

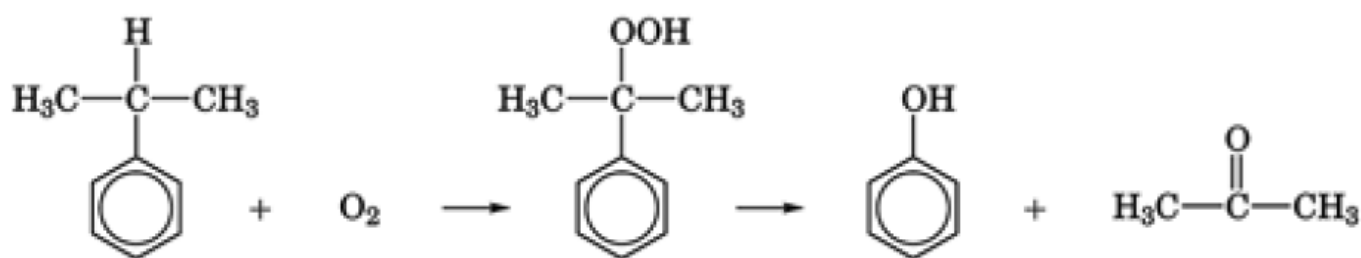
Phenol

Phenol is the specific name for hydroxybenzene, C_6H_5OH . Phenol has a melting point of $40.9\text{ }^{\circ}C$. At lower temperatures it crystallizes as a white mass. In the molten state it is a clear, colorless liquid. The melting and solidification point of phenol is lowered considerably by traces of water. The predominant uses of phenol are in bisphenol A, Phenolic resins, caprolactam, aniline, and alkylphenols.

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.

There are several licensed processes to produce phenol which are based on cumene. 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 (CHP) 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 (ACP) and dimethyl benzyl alcohol (DMBA). DMBA is dehydrated in the cleavage reaction to produce alphas-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 %.

Production of Cumene

Cumene is produced commercially through the alkylation of benzene with propylene over an acid catalyst. Over the years, many different catalysts have been proposed for this alkylation reaction, including boron trifluoride, hydrogen fluoride, aluminum chloride, and phosphoric acid. Among which >80% of the cumene in the world was produced by the solid phosphoric acid (SPA) process licensed by UOP.

Although SPA is a highly efficient and economical catalyst for cumene synthesis, it has two important limitations:

1. Cumene yield is limited to about 95 percent, because of the oligomerization of propylene and the formation of heavy alkylate by-products
2. The catalyst is not regenerable and must be disposed of at the end of each catalyst cycle.

The synthesis of cumene from benzene and propylene is a modified Friedel-Crafts alkylation, which can be accomplished by many different acid catalysts. The olefin forms a carbonium ion intermediate, which attacks the benzene ring in an electrophilic substitution. The addition to the olefin double bond is at the middle carbon of propylene, in accordance with Markovnikov's rule. The addition of the isopropyl group to the benzene ring weakly activates the ring toward further alkylation, producing di-isopropyl-benzene (DIPB) and heavier alkylate by-products.

Transalkylation of DIPB is the acid-catalyzed transfer of one isopropyl group from DIPB to a benzene molecule to form two molecules of cumene. After recovery of the cumene product by fractionation, the DIPB is reacted with recycle benzene at optimal conditions for transalkylation to produce additional cumene.

Phenol production:

Oxidation of Cumene to CHP

The oxidation of cumene as the first reaction step is usually carried out in a series of bubble column reactors. Fresh and recycle cumene are fed to the first reactor. Oxygen is used in each reactor as oxidant. The bubble columns are operated at pressures ranging from atmospheric to about 700 kPa and temperatures in the range 80-120°C. The temperature is controlled by internal or external heat exchangers. The final CHP concentration varies typically from 20 to 40%. Phenol is a strong inhibitor, so any recycled cumene must be treated to remove even traces of phenol. Formation of the byproducts DMBA and ACP depends on the CHP concentration. Depending on temperature, the residence time in the oxidizer train is between 4 and 20 h.

In the early years of the cumene oxidation process, the oxidation was carried out as a three phase reaction, so-called wet oxidation. In addition to cumene and air an aqueous sodium carbonate solution was continuously added to the reactors to extract and neutralize organic acids, which are formed during oxidation. Phenolchemie, now INEOS Phenol, was the first to operate the reactors without adding any caustic soda or sodium carbonate, a process known as dry oxidation.

The off-gas from the reactor is purified by two-step condensation of organic components with cooling water in condensers and chilled water or other refrigerants in another condenser. The CHP concentration in the oxidation product is increased by vacuum distillation to about 65 – 90 %.

B. Splitting of cumyl hydroperoxide

The hydroperoxide is a relatively stable compound, and at 100°C the induction period of its auto-catalytic decomposition is 8 h. Since it yields many undesirable components (aromatic alcohols and ketones), it must take place in specific conditions.

To achieve good phenol selectivity (94 to 95 molar per cent), splitting must take place catalytically. This can be done by using strong acids, such as sulfonic acids, ion exchange resins, etc., which offer the advantage of not requiring subsequent neutralization, but present the drawback of excessively slow conversion rates. It is preferred to use concentrated sulfuric acid (98 per cent weight) used in a low concentration (0.2 to 1 per cent weight), to avoid introducing water which slows down the decomposition and prevents it from being complete, and to limit new side reactions which, based on the acetone produced, yield compounds such as mesityl oxide, hydroxyacetone, alcohol diacetone and isophorone.

To prevent the thermal decomposition of cumyl hydroperoxide, which gives rise chiefly to acetophenone, dissociation takes place at a relatively low temperature (between 70 and 80°C), at low pressure (0.1 to 0.2 · 10⁶ Pa absolute), in an agitated reactor, suitably cooled to remove easily the heat generated by this decomposition. This is achieved either by allowing part of the reaction products (especially acetone) to be vaporized, and subsequently recondensed and recycled, or by means of an external circulation of the reaction medium, with pumping and heat exchange.

To minimize the risks of initiating undesirable chain reactions and explosions, the hydroperoxide must be totally converted at the reactor exit. This requirement can be met by maintaining a residence time of about 20 to 30 min. Hot spots and the accumulation of hydroperoxide in the splitting reactor are also avoided by homogenizing the medium by dilution with the main conversion products, acetone (Hercules process) and phenol (Rhône-Poulenc process).

To limit acid corrosion and avoid the use of high-alloy steels, the effluents must be neutralized upon leaving the reactor. The addition of caustic soda, sodium carbonate, lime etc., in the form of aqueous solutions or directly in solid form, presents many drawbacks (gelatinous or colloidal precipitates difficult to separate, handling of solids, slow reaction rates, etc.). It is preferable to use aqueous sodium phenate, which acts rapidly in stoichiometric quantities and yields sodium sulfate in solution, that is easy to remove. This phenate can also be obtained in the unit itself from the phenol produced.

C. Phenol purification

Several purification schemes are feasible. As a rule (Unisir version for example), the crude acetone is first separated at the top of a first distillation column (≅ 55 trays), followed by light ends separation (20 trays) of the light products (especially acetaldehyde) and heavy ends separation (50 trays) of the heavy products (cumylphenol, acetophenone, polymeric residues, small amounts of water, cumene and α -methylstyrene) ultimately yielding acetone to commercial specifications. The withdrawal from the first distillation

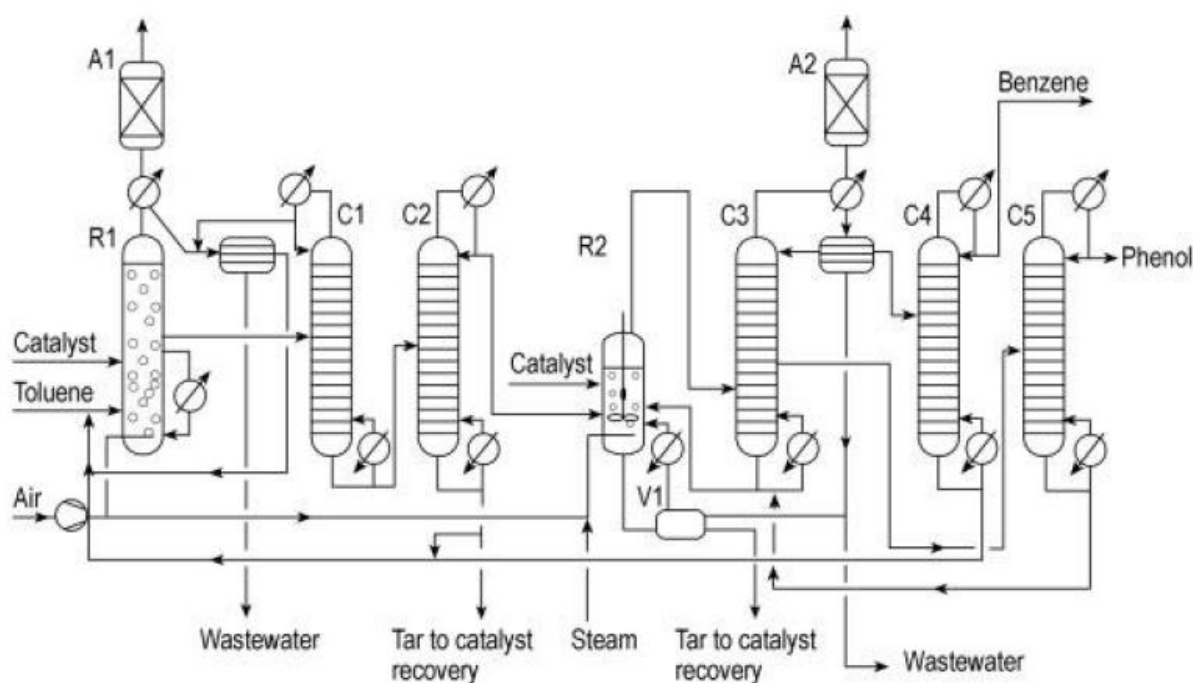
is itself retreated in a series of columns for the successive separation of the heavy products (20 trays), followed by hydrocarbons (more than 100 trays, for unconverted cumene and α -methylstyrene), and finally phenol, which is sent to final purification (60 trays). Given the closeness of the boiling points, it is preferable to avoid isolating the α -methylstyrene from the other components of the hydrocarbon cut, in favor of total selective hydrogenation in the liquid phase, around 90 to 95°C, in the presence of a nickel base catalyst. This operation generates additional amounts of cumene which are recycled to oxidation. It is exothermic and requires a division of the catalyst system into several beds, between which cold cumene is injected to control the temperature rise.

Phenol from toluene (Dow process)

The two-steps of the process are first the oxidation of toluene to benzoic acid, which was already well known, and second the oxidation of benzoic acid to phenol. In principle the conversion of toluene to phenol is a complete oxidation of the methyl group with the byproducts carbon dioxide and water.

The oxidation of toluene as the first step is carried out in the liquid phase at temperatures about 100 – 150 °C and a gauge pressure of about 2 bar. Atmospheric oxygen is used. A cobalt naphthenate is used as a soluble catalyst at concentrations between 0.1 and 0.3 %. The oxidation of toluene to benzoic acid has a complex radical chain mechanism. Benzyl alcohol and benzaldehyde are intermediates in the successive oxidation to benzoic acid. Byproducts such as benzyl benzoate and biphenyl are formed, as well as formic acid, acetic acid, and, in smaller amounts, carbon dioxide and carbon monoxide.

For the oxidation of benzoic acid as the second step molten benzoic acid is used as the reactant and solvent medium. The temperature is about 230 – 240 °C at atmospheric pressure. Benzoic acid reacts with atmospheric oxygen, steam, and soluble copper(II) benzoate as catalyst. Magnesium salts may be added to act as a promotor.



R1 toluene oxidation reactor; A1 adsorption unit; C1 toluene column; C2 benzoic acid column; R2 benzoic acid oxidation reactor; A2 adsorption unit; C3 crude phenol column; C4 benzene column; C5 pure phenol column; V1 tar extraction unit

Fresh and recycle toluene as well as air and the cobalt catalyst are charged to gas – liquid reactor R1, which can be, for example, a bubble column. The reactor has cooling devices to remove the reaction heat, for example, in an external circulation loop. The toluene conversion is limited to 40 %. The yield of benzoic acid is about 90 %. The off-gas from the reactor is cooled by passing it through a water-cooled condenser. The condensed toluene is recycled to the reactor, and the water phase is withdrawn for further wastewater treatment. The noncondensable gas, principally nitrogen, is treated in activated-carbon adsorption unit A1 to remove traces of toluene and other organic components. The liquid phase from the reactor is at first fractionated in column C1. Toluene and the intermediate benzaldehyde are taken overhead for recycle. The crude benzoic acid as the bottom product is purified in the second column C2. The catalyst containing high boilers (tar) is taken as the bottom product, which is partially recycled to the reactor. Purified benzoic acid is oxidized in the second reactor R2, which is a stirred gas – liquid reactor. In the presence of the copper(I/II) catalyst the acid is contacted with air and recycled vaporized water. In addition steam may be added to the air. Small amounts of magnesium benzoate may be added as a promoter. The benzoic acid conversion is 70 – 80% with a yield of phenol of about 90 %. Phenol, benzoic acid, water, and other organic components are vaporized continuously. The vapors are charged to column C3. Water and hydrocarbons are taken as the overhead fraction and separated into two liquid phases. The remaining gas phase is purified in adsorption unit A2. The separated water is used to extract benzoic acid from the tar which has to be removed from reactor R2. This is done in extraction unit V1, which consists of a series of several mixer – settlers. The aqueous phase from V1 is vaporized and recycled to reactor R1. The tar contains the copper salts. If it is burned special incineration equipment is required to insure that no heavy metal emissions occur. The organic phase from the overheads of column C3 contains mainly toluene and benzene. Benzene is separated from toluene in column C4. Toluene is recycled to the oxidation reactor R1. Crude phenol is taken as a side cut from column C3. In Column C5 pure phenol is taken as the overhead. Benzoic acid is withdrawn as the bottom product and recycled to reactor R2. Because of the corrosive character of benzoic acid apparatus must be constructed from stainless steel 1.4571 or even from Hastelloy.