PHENOL

1. Introduction

Phenol [108-95-2] is the common name of hydroxybenzene, C_6H_5OH, and belongs to the class of compounds, commonly referred to as phenols, containing one or more hydroxyl groups attached to an aromatic ring. Phenol has also been called carbolic acid, phenic acid, phenylic acid, phenyl hydroxide, or oxybenzene. The history of phenol goes back to 1834 when it was first isolated from coal tar and named carbolic acid. Until the advent of synthetic phenol production, just before World War I, coal tar remained the only source of phenol. The first synthetic phenol was produced by sulfonation of benzene and hydrolysis of the sulfonate.

More than 99% of phenol produced worldwide is from synthetic processes. In 2001, worldwide phenol production was nearly 6.4 million metric tons (1). The predominant uses of phenol are in bisphenol A, Phenolic resins (qv), caprolactam (qv), aniline, and alkylphenols (qv).

2. Physical Properties

At room temperature phenol is a white, crystalline mass. Phenol gradually turns pink if it contains impurities or is exposed to heat or light. It has a distinctive sweet, tarry odor, and burning taste. Phenol has limited solubility in water between 0 and 65°C. Above 65.3°C phenol and water are miscible in all proportions. It is very soluble in alcohol, benzene, chloroform, ether, and partially dissociated organics in general. It is less soluble in paraffinic hydrocarbons. The important physical properties of phenol are listed in Table 1.

3. Chemical Properties

Phenol's chemical properties are characterized by the influences of the hydroxyl group and the aromatic ring upon each other. Although the structure of phenol is similar to cyclohexanol, phenol is a much stronger acid. Its pK_a in aqueous solution at 25°C is 9.89×10^{-10} (8). This characteristic allows aqueous hydroxides to convert phenol into their salts. The salts, especially those of sodium and potassium, are converted back into phenol by aqueous mineral acids or carboxylic acids.

Beside being acidic, a significant industrial chemical property of phenol is the extremely high reactivity of its ring toward electrophilic substitution. If steric conditions permit, the substitution leads first to the formation of the 2- or 4-monoderivative, then to the 2,4- or 2,6-diderivative, and finally to the 2,4,6-triderivative. The halogenation of phenol produces mono-, di-, and trihalophenols.

The most important commercial chemical reactions of phenol are condensation reactions. The condensation reaction between phenol and formaldehyde yields phenolic resins whereas the condensation of phenol and acetone yields bisphenol A (2,2-bis-(4-hydroxyphenol)propane). Bisphenol A [80-05-7] and phenolic resins account for more than two-thirds of U.S. phenol consumption (9).

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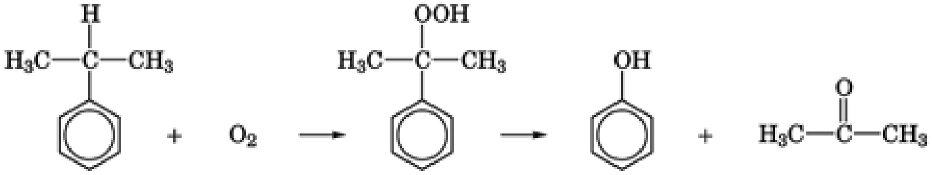
4. Manufacture

The cumene oxidation route is the leading commercial process of synthetic phenol production, accounting for more than 95% of phenol produced in the world. The remainder of synthetic phenol is produced by the toluene oxidation route via benzoic acid. Other processes including benzene via cyclohexane, benzene sulfonation, benzene chlorination, and benzene oxychlorination have also been used in the manufacture of phenol.

4.1. Cumene Process. There are several licensed processes to produce phenol which are based on cumene (qv) (10–13). All of these processes consist of two fundamental chemical reactions: cumene is oxidized with air to form cumene hydroperoxide, and cumene hydroperoxide is cleaved to yield phenol and acetone. In this process, approximately 0.46 kg of acetone and 0.75 kg of phenol are produced per kg of cumene feedstock.



A typical phenol plant based on the cumene hydroperoxide process can be divided into two principal areas. In the reaction area, cumene, formed by alkylation of benzene and propylene, is oxidized to form cumene hydroperoxide (CHP). The cumene hydroperoxide is concentrated and cleaved to produce phenol and acetone. By-products of the oxidation reaction are acetophenone and dimethyl benzyl alcohol (DMBA). DMBA is dehydrated in the cleavage reaction to produce alpha-methylstyrene (AMS).

The recovery area of the plant employs fractionation to recover and purify the phenol and acetone products. Also in this section the alpha-methylstyrene is recovered and may be hydrogenated back to cumene or recovered as AMS product. The hydrogenated AMS is recycled as feedstock to the reaction area. The overall yield for the cumene process is 96 mol %. Figure 1 is a simplified process diagram.

Oxidation of cumene to cumene hydroperoxide is usually achieved in three to four oxidizers in series, where the fractional conversion is about the same for each reactor. Fresh cumene and recycled cumene are fed to the first reactor. Air is bubbled in at the bottom of the reactor and leaves at the top of each reactor. The oxidizers are operated at low to moderate pressure. Due to the exothermic nature of the oxidation reaction, heat is generated and must be removed by external cooling. A portion of cumene reacts to form dimethylbenzyl alcohol and acetophenone. Methanol is formed in the acetophenone reaction and is further oxidized to formaldehyde and formic acid. A small amount of water is also formed by the various reactions. The selectivity of the oxidation reaction is a function of oxidation conditions: temperature, conversion level, residence time, and oxygen partial pressure. Typical commercial yield of cumene hydroperoxide is about 95 mol % in the oxidizers. The reaction effluent is stripped off unreacted cumene which is then recycled as feedstock. Spent air from the oxidizers is treated to recover 99.99% of the cumene and other volatile organic compounds.

The concentrated cumene hydroperoxide solution from the cumene stripping section is fed to the cleavage reaction. The cleavage reaction is carried out in the presence of an acid catalyst such as sulfuric acid. The cleavage reactor conditions are adjusted to maintain an optimum temperature to maximize phenol yield. Typical commercial yield of phenol from CHP in cleavage is greater than 98 mol %. The cleavage effluent contains the acid used as a catalyst for the cleavage reaction as well as formic and acetic acids which are by-products of the cleavage reactions. These must be neutralized and extracted to avoid corrosion problems downstream.

The neutralized cleavage product, consisting of acetone, phenol, water, hydrocarbons, and trace organic impurities, is separated in a series of distillation columns. Also in this section alpha-methylstyrene is either recovered as a product or hydrogenated to cumene.

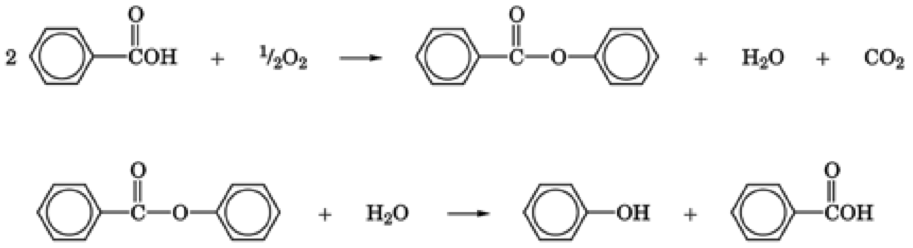
Due to environmental considerations, many phenol plants are equipped with a special water treatment facility where acetone and phenol are recovered from the wastewater stream. Also, recovered heavy residue is considered a K-022 waste material by the U.S. EPA and must be properly disposed of by incineration or other means (13).

Safety is a critical aspect in the design of phenol plants. Oxidation of cumene to CHP occurs at conditions close to the flammable limits. Furthermore, the CHP is a potentially unstable material which can violently decompose under certain conditions. Thus, phenol plants must be carefully designed and provided with well-designed control and safety systems.

4.2. Toluene–Benzoic Acid Process. The toluene–benzoic acid process was first introduced by Dow-Canada, Ltd. in 1961 (14). It accounts for 4% of the total synthetic phenol capacity in the world.

The three chemical reactions in the toluene–benzoic acid process are oxidation of toluene to form benzoic acid, oxidation of benzoic acid to form phenyl benzoate, and hydrolysis of phenyl benzoate to form phenol. A typical process consists of two continuous steps (14,15). In the first step, the oxidation of toluene to benzoic acid is achieved with air and cobalt salt catalyst at a temperature between 121 and 177°C. The reactor is operated at 206 kPa gauge (2.1 kg/cm^2 gauge) and the catalyst concentration is between 0.1 and 0.3%. The reactor effluent is distilled and the purified benzoic acid is collected. The overall yield of this process is believed to be about 68 mol % of toluene.

The second processing step, in which benzoic acid is oxidized and hydrolyzed to phenol, is carried out in two reactors in series. In the first reactor, the benzoic acid is oxidized to phenyl benzoate in the presence of air and a catalyst mixture of copper and magnesium salts. The reactor is operated at 234°C and 147 kPa gauge (1.5 kg/cm^2 gauge). The phenyl benzoate is then hydrolyzed with steam in the second reactor to yield phenol and carbon dioxide. This occurs at 200°C and atmospheric pressure. The overall yield of phenol from benzoic acid is around 88 mol %. Figure 2 shows a simplified diagram for the toluene–benzoic acid process.



4.3. Other Processes. *Phenol Via Cyclohexene.* In 1989 Mitsui Petrochemicals developed a process in which phenol was produced from cyclohexene. In this process, benzene is partially hydrogenated to cyclohexene in the presence of water and a ruthenium-containing catalyst. The cyclohexene then reacts with water to form cyclohexanol or oxygen to form cyclohexanone. The cyclohexanol or cyclohexanone is then dehydrogenated to phenol. No phenol plants have been built employing this process.

Benzene Sulfonation. In the benzene sulfonation process, benzene reacts with concentrated sulfuric acid to form benzenesulfonic acid at about 150°C. The benzenesulfonic acid is neutralized with sodium sulfate to produce sodium benzenesulfonate, which is then fused with caustic soda to yield sodium phenate. The sodium phenate is acidified with sulfur dioxide and a small amount of sulfuric acid to release the phenol from the sodium salt. The phenol yield by this process can be as high as 88 mol % to that of the theoretical value based on benzene. Plants employing this technology have been shut down for environmental and economic reasons.

Benzene Chlorination. In this process, benzene is chlorinated at 38–60°C in the presence of ferric chloride catalyst. The chlorobenzene is hydrolyzed with caustic soda at 400°C and 2.56 kPa (260 atm) to form sodium phenate. The impure sodium phenate reacts with hydrochloric acid to release the phenol from the sodium salt. The yield of phenol is about 82 mol % to that of the theoretical value based on benzene. Plants employing this technology have been shut down for environmental and economic reasons.

Benzene Oxychlorination. In the benzene oxychlorination process, also known as the Raschig Hooker process, benzene is oxychlorinated with hydrogen chloride, air, and with the presence of iron and copper chloride catalyst to form chlorobenzene. The reaction occurs at 200–260°C and atmospheric pressure. The chlorobenzene is hydrolyzed at 480°C in the presence of a suitable catalyst to produce phenol and chloride. The yield of phenol is ~90 mol% of theoretical. These plants have been shut down for environmental and economic reasons.

5. Economic Aspects

Table 2 gives the United States production of phenol and their capacities for 2002 (9).

In 2001, global production was 6.4×10^6t valued at $\$4 \times 10^9$. Global capacity utilization fell to 83% in 2001 from 86% in 2000 because of weaker demand and increased supply. Bisphenol A (BPA) accounted for 37% of global phenol consumption in 2001, 41% in 2002. In early 2004, the BPA market became extremely tight due to a limited supply of phenol feedstocks. Benzene costs tripled in 2004. This was of concern because benzene is a primary material in the cumene to phenol process (16).

Growth rates for end use markets will vary be region. BPA will continue to be a strong use for phenol. Consumption of phenol for phenol–formaldehyde resins shows more regional variation. In the United States, Western Europe, and Japan, phenol consumption for phenol-formaldehyde resins is forecasted to grow at 0.4–2% through 2006. The market in Southeast Asia is expected to grow at the rate of 3.3% per year and the market in and central and Eastern Europe is expected to grow at the rate of 5.7% through 2006 (1).

6. Specifications and Standards

DOT's Hazardous Materials Regulations (4,17) classifies phenol as a Class B poison. Drums and packages are to be labeled "Poison" and must comply with the regulations as contained in paragraph 173.369. Bulk containers must be properly placarded and marked. Shipping papers must include the required information regarding classification.

The *U.S. Pharmacopeia* (USP) specification for phenol includes (*1*) purity is to be no less than 98 wt %, (*2*) clear solubility of 1 part of phenol in 15 parts of water, (*3*) a congealing temperature to be not lower than 39°C, and (*4*) a content of nonvolatiles of no more than 0.05 wt %. Commercially, phenol specifications far exceed the USP requirement. Typical commercial phenol specifications are listed in Table 3. Higher purity material is required for some applications.

7. Analytical Methods

Phenol quality tests and analyses can be divided into two categories: wet lab and liquid and gas chromatography. In the wet lab, phenol is tested for pH, solidification point, solubility in water, bromine index, color, and distillation ranges. Phenol concentration, impurities, and CHP contents are analyzed using highly automated liquid and gas chromatography.

In the wet lab, the minimum solidification points of freezing point is determined according to ASTM D1493-67. The color is determined according to ASTM D1686-61. The concentration of water in phenol is determined according to ASTM D1631.

7.1. Storage.

Phenol is shipped in drums, tank trucks, and tank cars. It is loaded and shipped at elevated temperatures as a bulk liquid. In storage, phenol may acquire a yellow, pink, or brown discoloration which makes it unusable for some purposes. The discoloration is promoted by the action of water, light, air, and catalysts, eg, traces of iron or copper. When stored as a solid in the original drum or in nickel, glass-lined, or tanks lined with baked phenolic resin, phenol remains colorless for a number of weeks.

Storage tanks should be equipped with heating coils that pass upward through the entire vessel. Spillage and accidents have been caused by attempts to melt solid phenol using coils in the side of a tank which provide no escape for the expansion that occurs upon melting. Storage tanks may be constructed by either welding or riveting. Both horizontal and vertical tanks are suitable for phenol storage. Underground storage tanks are not recommended because leaks in the tanks are difficult to locate. Diking, draining, and tank support should be designed to conform with local regulations. Unloading and transfer should be operated so that there are no emissions into the atmosphere. Workmen should not be permitted to enter an empty tank which has been filled with phenol until it has been thoroughly cleaned.

8. Health and Safety Factors

Phenol fumes are irritating to the eyes, nose, and skin. According to the National Institute for Occupational Safety and Health (NIOSH), exposure to phenol should be controlled so that no employees are exposed to phenol concentrations >20 mg/m^3, which is a time-weighted average concentration for up to a 10-h work day, 40-h work week. Phenol is very toxic to fish and has a nearly unique property of tainting the taste of fish if present in marine environments at 0.1–1.0 ppm (7). Phenol presents no unusual fire hazard when handled at ambient temperatures, but burns if ignited. The lower flammability limit for the vapor is 1.5% in air. Phenol produces flammable, toxic vapors at elevated temperatures and has a flash point of 85°C (open cup).

Phenol is a general protoplasmic poison that is corrosive to any living tissue it contacts. It is a local anaesthetic, so that upon initial contact to the skin no pain is felt. By the time pain is felt, serious burns and absorption through skin may occur. Skin absorption occurs readily with a rapid onset of symptoms or death. Contact with eyes may cause severe damage and blindness. Upon contact with phenol, skin should be washed with water, then washed with poly(ethylene glycol) of molecular weight 300 (Macrogol 300) for at least 30 minutes. Eyes should be washed with flowing water for 10 minutes. Treatment for inhalation begins with removal of the exposed person to fresh air and provision of breathing support if needed.

Personnel who handle phenol should wear protective clothing, safety goggles, and rubber gloves, depending on the working conditions and amount of phenol handled.

OSHA PEL TWA is 5 ppm (skin); ACGIH TLV TWA is 5 ppm skin; NIOSH REL TWA is 20 mg/m^3 (18).

9. Uses

Uses of phenol in the United States for 2001 were Bisphenol A, 41%; phenolic resins, 28%; caprolactam, 13 %; alkylphenols, 5%; xylenols, 4%; aniline, 3%; miscellaneous, 6% (9).

9.1. Bisphenol A. Bisphenol A (BPA), the fastest growing user of phenol, is produced by the condensation reaction of two moles of phenol and one mole of acetone. BPA, in turn, has two significant applications, which consume more than 80% of the production: polycarbonates, ie, engineering thermoplastics used for compact disks, opthalmic lenses, automotive applications, and numerous other applications requiring the outstanding properties of polycarbonate; and epoxy resins, ie, thermosetting plastics employed in automotive coatings, electronic coatings, and other thermosetting applications.

9.2. Phenolic Resins. Phenolic resins are produced by the condensation of phenol or a substituted phenol, such as cresol, with formaldehyde. These low cost resins have been produced commercially for more than 100 years. They are employed as adhesives in the plywood industry and in numerous under-the-hood applications in the automotive industry. Because of the cyclic nature of the automotive and home building industry, the consumption of phenol for the production of phenolic resins is subject to cyclic swings greater than that of the economy as a whole.

9.3. Other. Some other phenol derivatives are somewhat local in application. For example, aniline is produced from phenol at only two plants, one in Japan and one in the United States. Likewise, phenol is used in the production of nylon, via caprolactam (qv) or adipic acid (qv) by only one United States producer and one European producer. These markets, like the phenolic resin and polycarbonate markets, are quite cyclical. Thus, the entire phenol market tends to be cyclical and closely tied to the housing and automotive markets.

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Table 1. **Physical Properties of Phenol**

Property	Value	Reference
molecular weight	94.11	2
boiling point at 101.3 kPa[a]	181.75	3
freezing point, °C	40.91	2
vapor pressure at 25°C, MPa[a]	46.84	4
flash point (closed cup), °C	79	2
density at 20°C (solid), g/cm^3	1.0722	3
critical temperature, °C	421.1	3
critical pressure, MPa[b]	6.13	3
specific heat at 14–25°C, J/g·K[c]	2.35	5
heat of fusion, J/g[c]	121.54	5
heat of vaporization, at bp, J/g[c]	528.7	3
heat of combustion, kJ/g[c]	−32.468	3
viscosity, mPa·(=cP)		
at 50°C	3.49	3
70°C	2.03	3
90°C	1.26	3
specific heat		
at 4.0°C (solid)	1.24	6
227°C (solid)	1.41	6
70–74°C (liquid)	2.22	7

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert MPa to atm, divide by 0.1013.

[c] To convert J to cal, divide by 4.184.

Table 2. **U.S. Producers of Phenol and Their Capacities, 2001**[a]

Producer	Capacity[b] $\times 10^3$t
Dakota Gasification, Beulah, N.D.	15.9
Dow, Freeport, Tex.	294.8
Georgia Gulf, Pasadena, Tex.	72.6
Georgia Gulf, Plaquemine, La.	226.8
INEOS Phenol, Theodore, Als.	399.1
JLM, Blue Island, III.	43.1
Merisol USA, Houston, Tex.	15.9
Mount Vernon Phenol Plant Partnership, Mount Vermon, Ind.	322
Noveon Kalama, Kalama, Wash.	34.0
Shell Chemical, Deer Park, Tex.	535.2
Sunoco, Haverhill, Ohio	426.3
Sunoco, Philadelphia, Pa.	499.0
Total	*2884.9*

[a] Ref. 9.

[b] Nearly 98 percent of US phenol capacity is based on oxidation of cumene.

Table 3. **Typical Commercial Phenol Specifications**

Property	Value
freezing points, °C	40.85
color, ASTM Pt–Co	5
phenol concentration, wt %, min	99.99
water concentration, wt %, max	0.01
impurities, ppm	
carbonyls	40
hydroxyacetone	10
α-methylstyrene plus cumene	5
acetophenone	3
2-methylbenzofuran	2
Total (dry)	*100*

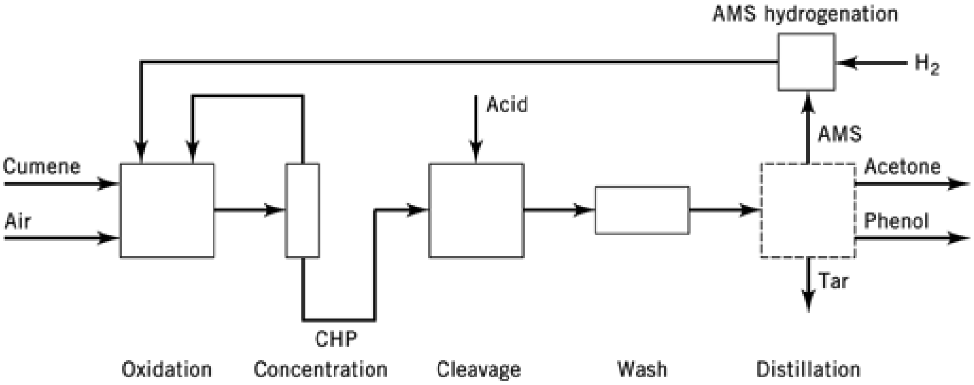

Fig. 1. Cumene process for phenol production.

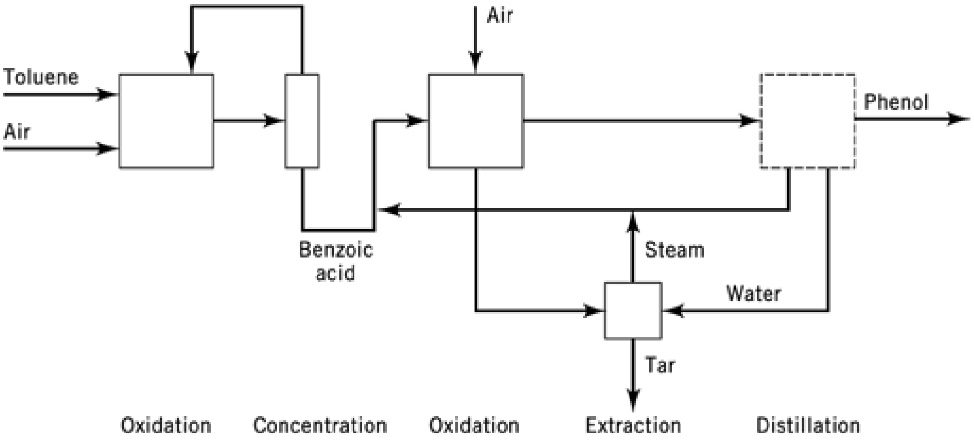

Fig. 2. Toluene–benzoic acid process for phenol production.