

## MANUFACTURING PROCESSES

### *Henkel Rearrangement of Benzoic acid and Phthalic anhydride:*

Henkel technology is based on the conversion of benzene carboxylic acids to their potassium salts. The salts are rearranged in the presence of carbon dioxide and a catalyst usually cadmium or zinc oxide to form dipotassium terephthalate, which is later converted to Terephthalic acid. This technology has become obsolete. The process involved the oxidation of naphthalene to phthalic anhydride, which was the starting material for Henkel process. The phthalic anhydride was converted sequentially to monopotassium o – phthalate and dipotassium o – phthalate by aqueous recycle streams of mono and di potassium terephthalate. The dipotassium o – terephthalate was recovered, spray dried and isomerised at a carbon di oxide pressure of 1000-5000Kpa at 350-450 °C, The product from the isomerisation was dissolved in water and recycled to the beginning of the process. Here Terephthalic acid crystals, which formed during the production of monopotassium o – phthalate were recovered by filtration, dried and conveyed and stored.

### *Henkel II:*

The Henkel II process involved the use of toluene to produce benzoic acid as a feed stock. The acid reacted with potassium hydroxide with consequent production of potassium benzoate. Dipotassium terephthalate was produced by a disproportionation reaction. The reaction conditions for this rearrangement were similar to those used in Henkel I process. Dipotassium terephthalate reacted with sulfuric acid and the resulting Terephthalic acid was recovered, filtered and dried. Benzene was a by-product and of the disproportionation and dipotassium sulfate was produced in product recovery. The terephthalic acid from this process typically contained trace amounts of potassium, sulfur and benzoic acid.

***Polymer Grade Terephthalic acid (Purification):***

Polymer grade Terephthalic acid is produced by a separate purification process. The Terephthalic acid produced by the above mentioned methods cannot be used in the manufacture of polymers.

***Amoco Purification method:***

This process is used to purify Terephthalic acid produced by bromine promoted air oxidation of p-Xylene. The product contains less than 25ppm of 4-formylbenzoic acid, which is main impurity in the feed. Crude Terephthalic acid and water are fed continuously into a mixing tank to give a slurry containing at least 10 wt% of Terephthalic acid. The slurry is pumped through a preheater and into a dissolver, which operates at  $\geq 250$  °C. The effluent from the dissolver is a solution and it flows through the hydrogenation reactor which contains noble-metal catalyst on a carbon support. The pressure in the reactor is maintained above the partial pressure of steam to maintain a liquid phase and to ensure an adequate supply of hydrogen.

***Mitsubishi Decarbonylation Process:***

In this process is used to purify Terephthalic acid produced by the liquid phase air oxidation of p-Xylene. Crude PTA dissolves in a solvent and the solution is passed into a reactor where the structures of principal organic impurities are altered. The solvent is usually water and the reaction step is usually the decarbonylation of 4-formylbenzoic acid, which takes place at 250-300°C in the presence of palladium on carbon catalyst. After the reaction Terephthalic acid is recovered by continuous crystallization and filtration.

***Modification of Henkel Processes:***

The Henkel processes can be modified to yield polymer grade Terephthalic acid. Henkel II process begins with the crystallization of dipotassium terephthalate from an aqueous solution. After recovery the crystals are redissolved in water and treated with alkali permanganate at 40-100°C and then passed through a bed of activated carbon for removal of colored impurities. Sulfuric acid is added to form very fine crystals of Terephthalic acid.

## CHOICE OF PROCESS

### **CATALYTIC, LIQUID PHASE-AIR OXIDATION OF p-XYLENE:**

This method is most widely used all over the world to produce technical grade Terephthalic acid. This method was developed by Mid –Century Corp. The process generally uses acetic acid as the solvent and a catalyst to oxidize p-Xylene in liquid phase by air oxidation. The process is also called as the Amoco process. This uses a catalyst usually a heavy metal eg. Cobalt. The process may use typically multivalent metals like manganese as catalyst for oxidation and bromine serves as the renewable source of free radicals.

Advantages of using this process:

- The reaction is very simple with a single step.
- The raw materials used in this process are easily available since it is a byproduct of a petroleum industry.
- The Terephthalic acid produced in this process has a yield of almost 100% with the presence of 4-formylbenzoic acid in trace amount.
- The oxidation process is highly efficient when compared to the other methods it brings about a conversion of about 95 wt%.
- The product purity is very high 99%.
- The process has very few pollution problems.
- The solvent and the catalyst can be recovered and reused. The recovery of solvent is possible till 90%.

#### ***Process Description:***

The process can be divided into different units:

- Reactor Unit
- Separation and Drying Unit
- Recovery Unit.

### Reactor Unit:

The reactor unit comprises of a reactor, a condenser and a G-L separator. The raw materials p-Xylene, air, acetic acid (solvent) and the catalyst (cobalt) are fed continuously into the reactor. The reactor is maintained at a temperature of 150°C and a pressure of 1500 kPa – 3000kPa. The air is added in greater stoichiometric ratio to minimize the formation of byproducts. The heat of reaction is removed by condensing and refluxing acetic acid. The reflux stream passes through the G-L separator where the excess air is removed and the liquid refluxed back into the reactor. The residence time of this reaction varies from 30 minutes to 3 hours. More than 95% of p-Xylene is converted to product. The outlet from the reactor is a slurry, since it is soluble to a limited extent in the solvent used.

### Separation And Drying Unit:

The separation and drying unit consists of a surge vessel, a centrifuge and a rotary drier. The surge vessel is maintained at a low temperature and pressure when compared to the reactor. The cooled slurry from the surge vessel is fed to a centrifuge. In the centrifuge most of the water content is removed from the product (Terephthalic acid). There are two streams leaving the centrifuge. One stream is sent to the recovery unit. And the other is sent to the rotary drier. The solid stream is sent to the drier. Preheated air is sent to the through the drier to remove the moisture present in the final product. The product from the drier is 99% pure Terephthalic acid.

### Recovery Unit:

The recovery unit comprises of two set of distillation columns, condensers and reboiler. The mother liquor from the centrifuge consists of three components p-Xylene (unreacted), catalyst, Acetic acid and water. This stream is fed to the residue still. The residue from the still contains acetic acid, p-xylene , water and the catalyst. The catalyst can be recovered from this residue. The distillate from the still has trace amount of p-Xylene, acetic acid and water. This is fed to a dehydration tower where the water is removed from acetic acid. Acetic acid is recycled back to the reactor in addition with a makeup acetic acid stream.

The process flow diagram is as shown below

**FLOW SHEET OF TEREPHTHALIC ACID PLANT**

