

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

In 1825, Faraday isolated benzene from a liquid condensed by compressing oil gas. Benzene was first synthesized by Mitscherlich in 1833 by distilling benzoic acid with lime. Benzene was first commercially recovered from light oil derived from coal tar in 1849 and from petroleum in 1941 (IARC 1982a).

Several years after the end of World War II, the rapidly expanding chemical industry created an increased demand for benzene that the coal carbonization industry could not fulfill. To meet this demand, benzene was produced by the petroleum and petrochemical industries by recovery from reformat and liquid byproducts of the ethylene manufacturing process (Fruscella 1992).

Currently, benzene is commercially recovered from both coal and petroleum sources. More than 98% of the benzene produced in the United States is derived from the petrochemical and petroleum refining industries (OSHA 1987). These sources include refinery streams (catalytic reformats), pyrolysis gasoline, and toluene hydrodealkylation. Catalytic reformat is the major source of benzene (Greek 1990). Between 1978 and 1981, catalytic reformats accounted for approximately 44–50% of the total U.S. benzene production (Fishbein 1988). During catalytic reforming, cycloparaffins (also known by the obsolescent term "naphthenes") such as cyclohexane, methyl cyclohexane, and dimethylcyclohexane are converted to benzene by isomerization, dehydrogenation, and dealkylation, and paraffins in naphtha (such as hexane) are converted to benzene by cyclodehydrogenation. The process conditions and the catalyst determine which reaction will predominate. The benzene is recovered by solvent extraction (e.g., with sulpholane or tetraethylene glycol). Pyrolysis gasoline is a liquid byproduct produced by the steam cracking of lower paraffins (gas oil) or heavier hydrocarbons (heavy naphtha). Pyrolysis gasoline contains unsaturated aliphatic hydrocarbons (such as ethylene and propylene) and aromatics. Several integrated pyrolysis gasoline treatment processes are available including partial hydrogenation and extractive distillation; hydrogenation, hydrodesulfurization, and solvent extraction; or partial hydrogenation, desulfurization, hydrocracking, hydrodealkylation, and distillation for the optimization of benzene yield and the recovery of benzene (Fruscella 1992; IARC 1982a). In the toluene hydrodealkylation process, toluene or toluene/xylene mixtures are reacted with hydrogen at temperatures ranging from 500 to 595 °C with usual pressures of 4–6 mPa (40–60 atm), and demethylated to produce benzene and methane. Another process whereby toluene is converted to benzene and xylenes by transalkylation or disproportionation is also used for the production of benzene (Fruscella 1992). Small quantities of benzene are also produced from destructive distillation of coal used for coke manufacture. Benzene is derived from the light oil fraction produced during the coking process (Greek 1990; Fruscella 1992). New coking, gasification, and

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liquefaction processes for coal are all potential sources of benzene (IARC 1982a). Of the total U.S. production capacity of 3.109 billion gallons in 2004, catalytic reformats constituted 45%, toluene and xylene 30%, pyrolysis gasoline 23%, and coke oven <2% (SRI 2004).

Benzene ranks in the top 20 most abundantly produced chemicals in the United States (C&EN 1994; Kirschner 1995; Reisch 1994). Production data from 1984 to 1994 indicate that the production of benzene increased by about 4% annually (C&EN 1995).

According to the Toxics Release Inventory (TRI), 2,528 facilities in the United States produced or processed benzene in 2004 (TRI04 2006). Table 5-1 lists the facilities in each state that manufacture or process benzene, the intended use, and the range of maximum amounts of benzene that are stored on site. The TRI data listed in Table 5-1 should be used with caution since only certain types of facilities were required to report. Therefore, this is not an exhaustive list.

SRI (2004) lists the companies producing benzene in the United States in 2004. This list is summarized in Table 5-2. Facilities listed as being responsible for producing the top 50% of regional capacity in the United States include: Exxon Mobil Chemical Company, 518 million gallons (16%); Equistar Chemicals LP, 330 million gallons (11%), Dow Chemical Company, 300 million gallons (10%); Flint Hills Resources LP, 250 million gallons (8%), and BP Oil Company 230 million gallons (7%) (SRI 2004).

5.2 IMPORT/EXPORT

Benzene is imported and exported to the United States as both the pure chemical and as a mixture of mineral fuels. The import of pure benzene into the United States is dependent on domestic production and demand. Imports of benzene (from mineral fuels and pure benzene) into the United States were approximately 5,252 million L (10,176 million pounds) in 2004, 6,024 million L (11,672 million pounds) in 2003, and 5,912 million L (11,455 million pounds) in 2002 (USITC 2005). The largest exporters of benzene to the United States during 2002-2004 were Canada, Iraq, Israel, Kuwait, Venezuela, and Saudi Arabia (USITC 2005).

As in the case of import, the export of benzene from the United States to other countries is dependent on domestic and world production and demand. The 2002–2004 data indicate an increase in export volumes for benzene during this period. Exports of benzene (both pure benzene and benzene derived from mineral fuels) to other countries were approximately 11 million L (21 million pounds) in 2002, 150 million L

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Table 5-1. Facilities that Produce, Process, or Use Benzene

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AK	26	0	99,999,999	1, 2, 3, 4, 5, 7, 8, 9, 11, 12
AL	85	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
AR	24	100	9,999,999	1, 2, 3, 4, 6, 8, 9, 11, 12, 13
AS	1	100,000	999,999	9
AZ	30	100	9,999,999	1, 2, 4, 5, 7, 9, 10, 11, 12, 13, 14
CA	172	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
CO	23	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13
CT	8	1,000	9,999,999	1, 4, 6, 7, 9, 10, 12
DE	13	1,000	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13
FL	36	0	499,999,999	1, 2, 3, 4, 5, 7, 8, 9, 10, 12, 13, 14
GA	33	0	49,999,999	1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
GU	6	100	9,999,999	2, 3, 4, 7, 9, 12
HI	15	100	49,999,999	1, 2, 3, 4, 5, 6, 7, 9, 12, 13, 14
IA	21	0	10,000,000,000	1, 2, 3, 4, 5, 7, 9, 10, 11, 12, 13, 14
ID	3	10,000	9,999,999	7, 9, 12
IL	102	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
IN	80	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
KS	59	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
KY	66	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
LA	212	0	10,000,000,000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
MA	15	100	99,999,999	2, 4, 7, 8, 9
MD	20	100	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12
ME	9	100	9,999,999	2, 3, 4, 7, 9, 12, 13
MI	108	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
MN	36	100	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
MO	30	0	9,999,999	1, 5, 7, 8, 9, 11, 12
MP	7	0	999,999	2, 3, 4, 7, 9
MS	43	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14
MT	27	10,000	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14
NC	34	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13
ND	9	0	49,999,999	1, 2, 3, 4, 5, 6, 9, 12, 13
NE	11	0	9,999,999	1, 7, 10, 12, 13
NH	9	0	999,999	1, 2, 7, 9, 12, 13
NJ	61	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
NM	32	100	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14
NV	5	100	99,999	1, 2, 4, 8, 9, 12, 13
NY	48	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
OH	101	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14

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State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
OK	48	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14
OR	12	1,000	9,999,999	1, 2, 3, 4, 5, 7, 9, 12, 13
PA	100	0	99,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
PR	52	0	10,000,000,000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
RI	9	10,000	9,999,999	1, 2, 4, 7, 8, 9
SC	26	0	9,999,999	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13
SD	8	100	999,999	2, 3, 4, 7, 8, 11, 12, 13, 14
TN	53	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
TX	361	0	10,000,000,000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14
UT	42	1,000	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
VA	36	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13
VI	8	10,000	499,999,999	1, 2, 3, 4, 6, 7, 8, 9
WA	57	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 13, 14
WI	27	0	9,999,999	1, 4, 5, 7, 8, 9, 11, 12, 13, 14
WV	32	0	99,999,999	1, 2, 4, 5, 6, 7, 8, 9, 12, 13
WY	37	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 9, 12, 13, 14

^aPost office state abbreviations used

^bAmounts on site reported by facilities in each state

^cActivities/Uses:

- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. Produce | 6. Impurity | 11. Chemical Processing Aid |
| 2. Import | 7. Reactant | 12. Manufacturing Aid |
| 3. Onsite use/processing | 8. Formulation Component | 13. Ancillary/Other Uses |
| 4. Sale/Distribution | 9. Article Component | 14. Process Impurity |
| 5. Byproduct | 10. Repackaging | |

Source: TRI04 2006 (Data are from 2004)

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Table 5-2. Current U.S. Manufacturers of Benzene^a

Company	Location (annual capacity millions of gallons)
ATOFINA Petrochemicals, Inc.	Port Arthur, Texas (87)
BASF FINA Petrochemicals, Inc.	Port Arthur, Texas (34)
BP America, Inc.	Texas City, Texas (230)
Ceveron Phillips Chemical Company, LP	Pascagoula, Mississippi (150)
Olefins and Polyolefins Business Unit	Port Arthur, Texas (35)
CITGO Petroleum Corporation	Corpus Christi, Texas (78) Lake Charles, Louisiana (55) Lemont, Illinois (19)
Conoco Phillips Refining Marketing and Transportation Division	Alliance Louisiana (65) Sweeny, Texas (39) Wood River Illinois (60)
Dow Chemical USA	Freeport, Texas (80) Plaquemine, Louisiana (317)
Equistar Chemicals, LP	Alvin, Texas (137) Channelveiw, Texas (90) Corpus Christi, Texas (103)
ExxonMobil Chemical Company	Baton Rouge Louisiana (100) Baytown, Texas (180) Beaumont, Texas (182) Chalmette, Louisiana (56) Corpus Christi, Texas (250)
Flint Hills Resources, LP	El Dorado, Kansas (15)
Frontier El Dorado Refining Company	St. Croix, Virgin Islands (60)
HOVENSA, LLC	Port Arthur, Texas (90)
Huntsman, LLC	Houston, Texas (50)
Lyondell-Citgo Refining, LP	Catlettsburg, Kentucky (58) Texas City, Texas (3)
Marathon Ashland Petroleum, LLC	Delaware City, Delaware (15)
Motiva Enterprises, LLC	Bayport, Texas (15)
NOVA Chemicals Corp.	Lima, Ohio (145)
The Premcor Refining Group Inc.	Deer Park, Texas (180)
Shell Chemical Company	Marcus Hook, Pennsylvania (60) Philadelphia, Pennsylvania (24) Toledo Ohio (20) Westville, New Jersey (18)
Sunoco, Inc.	Corpus Christi, Texas (82) Three Rivers, Texas (20)
Valero Energy Corporation	Lenexa, Kansas
Eagle-Pitcher Industries, Inc.	
Eagle-Pitcher Technologies, LLC	
Chem Syn Laboratories (¹⁴ C-benzene)	

^aDerived from Stanford Research Institute (SRI) 2004, receipt where otherwise noted. SRI reports production of chemicals produced in commercial quantities (defined as exceeding 5,000 pounds or \$10,000 in value annually) by the companies listed.

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(290 million pounds) in 2003, and 75 million L (145 million pounds) in 2004. These numbers are up from 15 million L (29 million pounds) in 2001 and 3.3 million L (6.4 million pounds) in 1993 (USITC 2005). The largest importers of benzene from the United States are Canada, the Netherlands, Taiwan, Spain, and Korea (USITC 2005).

5.3 USE

Benzene has been used extensively as a solvent in the chemical and drug industries, as a starting material and intermediate in the synthesis of numerous chemicals, and as a gasoline additive (NTP 1994).

Benzene recovered from petroleum and coal sources is used primarily as an intermediate in the manufacture of other chemicals and end products. The major uses of benzene are in the production of ethylbenzene, cumene, and cyclohexane. Ethylbenzene (55% of benzene production volume) is an intermediate in the synthesis of styrene, which is used to make plastics and elastomers. Cumene (24%) is used to produce phenol and acetone. Phenols are used in the manufacture of phenolic resins and nylon intermediates; acetone is used as a solvent and in the manufacture of pharmaceuticals. Cyclohexane (12%) is used to make nylon resins. Other industrial chemicals manufactured from benzene include nitrobenzene (5%), which is used in the production of aniline, urethanes, linear alkylbenzene sulfonates, chlorobenzene, and maleic anhydride (Eveleth 1990; Greek 1990; HSDB 2007). Benzene is also a component of gasoline since it occurs naturally in crude oil and since it is a byproduct of oil refining processes (Brief et al. 1980; Holmberg and Lundberg 1985). Benzene is especially important for unleaded gasoline because of its anti-knock characteristics. For this reason, the concentration of aromatics, such as benzene, in unleaded fuels has increased (Brief et al. 1980). The percentage by volume of benzene in unleaded gasoline is approximately 1–2% (NESCAUM 1989).

The EPA has listed benzene as a hazardous air pollutant and a hazardous waste (EPA 1977, 1981). In addition, there is sufficient evidence to support classifying benzene as a human carcinogen (Group A) (IRIS 2007). One result of EPA's action is that the widespread use of benzene as a solvent has decreased in recent years. Many products that used benzene as solvents in the past have replaced it with other organic solvents; however, benzene may still occur as a trace impurity in these products. Less than 2% of the amount produced is used as a solvent in products such as trade and industrial paints, rubber cements, adhesives, paint removers, artificial leather, and rubber goods. Benzene has also been used in the shoe manufacturing and rotogravure printing industries (EPA 1978; OSHA 1977). In the past, certain consumer products (such as some paint strippers, carburetor cleaners, denatured alcohol, and rubber

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cement used in tire patch kits and arts and crafts supplies) contained small amounts of benzene (Young et al. 1978). Other consumer products that contained benzene were certain types of carpet glue, textured carpet liquid detergent, and furniture wax (Wallace et al. 1987).

The Consumer Products Safety Commission (CPSC) withdrew an earlier proposal to ban consumer products, except gasoline and laboratory reagents, that contained benzene as an intentional ingredient or as a contaminant at >0.1% by volume. The withdrawal of the rulemaking was based on CPSC findings that benzene was no longer used as an intentional ingredient and that the contaminant levels remaining in certain consumer products were unlikely to result in significant exposures (NTP 1994). Products containing >5% benzene, and paint solvents and thinners containing <10% of petroleum distillates such as benzene, are required to meet established labeling requirements. In a guidance document targeting school science laboratories, the CPSC recommended that benzene not be used or stored in schools. The document identified benzene as a carcinogen and ascertained that the hazards posed by its use in high school laboratories may be greater than its potential usefulness.

The U.S. Food and Drug Administration (FDA) regulates benzene as an indirect food additive under the Food, Drug, and Cosmetics Act (FDCA). Under the FDCA, benzene is restricted to use only as a component of adhesives used on articles intended for packaging, transport, or holding foods (FDA 1977).

5.4 DISPOSAL

Benzene-containing wastes, such as commercial chemical products, manufacturing chemical intermediates, and spent solvents, are subject to federal and/or state hazardous waste regulations (HSDB 2007). Regulations governing the treatment and disposal of benzene-containing wastes are presented in Chapter 8. Waste byproducts from benzene production processes include acid and alkali sludges, liquid-solid slurries, and solids (EPA 1982b; Saxton and Narkus-Kramer 1975). In the past, landfilling and lagooning have been the major methods of disposal of benzene-containing industrial wastes (EPA 1982b). In addition to biodegradation, a portion of the benzene is expected to be lost due to volatilization. Unfortunately benzene, along with other hazardous contaminants, also leaches into groundwater from the lagooned wastes. Currently, the recommended method of disposal is to incinerate solvent mixtures and sludges at a temperature that ensures complete combustion. The recommended methods for combustion are liquid injection incineration at a temperature range of 650–1,600 °C and a residence time of 0.1–2 seconds; rotary kiln incineration at a temperature range of 820–1,600 °C and residence times of seconds for liquids and gases, and hours for solids; and fluidized bed incineration at a temperature range of 450–

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980 °C and residence times of seconds for liquids and gases and longer for solids (HSDB 2007). Since benzene burns with a very smoky flame, dilution with alcohol or acetone is suggested to minimize smoke. Small quantities of benzene waste can be destroyed by chemical reaction. For example, treating benzene with dichromate in strong sulfuric acid for 1–2 days is sufficient for total destruction (HSDB 2007).

Underground injection also appears to be an important disposal method in some states. Approximately 436,000 pounds of benzene (6% of the total environmental release) was disposed of by underground injection. This disposal via underground injection in 2006 was higher than the amount (356,000 pounds) released in 1992 (TRI90 1992), but lower than the release in 1990 (654,000 pounds) (TRI90 1992) and 2002 (692,000 pounds) (TRI02 2005). In addition, 24,000 pounds of benzene (0.3% of the total environmental release) was disposed of via land disposal (TRI04 2006). The amount discharged to soil in 2002 was less than one quarter of the amount (724,000 pounds) discharged in 1990 (TRI90 1992) and less than one third of the amount (340,000 pounds) discharged in 1992 (TRI92 1994).

Several methods exist for the treatment of waste water that contains benzene: biological treatment (aeration or activated sludge process), solvent extraction, air and/or steam stripping, and activated carbon process (EPA 1994a; IRPTC 1985). Full-scale chemical treatability studies have demonstrated 95–100% reductions in benzene concentrations for industrial waste waters receiving biological treatments (HSDB 2007). A combination of steam stripping and air stripping, and a vapor extraction system that removes the separated benzene vapor may be suitable for the treatment of contaminated groundwater and soil (Naft 1992). An *in situ* bioremediation process has been used to decontaminate a site by delivering a controlled amount of nitrate (to accelerate biodegradation of benzene) to the site under hydraulic control (Kennedy and Hutchins 1992).