

Lecture Eleven

CHAPTER EIGHT

Chemicals Based on Propylene

INTRODUCTION

Propylene, “the crown prince of petrochemicals,” is second to ethylene as the largest-volume hydrocarbon intermediate for the production of chemicals.

As an olefin, propylene is a reactive compound that can react with many common reagents used with ethylene such as water, chlorine, and oxygen. However, structural differences between these two olefins result in different reactivities toward these reagents. For example, direct oxidation of propylene using oxygen does not produce propylene oxide as in the case of ethylene. Instead, an unsaturated aldehyde, acrolein, is obtained. This could be attributed to the ease of oxidation of allylic

hydrogens in propylene. Similar to the oxidation reaction, the direct catalyzed chlorination of propylene produces allyl chloride through substitution of allylic hydrogens by chlorine. Substitution of vinyl hydrogens in ethylene by chlorine, however, does not occur under normal conditions.

The current chemical demand for propylene is a little over one half that for ethylene. This is somewhat surprising because the added complexity of the propylene molecule (due to presence of a methyl group) should permit a wider spectrum of end products and markets. However, such a difference can lead to the production of undesirable byproducts, and it frequently does. This may explain the relatively limited use of propylene in comparison to ethylene. Nevertheless, many important chemicals are produced from propylene.

The 1997 U.S. propylene demand was 31 billion pounds and most of it was used to produce polypropylene polymers and copolymers (about 46%). Other large volume uses are acrylonitrile for synthetic fibers (Ca 13%), propylene oxide (Ca 10%), cumene (Ca 8%) and oxo alcohols (Ca 7%).

Figure 8-1 shows the important chemicals based on propylene.

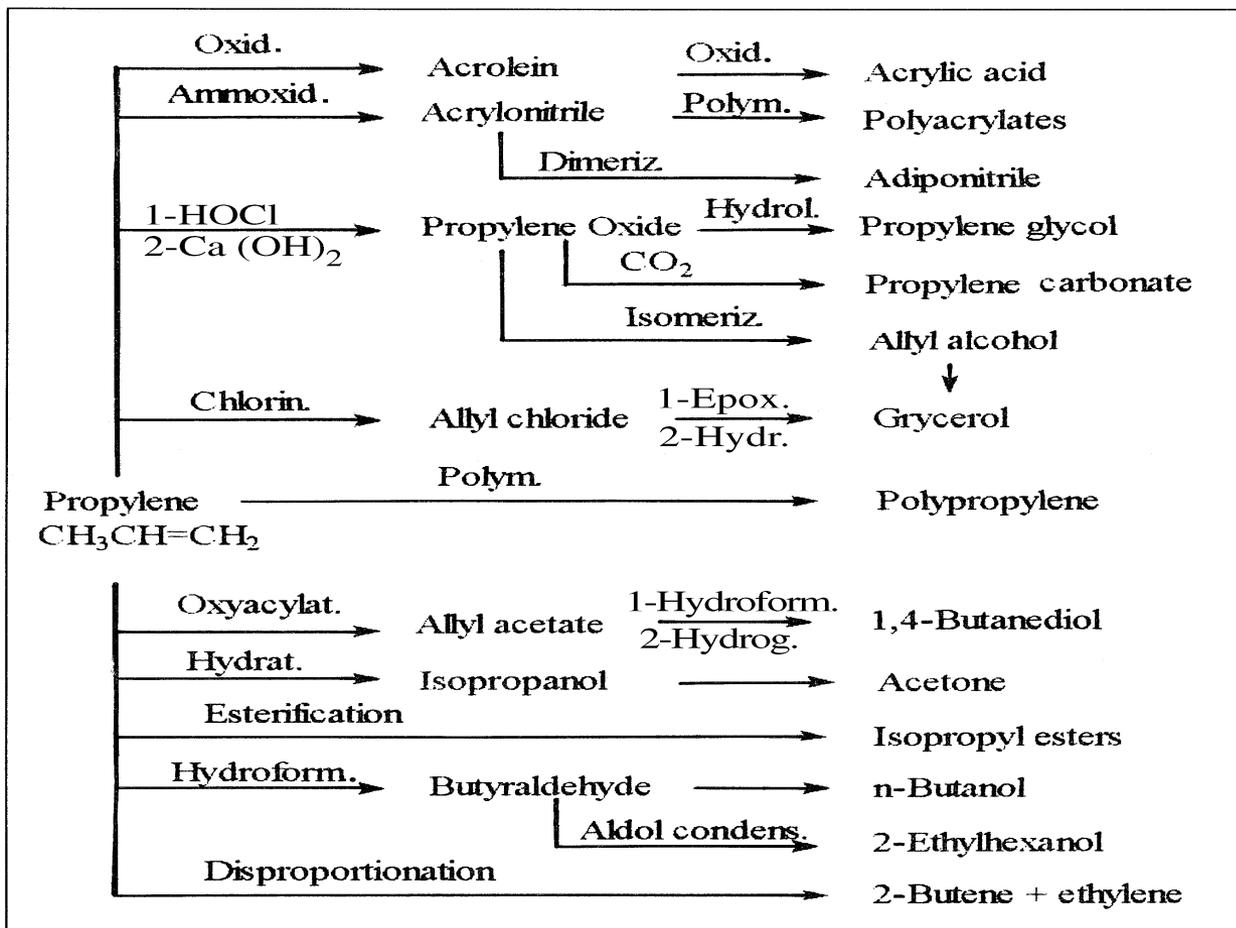


Figure 8-1. Important chemicals based on propylene.

AMMOXIDATION OF PROPYLENE

(Acrylonitrile [$\text{CH}_2=\text{CHCN}$])

Ammoxidation refers to a reaction in which a methyl group with allyl hydrogens is converted to a nitrile group using ammonia and oxygen in the presence of a mixed oxides-based catalyst. A successful application of this reaction produces acrylonitrile from propylene:



As with other oxidation reactions, ammoxidation of propylene is highly exothermic, so an efficient heat removal system is essential.

Acetonitrile and hydrogen cyanide are by-products that may be recovered for sale.

Acetonitrile (CH_3CN) is a high polarity aprotic solvent used in DNA synthesizers, high performance liquid chromatography (HPLC), and electrochemistry. It is an important solvent for extracting butadiene from C_4 streams.,

Both fixed and fluid-bed reactors are used to produce acrylonitrile, but most modern processes use fluid-bed systems. (Figure 8-2) uses a highly active catalyst that gives 95.6% propylene conversion and a selectivity above 80% for acrylonitrile.

The catalysts used in ammoxidation are similar to those used in propylene oxidation to acrolein. Oxidation of propylene occurs readily at 322°C over Bi-Mo catalysts. However, in the presence of ammonia, the conversion of propylene to acrylonitrile does not occur until about 402°C. This may be due to the adsorption of ammonia on catalytic sites that block propylene chemisorption. As with propylene oxidation, the first step in the ammoxidation reaction is the abstraction of an alpha hydrogen from propylene and formation of an allylic intermediate. Although the subsequent steps are not well established, it is believed that adsorbed ammonia dissociates on the catalyst surface by reacting with the lattice oxygen, producing water. The adsorbed NH species then reacts with a neighboring allylic intermediate to yield acrylonitrile.

Uses of Acrylonitrile

Acrylonitrile is mainly used to produce acrylic fibers, resins, and elastomers. Copolymers of acrylonitrile with butadiene and styrene are the ABS resins and those with styrene are the styrene-acrylonitrile resins SAN that are important plastics. The 1998 U.S. production of acrylonitrile was approximately 3.1 billion pounds. Most of the production was used for ABS resins and acrylic and modacrylic fibers. Acrylonitrile is also a precursor for acrylic acid (by hydrolysis) and for adiponitrile (by an electro-dimerization).

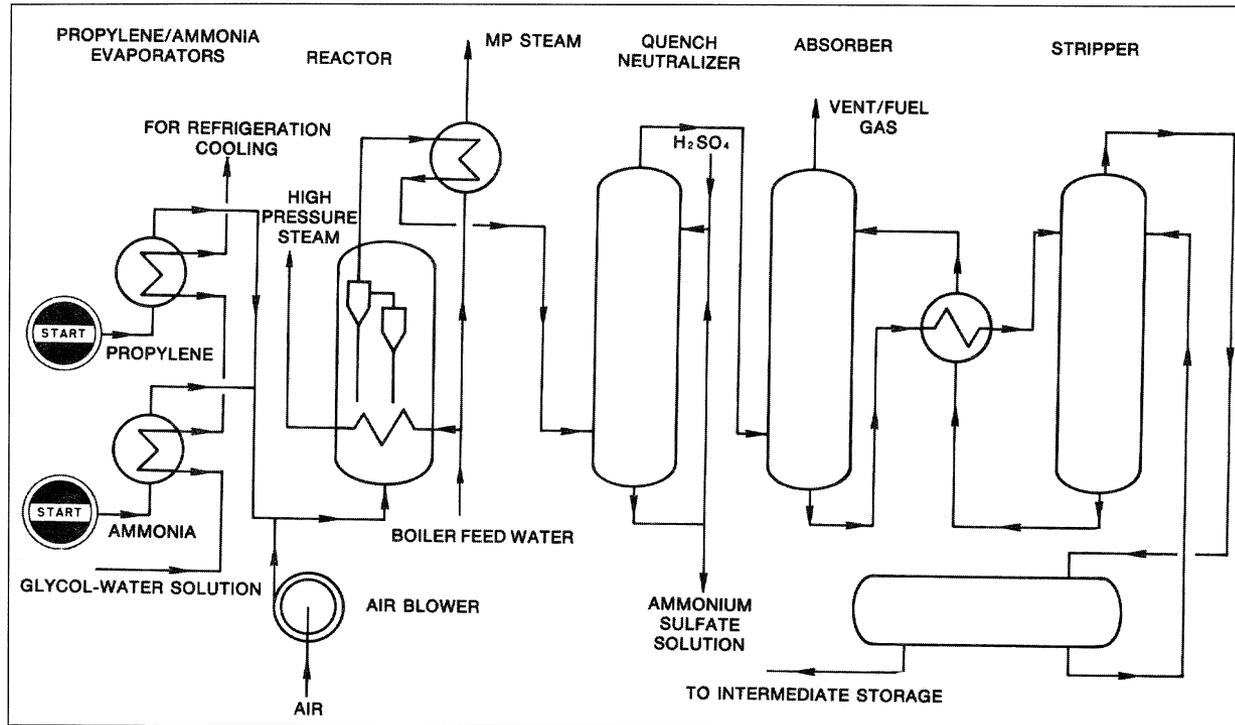


Figure 8-2. A flow diagram of the Montedison-UOP acrylonitrile process.

CHAPTER NINE

C₄ Olefins and Diolefins Based Chemicals

INTRODUCTION

The C₄ olefins produce fewer chemicals than either ethylene or propylene. However, C₄ olefins and diolefins are precursors for some significant big-volume chemicals and polymers such as methyl-ter-butyl ether adiponitrile, 1,4-butanediol, and polybutadiene.

Butadiene is not only the most important monomer for synthetic rubber production, but also a chemical intermediate with a high potential for producing useful compounds such as sulfolane by reaction with SO₂, 1,4-butanediol by acetoxylation-hydrogenation, and chloroprene by chlorination-dehydrochlorination.

ADIPIC ACID (HOOC(CH₂)₄COOH)

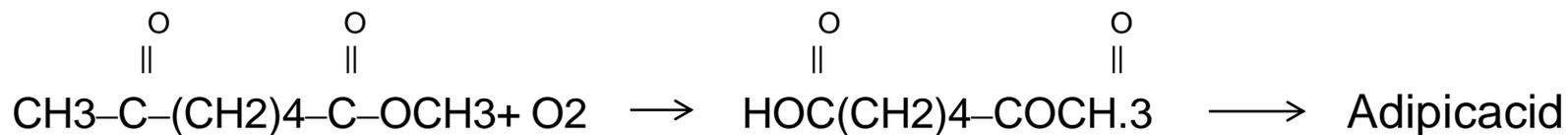
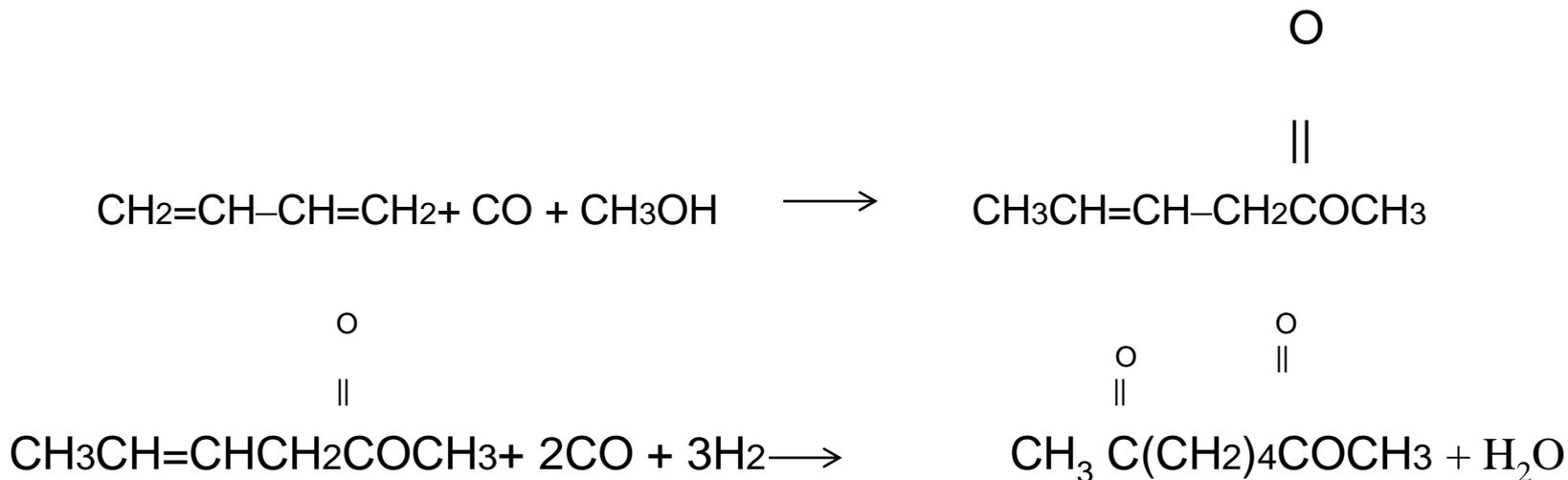
Adipic acid may be produced by a liquid-phase catalytic carbonylation of butadiene.

A catalyst of RhCl₂ and CH₃I is used at approximately 220°C and 75 atmospheres.

Adipic acid yield is about 49%. Both α-gultaric acid (25%) and valeric acid (26%) are coproduced:



A new route to adipic acid occurs via a sequential carbonylation, isomerization, hydroformylation reactions. The following illustrates these steps:



The main process for obtaining adipic acid is the catalyzed oxidation of Cyclohexane.

CHAPTER TEN

Chemicals Based on Benzene, Toluene, and Xylenes

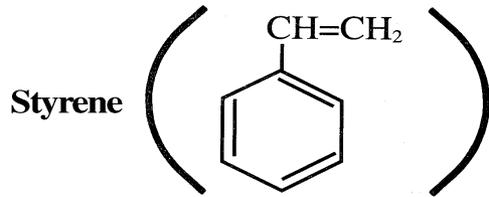
INTRODUCTION

The primary sources of benzene, toluene, and xylenes (BTX) are refinery streams, especially from catalytic reforming and cracking, and pyrolysis gasoline from steam cracking and from coal liquids. BTX and ethyl benzene are extracted from these streams using selective solvents such as sulfolene or ethylene glycol. The extracted components are separated through lengthy fractional distillation, crystallization, and isomerization processes .

The reactivity of C₆, C₇, C₈ aromatics is mainly associated with the benzene ring. Aromatic compounds in general are liable for electrophilic substitution. Most of the chemicals produced directly from benzene are obtained from its reactions with electrophilic reagents. Benzene could be alkylated, nitrated, or chlorinated to important chemicals that are precursors for many commercial products.

Toluene and xylenes (methylbenzenes) are substituted benzenes.

Although the presence of methyl substituents activates the benzene ring for electrophilic attack, the chemistry of methyl benzenes for producing commercial products is more related to reactions with the methyl than with the phenyl group. As an electron-withdrawing substituent (of methane), the phenyl group influences the methyl hydrogens and makes them more available for chemical attack. The methyl group could be easily oxidized or chlorinated as a result of the presence of the phenyl substituent.



Styrene (vinylbenzene) is a liquid (b.p. 145.2°C) that polymerizes easily when initiated by a free radical or when exposed to light. The 1998 U.S. production of styrene was approximately 11 billion pounds. Dehydrogenation of ethylbenzene to styrene occurs over a wide variety of metal oxide catalysts. Oxides of Fe, Cr, Si, Co, Zn, or their mixtures can be used for the dehydrogenation reaction. Typical reaction conditions for the vapor-phase process are 600–700°C, at or below atmospheric pressure. Approximately 90% styrene yield is obtained at 30–40% conversion:

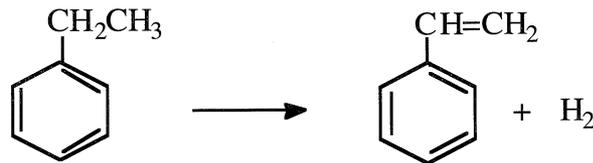


Figure (10-3), fresh ethylbenzene with recycled unconverted ethylbenzene are mixed with superheated steam. The steam acts as a heating medium and as a diluent. The endothermic reaction is carried out in multiple radial bed reactors filled with proprietary catalysts. Radial beds minimize pressure drops across the reactor. Figure 10-4 shows the effect of steam-to-EB ratio, temperature, and pressure on the equilibrium conversion of ethylbenzene.

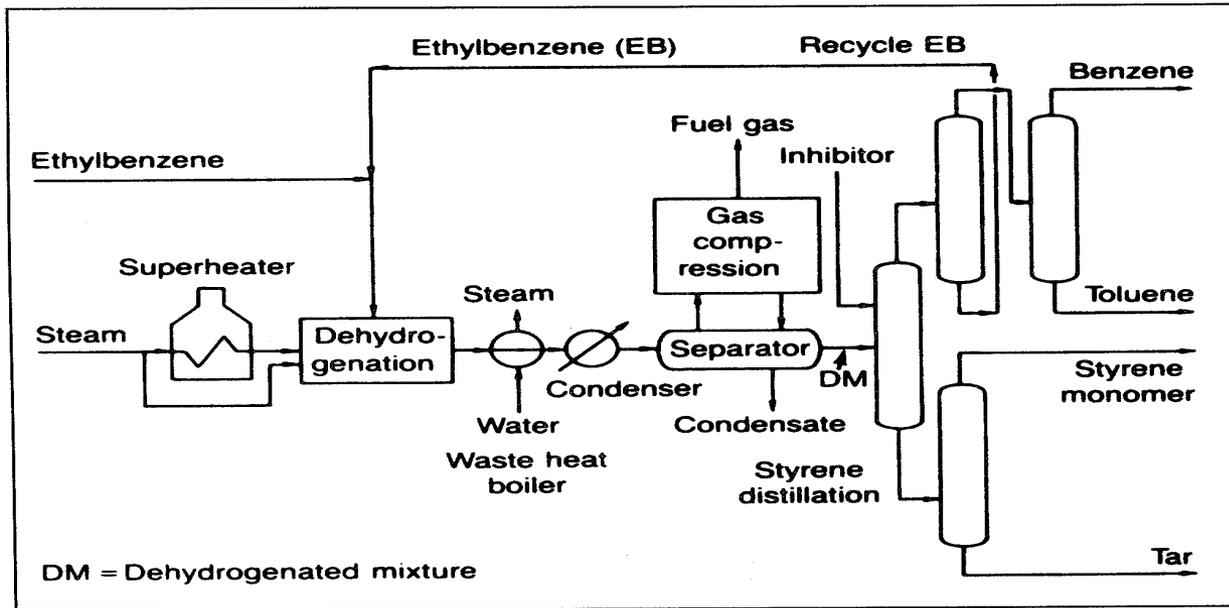


Figure 10-3. Schematic diagram of the Monsanto/Lummus Crest styrene plant.

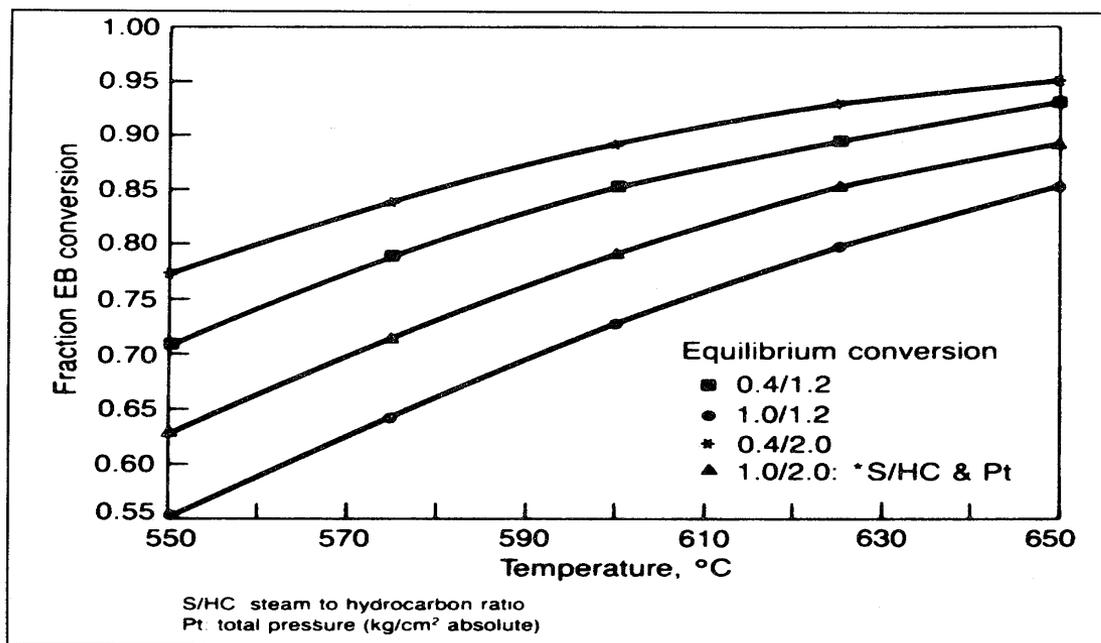
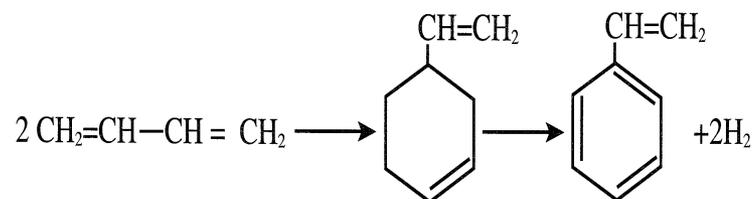


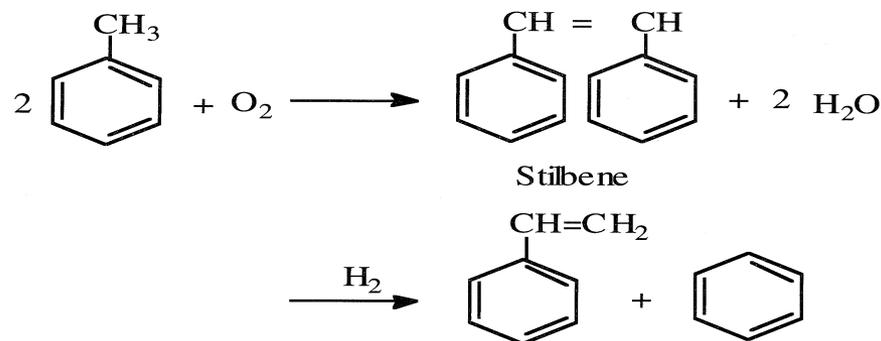
Figure 10-4. Effect of steam/EB, temperature, and pressure on the conversion of ethylbenzene.

Alternative routes for producing styrene have been sought. One approach is to dimerize butadiene to 4-vinyl-1-cyclohexene, followed by catalytic dehydrogenation to styrene:



The process which was developed by DOW involves cyclodimerization of butadiene over a proprietary copper-loaded zeolite catalyst at moderate temperature and pressure (100°C and 250 psig). To increase the yield, the cyclodimerization step takes place in a liquid phase process over the catalyst. Selectivity for vinylcyclohexene (VCH) was over 99%. In the second step VCH is oxidized with oxygen over a proprietary oxide catalyst in presence of steam. Conversion over 90% and selectivity to styrene of 92% could be achieved.

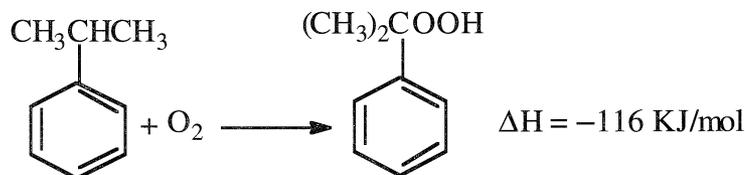
Another approach is the oxidative coupling of toluene to stilbene followed by disproportionation to styrene and benzene:



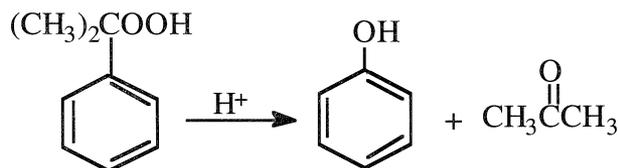
High temperatures are needed for this reaction, and the yields are low.

Phenol and Acetone from Cumene

Phenol, C₆H₅OH (hydroxybenzene), is produced from cumene by a two-step process. In the first step, cumene is oxidized with air to cumene hydroperoxide. The reaction conditions are approximately 100–130°C and 2–3 atmospheres in the presence of a metal salt catalyst:



In the second step, the hydroperoxide is decomposed in the presence of an acid to phenol and acetone. The reaction conditions are approximately 80°C and slightly below atmospheric:



In this process (Figure 10-6), cumene is oxidized in the liquid phase.

The oxidation product is concentrated to 80% cumenehydroperoxide by vacuum distillation. To avoid decomposition of the hydroperoxide, it is transferred immediately to the cleavage reactor in the presence of a small amount of H₂SO. The cleavage product is neutralized with alkali before it is finally purified.

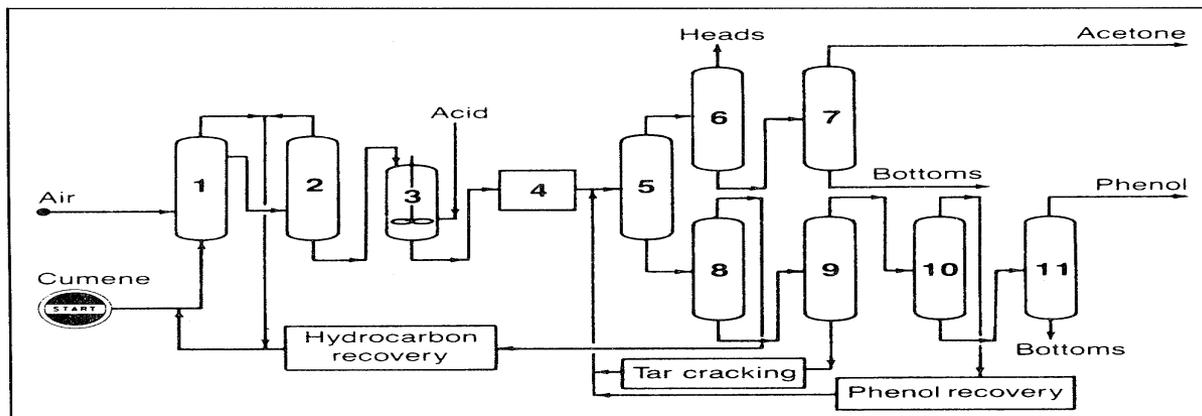


Figure 10-6. The Mitsui Petrochemical Industries process for producing phenol and acetone from cumene:(1) autooxidation reactor, (2) vacuum tower, (3) cleavage reactor, (4) neutralizer, (5–11) purification train.

After an initial distillation to split the coproducts phenol and acetone, each is purified in separate distillation and treating trains. An acetone finishing column distills product acetone from an acetone/water/oil mixture. The oil, which is mostly unreacted cumene, is sent to cumene recovery. Acidic impurities, such as acetic acid and phenol, are neutralized by caustic injection.

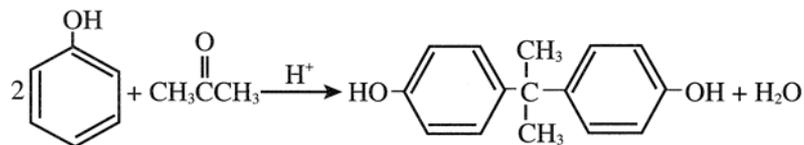
Cumene processes are currently the major source for phenol and coproduct acetone. Previously, phenol was produced from benzene by sulfonation followed by caustic fusion to sodium phenate. Phenol is released from the sodium salt of phenol by the action of carbon dioxide or sulfur dioxide.

Direct hydroxylation of benzene to phenol could be achieved using zeolite catalysts containing rhodium, platinum, palladium, or irridium. The oxidizing agent is nitrous oxide, which is unavoidable a byproduct from the oxidation of KA oil to adipic acid using nitric acid as the oxidant.

Phenol is also produced from chlorobenzene and from toluene via a benzoic acid intermediate.

Properties and Uses of Phenol

Phenol, a white crystalline mass with a distinctive odor, becomes reddish when subjected to light. It is highly soluble in water, and the solution is weakly acidic. Phenol was the 33rd highest-volume chemical. The 1994 U.S. production of phenol was approximately 4 billion pounds. The current world capacity is approximately 15 billion pounds. Many chemicals and polymers derive from phenol. Approximately 50% of production goes to phenolic resins. Phenol and acetone produce bis-phenol A, an important monomer for epoxy resins and polycarbonates. It is produced by condensing acetone and phenol in the presence of HCl, or by using a cation exchange resin. Figure 10-8 shows the bisphenol A process.



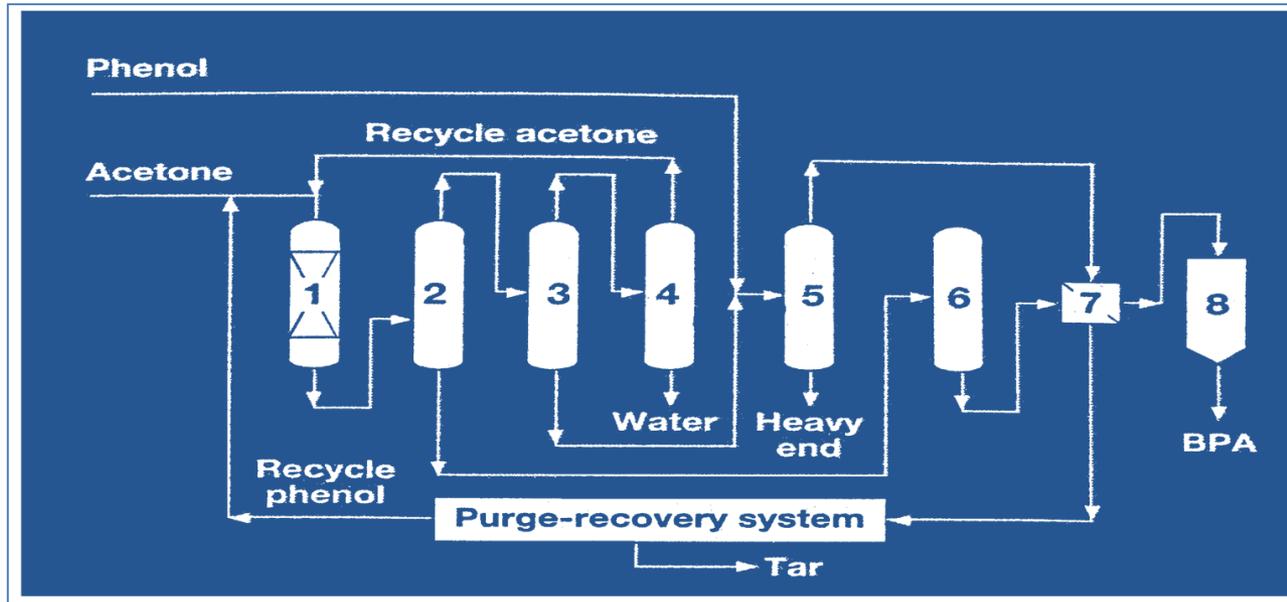
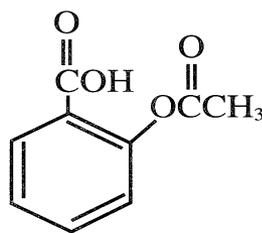


Figure 10-8. The CT-BISA (Chiyoda Corp.) process for producing bis-phenol A from acetone and phenol.(1) reactor, (2–4) distillation columns, (5) phenol distillation column, (6) crystallizer, (7) solid/liquid separator, (8) prilling tower.

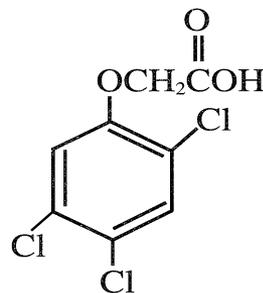
Important chemicals derived from phenol are salicylic acid; acetylsalicylic acid (aspirin); 2,4-dichlorophenoxy acetic acid (2,4-D), and 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), which are selective herbicides; and pentachlorophenol, a wood preservative:



Salicylic acid



Aspirin



2,4,5-T

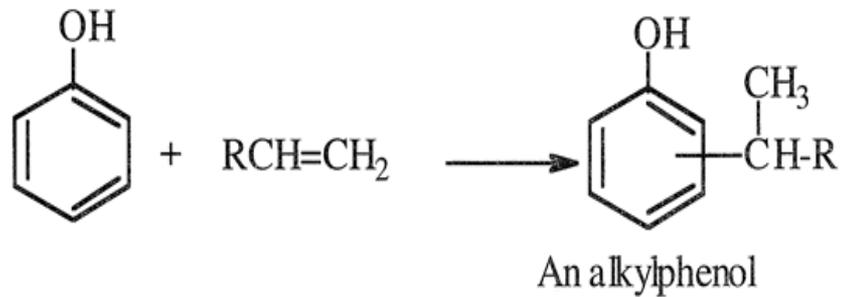
Other halophenols are miticides, bactericides, and leather preservatives.

Halophenols account for about 5% of phenol uses.

About 12% of phenol demand is used to produce caprolactam, a monomer for nylon 6.

The main source for caprolactam, however, is toluene.

Phenol can be alkylated to alkylphenols. These compounds are widely used as nonionic surfactants, antioxidants, and monomers in resin polymer applications:



Phenol is also a precursor for aniline. The major process for aniline ($\text{C}_6\text{H}_5\text{NH}_2$) is the hydrogenation of nitrobenzene .