

## BENZALDEHYDE

### 1. Introduction

Benzaldehyde [100-52-71]  $\text{C}_6\text{H}_5\text{CHO}$ , is the simplest and quite possibly the most industrially useful member of the family of aromatic aldehydes. Benzaldehyde exists in nature, primarily in combined forms such as a glycoside in almond, apricot, cherry, and peach seeds. The characteristic benzaldehyde odor of oil of bitter almond occurs because of trace amounts of free benzaldehyde formed by hydrolysis of the glycoside amygdalin. Amygdalin was first isolated in 1830 from the seeds of the bitter almond (*Prunus amygdalus*). Sometime later, Liebig and Wöhler found that when amygdalin was hydrolyzed with water and emulsin, benzaldehyde, hydrogen cyanide, and D-glucose were formed (1).

### 2. Physical Properties

Physical properties of benzaldehyde are listed in Tables 1 and 2; boiling points and concentrations of certain selected binary azeotropes are given in Table 3. For a more complete listing of benzaldehyde azeotropes, see (3).

### 3. Manufacture

The only industrially important processes for the manufacturing of synthetic benzaldehyde involve the hydrolysis of benzal chloride [98-87-31] and the air oxidation of toluene. The hydrolysis of benzal chloride, which is produced by the side-chain chlorination of toluene, is the older of the two processes. It is

Table 1. Physical Properties of Benzaldehyde

Property	Value
molecular formula	$\text{C}_7\text{H}_6\text{O}$
molecular weight	106.12
boiling point, °C at 101.3 kPa <sup>a</sup>	179
melting point, °C	-26
flash point, closed cup, °C	63
autoignition temperature, °C	192
refractive index, $n^{20}$	1.5455
viscosity, mPa · s (=cP) at 25°C	1.321
density, g/cm <sup>3</sup> at 25°C	1.046
specific heat (liquid) at 25°C, J/g · K <sup>b</sup>	1.615
latent heat of vaporization <sup>c</sup> , J/g <sup>b</sup>	362
standard heat of combustion, kJ/g <sup>b</sup>	-31.9
solubility in water at 20°C, wt %	~0.6
solubility of water in at 20°C, wt %	~1.5

<sup>a</sup> To convert kPa to atm, divide by 101.3.

<sup>b</sup> To convert J to cal, divide by 4.184.

<sup>c</sup> At the boiling point (179°C).

Table 2. Vapor Pressure vs Temperature<sup>a</sup>

Temperature, °C	Pressure, kPa <sup>b</sup>
26.2	0.13
50.1	0.67
62.0	1.33
75.0	2.66
90.1	5.32
99.6	8.0
112.5	13.3
131.7	26.6
154.1	53.3
179.0	101.3

<sup>a</sup> Ref. 2.<sup>b</sup> To convert kPa to mm Hg, multiply by 7.5.

not utilized in the United States but is used in Europe, India, and China. Other processes, including the oxidation of benzyl alcohol, the reduction of benzoyl chloride, and the reaction of carbon monoxide and benzene, have been utilized in the past, but they no longer have any industrial application. [For an historical article regarding the chlorination of toluene and the subsequent production of benzaldehyde, benzyl alcohol, and benzoic acid, see (4).]

The air oxidation of toluene is the source of the majority of the world's synthetic benzaldehyde. Both vapor- and liquid-phase air oxidation processes have been used. In the vapor-phase process, a mixture of air and toluene vapor is passed over a catalyst consisting of the oxides of uranium, molybdenum, or related metals. High temperatures and short contact times are essential to maximize yields. Small amounts of copper oxide may be added to the catalyst mixture to reduce formation of by-product maleic anhydride. Conversion per pass is reported to be low, 10–20%, with equally low yields, 30–50% (5). The vapor-phase oxidation of toluene was the dominant toluene oxidation process in the 1950s and early 1960s, but is no longer of industrial importance. The liquid-phase process now dominates.

In the liquid-phase process, both benzaldehyde and benzoic acid are recovered. This process was introduced and developed in the late 1950s by the Dow Chemical Company, as a part of their toluene-to-phenol process, and by Snia Viscosa for their toluene-to-caprolactam process. The benzaldehyde recovered from the liquid-phase air oxidation of toluene may be purified by either

Table 3. Binary Azeotropes of Benzaldehyde<sup>a</sup>

Component	Azeotrope, Boiling point, °C	Benzaldehyde, %
benzyl chloride	177.9	50
<i>o</i> -cresol	192	23
D-limonene	171.2	43
cineole	172	36
phenol	185.6	49

<sup>a</sup> Ref. 3.

Table 4. National Formulary and Food Chemicals Codex Specifications

Item	The National Formulary <sup>a</sup>	Food Chemicals Codex <sup>b</sup>
identification		passes FCC Test
assay (by oximation method)	contains not <98.0% and not >100.5% of C <sub>7</sub> H <sub>6</sub> O.	98.0%, Minimum of C <sub>7</sub> H <sub>6</sub> O.
specific gravity (@ 25°C)	between 1.041 and 1.046	1.041–1.046
refractive index (@ 20°C)	between 1.544 and 1.546	1.544–1.547
hydrocyanic acid	passes NF Test	passes FCC Test
nitrobenzene	passes NF Test	
chlorinated compounds	passes NF Test	passes FCC Test
organic volatile impurities	passes NF Test	

<sup>a</sup> NF 21st ed.—Effective 1/1/2003.<sup>b</sup> FCC 4th ed.—Effective 7/1/1996.

batch or continuous distillation. Liquid-phase air oxidation of toluene is covered more fully (see BENZOIC ACID).

#### 4. Economic Aspects

Benzaldehyde is produced in the United States by Noveon Kalama, Inc., Kalama, Washington (formerly Kalama Chemical). The Noveon plant was originally constructed by The Dow Chemical Company in the early 1960s to produce phenol from benzoic acid and currently recovers benzaldehyde as a by-product of that process (6). Production and sales figures for benzaldehyde are not available.

#### 5. Specifications and Test Methods

Benzaldehyde is sold as technical grade or as meeting the specifications of the National Formulary (NF) (7), the Food Chemicals Codex (FCC) (8), or the British Pharmacopeia (BP) (9) (Tables 4 and 5). The test methods used for the analysis of benzaldehyde are standard methods, with the exception of the assay method.

The assay method involves the reaction of benzaldehyde with hydroxylamine hydrochloride in an alcoholic solution. Benzaldehyde oxime, water, and

Table 5. British Pharmacopeia and Technical Grade Specifications

Item	British Pharmacopeia <sup>a</sup>	Technical
assay (by oximation method)	benzaldehyde contains not <98.0% w/w and not >100.5% w/w of C <sub>7</sub> H <sub>6</sub> O	99.0%, minimum
refractive index @ 20°C		
weight per mL @ 20°C		
free acid	not >1.0% w/v, calculated as benzoic acid	
chlorinated compounds	not >0.05% w/v, calculated as Cl <sup>-</sup>	none
color		colorless to pale yellow
toluene		0.1 %, maximum

<sup>a</sup> BP 2002—Effective 1 December, 2002.

hydrochloric acid are the products of the reaction. The hydrochloric acid formed is then titrated with standard caustic solution to determine the benzaldehyde assay. Performing the titration to a potentiometric end point, rather than to a colored end point, has been shown to be the more accurate method. Since other carbonyl containing compounds also react to form the oxime and release hydrochloric acid, this test is not specific for benzaldehyde. The levels of trace impurities in the product benzaldehyde are often more important than the product assay. Gas chromatographic (gc) methods for the determination of those trace impurities are widely used.

Benzaldehyde is not included in the European or the Japanese Pharmacopias.

## 6. Health and Safety Factors

The oral LD<sub>50</sub> for benzaldehyde is reported as 1300 mg/kg in rats and as 1000 mg/kg in guinea pigs. Based upon these values, benzaldehyde is considered a moderately toxic substance when ingested. The subcutaneous lethal dose in rats is ~5 g/kg. The fatal oral dose in humans is estimated to be ~56.7 g (2 oz) (10). Benzaldehyde tested negative for mutagenicity in salmonella assays in the 1988 National Toxicology Program. Studies of the carcinogenic effects of benzaldehyde are currently in progress (11). In the industrial setting, exposure to benzaldehyde through eye and skin contact and inhalation is far more prevalent than ingestion incidence. Overexposure to benzaldehyde vapors is irritating to the upper respiratory tract and produces central nervous system depression with possible respiratory failure. Epileptiform convulsions have been observed in rabbits (10). Contact may cause eye and skin irritation. Some individuals are more sensitive to skin contact than others. See (12) for more toxicological information.

## 7. Handling

The low autoignition temperature of benzaldehyde (192°C) presents safety problems since benzaldehyde can be ignited by exposure to low pressure steam piping, for example. Benzaldehyde may also spontaneously ignite when soaked into rags or clothing or adsorbed onto activated carbon (13). Bulk storage of benzaldehyde should be made under a nitrogen blanket, since benzaldehyde is easily oxidized to benzoic acid upon exposure to air. All storage tank openings should be easily accessible for cleaning, since they will have a tendency to plug with benzoic acid. Benzaldehyde is stored in noninsulated type 304 stainless steel storage tanks. If storage in very cold climates is contemplated, consideration should be given to insulating and steam-tracing the tank. A baked, phenolic, resin-lined tank is also suitable. Copper or brass are to be avoided since they are readily attacked by benzaldehyde and benzoic acid. Because of the low surface tension of benzaldehyde, the use of screwed piping fittings should be avoided (14).

## 8. Uses

Benzaldehyde is a synthetic flavoring substance, sanctioned by the U.S. Food and Drug Administration (FDA) to be generally recognized as safe (GRAS) for foods (21 CFR 182.60). Both "pure almond extract" and "imitation almond extract" are offered for sale. Each contains 2.0–2.5 wt% benzaldehyde in an aqueous solution containing approximately one-third ethyl alcohol.

"Natural" benzaldehyde can be produced in a number of ways. The FDA regulations regarding natural products are found in 21 CFR 101.22. At present, there is a controversy over what the term natural really means with regard to benzaldehyde. Whether a particular benzaldehyde product is natural or not becomes an issue only if the final product is said to contain natural flavors. There are at least two routes currently being used to produce natural benzaldehyde. Principal flavor houses are reported to market a product that is derived from cassia oil. The chief constituent of cassia oil is cinnamic aldehyde, which is hydrolyzed into its benzaldehyde and acetaldehyde constituents, which is a fermentative retro-aldol reaction. Whether this hydrolysis allows the final benzaldehyde product to be considered natural is of great concern. The FDA has reportedly issued an opinion letter that benzaldehyde produced from cassia oil is not natural (15).

The other significant production method for natural benzaldehyde involves the steam distillation of bitter almond oil, which has been derived from the kernels of fruit such as apricots, peaches, cherries, plums, or prunes. The benzaldehyde product obtained in this fashion is claimed to have a superior flavor profile. The use of peach and apricot pits to produce the more profitable product laetrile apparently affects the supply available to natural benzaldehyde producers. The subject of natural benzaldehyde came to the forefront in 1984 when it was found that a natural benzaldehyde product, labeled "oil of benzaldehyde", was actually made synthetically by the air oxidation of toluene followed by careful fractionation to remove trace impurities. This finding was accomplished by the Center for Applied Isotopic Studies, University of Georgia, and involved measuring the amounts of  $^{13}\text{C}$  and  $^{14}\text{C}$  in that material.

Benzaldehyde is widely used in organic synthesis, where it is the raw material for a large number of products. In this regard, a considerable amount of benzaldehyde is utilized to produce various aldehydes, such as cinnamic and methyl, butyl, amyl, and hexyl cinnamic aldehydes. The single largest use for benzaldehyde, however, is the production of benzyl alcohol via hydrogenation.

## 9. Derivatives

Benzoin [119-53-9],  $\alpha$ -hydroxy- $\alpha$ -phenylacetophenone,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COC}_6\text{H}_5$  (mp, 133–137°C; bp, 343–344°C at 101.3 kPa), is formed by the self-condensation of benzaldehyde in the presence of potassium cyanide. It is used on a small scale as a polymerization catalyst in polyester resin manufacture.

Benzil [134-81-6], diphenyl- $\alpha,\beta$ -diketone,  $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$  (mp, 95°C; bp, 346–348°C at 101.3 kPa), formed by oxidizing benzoin is used as an intermediate in chemical synthesis.

Benzyl alcohol [100-51-6],  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (bp, 205AT at 101.3 kPa), produced by the hydrogenation of benzaldehyde is used in color photography, as a parenteral solution preservative, as a general solvent, and as an intermediate in the manufacture of various benzoate esters for the soap, perfume, and flavor industries (see BENZYL ALCOHOL AND  $\beta$ -PHENETHYL ALCOHOL).

Benzoyl chloride [98-88-4],  $\text{C}_6\text{H}_5\text{COCl}$  (mp,  $-1^\circ\text{C}$ ; bp,  $197.2^\circ\text{C}$  at 1–01.3 kPa;  $d_4^{25}$ , 1.2070;  $n_D^{20}$ , 1.55369), is a colorless liquid that fumes upon exposure to the atmosphere. It has a sharp odor and, in vapor form, is a strong lachrimator. It is decomposed by water and alcohol, and is miscible with ether, benzene, carbon disulfide, and oils.

Benzylamine [100-46-9],  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (bp,  $184^\circ\text{C}$  at 101.3 kPa) produced by reaction of ammonia with benzaldehyde and hydrogenation of the resulting Schiffs base, is used as the raw material for the production of biotin (Vitamin H), as an intermediate for certain photographic materials, and as an intermediate in the manufacture of certain pharmaceutical products.

Benzylideneacetone [122-57-6],  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$  (bp,  $260\text{--}262^\circ\text{C}$  at 101.3 kPa; mp,  $35\text{--}39^\circ\text{C}$ ) is produced by condensing acetone and benzaldehyde. It is used as an electroplating additive.

Benzylacetone [2550-26-7],  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COCH}_3$  (bp,  $233\text{--}234^\circ\text{C}$  at 101.3 kPa) is produced by condensing acetone and benzaldehyde, followed by selective hydrogenation, and is used in soap perfumes.

Dibenzylamine [103-49-1],  $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_5$  (bp,  $300^\circ\text{C}$  at 101.3 kPa) is produced by reaction of benzyl amine with benzaldehyde and hydrogenation of the Schiffs base. It is used in rubber and tire compounding, as a corrosion inhibitor, and as an intermediate in the production of rubber compounds and pharmaceutical products.

Cinnamaldehyde [14371-10-9],  $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$  (bp,  $253^\circ\text{C}$  at 101.3 kPa), produced by the alkaline condensation of benzaldehyde and acetaldehyde is the main ingredient in cassia oil. It is used in soap perfumes and as an intermediate in the production of other flavor and fragrance compounds.

$\alpha$ -Methylcinnamaldehyde [101-39-3],  $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$ , is produced by the alkaline condensation of benzaldehyde and propionaldehyde. Its principal use is as the raw material for *p*-*tert*-butyl- $\alpha$ -methyl dihydrocinnamic aldehyde, [8054-61], a lily of the valley fragrance intermediate.

$\alpha$ -Amylcinnamaldehyde [122-40-7],  $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_5\text{H}_{11})\text{CHO}$  (bp,  $140^\circ\text{C}$  at 0.7 kPa), produced by the alkaline condensation of benzaldehyde and *n*-heptaldehyde, produces a jasminelike floralness and is used extensively as a perfume for soap products.

$\alpha$ -Hexylcinnamaldehyde [101-86-0],  $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_{13})\text{CHO}$  (bp,  $174\text{--}176^\circ\text{C}$  at 2 kPa), produced by the alkaline condensation of benzaldehyde and *n*-octaldehyde, also produces a jasminelike floralness and is also used extensively as a perfume for soap products.

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## BENZENE

### 1. Introduction

Benzene [71-43-2],  $C_6H_6$ , is a volatile, colorless, and flammable liquid aromatic hydrocarbon possessing a distinct, characteristic odor. Benzene is used as a chemical intermediate for the production of many important industrial compounds,

such as styrene (polystyrene and synthetic rubber), phenol (phenolic resins), cyclohexane (nylon), aniline (dyes), alkylbenzenes (detergents), and chlorobenzenes. These intermediates, in turn, supply numerous sectors of the chemical industry producing pharmaceuticals, specialty chemicals, plastics, resins, dyes, and pesticides. In the past, benzene has been used in the shoe and garment industry as a solvent for natural rubber. Benzene has also found limited application in medicine for the treatment of certain blood disorders, such as polycythemia and malignant lymphoma (1), and further in veterinary medicine as a disinfectant. Benzene, along with other light high octane aromatic hydrocarbons such as toluene and xylene, is used as a component of motor gasoline. Although this use has been largely reduced in the United States, benzene is still used extensively in many countries for the production of commercial gasoline. Benzene is no longer used in appreciable quantity as a solvent because of the health hazards associated with it.

Benzene was first isolated by Michael Faraday in 1825 from the liquid condensed by compressing oil gas. He proposed the name bicarburet of hydrogen for the new compound. In 1833, Eilhard Mitscherlich synthesized bicarburet of hydrogen by distilling benzoic acid, obtained from gum benzoin, with lime and suggested the name benzin for the compound. In 1845, A. W. Hoffman and C. Mansfield found benzene in light oil derived from coal tar. The first practical industrial process for recovery of benzene from coal tar was reported by Mansfield in 1849. Coal tar soon became the largest source of benzene. Soon afterward, benzene was discovered in coal gas and this initiated the recovery of coal gas light oil as a source of benzene.

Until the 1940s, light oil obtained from the destructive distillation of coal was the principal source of benzene. Except for part of the World War II period, the quantity of benzene produced by the coal carbonization industry was sufficient to supply the demand even when a large portion of benzene was used for gasoline blending.

After 1950, benzene in motor fuel was largely replaced by tetraethyllead but the demand for benzene in the chemical industry persisted and soon exceeded the total production by the coal carbonization industry. To meet this growing demand, methods for producing benzene directly from petroleum sources were developed.

Since the 1950s, benzene production from petroleum feedstocks has been very successful and accounts for ~95% of all benzene obtained. Less than 5% of commercial benzene is derived from coke oven light oil.

Benzene is the simplest and most important member of the aromatic hydrocarbons and should not be confused with benzine, a low boiling petroleum fraction composed chiefly of aliphatic hydrocarbons. The term benzole, which denotes commercial products that are largely benzene, is not common in the United States, but is still used in Europe.

## 2. Physical Properties

The physical and thermodynamic properties of benzene are shown in Table 1 (2). Azeotrope data for benzene with selected compounds are shown in Table 2 (3).



Table 1. **Physical and Thermodynamic Properties of Benzene**<sup>a</sup>

Property	Value
mol wt	78.115
freezing point, °C in air at 101.3 kPa <sup>b</sup>	5.530
boiling point, °C at 101.3 kPa <sup>b</sup>	80.094
density, g/cm <sup>3</sup>	
20°C	0.8789
25°C	0.8736
vapor pressure, 25°C, kPa <sup>c</sup>	12.6
refractive index, $n_D$ , 25°C	1.49792
surface tension, 25°C, mN/m (= dyn/cm)	28.20
viscosity, absolute, 25°C in mPa · s (= cP)	0.6010
critical temperature, °C	289.01
critical pressure, kPa <sup>b</sup>	$4.898 \times 10^3$
critical volume, cm <sup>3</sup> /mol	259.0
heat of formation	
g, kJ/mol	82.93
L, kJ/mol	49.08
heat of combustion, kJ/mol <sup>d,e</sup>	$3.2676 \times 10^3$
heat of fusion, kJ/mol	9.866
heat of vaporization, 25°C, kJ/mol	33.899
solubility in H <sub>2</sub> O, 25°C, g/100 g H <sub>2</sub> O	0.180

<sup>a</sup> Ref.2. Courtesy of the Thermodynamics Research Center, The Texas A&M University System.

<sup>b</sup> To convert kPa to atm, divide by 101.3.

<sup>c</sup> To convert kPa to mmHg, multiply by 7.5.

<sup>d</sup> To convert kJ to kcal, divide by 4.184.

<sup>e</sup> At 298.15 K and constant pressure to CO<sub>2</sub> and H<sub>2</sub>O.

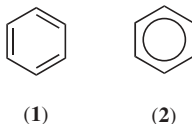
Benzene forms minimum-boiling azeotropes with many alcohols and hydrocarbons. Benzene also forms ternary azeotropes.

**2.1. Structure.** The representation of the benzene molecule has evolved from the Kekulé ring formula (1) to the more electronically accurate (2), which indicates all carbon–carbon bonds are identical.

Table 2. **Azeotropes of Benzene**<sup>a</sup>

Component	CAS Registry Number	Bp, °C	Azeotrope	
			Bp, °C	Wt % benzene
cyclohexane	[110-82-7]	80.75	77.56	51.9
cyclohexene	[110-83-8]	82.1	78.9	64.7
methylcyclopentane	[96-37-7]	71.8	71.5	9.4
<i>n</i> -heptane	[142-82-5]	98.4	80.1	99.3
2,2-dimethylpentane	[590-35-2]	79.1	75.85	46.3
2,2,4-trimethylpentane	[540-84-1]	99.2	80.1	97.7
methanol	[67-56-1]	64.72	57.50	60.9
ethanol	[64-17-5]	78.3	68.24	67.6
2-propanol	[67-63-0]	82.45	71.92	66.7
2-butanol	[78-92-2]	99.5	78.5	84.6
<i>tert</i> -butyl alcohol	[75-65-0]	82.9	73.95	63.4
water	[7732-18-5]	100	69.25	91.17

<sup>a</sup> Ref.3.



The bond angles and distances in benzene are known accurately from X-ray diffraction studies. The six carbon atoms form a regular hexagon in which each carbon atom is 0.139 nm from each of the two adjacent carbon atoms. The carbon-carbon bond lengths in benzene are intermediate in length between single and double carbon-carbon bonds. Each hydrogen atom is 0.108 nm from the carbon atom to which it is bonded. All 12 atoms lie in a single plane. All bond angles in benzene are exactly  $120^\circ$ .

**Resonance Stabilization.** Benzene has great thermal stability. It has a lower heat of formation from the elements than the corresponding structure (1) possessing three fixed, ethylene-type double bonds. Similarly, when benzene is decomposed into carbon and hydrogen, it absorbs more energy than is predicted by the Kekulé formula. The hydrogenation of benzene is exothermic by  $\sim 208$  kJ/mol (49.8 kcal/mol),  $\sim 151$  kJ (36.0 kcal) less than three times the value for cyclohexene. This difference between the energy taken up during the formation of three double bonds and that obtained experimentally for benzene formation is termed the resonance energy for benzene (4,5).

### 3. Chemical Properties

Benzene undergoes substitution, addition, and cleavage of the ring; substitution reactions are the most important for industrial applications.

**3.1. Electrophilic Aromatic Substitution.** Benzene undergoes substitution of one or more of its hydrogen atoms by various groups such as halogen, nitro, sulfonic acid, or alkyl. Reactions with chlorine, bromine, or nitric acid are termed electrophilic aromatic substitution because they involve attack of electron-seeking reagents on the delocalized  $\pi$ -electrons of the aromatic ring. Similarly, benzene derivatives substituted with electronegative or electron-withdrawing groups undergo nucleophilic substitution reactions with electron-donating reagents. Benzene yields only one monosubstitution product and three possible disubstitution products, classified as ortho, meta, or para.

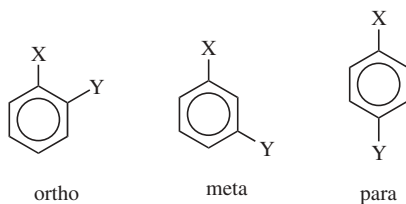


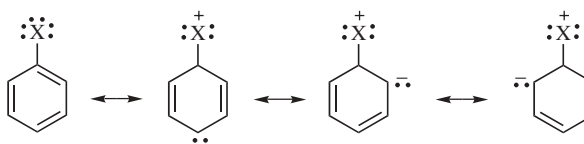
Table 3 shows the number of structural isomers possible when one, two, three, or four substituents, X, Y, and Z, replace the hydrogens of benzene.

**Orientation in Electrophilic Aromatic Substitution.** A substituent group that increases the rate of electrophilic substitution relative to benzene itself is

Table 3. Number of Structural Isomers of the Substitution Products of Benzene

Substituents	Number of isomers
X	1
X, X	3
X, Y	3
X, X, X	3
X, X, Y	6
X, Y, Z	10
X, X, X, X	3
X, X, X, Y	6
X, X, Y, Y	11
X, X, Y, Z	16

called an activating group. Activating groups often have unshared electron pairs on atoms directly attached to the benzene ring and are characterized by their ability to contribute electron density to the  $\pi$ -orbitals of the aromatic ring, thus stabilizing the electrophile's influence on the ring (5,6). An example of a resonance effect is shown.



Resonance effects are the primary influence on orientation and reactivity in electrophilic substitution. The common activating groups in electrophilic aromatic substitution, in approximate order of decreasing effectiveness, are  $-\text{NR}_2$ ,  $-\text{NHR}$ ,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{NO}$ ,  $-\text{NHCOR}$ ,  $-\text{OCOR}$ , alkyls,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ , aryls,  $-\text{CH}_2\text{COOH}$ , and  $=\text{CH}=\text{CH}-\text{COOH}$ . Activating groups are ortho- and para-directing. Mixtures of ortho- and para-isomers are frequently produced; the exact proportions are usually a function of steric effects and reaction conditions.

Deactivating groups decrease the rate at which electrophilic aromatic substitution occurs. They lack an unshared electron pair on the atom directly connected to the aromatic ring and frequently are attached to an electronegative atom by double or triple bonds. The typical deactivating groups, in approximate order of decreasing effectiveness, are  $-\text{NR}_3^+$ ,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CHO}$ ,  $-\text{COOR}$ ,  $-\text{COOH}$ ,  $-\text{CONH}_2$ , and  $-\text{CCl}_3$ . Deactivating groups withdraw electron density from the  $\pi$ -electron cloud making the  $\pi$ -electrons less available for electrophilic reagents. It necessarily follows that, because of resonance effects, deactivating groups direct electrophilic substitution almost exclusively to the meta-position.

The entrance of a third or fourth substituent can be predicted by Beilstein's rule. If a substituent Z-enters into a compound  $\text{C}_6\text{H}_4\text{XY}$ , both X and Y exert an influence, but the group with the predominant influence directs Z- to the position it will occupy. Since all meta-directing groups are deactivating, it follows that

ortho-para activating groups predominate when one of them is present on the benzene ring.

**3.2. Nucleophilic Substitutions of Benzene Derivatives.** Benzene itself does not normally react with nucleophiles such as halide ions, cyanide, hydroxide, or alkoxides (7). However, aromatic rings containing one or more electron-withdrawing groups, usually halogen, react with nucleophiles to give substitution products. An example of this type of reaction is the industrial conversion of chlorobenzene to phenol with sodium hydroxide at 400°C (8).

In nucleophilic aromatic substitutions, required reaction conditions become milder as the number of electron-withdrawing groups on the ring is increased. For example, the conversion of *p*-nitrochlorobenzene to *p*-nitrophenol occurs with sodium hydroxide solution at ~160°C. The conversion of 2,4-dinitrochlorobenzene to 2,4-dinitrophenol occurs with sodium carbonate solution at about 130°C. Picric acid (2,4,6-trinitrophenol) is obtained from the chloride by brief warming with water (9). The reaction occurs preferentially at ortho- and para-positions to electron-withdrawing substituents. In contrast to electrophilic aromatic substitution, electron-withdrawing groups such as NO<sub>2</sub> and CN are activating and ortho-para directing in nucleophilic aromatic substitution.

Nucleophilic aromatic substitutions involving loss of hydrogen are known. The reaction usually occurs with oxidation of the intermediate either intramolecularly or by an added oxidizing agent such as air or iodine. A noteworthy example is the formation of 6-methoxy-2-nitrobenzonitrile from reaction of 1,3-dinitrobenzene with a methanol solution of potassium cyanide. In this reaction, it appears that the nitro compound itself functions as the oxidizing agent (10).

**3.3. Oxidation.** Benzene can be oxidized to a number of different products. Strong oxidizing agents such as permanganate or dichromate oxidize benzene to carbon dioxide and water under rigorous conditions. Benzene can be selectively oxidized in the vapor phase to maleic anhydride. The reaction occurs in the presence of air with a promoted vanadium pentoxide catalyst (11). Prior to 1986, this process provided most of the world's maleic anhydride [108-31-6], C<sub>4</sub>H<sub>2</sub>O<sub>3</sub>. Currently maleic anhydride is manufactured from the air oxidation of *n*-butane also employing a vanadium pentoxide catalyst. Benzoquinone [106-51-4], C<sub>6</sub>H<sub>4</sub>O<sub>2</sub> (quinone) has been reported as a by-product of benzene oxidation at 410–430°C. Benzene can be oxidized to phenols with hydrogen peroxide and reducing agents such as Fe(II) and Ti(II). Frequently, ferrous sulfate and hydrogen peroxide are used (Fenton's reagent), but yields are generally low (12) and the procedure is of limited utility. Benzene has also been oxidized in the vapor phase to phenol in low yield at 450–800°C in air without a catalyst (13).

**3.4. Reduction.** Benzene can be reduced to cyclohexane [110-82-7], C<sub>6</sub>H<sub>12</sub>, or cycloolefins. At room temperature and ordinary pressure, benzene, either alone or in hydrocarbon solvents, is quantitatively reduced to cyclohexane with hydrogen and nickel or cobalt (14) catalysts. Catalytic vapor-phase hydrogenation of benzene is readily accomplished at ~200°C with nickel catalysts. Nickel or platinum catalysts are deactivated by the presence of sulfur-containing impurities in the benzene and these metals should only be used with thiophene-free benzene. Catalysts less active and less sensitive to sulfur, such as molybdenum oxide or sulfide, can be used when benzene is contaminated with sulfur-containing impurities. Benzene is reduced to 1,4-cyclohexadiene

[628-41-1],  $C_6H_8$ , with alkali metals in liquid ammonia solution in the presence of alcohols (15).

**3.5. Halogenation.** Depending on the conditions either substitution or addition products can be obtained by the halogenation of benzene. Chlorine or bromine react with benzene in the presence of carriers, such as ferric halides, aluminum halides, or transition metal halides, to give substitution products such as chlorobenzene or bromobenzene [108-86-1],  $C_6H_5Br$ ; occasionally para-disubstitution products are formed. Chlorobenzene [108-90-7],  $C_6H_5Cl$ , is produced commercially in the liquid phase by passing chlorine gas into benzene in the presence of molybdenum chloride at 30–50°C and atmospheric pressure. This continuous process yields a 14:1 ratio of chlorobenzene to *p*-dichlorobenzene [106-46-7],  $C_6H_4Cl_2$ . The reaction of iodine with benzene takes place only in the presence of oxidizing agents such as nitric acid. Iodobenzene [591-50-4],  $C_6H_5I$ , is thus produced from reaction of benzene, iodine, and excess nitric acid at 50°C (16). Benzene is fluorinated by direct liquid-phase reaction with fluorine in acetonitrile solution at –35°C. The reaction gives predominantly fluorobenzene with small amounts of *o*-, *m*-, and *p*-difluorobenzene by-products (17). Direct fluorination of benzene with fluorine has not yet gained commercial importance. Fluorobenzene [462-06-6],  $C_6H_5F$ , is most commonly prepared from thermal decomposition of dry benzenediazonium tetrafluoroborate [446-46-8] (18).

Chlorine and bromine add to benzene in the absence of oxygen and presence of light to yield hexachloro- [27154-44-5] and hexabromocyclohexane [30105-41-0],  $C_6H_6Br_6$ . Technical benzene hexachloride is produced by either batch or continuous methods at 15–25°C in glass reactors. Five stereoisomers are produced in the reaction and these are separated by fractional crystallization. The gamma isomer (BHC), which composes 12–14% of the reaction product, was formerly used as an insecticide. Benzene hexachloride [608-73-1],  $C_6H_6Cl_6$ , is converted into hexachlorobenzene [118-74-1],  $C_6Cl_6$ , upon reaction with ferric chloride in chlorobenzene solution.

**3.6. Nitration.** The nitration of benzene to nitrobenzene [98-95-3],  $C_6H_5NO_2$ , occurs in yields often >95% when a mixture of concentrated nitric and sulfuric acids is used at 50–55°C. Because the meta-directing nitro group is deactivating, the extent of nitration is rather easily controlled. To produce *m*-dinitrobenzene, more vigorous conditions are required, e.g., nitric and sulfuric acids at 100°C. 1,3,5-Trinitrobenzene [99-35-4],  $C_6H_3N_3O_6$ , is obtained from benzene with a large excess of fuming sulfuric and nitric acids at higher temperatures (19). When benzene reacts with mercuric nitrate and concentrated nitric acid, oxynitration occurs with the formation of either 2,4-dinitrophenol [51-28-5],  $C_6H_4N_2O_5$ , or 2,4,6-trinitrophenol [88-89-1],  $C_6H_3N_3O_7$ , depending on the reaction conditions (20).

**3.7. Sulfonation.** Benzene is converted into benzenesulfonic acid [98-11-3],  $C_6H_6SO_3$ , upon reaction with fuming sulfuric acid (oleum) or chlorosulfonic acid. *m*-Benzenedisulfonic acid [98-48-6],  $C_6H_6S_2O_6$ , is prepared by reaction of benzene-sulfonic acid with oleum for 8 h at 85°C. Often under these conditions, appreciable quantities of *p*-benzenedisulfonic acid [31375-02-7] are produced. 1,3,5-Benzenetrisulfonic acid [617-99-2],  $C_6H_6S_3O_9$ , is produced by heating the disulfonic acid with oleum at 230°C (21).

**3.8. Alkylation.** Friedel-Crafts alkylation (qv) of benzene with ethylene or propylene to produce ethylbenzene [100-41-4],  $C_8H_{10}$ , or isopropylbenzene [98-82-8],  $C_9H_{12}$  (cumene) is readily accomplished in the liquid or vapor phase with various catalysts such as  $BF_3$  (22), aluminum chloride, or supported polyphosphoric acid. The oldest method of alkylation employs the liquid-phase reaction of benzene with anhydrous aluminum chloride and ethylene (23). Ethylbenzene is produced commercially almost entirely for styrene manufacture. Cumene [98-82-8] is catalytically oxidized to cumene hydroperoxide, which is used to manufacture phenol and acetone. Benzene is also alkylated with  $C_{10}$ – $C_{20}$  linear alkenes to produce linear alkyl aromatics. Sulfonation of these compounds produces linear alkane sulfonates (LAS) that are used as biodegradable detergents.

In recent years, alkylations have been accomplished with acidic zeolite catalysts, most notably ZSM-5. A ZSM-5 ethylbenzene process was commercialized jointly by Mobil Co. and Badger America in 1976 (24). The vapor-phase reaction occurs at temperatures  $>370^\circ C$  over a fixed bed of catalyst at 1.4–2.8 MPa (200–400 psi) with high ethylene space velocities. A typical molar ethylene to benzene ratio is  $\sim 1$ –1.2. The conversion to ethylbenzene is quantitative. The principal advantages of zeolite-based routes are easy recovery of products, elimination of corrosive or environmentally unacceptable by-products, high product yields and selectivities, and high process heat recovery (25,26).

ABB Lummus Crest Inc. and Unocal Corp. have licensed a benzene alkylation process using a proprietary zeolite catalyst. Unlike the Mobil-Badger process, the Unocal-Lummus process is suitable for either ethylbenzene or cumene manufacture (27,28).

**3.9. Other Reactions.** Benzene undergoes a number of other useful reactions.

*Chloromethylation (Blanc–Quelet Reaction).* Benzene reacts with formaldehyde and hydrochloric acid in the presence of zinc chloride to yield chloromethylbenzene [100-44-7],  $C_7H_7Cl$  (benzyl chloride) (29), a chemical intermediate.

*Friedel-Crafts Acylation.* The Friedel-Crafts acylation procedure is the most important method for preparing aromatic ketones and their derivatives. Acetyl chloride (acetic anhydride) reacts with benzene in the presence of aluminum chloride or acid catalysts to produce acetophenone [98-86-2],  $C_8H_8O$  (1-phenylethanone). Benzene can also be condensed with dicarboxylic acid anhydrides to yield benzoyl derivatives of carboxylic acids. These benzoyl derivatives are often used for constructing polycyclic molecules (Haworth reaction). For example, benzene reacts with succinic anhydride in the presence of aluminum chloride to produce  $\beta$ -benzoylpropionic acid [2051-95-8], which is converted into  $\alpha$ -tetralone [529-34-0] (30).

*Mercuration–Thallation.* Mercuric acetate and thallium trifluoroacetate react with benzene to yield phenylmercuric acetate [62-38-4] or phenylthallic trifluoroacetate. The arylthallium compounds can be converted into phenols, nitriles, or aryl iodides (31).

*Metalation.* Benzene reacts with alkali metal derivatives such as methyl or ethyllithium in hydrocarbon solvents to produce phenyllithium [591-51-5],  $C_6H_5Li$ , and methane or ethane. Chloro-, bromo-, or iodobenzene will react

with magnesium metal in ethereal solvents to produce phenylmagnesium chloride [100-59-4],  $C_6H_5MgCl$ , bromide, or iodide (Grignard reagents) (32).

**Pyrolysis.** Benzene undergoes thermal dehydrocondensation at high temperatures to produce small amounts of biphenyls and terphenyls (see BIPHENYL AND TERPHENYLS). Before the 1970s most commercial biphenyl was produced from benzene pyrolysis. In a typical procedure, benzene vapors are passed through a reactor, usually at temperatures  $> 650^\circ C$ . The decomposition of benzene into carbon and hydrogen is a competing reaction at temperatures of  $\sim 750^\circ C$ . Biphenyls are also formed when benzene and ethylene are heated to  $130\text{--}160^\circ C$  in the presence of alkali metals on activated  $Al_2O_3$  (33).

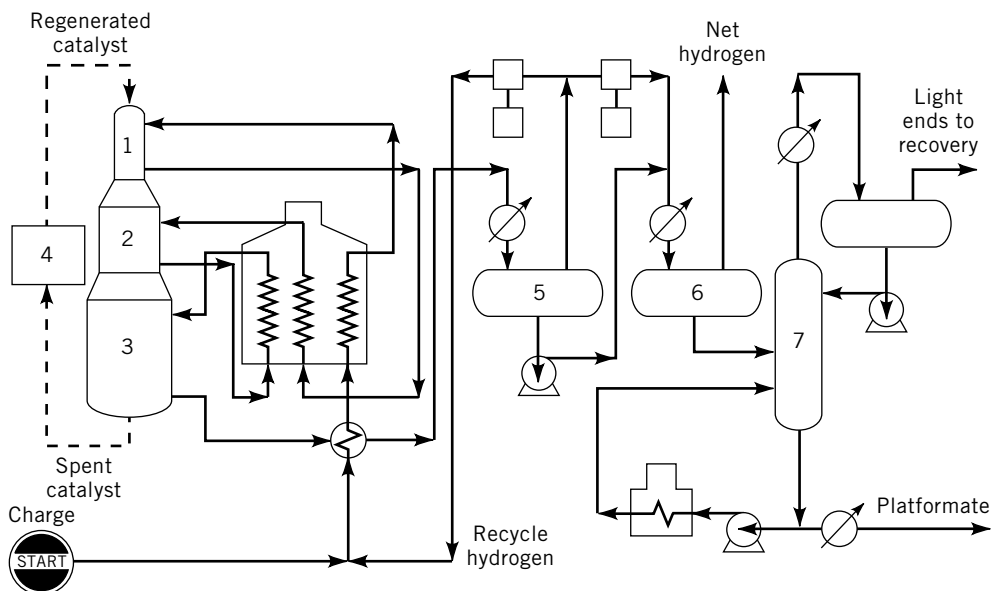
## 4. Manufacture

Benzene is a natural component of petroleum, but the amount of benzene present in most crude oils is small, often  $<1.0\%$  by weight (34). Therefore the recovery of benzene from crude oil is uneconomical and was not attempted on a commercial scale until 1941. To add further complications, benzene cannot be separated from crude oil by simple distillation because of azeotrope formation with various other hydrocarbons. Recovery is more economical if the petroleum fraction is subjected to a thermal or catalytic process that increases the concentration of benzene.

After 1950, the demand for benzene exceeded the output by the coal carbonization industry and to supply the increasing demand, processes were developed for producing and separating benzene directly from petroleum feedstocks. The production of benzene from petroleum increased rapidly thereafter, and by the early 1960s the amount of benzene derived from petroleum was several times greater than that derived from coal. By the late 1970s coal-derived benzene accounted for  $<10\%$  of total benzene produced. Although coke oven light oil often contains useful quantities of benzene, it is expected to further decrease as a source of aromatics as the number of steel companies that produce metallurgical coke from coal decreases.

Petroleum-derived benzene is commercially produced by reforming and separation, thermal or catalytic dealkylation of toluene, and disproportionation. Benzene is also obtained from pyrolysis gasoline formed in the steam cracking of olefins (35).

**4.1. Catalytic Reforming.** Worldwide,  $\sim 30\%$  of commercial benzene is produced by catalytic reforming, a process in which aromatic molecules are produced from the dehydrogenation of cycloparaffins, dehydroisomerization of alkyl cyclopentanes, and the cyclization and subsequent dehydrogenation of paraffins (36). The feed to the catalytic reformer may be a straight-run, hydrocracked, or thermally cracked naphtha fraction in the  $C_6$  to  $200^\circ C$  range. If benzene is the main product desired, a narrow naphtha cut of  $71\text{--}104^\circ C$  is fed to the reformer. The reforming catalyst most frequently consists of platinum–rhenium on a high surface area alumina support. The reformer operating conditions and type of feedstock largely determine the amount of benzene that can be produced. The benzene product is most often recovered from the reformate by solvent extraction techniques.



**Fig. 1.** Universal Oil Products Platforming process. Courtesy Gulf Publishing Co., Houston, Tex. (41).

Several significant reforming processes are in use (37,38). These include Powerforming, Ultraforming Co., Rheniforming (Chevron), Catalytic Reforming, and Platforming. Several other reforming processes are in use but these are limited to a few installations and are not of general interest (39). Platforming is a noteworthy example of current commercial reforming technology.

**Platforming.** The feedstock is usually a straight-run, thermally cracked, catalytically cracked, or hydrocracked  $C_6$  to  $200^\circ\text{C}$  naphtha (40,41) (Fig. 1). The feed is first hydrotreated to remove sulfur, nitrogen, or oxygen compounds that would foul the catalyst, and also to remove olefins present in cracked naphthas. The hydrotreated feed is then mixed with recycled hydrogen and preheated to  $495\text{--}525^\circ\text{C}$  at pressures of  $0.8\text{--}5\text{ MPa}$  ( $116\text{--}725\text{ psi}$ ) (42). Typical hydrogen charge ratios of 4000 to 8000 standard cubic feet per barrel (scf/bbl) of feed are necessary (40). This is approximately equivalent to  $700\text{--}1400\text{ m}^3$  hydrogen per  $\text{m}^3$  of feed.

The feed is then passed through a stacked series of reactors. Usually three or four reactors are used (43,44). All of the reforming catalysts in general use contain platinum chloride or rhenium chloride supported on silica or silica-alumina. The catalyst pellets are generally supported on a bed of ceramic spheres  $\sim 30\text{--}40\text{ cm}$  deep. The spheres vary in size from  $\sim 2.5\text{ cm}$  in diameter on the bottom to  $\sim 9\text{ mm}$  in diameter at the top. Two types of Platforming processes are currently in use. The Semiregenerative Platforming process uses three or four reactors in series in which catalyst activity is regenerated at 6–12 month intervals. In the Continuous Platforming process catalyst activity is maintained by continuously withdrawing a small portion of catalyst and passing it through a

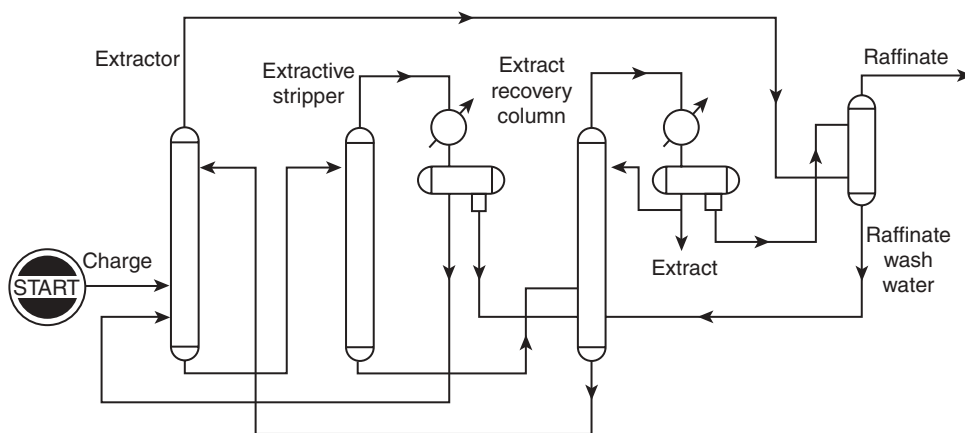


regeneration tower where coke, a natural by-product of the reforming process, is burned off (45).

The product coming out of the reactor consists of excess hydrogen and a reformate rich in aromatics. Typically the dehydrogenation of naphthenes approaches 100%. From 0 to 70% of the paraffins are dehydrocyclized. The liquid product from the separator goes to a stabilizer where light hydrocarbons are removed and sent to a debutanizer. The debutanized platformate is then sent to a splitter where  $C_8$  and  $C_9$  aromatics are removed. The platformate splitter overhead, consisting of benzene, toluene, and nonaromatics, is then solvent extracted (46).

**Aromatics Extraction.** Even when rigorous reforming conditions are employed, the platformate splitter overhead usually contains significant amounts of nonaromatics that must be removed to provide an acceptable commercial benzene product. Numerous solvents are available for extraction of aromatics from an aromatic-aliphatic mixture. These include diethylene glycol (Udex process), *N*-methylpyrrolidinone (Arosolvan process), *N,N*-dimethylformamide (REDEX process), liquid  $SO_2$  extraction (Edelaru process), tetramethylene sulfone [126-33-0] (Sulfolane process), and tetraethylene glycol (Tetra process, Union Carbide). The Udex process was the first solvent extraction process to find widespread usage prior to 1963. Since then, the Sulfolane process has become the most popular. This method, developed by Shell and licensed through UOP, was first reported in 1959 (47). A diagram of the Sulfolane extraction process is shown in Figure 2 (48). Feed is charged to a contactor for the countercurrent extraction of the aromatic components. Solvent from the extractor is charged to an extractive stripper. The stripper vapors are condensed and collected in a separator from which hydrocarbons are returned to the extractor. The stripper bottoms are charged to a recovery column that produces solvent-free aromatics. The aromatics are then fractionated to recover pure benzene.

**4.2. Toluene Hydrodealkylation.** Benzene is produced from the hydrodemethylation of toluene under catalytic or thermal conditions. The main



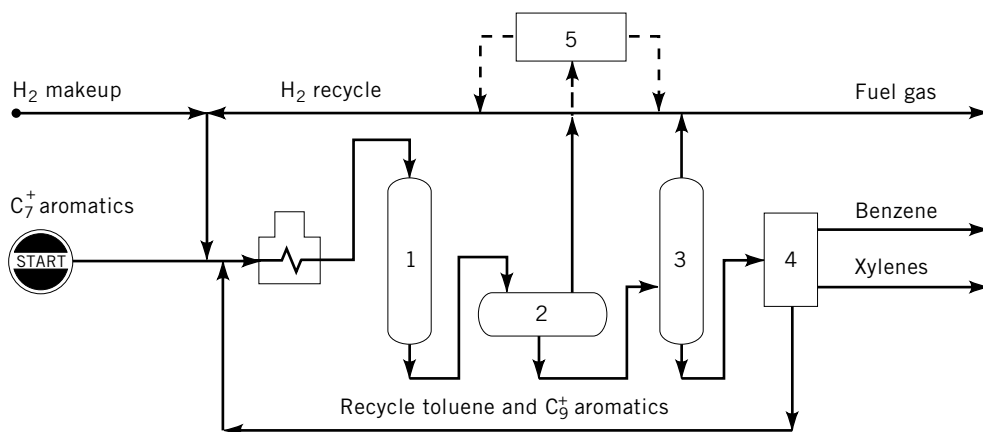
**Fig. 2.** Shell-UOP Sulfolane extraction process. Courtesy Gulf Publishing Co., Houston, Tex. (48).

catalytic hydrodealkylation processes are Hydeal and DETOL (49). Two widely used thermal processes are HDA and THD. These processes contribute 25–30% of the world's total benzene supply.

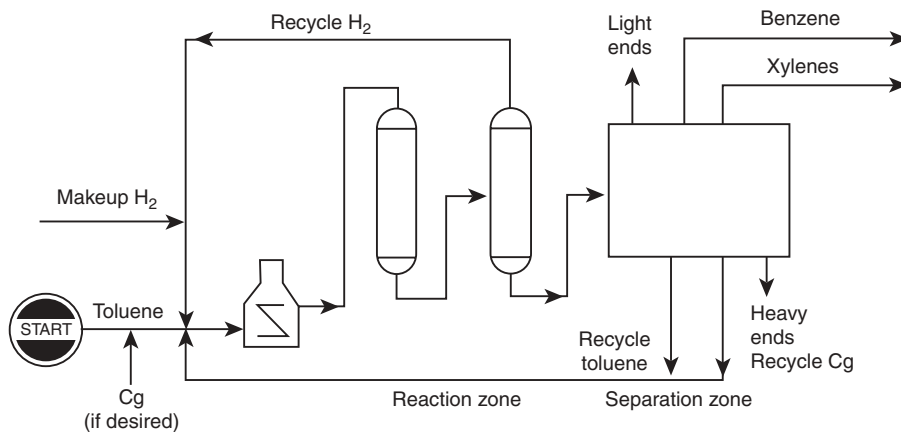
In catalytic toluene hydrodealkylation, toluene is mixed with a hydrogen stream and passed through a vessel packed with a catalyst, usually supported chromium or molybdenum oxides, platinum or platinum oxides, on silica or alumina (50). The operating temperatures range from 500 to 595°C and pressures are usually 4–6 MPa (40–60 atm). The reaction is highly exothermic and the temperature is controlled by injection of quench hydrogen at several places along the reaction. Conversions per pass typically reach 90% and selectivity to benzene is often >95%. The catalytic process occurs at lower temperatures and offers higher selectivities but requires frequent regeneration of the catalyst. Products leaving the reactor pass through a separator where unreacted hydrogen is removed and recycled to the feed. Further fractionation separates methane from the benzene product.

A typical catalytic hydrodealkylation scheme is shown in Figure 3 (49). The most common feedstock is toluene, but xylenes can also be used. Recent studies have demonstrated that C<sub>9</sub> and heavier monoaromatics produce benzene in a conventional hydrodealkylation unit in yields comparable to that of toluene (51). The use of feeds containing up to 100% of C<sub>9</sub>–C<sub>11</sub> aromatics increases the flexibility of the hydrodealkylation procedure that is sensitive to the price differential of benzene and toluene. When toluene is in demand, benzene supplies can be maintained from dealkylation of heavy feedstocks.

**4.3. Transalkylation.** Two molecules of toluene are converted into one molecule of benzene and one molecule of mixed-xylene isomers in a sequence called transalkylation or disproportionation. Economic feasibility of the process strongly depends on the relative prices of benzene, toluene, and xylene. Operation of a transalkylation unit is practical only when there is an excess of toluene and a strong demand for benzene. In recent years, xylene and benzene prices have generally been higher than toluene prices so transalkylation is presently an attractive alternative to hydrodealkylation (see also BTX PROCESSING).



**Fig. 3.** DETOL hydrodealkylation process. Courtesy Gulf Publishing Co., Houston, Tex. (49).



**Fig. 4.** Tatoray toluene disproportionation process. Courtesy Gulf Publishing Co., Houston, Tex. (52).

An example of toluene disproportionation, the Tatoray process, is shown in Figure 4(52). Toluene and  $C_9$  aromatics are mixed with liquid recycle and recycle hydrogen, heated to  $350\text{--}530^\circ\text{C}$  at  $1\text{--}5\text{ MPa}$  ( $10\text{--}50\text{ atm}$ ), and charged to a reactor containing a fixed bed of noble metal or rare earth catalyst. Hydrogen to feed-stock mole ratios of  $5:1$  to  $12:1$  are typically required. Following removal of gases, the separator liquid is freed of light ends and the bottoms are then clay treated and fractionated to produce high purity benzene and xylenes. The yield of benzene and xylene obtained from this procedure is  $\sim 92\%$  of the theoretical. Since the disproportionation is an equilibrium reaction, by varying the feedstock and experimental conditions the ratio of xylene to benzene can be changed.

Lyondell and Sun Oil Co. are the main producers of benzene by disproportionation. Fina Oil Co. of Texas has developed the Fina T2BX process for toluene disproportionation using a proprietary catalyst. The new catalyst is claimed to reduce hydrogen consumption and is suitable for feeds containing small amounts of moisture (53). A process for reacting impure toluene to obtain benzene, toluene, and a para-rich xylene stream that is substantially free of close-boiling nonaromatics by combining aromatization and selective disproportionation has been patented (54).

**4.4. Pyrolysis Gasoline.** The steam cracking of heavy naphthas or light hydrocarbons such as propane or butane to produce ethylene yields a liquid by-product rich in aromatic content called pyrolysis gasoline, dripolene, or drip oil (55). A typical pyrolysis gasoline contains up to  $\sim 65\%$  aromatics,  $\sim 50\%$  of which is benzene. Approximately  $30\text{--}35\%$  of benzene produced worldwide is derived from pyrolysis gasoline. The remainder of the product is composed of mono- and diolefins. These olefinic substances are removed by a mild hydrogenation step. Following hydrogenation, the resulting pyrolysis gasoline is used in motor gasoline. Alternatively, pure benzene could be recovered from the pyrolysis gasoline by solvent extraction and subsequent distillation.

**4.5. Miscellaneous Sources of Benzene.** Benzene has been recovered from coal tar. The lowest boiling fraction is extracted with caustic soda to remove tar acids. The base washed oil is then distilled and further purified by hydrodealkylation.

The synthesis of aromatics from methane, and other light C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> hydrocarbons has been the subject of investigation since the 1980s. One recent example of this is British Petroleum's Cyclar process, modified with UOPs continuous catalyst regeneration technology (56). The process is claimed to produce high purity benzene, toluene, and xylenes from propane, isobutane, or *n*-butane feedstocks. The conversion of synthesis gas into aromatic hydrocarbons with metal zeolite catalysts such as ZSM-5 has also been reported (57). ZSM-5 has also been found to convert light paraffins, olefins, and naphthenes to aromatics and light gases (58). The name M2-Forming has been suggested to describe this recently discovered aromatization process. The production of aromatics and gasoline hydrocarbons from methanol has also received attention (59–61). The future may bring practical methods for converting methane into benzene (62,63). A process for generating benzene from reformed gasoline has been reported (64). A purification process for benzene that comprises two permeation stages has also been reported (65).

## 5. Handling and Shipping

Manufacturers of benzene are required by federal law to publish Material Safety Data Sheets (MSDS) that describe in detail the procedures for its safe handling. Benzene is classified as a flammable liquid and should be stored away from any potential source of ignition. Fire and explosion hazard data for benzene are shown (66).

flash point, closed cup, °C	–11
autoignition temperature, °C	560
flammable limits, vol% in air	1.4 (lower)–8.0 (upper)

Benzene is shipped by rail tank cars, trucks, barges, and tankers. Because of the flammability, toxicity, and volatility of benzene, transfers from one vessel to another are conducted in closed systems. Metal tanks and storage containers should be grounded during transfers. Smaller quantities of benzene are routinely shipped in steel or glass containers. Benzene should be handled only where adequate ventilation is provided; protective clothing and self-contained respirators are recommended. Labeling, packaging, and domestic or international transportation of benzene must comply with regulations described in the *Code of Federal Regulations* (CFR) Title 49. OSHA regulations are described in 29 CFR, Parts 1501, 1502, and 1503. New exposure limits for benzene are published in 29 CFR, Part 1910.1028.

## 6. Economic Aspects

U.S. producers of benzene and their approximate production capacities are shown in Table 4. These figures are inexact because of the size of the market and instability of benzene prices causes frequent changes in capacity. The data in Table 4 include benzene from naphtha reforming, toluene hydroalkylation, or toluene disproportionation, and extraction from pyrolysis gasoline fractions derived from ethylene plant cracked naphthas or heavier feedstocks.

Table 4. **U.S. Producers of Benzene and Annual Capacities<sup>a</sup>**

Producer	Capacity /10 <sup>6</sup> gal <sup>b</sup>
<i>Continental United States</i>	
BP Amoco, Alliance, La.; Lima, Ohio; Texas City, Tex.	270
Chevron, Pascagoula, Miss.; Port Arthur, Tex.; Richmond, Calif.	240
Citgo, Corpus Christi, Tex.; Lake Charles, La.; Lemont, Ill.	170
Coastal, Corpus Christi, Tex.; Westville, N.J.	75
Dow Chemical, Freeport, Tex.; Plaque- mine, La.	220
Equilon Enterprises, El Dorado, Kan.	15
Equistar Chemicals, Alvin, Tex.; Chan- nelview, Tex.; Corpus Christi, Tex.	365
Exxon, Baton Rouge, La.; Baytown, Tex.	335
Fina Oil, Port Arthur, Tex.	95
Huntsman, Port Arthur, Tex.	60
Koch Petroleum, Corpus Christi, Tex.	250
Lyondell, Houston, Tex.	50
Marathon Ashland, Catlettsburg, Ky.; Texas City, Tex.	55
Mobile, Beaumont, Tex.; Chalmette, La.	270
Motiva, Delaware City, Del.	15
Nova, Bayport, Tex.	15
Shell Chemical, Deer Park, Tex.	390
Sunoco, Marcus Hook, Pa.; Sunoco, Mar- cus Hook, Pa.; Philadelphia, Pa.; Toledo Ohio	140
Ultramar Diamond Shamrock, Three Rivers, Tex.	20
Valero Energy, Houston, Tex.	5
<i>Virgin Islands and Puerto Rico</i>	
HOVENSA, St. Croix, V.I.	75
Phillips, Guayama, P.R.; Sweeny, Tex.	145
<i>Total</i>	<i>3275</i>

<sup>a</sup> From Ref. 68, as of Dec. 1999.<sup>b</sup> To convert gal to t, divide by 300.

Estimated demand for 2002 is 2.78 billion gal (68).

Historical (1993–1998) prices were \$1.55/gal, barge, spot, works, as a high and \$0.82 as a low. In Dec. 1999 the price was \$0.75/gal (68).

Benzene production by various foreign countries is shown in Table 5

## 7. Specifications, Standards, and Test Methods

Several different grades of benzene are commercially available. The most common grades are benzene 535, benzene 485 (nitration grade), benzene 545, and thiophene-free benzene. Specifications and the corresponding American Society

Table 5. **Benzene Production by Various Foreign Countries,**<sup>a</sup> 10<sup>3</sup> t<sup>b</sup>

Producers	Quantity
<i>North America</i>	
Petroleos Mexicanos	400
<i>Western Europe</i>	
Germany	
Deutsche Shell	510
Rühr Ol	380
Redistillationsgemeinschaft	240
Erdölchemie	220
OMV	120
PCK	80
Wintershall	75
DEA	65
Others	60
France	
Elf Atochem	610
Gexaro	200
AAF	110
Total	140
Shell Chimie	95
Italy	
EniChem	700
Netherlands	
Dow Europe	900
Exxon Chemical	480
DSM	300
United Kingdom	
ICI	573
Shell U.K.	240
BP Chemicals	217
Conoco	200
Belgium	
Finaneste	170
Portugal	
Petrogal	60
Spain	
Cepsa	304
<i>Eastern Europe</i>	5,007
<i>Asia</i>	
Japan	
Mitsubishi Chemical	843
Idemitsu	804
Nippon Steel	367
Taiyo Oil	330
Maruzen Petrochemical	350
Sanyo Petrochemical	340
Mitsubishi Oil	345
Koa Oil	204
Mitsui Chemicals	161
Showa Shell Sekiyu	160
Osaka Petrochemical	130
Sumitomo Chemical	122
Tosoh	120

Table 5 (Continued)

Producers	Quantity
Kawasaki Steel	116
Nikko Petrochemicals	100
Nippon Petrochemical	90
Others	600
South Korea	
SK	490
Samsung	425
Daelim	190
Hyundai Petrochemical	100
Honam Oil	100
Others	420
Singapore	
Mobil Chemical	250
PCS	220
Taiwan	
Chinese Petroleum	493
China Steel	30
Indonesia	
Pertamina	115
Middle East	
Saudi Arabia	
Sabic	290
Iran	405
<i>South America</i>	
Brazil	
Copene	430
Copesul	263
Petroquímica União	198
Petrobras	38
Others	30
Argentina	
YPF	120
PASA	80
Venezuela	
Pequiven	70
Colombia	
Ecopetrol	65

<sup>a</sup> From Ref. 69. Sources: De Witt & Co. (Houston); SRI Consulting (Menlo Park, Calif.); CW estimates.

<sup>b</sup> To convert t to gal, multiply by 300.

for Testing and Material (ASTM) test procedures for these various types are shown in Table 6 (70). American Chemical Society (ACS) specifications for reagent grade benzene are shown in Table 7 (71). Industrial-grade benzene is used primarily in applications that are insensitive to impurities. Nitration-grade benzene is a high quality product used for preparing nitrobenzene and derivatives. Thiophene-free benzene is used as a reagent in ASTM standards and is specially treated to remove thiophene. Thiophene and organic sulfur compounds foul many catalysts used in reactions of benzene.

Table 6. Specifications for Commercial Grades of Benzene<sup>a</sup>

ASTM test	Benzene 535 <sup>b</sup>	Benzene 485 <sup>c</sup>	Industrial-grade <sup>d</sup>
appearance	clear liquid, free from sediment or haze at 18–24°C	clear liquid, free from sediment or haze at 18–24°C	clear liquid, free from sediment at 18–24°C
relative density, 14.56–15.56°C, D3505	0.8820–0.8860	0.8820–0.8860	0.875–0.886
density, 20°C, g/cm <sup>3</sup> , D4052	0.8780–0.8820	0.8780–0.8820	0.871–0.882
color pt-co scale, D1209	20 max	20 max	20 max
total distillation range, 101.3 kPa, <sup>e</sup> D850	1.0°C max, including the temperature of 80.1°C	1.0°C max, including the temperature of 80.1°C	2.0°C max, including the temperature of 80.1°C
solidification point, D852	5.35°C (anhydrous)	not lower than 4.85°C (anhydrous)	
acid wash color, D848	1 max	2 max	3 max
acidity, D847	none detected	none detected	none detected
H <sub>2</sub> S and SO <sub>2</sub> , D853	none detected	none detected	none detected
thiophene, D1685	1 mg/kg max		
copper corrosion, D849	pass	pass	copper strip shall not show iridescence, a gray or black deposit, or discoloration
nonaromatics, D2360	0.15 wt% max		

<sup>a</sup> Ref. 70.<sup>b</sup> ASTM D2359-85a.<sup>c</sup> Nitration-grade, ASTM D835-85.<sup>d</sup> ASTM D836-84.<sup>e</sup> To convert kPa to mmHg, multiply by 7.5.

The purity of benzene marketed for most laboratory purposes is usually >95.5% with the principal impurities being toluene and other hydrocarbons with boiling points similar to that of benzene. Methods used to assess the quality of benzene include determination of density, boiling point, distillation characteristics, and specific gravity. Benzene of high purity samples is conveniently

Table 7. Specifications for ACS Reagent-Grade Benzene<sup>a</sup>

Specification	Value
color (APHA)	not more than 10
boiling range	entirely within 1.0°C range including 80.1 ± 0.1°C
freezing point	not below 5.2°C
residue after evaporation	not more than 0.001%
substances darkened by sulfuric acid	to pass test
thiophene	to pass test (limit ≈1 ppm)
sulfur compounds (as S)	not more than 0.005%
water	not more than 0.05%

<sup>a</sup> Ref. 71.



measured by freezing point, as outlined in ASTM D1016. The acid wash test consists of shaking a mixture of 96% sulfuric acid with benzene and comparing the color of the (lower) acid layer with a set of color standards. Other qualitative tests include those for  $\text{SO}_2$  and  $\text{H}_2\text{S}$  determination. The copper strip corrosion test indicates the presence of acidic or corrosive sulfur impurities. The test for thiophene is colorimetric.

**7.1. Analysis.** The infrared (ir), ultraviolet (uv), and nuclear magnetic resonance (nmr) spectra are distinct and characteristic for benzene and are widely used in analysis (72–74). Benzene also produces diagnostic ions in the mass spectrum (75,76) (see ANALYTICAL METHODS).

The identification of benzene is most easily carried out by gas chromatography (77). Gas chromatographic analysis of benzene is the method of choice for determining benzene concentrations in many diverse media such as petroleum products or reformat, water, soil, air, or blood. Benzene in air can be measured by injection of a sample obtained from a syringe directly into a gas chromatograph (78).

In recent years, gas chromatograph–mass spectrometer (gc–ms) systems have become popular for analyzing trace amounts of benzene (79). The gc–ms method gives higher accuracy and precision than conventional gc methods because components are identified by molecular weight, even when benzene may overlap with other compounds. With multichanneled, double-focusing instruments, detection limits of 0.1 ppb in air or breath samples are claimed by a selective ion monitoring gc–ms procedure (sim–gc–ms) (80).

Rapid, simple, qualitative methods suitable for determining the presence of benzene in the workplace or surroundings have been utilized since the 1930s. Many early tests offered methods for detection of aromatics but were not specific for benzene. A straightforward test allowing selective detection of benzene involves nitration of a sample to *m*-dinitrobenzene and reaction of the resultant ether extract with an ethanolic solution of sodium hydroxide and methyl ethyl ketone (2-butanone), followed by the addition of acetic acid to eliminate interferences from toluene and xylenes. Benzene imparts a persistent red color to the solution (81). The method is claimed to be sensitive to concentrations as low as 0.27 ppm benzene from 10-mL air samples.

Benzene reacts with concentrated sulfuric acid and formaldehyde to produce a brown precipitate. A similar reaction occurs with ferrous sulfate and hydrogen peroxide. The resulting brown solid is dissolved in nitric acid for comparison with color standards.

Colorimetric methods have led to the development of visual devices for measurement of benzene concentration. These visual detection tubes have been popular since the 1960s and have provided a simple and reliable method for evaluating ambient aromatic vapor contamination. These products are available from a number of manufacturers such as Dräger (Lubeck, Germany), Gastec (Tokyo, Japan), Kitagawa (Kawasaki, Japan), DuPont (Wilmington, Delaware, USA), and 3M (St. Paul, Minnesota, USA) (79).

Various types of detector tubes have been devised. The NIOSH standard number S-311 employs a tube filled with 420–840  $\mu\text{m}$  (20/40 mesh) activated charcoal. A known volume of air is passed through the tube by either a handheld or vacuum pump. Carbon disulfide is used as the desorbing solvent and the

solution is then analyzed by gc using a flame-ionization detector (82). Other adsorbents such as silica gel and desorbents such as acetone have been employed. Passive (diffuse samplers) have also been developed. Passive samplers are useful for determining the time-weighted average (TWA) concentration of benzene vapor (83). Passive dosimeters allow permeation or diffusion-controlled mass transport across a membrane or adsorbent bed, ie, activated charcoal. The activated charcoal is removed, extracted with solvent, and analyzed by gc. Passive dosimeters with instant readout capability have also been devised (79).

Determination of benzene in air samples has been achieved by bubbling contaminated air through various solvents, followed by uv or ir analysis of the solution (84). Methods for identifying benzene in soil, water, and biological media are further described in References 78 and 79.

## 8. Environmental Considerations

Benzene is classified as a hazardous waste by the Environmental Protection Agency (EPA) under subtitle C of the Resource and Recovery Act (RCRA) (85). Effective Sept. 25, 1990, solid wastes containing more than 0.5-mg/mL benzene must be treated in accordance with applicable RCRA regulations. Benzene is also subject to annual reporting of environmental releases as described in Section 313 of the Emergency and Community Right to Know Act of 1986 (86). Benzene emissions and effluent streams from petroleum refineries or benzene processing plants are also subject to strict federal regulations. Federal waste management procedures must be complied with for any industrial process involving manufacture, transport, treatment, or disposal of benzene. A complete description of the new EPA regulations concerning benzene and other hazardous wastes is found in the *Federal Register* (87). Further information regarding the handling and disposal of toxic or hazardous wastes is in the CFR, Vol. 40.

## 9. Health and Safety Factors

At room temperature and atmospheric pressure, benzene is sufficiently vaporized to pose an inhalation hazard. Benzene is a toxic substance that can produce both acute and chronic adverse health effects. It is generally recognized that prolonged or repeated exposure to benzene can result in serious damage to the blood-forming elements. The first indications of benzene toxicity during occupational exposure were reported in Sweden in 1897 (88). By the early 1900s, it was clear that humans chronically exposed to benzene suffered bone marrow damage.

Prolonged or repeated exposure to benzene vapor results in blood dyscrasias including lympho-, thrombo-, and pancytopenia, a decrease in all types of circulating blood cells (89–91). The decrease in blood components, caused by the action of benzene on bone marrow, is referred to as aplastic anemia and is the disease most commonly associated with benzene exposure (91). Cases of benzene poisoning resulting in hematological disturbances have been reported from repeated exposures to amounts as low as 60 ppm (92). In the early stages of chronic exposure the blood changes are variable, but as the disease becomes

established a decrease in polymorphonuclear leucocytes and a relative lymphocytosis are found (93). If benzene exposure is stopped, the blood changes may or may not be reversed, and the blood morphology may require several years to return to normal (94).

A less frequent, but more serious, health complication resulting from chronic benzene exposure is the development of leukemia. The relationship between benzene and leukemia was suggested in the late 1920s. By the late 1930s, 10 cases of leukemia linked to benzene had been documented worldwide. A number of clinical case reports and several epidemiological studies followed and by the late 1970s benzene was clearly recognized as a carcinogen (leukemogen). Acute myelogenous leukemia (AML) is the most common form of the disease associated with benzene exposure (88,95,96). It is believed that most, if not all, benzene-induced leukemias are preceded by pancytopenia or aplastic anemia (97) followed by a latency period of at least several years. Currently, the long-term prognosis for AML is poor and the outcome is usually fatal. Benzene has been linked to other, less common forms of leukemia, including lymphoid, myeloblastic, erythroblastic, and the hairy-cell varieties (98,99).

Neither the mechanism by which benzene damages bone marrow nor its role in the leukemia process are well understood. It is generally believed that the toxic factor(s) is a metabolite of benzene (100). Benzene is oxidized in the liver to phenol [108-95-2] as the primary metabolite with hydroquinone [123-31-9], catechol [120-80-9], muconic acid[505-70-4], and 1,2,4-trihydroxybenzene[533-73-3] as significant secondary metabolites (101). Although the identity of the actual toxic metabolite or combination of metabolites responsible for the hematological abnormalities is not known, evidence suggests that benzene oxide, hydroquinone, benzoquinone, or muconic acid derivatives are possibly the ultimate carcinogenic species (89,96,100–105).

Recently, the myelotoxicity has been proposed to occur through initial conversion of benzene to phenol and hydroquinone in the liver, selective accumulation of hydroquinone in the bone marrow, followed by conversion of hydroquinone to benzoquinone via bone marrow myeloperoxidase. Benzoquinone is then proposed to react with macromolecules disrupting cellular processes (101).

Benzene is rapidly absorbed from the lungs into the bloodstream. Studies on the inhalation of benzene have given a retention at rest of ~50% (100). The half-life for benzene disappearance in the body is ~0.4–1.6 h (106). Benzene accumulates in fatty tissues and continues to be excreted long after exposure. In one particular study, volunteers were exposed to 200 ppm benzene per hour over an 8-h workday for 5 days. After the fifth day of exposure, the volunteers exhaled twice as much benzene as on the first day of exposure (107). In another study, it was observed that 26% of absorbed benzene was exhaled unmetabolized and was excreted in the urine as 61% phenol, 6.4% catechol, and 2% hydroquinone (108). Because benzene is oxidized mainly to phenol, the urinary phenol test is a widely used method for detecting benzene exposure. Urinary phenol content of nonoccupationally exposed subjects does not usually exceed 20 mg/L (109). Determining the ratio of inorganic to organic sulfate in urine is no longer recommended for evaluating benzene exposure because of its recognized low specificity to phenol (110).

Aplastic anemia and leukemia are not the only health effects ascribed to benzene exposure. A number of recent studies have associated benzene exposure with chromosomal changes (aberrations) (111). Other studies have shown abnormalities in porphyrin metabolism and decrease in leucocyte alkaline phosphatase activity in apparently healthy workers exposed to 10–20 ppm benzene (112,113). Increases in leukoagglutinins, as well as increases in blood fibrinolytic activity, have also been reported and are believed to be responsible for the persistent hemorrhages in chronic benzene poisoning (114,115).

Inhalation of 3000 ppm benzene can be tolerated for 0.5–1 h; 7500 ppm causes toxic effects in 0.5–1 h; and 20,000 ppm is fatal in 5–10 min (116). The lethal oral dose for an adult is ~15 mL (117). Repeated skin contact is reported to cause drying, defatting, dermatitis, and the risk of secondary infection if fissuring occurs.

In chronic benzene intoxication, mild poisoning produces headache, dizziness, nausea, stomach pain, anorexia, and hypothermia. In severe cases, pale skin, weakness, blurred vision, and dyspnea occur on exertion. Hemorrhagic tendencies include petechia, easy bruising, and bleeding gums. Bone marrow depression produces a decrease in circulating peripheral erythrocytes and leucocytes (94). Fatalities from chronic exposure show at autopsy severe bone marrow aplasia, and necrosis or fatty degeneration of the heart, liver, and adrenals (118).

Acute benzene poisoning results in central nervous system (CNS) depression and is characterized by an initial euphoria followed by staggered gait, stupor, coma, and convulsions. Exposure to ~4000 ppm benzene results in complete loss of consciousness. Insomnia, agitation, headache, nausea, and drowsiness may persist for weeks after exposure (119). Continued inhalation of benzene to the point of euphoria has caused irreversible encephalopathy with tremulousness, emotional lability, and diffuse cerebral atrophy (118). In deaths arising from acute exposure, respiratory tract infection, hypo- and hyperplasia of sternal bone marrow, congested kidneys, and cerebral edema have been found at autopsy.

Treatment for acute exposure to benzene vapor involves removing the subject from the affected area, followed by artificial respiration with oxygen; intubation and cardiac monitors may be necessary for severe acute exposures (118,120). Because of its low surface tension, benzene poses a significant aspiration hazard if the liquid enters the lungs. Emesis is indicated in alert patients if more than 1 mL of benzene per kg of body weight has been ingested and less than two hours have passed between ingestion and treatment (120).

Treatment for chronic benzene poisoning is supportive and symptomatic, with chemotherapy and bone marrow transplants as therapeutic agents for leukemia and aplastic anemia (120).

## 10. Regulations

Because of the potential hazards associated with benzene, exposure to benzene in the workplace has been heavily regulated in the United States. Benzene is considered one of the ~40 known human carcinogens. Benzene is listed as an ACGIH suspected human carcinogen, an NTP human carcinogen, and an

Table 8. National Exposure Limits for Benzene<sup>a</sup>

Country		Concentration	Status
Australia	TWA	5 ppm (16 mg/m <sup>3</sup> )	carcinogen
Belgium	TWA	10 ppm (32 mg/m <sup>3</sup> )	carcinogen
Czechoslovakia	TWA	10 mg/m <sup>3</sup> ; STEL 20 mg/m <sup>3</sup>	
Denmark	TWA	5 ppm (16 mg/m <sup>3</sup> )	skin, carcinogen
Finland	TWA	5 ppm (15 mg/m <sup>3</sup> ); STEL 10 ppm (30 mg/m <sup>3</sup> )	skin
France	TWA	5 ppm (16 mg/m <sup>3</sup> )	carcinogen
Germany (DFG MAK)	none		
Hungary	STEL	5 mg/m <sup>3</sup>	skin, carcinogen
India	TWA	10 ppm (30 mg/m <sup>3</sup> )	carcinogen
Ireland	TWA	5 ppm (16 mg/m <sup>3</sup> )	carcinogen
Japan (JSOH)			carcinogen
The Netherlands	TWA	2.3 ppm (7.5 mg/m <sup>3</sup> )	skin
The Philippines	TWA	25 ppm (80 mg/m <sup>3</sup> )	skin
Poland	TWA	10 mg/m <sup>3</sup> ; STEL 40 mg/m <sup>3</sup>	skin
Russia	TWA	10 ppm (5 mg/m <sup>3</sup> ); STEL 25 ppm (15 mg/m <sup>3</sup> )	skin, carcinogen
Sweden	TWA	1 ppm (3 mg/m <sup>3</sup> ); STEL 5 ppm (16 mg/m <sup>3</sup> )	skin, carcinogen
Switzerland	TWA	5 ppm (16 mg/m <sup>3</sup> )	skin, carcinogen
Thailand	TWA	10 ppm (30 mg/m <sup>3</sup> ); STEL 25 ppm (75 mg/m <sup>3</sup> )	skin
Turkey	TWA	20 ppm (64 mg/m <sup>3</sup> )	skin
United Kingdom (HSE MEL)	TWA	5 ppm (16 mg/m <sup>3</sup> )	

<sup>a</sup> Ref. 122.

IARC human carcinogen. Six foreign countries, including Germany, Italy, Japan, Sweden, and Switzerland, recognize benzene as a carcinogen (88). In the United States, the earliest limit on benzene exposure was recommended in 1927 at 100 ppm (121). Over the decades the upper allowable limits were reduced to 50, 35, then 25 ppm (88). Twenty countries have been reported to limit occupational exposure to benzene by regulation or recommended guideline. These occupational exposure limits are shown in Table 8 (122).

In 1971, the Occupational Safety and Health Administration (OSHA) standard for benzene (20 CFR, Part 1910.0000) adopted a permissible exposure limit (PEL) of 10 ppm benzene measured as an 8-h TWA. In October of 1976, NIOSH updated its earlier criteria document on benzene and recommended that OSHA lower the benzene exposure standard from 10 to 1 ppm. This proposed implementation was blocked by the U.S. Supreme Court in 1980 on the basis of insufficient evidence linking benzene to cancer deaths. OSHA permissible exposure limit (PEL) is 1 ppm (3 mg/m<sup>3</sup>) with a short-term exposure limit (STEL) of 5 ppm (15 mg/m<sup>3</sup>); the American Conference of Governmental Industrial Hygienists (ACGIH) TLV is 0.5 ppm (1.6 mg/m<sup>3</sup>) and an STEL/ceiling level of 2.5 ppm (8 mg/m<sup>3</sup>) with an A1 notation. The NIOSH REL is 0.1 ppm with a STEL of 1 ppm (123).

Further, this standard provides for methods of compliance, personal protective equipment, adequate communication of benzene hazards to employees,

regulated areas, and medical surveillance of workers who are or may be exposed to benzene. Any employee routinely exposed to benzene should, in addition to wearing protective equipment, receive periodic blood tests.

## 11. Uses

In the early part of the twentieth century, benzene was used as a universal solvent and degreaser and found widespread use throughout the rubber industry in the manufacture of tires. By the late 1920s, following reports of deaths due to benzene exposure, it was largely replaced by toluene and aliphatic solvents (124).

Before World War II, the largest market for benzene was in gasoline blending to improve octane ratings. After 1950, benzene in gasoline was largely replaced with tetraethyllead. In recent years, with the recognition of the hazards of lead in the environment, the EPA has limited the amount of lead in gasoline to 0.1 g/lead gallon (125). In addition, the EPA has suggested limits for benzene content of gasoline. The California Air Resources Board (CARB) has proposed limits on benzene in motor gasoline of 0.8 vol% after September, 1990. It is possible in the future that other aromatics in gasoline, especially xylenes, will face similar restrictions. Benzene content of U.S. motor gasoline currently ranges from ~0.1 – 4.4 vol% (126).

Benzene is still used extensively as a gasoline component in Europe and many countries do not limit the benzene content (127). Exceptions are Austria, Norway, Sweden, and Switzerland, which set the maximum at 5.0 vol% (127). Over 90% of European motor gasolines are below the 5.0 vol% limit set by these countries. It is likely that benzene content of European gasoline will be further reduced in the future.

Benzene is now used primarily as an intermediate in the manufacture of industrial chemicals. Approximately 95% of U.S. benzene is consumed by industry for the preparation of polymers, detergents, pesticides, pharmaceuticals, and allied products.

Estimates of benzene consumption for nonfuel uses are shown in Table 9 (68). Benzene consumption worldwide is dominated by the production of three main derivatives, styrene, cumene, and cyclohexane, which account for nearly 86% of the total.

Benzene is alkylated with ethylene to produce ethylbenzene, which is then dehydrogenated to styrene, the most important chemical intermediate derived

Table 9. **United States Use Pattern for Benzene, 1999<sup>a</sup>**

Use	Total consumption, %
ethylbenzene	50
cumene	24
cyclohexane	12
aniline	6
alkylbenzene	2
chlorobenzenes	1
other	5

<sup>a</sup> Ref.68.

from benzene. Styrene is a raw material for the production of polystyrene and styrene copolymers such as acrylonitrile–butadiene–styrene (ABS) and SAN. Ethylbenzene accounted for nearly 50% of benzene consumption in 1999.

Benzene is alkylated with propylene to yield cumene (qv). Cumene is catalytically oxidized in the presence of air to cumene hydroperoxide, which is decomposed into phenol and acetone (qv). Phenol is used to manufacture caprolactam (nylon) and phenolic resins such as bisphenol A. Approximately 24% of benzene produced in 1999 was used to manufacture cumene.

Benzene is hydrogenated to cyclohexane. Cyclohexane is then oxidized to cyclohexanol, cyclohexanone, or adipic acid (qv). Adipic acid is used to produce nylon. Cyclohexane manufacture was responsible for about 12% of benzene consumption in 1999.

Nitration of benzene yields nitrobenzene, which is reduced to aniline, an important intermediate for dyes and pharmaceuticals. Benzene is chlorinated to produce chlorobenzene, which finds use in the preparation of pesticides, solvents, and dyes.

A novel herbicidal and defoliant composition containing substitution benzene compounds has been patented. Control of undesired plants is obtained by low concentrations of these compounds (128).

Some of benzene consumed was used for the manufacture of straight- or branched-chain detergent alkylate. Linear alkane sulfonates (LAS) are widely used as household and laundry detergents.

Prior to 1975, benzene was catalytically oxidized to produce maleic anhydride, an intermediate in synthesis of polyester resins, lubricant additives, and agricultural chemicals.

**11.1. Minor Uses.** Small amounts of benzene find use in production of benzene–sulfonic acid. *m*-Benzenedisulfonic acid is used to produce resorcinol[108-46-3],  $C_6H_6O_2$ , (1,3-dihydroxybenzene). Benzene is thermally dimerized to yield biphenyl[92-52-4],  $C_{12}H_{10}$ . Benzene can also be converted into *p*-diisopropylbenzene[100-18-5],  $C_{12}H_{18}$ , which is oxidized to hydroquinone(1,4-dihydroxybenzene), a useful antioxidant. Because of its well-recognized toxicity, little benzene is employed for solvent purposes, and then only when no suitable substitutes are available.

Substitute benzene compounds find use as an antiproliferative and cholesterol lowering drug (129), as an immunosuppressive agents, antifungal agent, and hair growth stimulant (130), and in treating ischemic diseases (131).

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