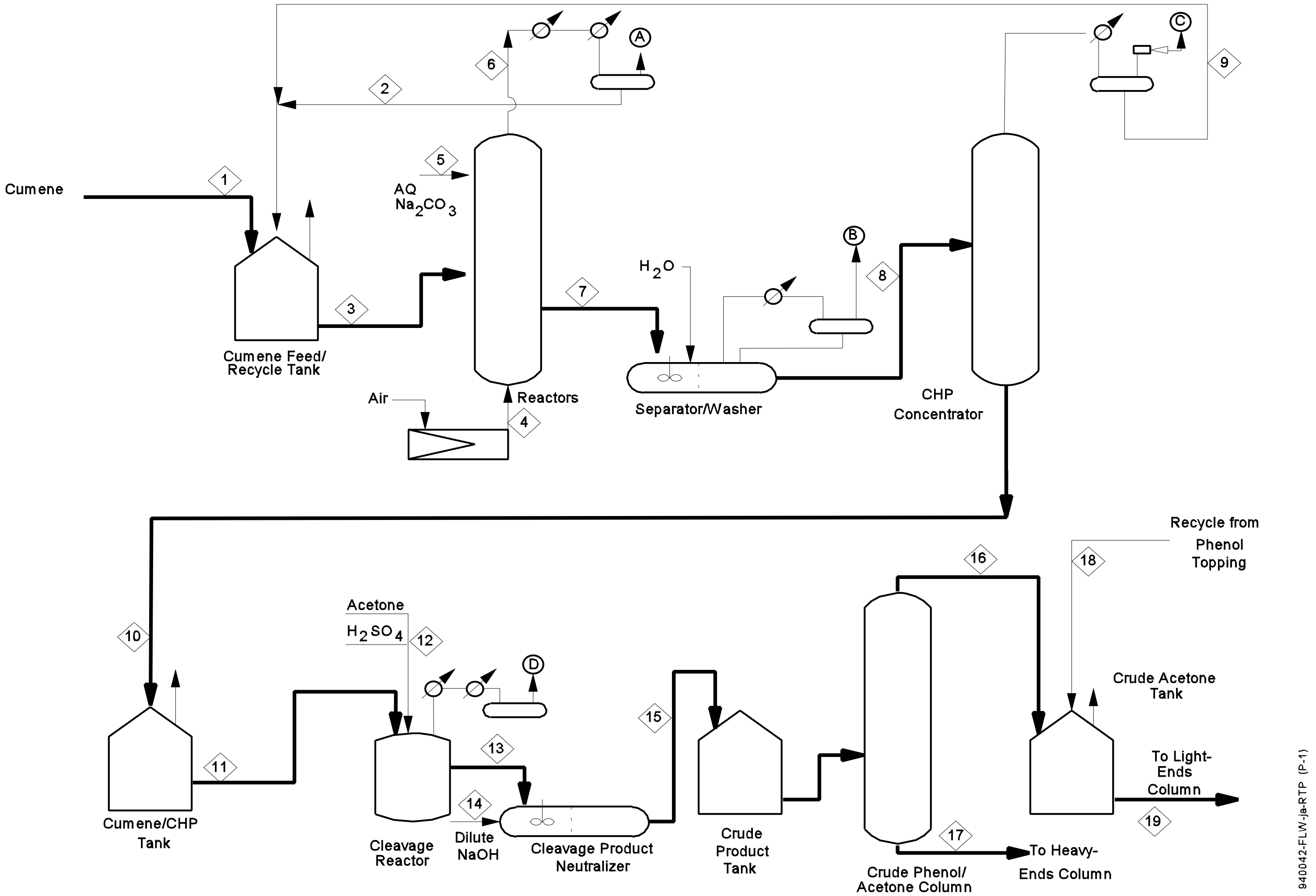
The bottoms from the phenol refining column (Stream 25) are further processed to recover phenol. The bottoms are sent to a phenol topping column, from which the overhead stream is condensed (Stream 26) and fed to phenol product storage. Uncondensed vapors from the condenser after the phenol topping column are vented (Vent K). The bottoms from the phenol topping column (Stream 27) are fed to a phenol residue stripping column, which removes phenol residue in the bottoms (Stream 29). The phenol residue may be used as fuel for on-site industrial boilers. The overheads from the phenol residue stripping column are condensed (Stream 28) and fed back to the phenol topping column to further recover phenol product. The uncondensed vapors from the condenser following the phenol residue stripping column are vented (Vent L).[84,85]

The phenolic wastewater generated by the Allied process (e.g., generated by recovery devices, such as condensers and scrubbers) is fed through distillation columns to further recover acetone and phenol products. This batch distillation cycle, which is not a continuous process, is not shown in Figure 5-9. Phenolic wastewater is fed through a dephenolizer (i.e., a steam stripping process) and one or two batch distillation columns. The recovered product is crude phenol or acetol phenol.[84-86]

Hercules Process

Figure 5-10 shows a typical flow diagram for the manufacture of acetone and phenol by the Hercules process.[79] Cumene from storage (Stream 1) and recycle cumene (Streams 2 and 9) are combined (Stream 3) and then fed with air (Stream 4) to the multiple-reactor system. Additionally, an aqueous sodium carbonate solution (Stream 5) is fed to the reactor system to promote the peroxidation reaction. In the reactor system, cumene is peroxidized to cumene hydroperoxide. Unreacted cumene is carried out of the reactors with the spent air (Stream 6) to a refrigerated vent system, where part of the cumene is recovered and recycled (Stream 2). Uncondensed vapors are vented (Vent A).[80]

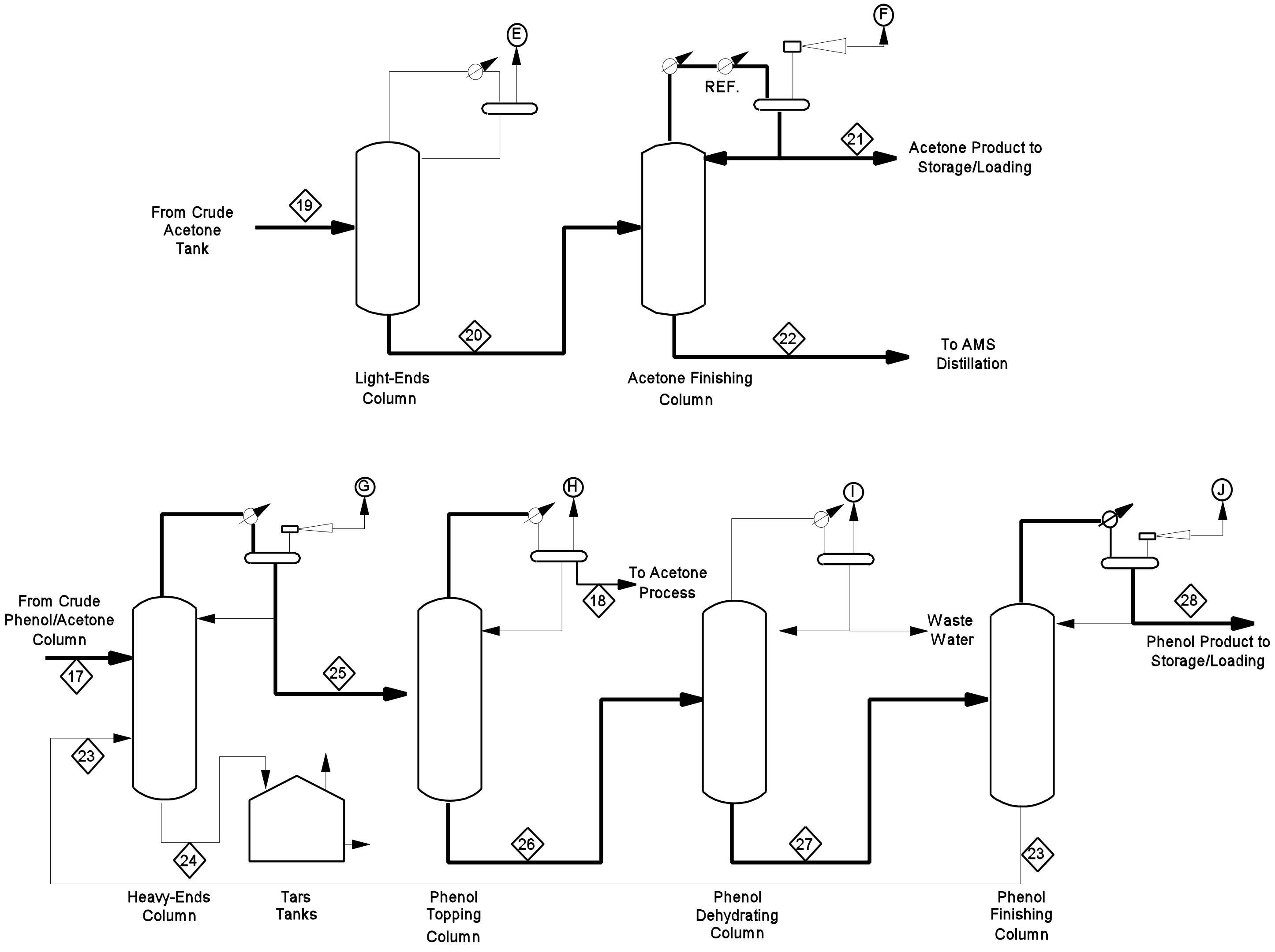
The oxidation reaction product (Stream 7) flows into a separator to remove spent carbonate solution and then is washed with water to remove remaining carbonate and other soluble components. The air stream removed is sent to a condenser from which uncondensed vapors are vented (Vent B). The washed product (Stream 8) is fed to a distillation column operated under vacuum, where the cumene hydroperoxide is separated from the cumene. The overheads from the CHP concentrator are condensed and the recovered



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. Flow Diagram for Phenol Production Using the Hercules Process

Source: Reference 79.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions. Lines in bold indicate the flow of the product stream.

Figure 5-10. (Continued)

cumene (Stream 9) is recycled. The uncondensed vapors from the condenser are vented (Vent C).

The concentrated CHP (Stream 10) is transferred through a surge tank to the cleavage reactor (Stream 11). Sulfuric acid, diluted to 5 to 10 percent with acetone (Stream 12), is added to catalyze the decomposition of CHP to acetone and phenol.[80] Uncondensed vapors captured from the cleavage reactor are vented (Vent D). Excess acid in the cleaved mixture (Stream 13) is neutralized with sodium hydroxide solution (Stream 14). The neutralized product (Stream 15) flows through the crude-product surge tank to a multi-column distillation train to produce product-grade acetone, phenol, and AMS.[80]

The crude product is separated in the first distillation column into a crude acetone fraction (Stream 16) and a crude phenol stream (Stream 17). The crude acetone (Stream 16) is combined with recycled hydrocarbons from the phenol topping column (Stream 18) and fed through a surge tank to the light-ends column (Stream 19) to strip low-boiling hydrocarbon impurities, such as acetaldehyde and formaldehyde, which are vented to the atmosphere (Vent E).

The bottoms stream from the light-ends column (Stream 20) is fed to the acetone finishing column, where the acetone is distilled overhead, condensed (Stream 21), and sent to day tanks and subsequently to acetone product storage and loading. Uncondensed vapors are vented (Vent F). The bottoms stream (Stream 22) is processed to produce AMS (not shown).[80]

The crude phenol stream (Stream 17) and the bottoms from the phenol finishing column (Stream 23) are fed to the heavy-ends column and distilled under vacuum to separate tars (Stream 24) from the impure phenol stream (Stream 25).[80] Uncondensed vapors from the condenser following the heavy-ends column are vented (Vent G).

The impure phenol is fed to the phenol topping column to remove hydrocarbons such as cumene and AMS. The overhead stream from the phenol topping column (Stream 18) may be condensed and recycled to the light-ends column of the acetone process for removal of residual acetone, cumene, and AMS. The uncondensed vapors from the condenser following the phenol topping column are vented (Vent H). The phenolic stream (Stream 26) is then fed to a dehydrating column, where water is removed overhead as a phenol/water azeotrope. Uncondensed vapors are vented (Vent I).[80]

The dried phenol stream (Stream 27) is distilled under vacuum in the phenol finishing column to separate product-quality phenol (Stream 28) from higher boiling components (Stream 23), which are recycled to the heavy ends column. Uncondensed vapors from the condenser after the phenol finishing column are vented (Vent J). The product-quality phenol is stored in tanks for subsequent loading.[80]

Toluene Oxidation Process

In this process, toluene is oxidized by air to benzoic acid. Following separation, the benzoic acid is catalytically converted to phenol.

5.4.2 Benzene Emissions from Phenol Production

Information related to benzene emissions from process vents, equipment leaks, storage vessels, wastewater collection and treatment systems, and product loading and transport operations associated with phenol production is presented below. Where a literature review revealed no source-specific emission factors for uncontrolled or controlled benzene emissions from these emission points, the reader is referred to Section 5.10 of this chapter, which provides a general discussion of methods for estimating uncontrolled and controlled benzene emissions from these types of emission points.

“Spent air” from the oxidizer reactor (Vent A, Figure 5-9) is the largest source of benzene emissions at phenol production plants utilizing the Allied process.[87] Table 5-7 provides uncontrolled and controlled (i.e., thermal oxidizer) emission factors from the oxidizer

TABLE 5-7. SUMMARY OF EMISSION FACTORS FOR PHENOL PRODUCTION BY THE PEROXIDATION OF CUMENE

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg)[a]	Factor Rating	Reference
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Uncontrolled[b]	4.00 x 10^{-3} (2.00 x 10^{-3})	U	3
3-01-202-02 Phenol Manufacturing - Cumene Oxidation	Process Vent	Thermal Oxidizer	1.16 x 10^{-4} (5.82 x 10^{-5})	D	88, 89

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[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)

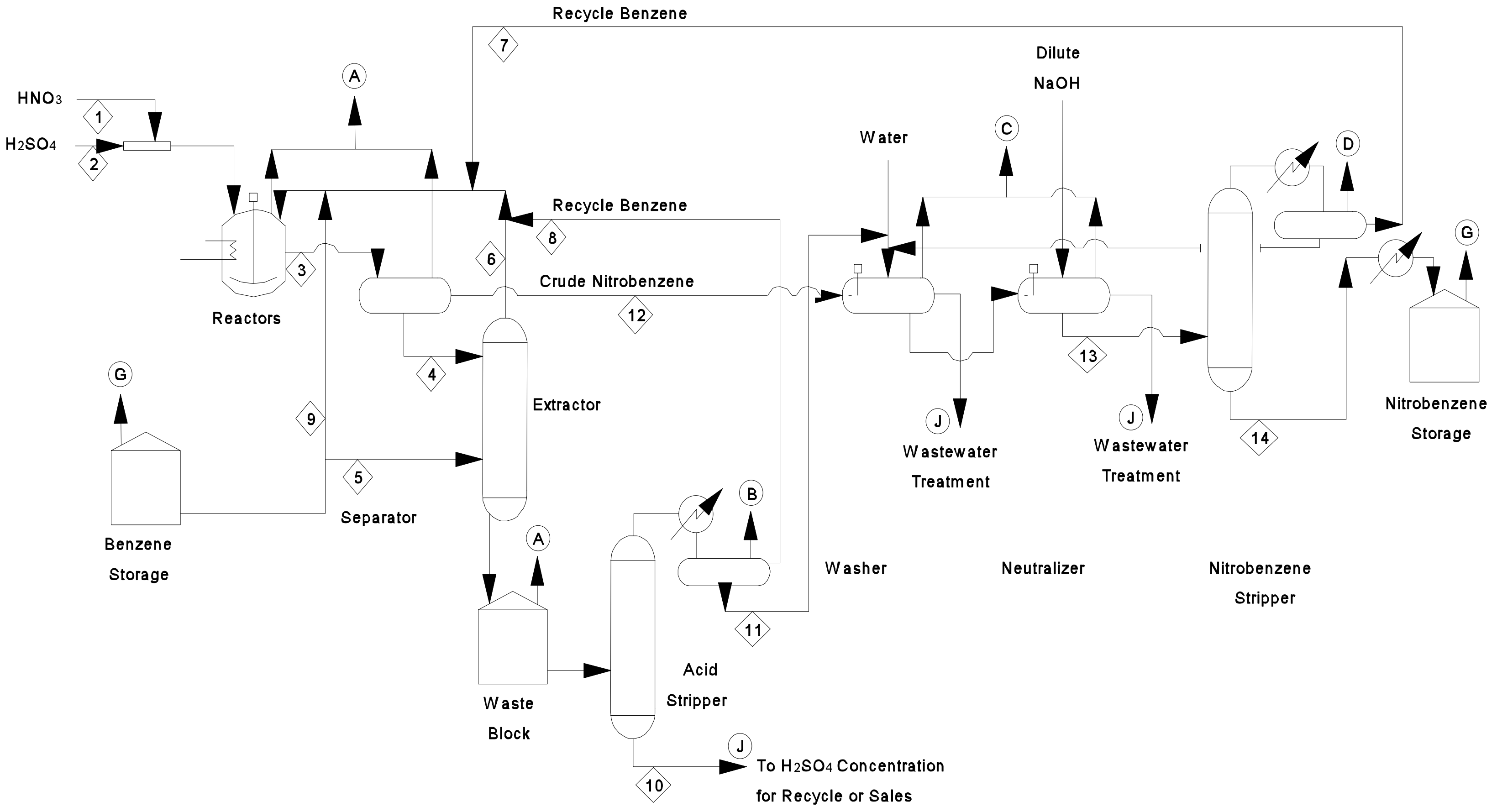
Source: Reference 11.

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.



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-11. Process Flow Diagram for Manufacture of Nitrobenzene

Following nitration, the crude reaction mixture (Stream 3) flows to the decanter, where the organic phase of crude nitrobenzene is separated from the aqueous waste acid. The crude nitrobenzene (Stream 12) subsequently flows to the washer and neutralizer, where mineral (inorganic) and organic acids are removed. The washer and neutralizer effluent are discharged to wastewater treatment. The organic layer (Stream 13) is fed to the nitrobenzene stripper, where water and most of the benzene and other low-boiling-point components are carried overhead. The organic phase carried overhead is primarily benzene and is recycled (Stream 7) to the reactor. The aqueous phase (carried overhead) is sent to the washer. Stripped nitrobenzene (Stream 14) is cooled and then transferred to nitrobenzene storage.

The treatment, recycling, or discharge of process streams is also shown in the flow diagram. Aqueous waste acid (Stream 4) from the decanter flows to the extractor, where it is denitrated. There, the acid is treated with fresh benzene from storage (Stream 5) to extract most of the dissolved nitrobenzene and nitric acid. The benzene extract (Stream 6) flows back to the nitrating reactor, whereas the denitrated acid is stored in the waste acid tank.

Benzene is commonly recovered from the waste acid by distillation in the acid stripper. The benzene recovered is recycled (Stream 8), and water carried overhead with the benzene is forwarded (Stream 11) to the washer. The stripped acid (Stream 10) is usually reconcentrated on site but may be sold.[93]

Typically, many of the process steps are padded with nitrogen gas to reduce the chances of fire or explosion. This nitrogen padding gas and other inert gases are purged from vents associated with the reactor and separator (Vent A in Figure 5-11), the condenser on the acid stripper (Vent B), the washer and neutralizer (Vent C), and the condenser on the nitrobenzene stripper (Vent D).

5.5.2 Benzene Emissions from Nitrobenzene Production

Benzene emissions may occur at numerous points during the manufacture of nitrobenzene. These emissions may be divided into four types: process emissions, storage emissions, equipment leak emissions, and secondary emissions.

Process emissions occur at the following four gas-purge vents: the reactor and separator vent (A), the acid stripper vent (B), the washer and neutralizer vent (C), and the nitrobenzene stripper vent (D). The bulk of benzene emissions occur from the reactor and separator vent. This vent releases about three times the level of benzene released from Vents B and D (Figure 5-11), and about 120 times that released from Vent C. For all of these vents, the majority of VOC emissions is in the form of benzene. Benzene accounts for 99, 100, 76, and 99 percent of total VOC emissions from Vents A, B, C, and D, respectively. Table 5-9 shows estimated emission factors for benzene from these sources.[93]

Other emissions include storage, equipment leak, and secondary emissions. Storage emissions (G) occur from tanks storing benzene, waste acid, and nitrobenzene. Equipment leak emissions of benzene can occur when leaks develop in valves, pump seals, and other equipment. Leaks can also occur from corrosion by the sulfuric and nitric acids and can hinder control of fugitive emissions.

Secondary emissions can result from the handling and disposal of process waste liquid. Three potential sources of secondary benzene emissions (J) are the wastewater from the nitrobenzene washer, waste caustic from the nitrobenzene neutralizer, and waste acid from the acid stripper. Where waste acid is not stripped before its sale or reconcentration, secondary emissions will be significantly affected (increased) unless the reconcentration process is adequately controlled.

Table 5-9 gives benzene emission factors before and after the application of possible controls for two hypothetical plants using the continuous nitration process. The two

TABLE 5-9. SUMMARY OF EMISSION FACTORS FOR HYPOTHETICAL NITROBENZENE PRODUCTION PLANTS

SCC and Description	Emissions Source[a]	Control Device	Emission Factor in lb/ton (g/kg)[b]	Factor Rating
3-01-195-01 Nitrobenzene - General	Small Benzene Storage[c] (Point G)	Uncontrolled	0.156 (0.078)[d]	U
			0.154 (0.077)[e]	U
3-01-195-01 Nitrobenzene - General	Benzene Storage[c] (Point G)	Uncontrolled	0.566 (0.283)[d]	U
			0.562 (0.281)[e]	U
		Internal Floating Roof	0.085 (0.0425)[d,e]	U
3-01-195-01 Nitrobenzene - General	Secondary (Point J)	Uncontrolled	0.20 (0.10)[d,e]	U
3-01-195-01 Nitrobenzene - General	Total	Uncontrolled	4.9 (2.45)[d]	U
			4.4 (2.19)[e]	U
		Vent Adsorber	0.78 (0.39)[d]	U
			0.64 (0.32)[e]	U
		Thermal Oxidizer	0.44 (0.22)[d]	U
			0.52 (0.26)[e]	U
3-01-195-03 Nitrobenzene - Acid Stripper Vent	Waste-Acid Stripper (Point B)	Uncontrolled	0.034 (0.170)[d,e]	U
3-01-195-04 Nitrobenzene - Washer/Neutralizer Vent	Wash and Neutralization (Point C)	Uncontrolled	0.0162 (0.0081)[d,e]	U
		Vent Adsorber	0.155 (0.0776)[d,e]	U

(continued)

TABLE 5-9. CONTINUED

SCC and Description	Emissions Source[a]	Control Device	Emission Factor in lb/ton (g/kg)[b]	Factor Rating
3-01-195-05 Nitrobenzene - Nitrobenzene Stripper Vent	Nitrobenzene Stripper (Point D)	Uncontrolled	0.34 (0.170)[d,e]	U
		Thermal Oxidizer	0.0288 (0.0144)[d,e]	U
3-01-195-06 Nitrobenzene - Waste Acid Storage	Waste Acid Storage (Point G)	Uncontrolled	0.102 (0.051)[d,e]	U
			0.96 (0.048)[d,e]	U
3-01-195-80 Nitrobenzene - Equipment Leak Emissions	Process Pumps and Valves[f]	Uncontrolled	1.26 (0.63)[d]	U
			0.76 (0.38)[e]	U
		LD&R plus mechanical seals	0.33 (0.165)[d]	U
			0.198 (0.099)[e]	U

Source: Reference 93.

[a] Emission points refer to Figure 5-11.

[b] Factors are expressed as lb (g) benzene emitted per ton (kg) nitrobenzene produced.

[c] Storage emission factors are based on these tank parameters:

For 198 million lb/yr (90,000 Mg/yr) Model Plant

	Tank Size ft^3 (m^3)	Turnovers/Year	Bulk Liquid Temperature °F (°C)
Benzene (large tank)	100,292 (2,840)	24	68 (20)
Benzene (small tank)	10,029 (284)	236	68 (20)

For 331 million lb/yr (150,000 Mg/yr) Model Plant

	Tank Size ft^3 (m^3)	Turnovers/Year	Bulk Liquid Temperature °F (°C)
Benzene (large tank)	160,035 (4,730)	24	68 (20)
Benzene (small tank)	16,704 (473)	236	68 (20)

(continued)

TABLE 5-9. CONTINUED

[d] Emission factor for a hypothetical 198 million lb/yr (90,000 Mg/yr) capacity plant.

[e] Emission factor for a hypothetical 331 million lb/yr (150,000 Mg/yr) capacity plant.

[f] Process pumps and valves are potential sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves based on data from an existing facility. All pumps have mechanical seals. Twenty-five percent of these pumps and valves are being used in benzene service. The fugitive emissions included in this table are based on the factors given in Section 4.5.2.

plants differ in capacity; one produces 198 million lb/yr (90,000 Mg/yr) and the other 331 million lb/yr (150,000 Mg/yr) of nitrobenzene. Both plants use a vent absorber or thermal oxidizer to control process emissions in conjunction with waste-acid storage and small benzene storage emissions.

The values presented for the main benzene storage emissions were calculated by assuming that a contact-type internal floating roof with secondary seals will reduce fixed-roof tank emissions by 85 percent. The values presented for controlled equipment leak emissions are based on the assumption that leaks from valves and pumps, resulting in concentrations greater than 10,000 ppm on a volume basis, are detected, and that appropriate measures are taken to correct the leaks.

Secondary emissions and nitrobenzene storage emissions are assumed to be uncontrolled. Uncontrolled emission factors are based on the assumptions given in the footnotes to Table 5-9. The total controlled emission factors for these hypothetical plants range from 0.44 to 0.78 lb/ton (0.22 to 0.39 kg/Mg). Actual emissions from nitrobenzene plants would be expected to vary, depending on process variations, operating conditions, and control methods.[93]

A variety of control devices may be used to reduce emissions during nitrobenzene production, but insufficient information is available to determine which devices nitrobenzene producers are using currently. Process emissions may be reduced by vent absorbers, water scrubbers, condensers, incinerators, and/or thermal oxidizers.

Storage emissions from the waste-acid storage tank and the small benzene storage tank can be readily controlled in conjunction with the process emissions. (A small storage tank contains approximately one day's supply of benzene; the larger tank is the main benzene storage tank.) In contrast, emissions from the main benzene storage tanks are controlled by using floating-roof storage tanks.

Equipment leak emissions are generally controlled by leak detection and repair, whereas secondary emissions are generally uncontrolled.

5.6 ANILINE PRODUCTION

Almost 97 percent of the nitrobenzene produced in the United States is converted to aniline.[91] Because of its presence as an impurity in nitrobenzene, benzene may be emitted during aniline production. Therefore, a brief discussion of the production of aniline from nitrobenzene and its associated benzene emissions is included in this document.

Table 5-10 lists the U.S. producers of aniline and the production method.[11] The main derivative of aniline (75 percent) is p.p.-methylene diphenyl diisocyanate (MDI). The growth outlook for aniline is expected to remain strong because of its continued use in housing and automobile parts.[95]

5.6.1 Process Descriptions for Aniline Production for Nitrobenzene

A process flow diagram of the most widely used process for manufacturing of aniline--by hydrogen reduction of nitrobenzene--is shown in Figure 5-12.[96] As shown in the figure, nitrobenzene (Stream 1) is vaporized and fed with excess hydrogen (Stream 2) to a fluidized-bed reactor. The product gases (Stream 3) are passed through a condenser. The condensed materials are decanted (Stream 4), and non-condensible materials are recycled to the reactor (Stream 5). In the decanter, one phase (Stream 6) is crude aniline and the other is an aqueous phase (Stream 7).

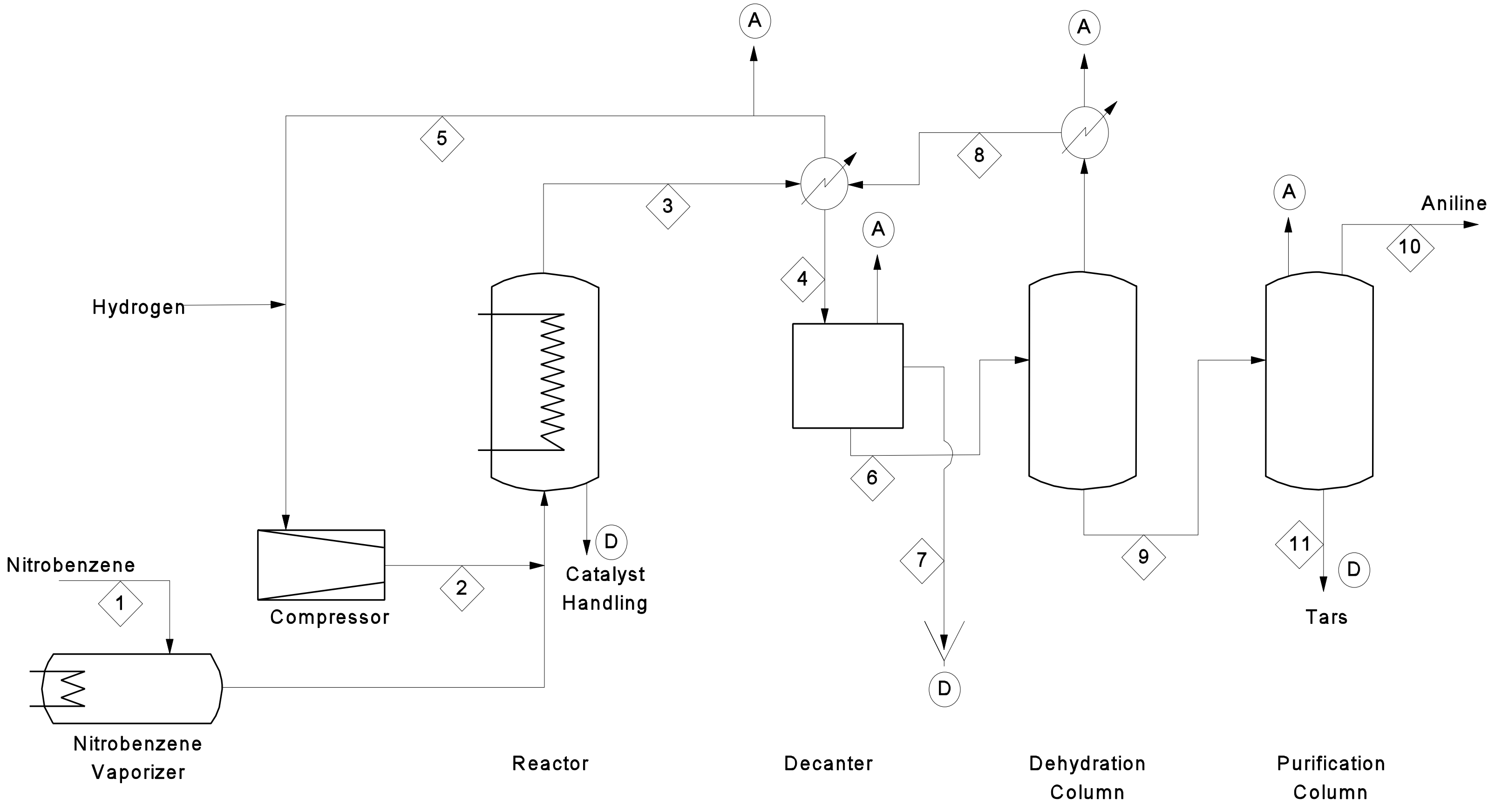
The crude aniline phase is routed to a dehydration column that operates under vacuum. Aniline is recovered from the aqueous phase by stripping or extraction with nitrobenzene. Overheads from the dehydration column (Stream 8) are condensed and recycled to the decanter. The bottoms from the dehydration column (Stream 9), which contain aniline,

TABLE 5-10. U.S. PRODUCERS OF ANILINE

Facility	Location	Annual Capacity in million gal/yr (million kg/yr)	Process and Remarks
Aristech Chemical Corporation	Haverhill, OH	200 (90)	Ammonolysis of phenol (Halcon process)
E.I. duPont de Nemours and Company, Inc.			
duPont Chemicals	Beaumont, TX	260 (120)	Hydrogen reduction of nitrobenzene
First Chemical Corporation	Pascagoula, MS	275 (130)	Hydrogen reduction of nitrobenzene
ICI American Holdings, Inc. and Uniroyal, Inc. Affiliate			
Rubicon, Inc.	Geismar, LA	400 (180)	Hydrogen reduction of nitrobenzene
Miles, Inc.			
Polymers Polyurethane Division	New Martinsville, WV	40 (20)	Nitrobenzene (acid-iron reduction process)
BASF Corporation Polymers Division Urethanes	Geismar, LA	190 (90)	
TOTAL		1,365 (630)	

Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These data on producers and locations were current as of January 1, 1993.



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.

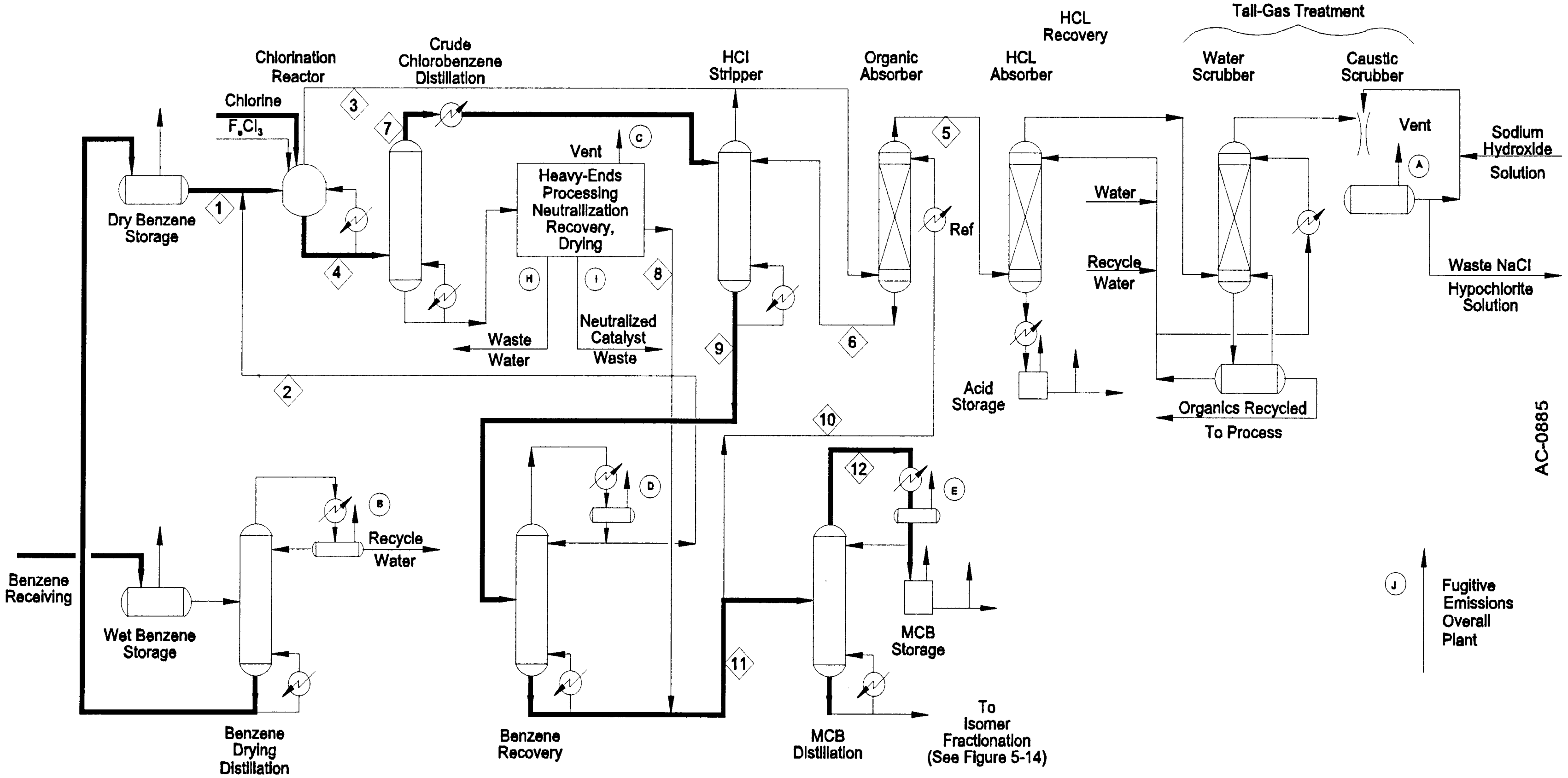


Figure 5-13. Monochlorobenzene Continuous Production Process Diagram

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]

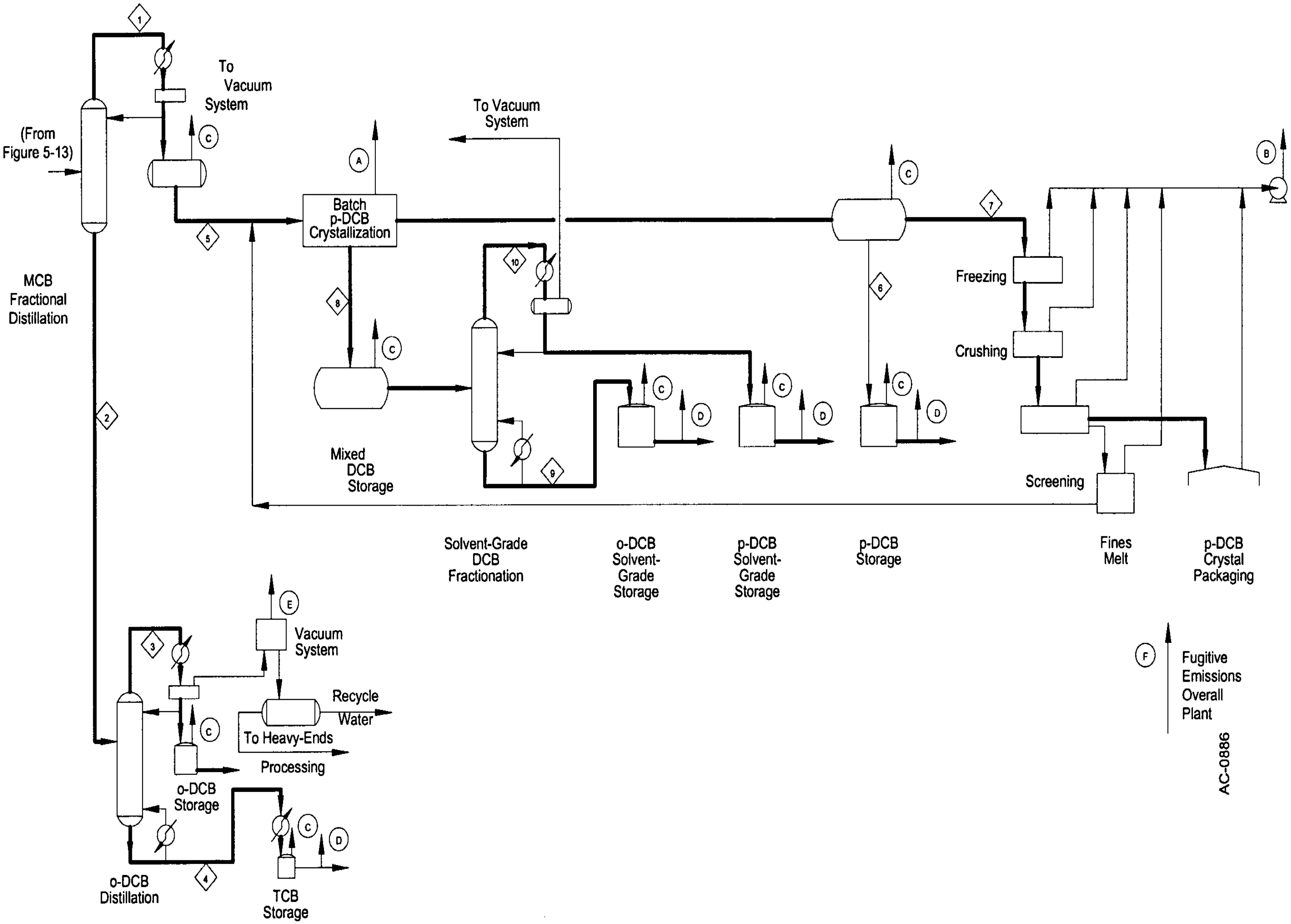


Figure 5-14. Dichlorobenzene and Trichlorobenzene Continuous Production Diagram

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.

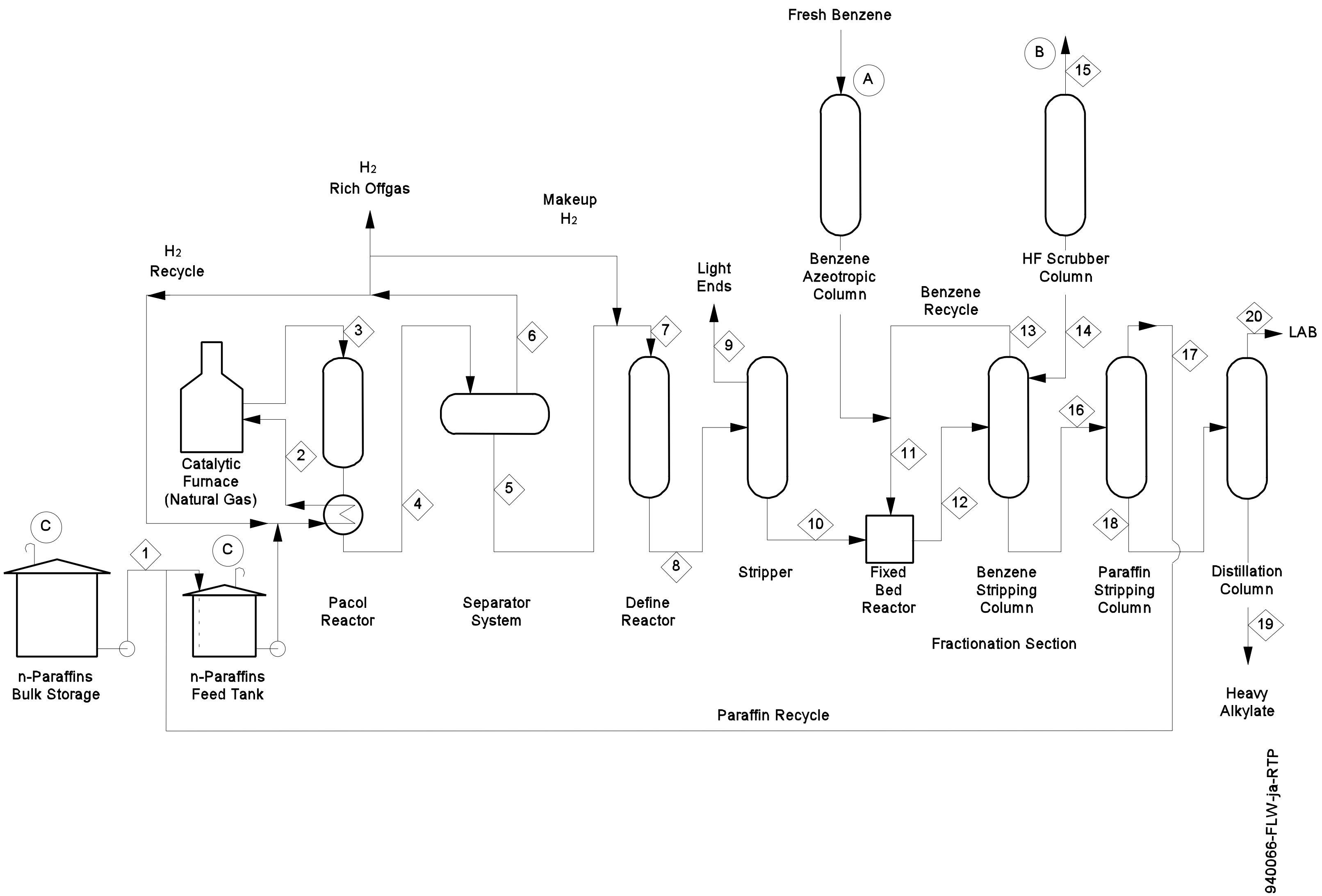


Figure 5-15. Linear Alkybenzene Production Using the Olefin Process

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.

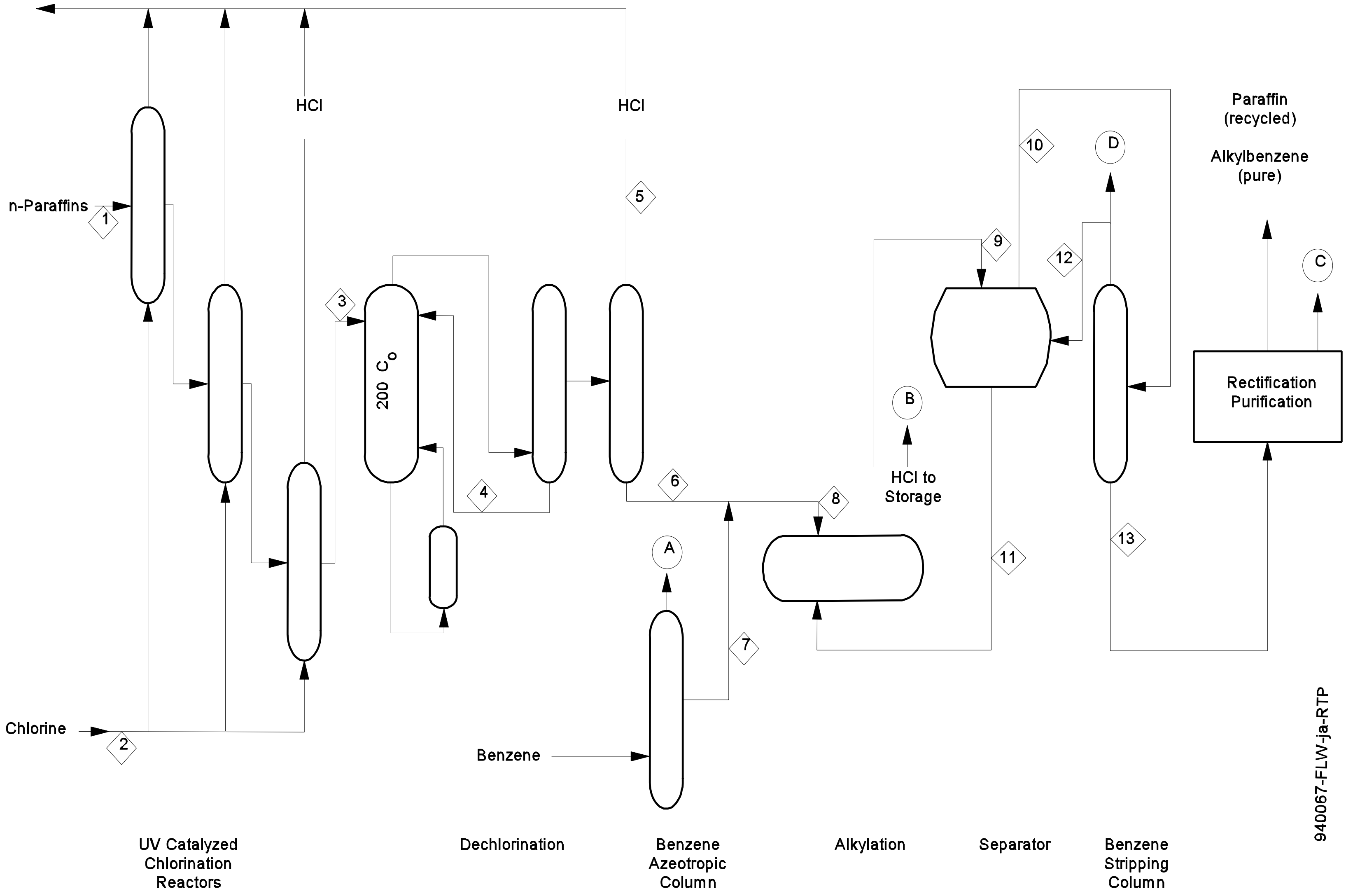
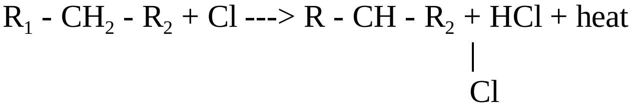


Figure 5-16. Production of Linear Alkybenzenes via Chlorination

Source: Reference 100.

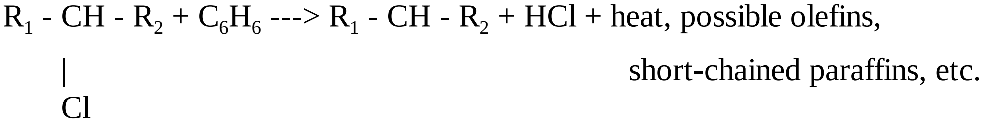
are converted at 212°F (100°C) to a mixture of about 35 percent chlorinated paraffins, and the remainder to paraffins and HCl as shown in the following reaction:



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

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:



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

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	700 (2,650)
	Walhalla, ND	11 (42)
Biocom USA Ltd.	Jennings, LA	40 (151)
Cargill, Incorporated Domestic Corn Milling Division	Eddyville, IA	30 (113)
Chief Ethanol Fuels Inc.	Hastings, NB	14 (53)
Eastman Chemical Company Texas Eastman Division	Longview, TX	25 (95)
Georgia-Pacific Corporation Chemical Division	Bellingham, WA	12 (45)
Giant Refining Co.	Portales, NM	10 (38)
Grain Processing Corporation	Muscatine, IA	60 (227)
High Plains Corp.	Colwich, KS	15 (57)
Hubinger-Roquette Americas, Inc.	Keokuk, IA	11 (42)
Midwest Grain Products, Inc.	Atchison, KS	22 (83)
	Pekin, IL	19 (72)
Minnesota Corn Processors	Columbus, NB	NA
	Marshall, MN	28 (106)
New Energy Company of Indiana	South Bend, IN	70 (265)
Pekin Energy Company	Pekin, IL	80 (303)
Quantum Chemical Corp. USI Division	Tuscola, IL	68 (257)
South Point Ethanol	South Point, OH	60 (227)
A. E. Staley Manufacturing Company Sweetner Business Group Ethanol Division	Loudon, TN	60 (227)

(continued)

TABLE 5-17. CONTINUED

Facility	Location	Annual Capacity million gal (million L)
Ethanol (continued)		
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	123 (466)
	TOTAL	1,458 (5,519)
Isopropanol		
Exxon Chemical Company Exxon Chemical Americas	Baton Rouge, LA	650 (2,460)
Lyondell Petrochemical Company	Channelview, TX	65 (246)
Shell Chemical Company	Deer Park, TX	600 (2,271)
Union Carbide Corporation Solvents and Coatings Materials Division	Texas City, TX	530 (2,006)
	TOTAL	1,845 (6,984)

Source: References 11 and 111.

[a] Emissions listed are those reported in the 1992 TRI.

NA = Not available

-- = no emissions reported

Table 5-18.[11,111] Of the three facilities, DSM and BASF use benzene as a solvent, and Allied Signal produces benzene as a co-product.[113]

Benzene is also used as a solvent in the blending and shipping of aluminum alkyls.[113]

Emission points identified for solvent benzene are process vents, dryer vents, and building ventilation systems.[107] As shown in Table 5-19, only one emission factor was identified for any of the solvent use categories.[114] The emission factor presented is for the vacuum dryer vent controlled with a venturi scrubber in pharmaceutical manufacturing.

TABLE 5-18. U.S. PRODUCERS OF CAPROLACTAM

Facility	Location	Annual Capacity million lb (million kg)	Raw Material
Allied-Signal, Inc. Engineered Materials Sector	Hopewell, VA	660 (299)	Phenol
BASF Corporation Chemicals Division Fiber Raw Materials	Freeport, TX	420 (191)	Cyclohexane
DSM Chemicals North America, Inc.	August, GA	360 (163)	Cyclohexane
	TOTAL	1,440 (653)	

Source: References 11 and 111.

[a] Emissions listed are those reported in the 1992 TRI.

"--" = no emissions reported.

TABLE 5-19. SUMMARY OF EMISSION FACTORS FOR BENZENE USE AS A SOLVENT

SCC and Description	Emissions Source	Control Device	Emission Factor[a] lb/1,000 gal (g/L)	Factor Rating
3-01-060-01 Pharmaceuticals - General Process - Vacuum Dryers	Vacuum Dryer Vent	Venturi Scrubber (99.10% efficiency)	2.1 (0.25)	B

Source: Reference 114.

[a] Factor is expressed as lb (kg) benzene emitted per 1,000 gal (L) pharmaceutical product produced.