MANUFACTURING PROCESSES

The major processes for producing benzene include:

* Catalytic reforming
* Toluene hydrodealkylation and disproportionation
* Pyrolysis gasoline
* Production from coal tar

Catalytic Reforming:

Catalytic Reforming was first used in the 1940's. This process accounts for 30% of the world's benzene production. Catalytic reforming involves the dehydrogenation of naphthenes to aromatics, or the isomerizatoin of alkylnaphthenes and the dehydrogenation of them. Paraffins are also dehydrocyclized to aromatics, but the reaction is slow.

The feed for this process is naptha, which may be straight-run, hydrocracked, thermally cracked, or catalytically cracked. First the naptha is hydrotreated to remove sulfur, which may be present. Recycled hydrogen is then added to it, mixed and heated. This stream is sent to the catalytic reactors where paraffins are converted to aromatic compounds. The catalyst involved in these reactors is usually platinum or rhenium chloride. The exiting stream, is made up of excess hydrogen and a reformate which is rich in aromatics. This stream is then sent to the separation section of the process. Here, the hydrogen is separated from the liquid product, and recycled back to the initial feed. The liquid product, on the other hand, is fed to a stabilizer. A stabilizer separates the light, volatile hydrocarbons from the liquid product. The liquid is then sent to a debutanizer. Benzene, as well as toluene and xylenes (all called aromatics) are then extracted from this stable reformate.

Different solvents are used to extract the aromatics from the stabilized reformate stream. The most common solvents used are glycol and sulfolane. Both processes are similar, and the below diagram shows the glycol process. Firstly, the aromatics are separated from the reformate inside the extractor. The raffinate is then washed with water and stored, while steam is used to strip the dissolved aromatics and hydrocarbons are separated from the solvent. The hydrocarbons are then washed with water to remove any solvent, and then heated, and fed through clay towers to remove olefins. Benzene, toluene and xylene are then separated by means of fractionation. The conversion rate of naphtha feedstocks approach 100%.

Toluene Hydrodealkylation:

Hydrodealkylation of aromatics, usually toluene, is used though heavier aromatics are used as well. The reaction that takes place is as follows:

$C_6H_5CH_3 + H_2$ ------------> $C_6H_6 + CH_4$

The reaction with more alkylated benzenes is:

$C_6H_4(CH_3)_2 + H_2$ --------------> $C_6H_5CH_3$ --------------> $C_6H_6 + CH_4$

Hydrodealkylation of toluene can be operated under catalytic or thermal conditions . Toluene is mixed with heavier aromatics or paraffins from the benzene fractionation column. They are then heated with a gas containing hydrogen at a specific pressure. The stream is then moved past a dealkylation catalyst contained in the reactor. Here, the toluene reacts with the hydrogen, and benzene and methane are produced. Benzene is then separated from the methane using a separator, which operates at high pressures. Here the gas containing the methane is removed. The product is then sent to a fractionalization column where distillation is used to recover the benzene . The benzene is then sent to be stored. Unreacted toluene and other heavier aromatic by-products are recycled back to the feed. There is a 70 to 85 percent conversion rate of toluene to benzene through this process.

Toluene disproportionation:

Alkylated aromatics are transalkylated to produce benzene and alkylated benzenes. An example of such a method is the Tatoray process. In this process, toluene or toluene and C_9 aromatics are converted to benzene and xylenes.

$2C_6H_5CH_3$ --------------> $C_6H_6 + C_6H_4(CH_3)_2$

$C_6H_5 + C_6H_3(CH_3)_3$ -------------> $2C_6H_4(CH_3)_2$

The toluene is sent to a separator to remove gases. The product stream is then sent through clay towers which separate the benzene, toluene, and xylene using distillation. Unreacted toluene is also recycled. Highly pure benzene and xylenes are produced. If the feed is C_9 and C_{10} aromatics, a mix of benzene, toluene and xylenes is produced and the yield for the benzene is lower.

Pyrolysis gasoline:

Pyrolysis gasoline is the by-product of steam cracking of paraffin gases, naphthas, gas oils and other hyrdrocarbons used to make ethylene. Pyrolysis gasoline can contain up to and including 5% diolefins. This makes the compound unstable. It also contains 60% aromatics, 50% of which is benzene. In order to remove the diolefins, it is possible to distill them away since they have a lower boiling point, but they tend to polymerize, so they first have to be converted to olefins through hydrotreating. This then, can be used for gasoline, or can be further hydrotreated to saturate the olefins and remove sulfur. Benzene is extracted through solvent extraction and then distillation. This process makes up 30%-35% of the world's benzene production.

Production from coal tar:

This method was replaced with the method of producing benzene from petroleum during the 1930's and 1940's, due to the low percentage yield of benzene. This process accounts for less than 5% of the world's production of benzene. It involves recovering benzene from coal tar. It is works by extracting the lowest boiling point fraction, and using caustic soda to remove tar acids. The oil that remains is then further distilled and then purified by hydrodealkylation.

Selection of the process:

Toluene hydrodealkylation can be done by catalytic or thermal processes. Both are quite similar. Toluene is heated to 590-650^{o}C and 25-40 atm for catalytic hydrodealkylation or to as high as 760^{o}C in the thermal processes. Conversions for both types of processes are 70-85% per pass with ultimate yields of 95-98% of theoretical. The catalytic process have the advantage of lower heat loads but they have catalyst costs & require somewhat more down time than the thermal processes. Hence, here thermal, non-catalytic hydrodealkyaltion process is taken.