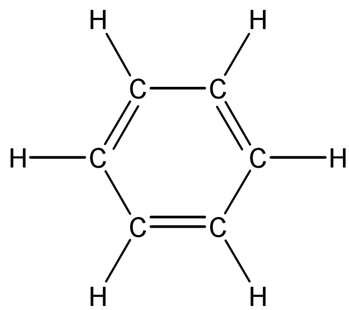
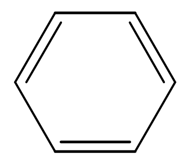
Benzene

US Production: 10.92 x 10^6 tons per year
Worldwide Production: 40 x 10^6 tons/year
Price: $3.32 per gallon ($996 per ton) as of 4-Jan-07
Growth rate: unstable



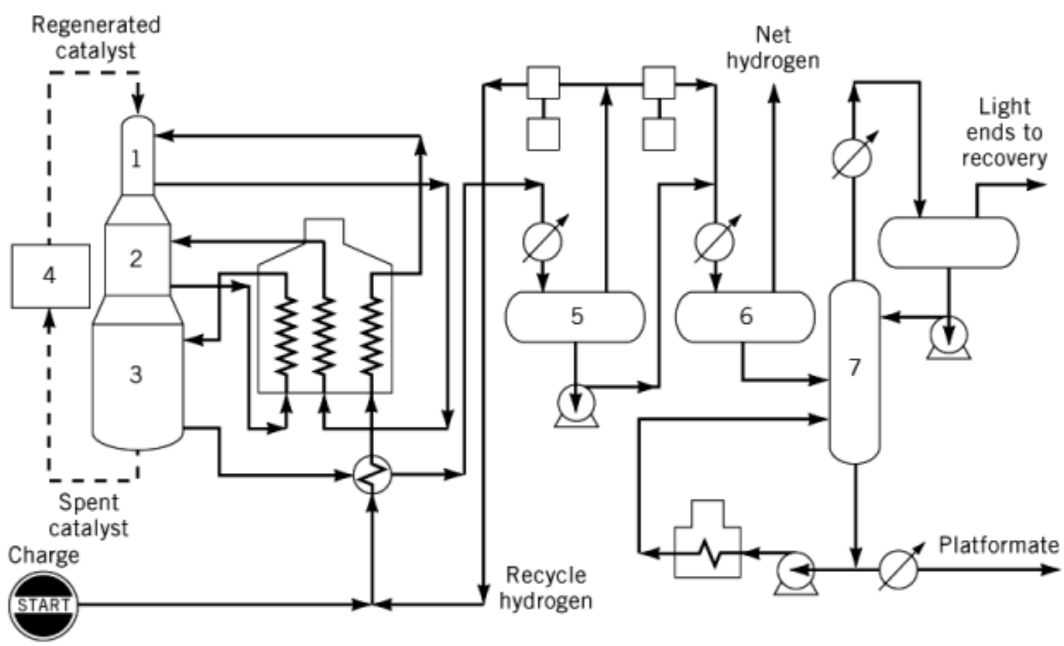


Benzene is very important because it is used to produce a series of molecules used as intermediates in turn to produce polymers, dyes, pharmaceuticals, and solvents. For example, benzene is alkylated with ethylene to make ethylbenzene, which is then dehydrogenated to form styrene. Styrene is the most important chemical derived from benzene, and about half of all benzene used in the United States is used for this purpose. Benzene is alkylated with propylene to form cumene, which is catalytically oxidized with air to produce cumene hydroperoxide, which is decomposed into phenol and acetone. Phenol is used to make nylon. Benzene is hydrogenated to form cyclohexane, which is then oxidized to form cyclohexanol, cyclohexanone, and adipic acid. Adipic acid is also used to make nylon. Nitration of benzene leads to nitrobenzene, which is used in a wide range of dyes and pharmaceuticals. Benzene is chlorinated to make chlorobenzene, which is used to make pesticides, solvents, and dyes. [1]

Before WWII, the biggest market fore benzene was as a gasoline additive to improve octane. After 1950, this was largely replaced with tetraethyl lead. However, benzene is still used in European gasoline, and in other countries where its use is not regulated. However, because of it is a known carcinogen, use expected to decline. The growth rate of benzene use is difficult to forecast, because the plastics and chemicals demand is expected to continue to grow.[2]

There are a number of ways to manufacture benzene. It can be distilled from petroleum, but is less than 1.0% by weight of crude oil. To further complicate matters, benzene purity from distillation of crude is limited by the presence of an azeotrope. Therefore, direct distillation from crude is generally considered uneconomical. However, benzene is produced economically from crude oil by catalytic reforming.[3] Catalytic reforming is a process by which aromatic molecules are produced from the dehydrogenation of cycloparafins, dehydroisomerization of alkyl cyclopentanes, and the cyclization and subsequent dehydrogenation of paraffins.

The catalytic reforming process most commonly used is called "Platforming." Platformiong was originally developed by Universal Oil Products.[4] The process is shown in schematic form below. Before entering the process, the feed is first hydrotreated to remove sulfur, nitrogen, and oxygen compounds that tend to foul the catalyst. Hyrodrotreating the feed also removes olefins present in cracked petroleum. From the "Start" position in the diagram, the hydrotreated feed is mixed with recycle hydrogen and preheated to 495-525 °C at pressures of 0.8 to 5 bar. Typical hydrogen charge ratios of 700 to 1400 m^3 of hydrogen per m^3 of gaseous feed are required. The feed is then passed through a stacked series of reactors, labeled 1, 2, and 3 in the schematic. Usually 3 or 4 reactors are used. The catalyst is mounted in fixed beds inside the reactors. The catalyst is either platinum chloride or rhenium chloride supported on silica or silica-alumina. Catalyst activity is maintained by continuously withdrawing a small portion of the catalyst and passing it through a regenerative tower, 4, where carbonaceous deposits (coke) are burned off. The product coming out of the reactor is



sent through a series of flash separators, 5, 6, and 7, to recover the hydrogen.

Benzene needs to be separated from the "platformate" product that leaves the process. The most common method is a combination of liquid-liquid extraction and followed by stripping with air.[5] The common solvents for the extraction process are diethylene glycol (Udex process), n-methylpyrrolidine (Arosolvan process), liquid SO_2 (Edelanu process), or tetramethylene sulfone (Sulfalone process).

References

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2. Consequences of Limiting Benzene Content of Motor Gasoline, CONCAWE, den Haag, The Netherlands, Dec. 1983, pp. 1-17.
3. D.M. Little, *Catalytic Reforming*, Penn Well Books, Tulsa, Okla.,1985.
4. Hydrocarbon Processing, **81**, (September, 1988).
5. Hydrocarbon Processing, **216**, (September, 1976).