PERP Program – New Report Alert

November 2004

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Medium Quality Terephthalic Acid (03/04S6)***.

Introduction

The development of purified terephthalic acid (PTA) triggered the widespread replacement of dimethyl terephthalate (DMT) in the production of most polyester applications, especially bottle-grade resin, the fastest growing end-use. PTA, which is cheaper and easier to handle and transport than DMT, and allows for faster reaction times, became the raw material of choice in most new polyethylene terephthalate plants and caused a revamping of existing plants.

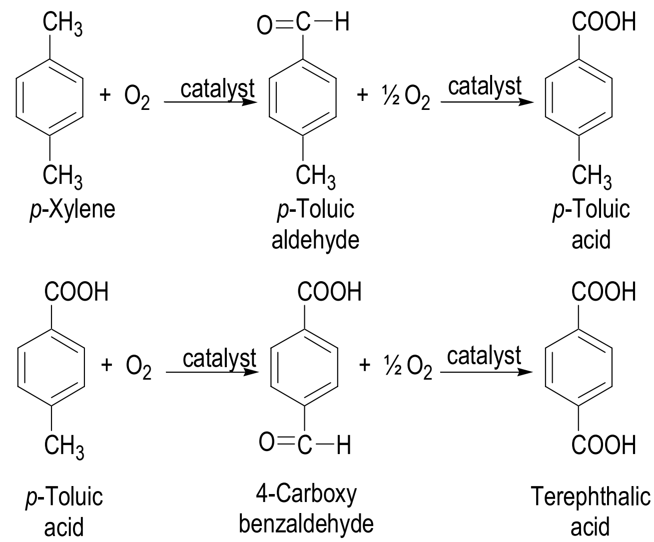
A relatively recent development in terephthalic acid process technology is the availability of so-called medium quality terephthalic acid, variously known as MTA, QTA or EPTA. MTA is now making inroads in the polyester markets. Eastman has long produced bottle-resin from its own proprietary medium quality terephthalic process without limitations in the marketplace, and is now offering their technology, EPTA, for license. Mitsubishi Chemical is also offering their own proprietary medium quality terephthalic acid process (QTA) for license. In addition, producers such as Sam Nam in Korea, are marketing their QTA (qualified terephthalic acid) as compatible with virtually all polyester applications, including bottle, fiber and film.

With the growth of medium quality terephthalic acid, both the process technology for making it and product in the market, there is now an alternative to PTA that has been proven applicable in most fiber and film applications and is starting to threaten PTA's prominence in the high growth bottle-resin applications. At a discount of $20-$30 per ton below PTA prices, MTA may not only take market share from PTA, but also may change the price and margin structure of the polyester products it produces.

The cost to produce of MTA is claimed to be lower than that of PTA and can result in very competitively priced polyester for an integrated producer or can provide a market edge for merchant sales. Also, the process is claimed to have a lower investment capital cost, which can have a large impact for polyester producers interested in licensing and back-integrating into terephthalic acid. This report examines the process technology for making MTA, its production economics, and the market issues surrounding the use of MTA.

Conventional Purified Terephthalic Acid (PTA)

The oxidation of *para*-xylene to crude terephthalic acid (CTA) catalyzed by metals (e.g. Co^{+2}, Mn^{+2}) and bromide is accomplished in acetic acid. The CTA is then purified to obtain purified terephthalic acid (PTA). Although there are undoubtedly differences in this technology as practiced by the various technology holders and licensors, the general outline is common to all. The reactions of importance are shown in the following chemical equations (the two moles of water formed by the selective oxidation of *para*-xylene are not shown):



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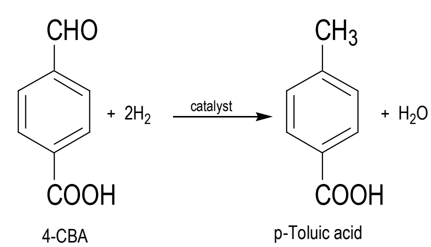
Purification of CTA requires at least one chemical step in addition to the physical procedures (e.g. crystallization, washing). One of the major impurities, 4-carboxybenzaldehyde (4-CBA), is quite difficult to remove by physical means but can be converted to *para*-toluic acid by catalytic hydrogenation in an aqueous solution, as shown in the following equation:



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The technology consists of the following major processing steps:

- *para*-Xylene oxidation (CTA synthesis)
- CTA crystallization
- CTA centrifugation or filtration
- CTA drying
- CTA dissolution
- Hydrogenation (CTA purification to PTA)

- PTA crystallization and filtration
- PTA centrifugation
- PTA drying

In the process *para*-xylene is catalytically oxidized to terephthalic acid in one step. The catalysts (cobalt and manganese acetates and a source of bromide) and some recycled acetic acid solvent are pumped to the oxidation reactors. Titanium reactors are needed because of the corrosive environment posed by the acetic acid and bromide solution. The amount of catalyst and solvent used and operating conditions must be tailored for optimum yields and product quality. The weight ratio of solvent to hydrocarbon in the oxidation reactor may range from 3 to 5. The catalyst is usually 0.1 to 0.2 weight percent of the solvent used. The ratio of bromide promoter to catalyst may vary widely from 1/10 to 10/1 atoms of catalyst per atom of bromine.

Modern plants use continuous oxidizers with air sparged through agitated vessels. The heat of reaction is removed by condensing, usually by raising steam, and refluxing solvent, *para*-xylene, and water vapors. Temperature and pressure in the reactor are typically between 185 and 204°C and 12 and 17.2 bar. Residence time is typically less than one hour for nearly complete conversion of *para*-xylene, and the yield from this step is about 98 mole percent.

Oxygen, usually from air, although oxygen-enriched air can be used, must be supplied to the reaction zone in excess of the stoichiometric requirements. It is normally maintained at 2 to 4 mole percent (volatile-free basis) in the vapor space above the reaction zone. Some acetic acid is destroyed by oxidation. The offgas from reaction is processed in a number of ways before discharging to the atmosphere to meet environmental standards. The reactor products are continuously discharged from the reactor as a hot slurry of CTA in acetic acid into a crystallizer where cooling takes place by flashing off part of the acetic acid, small amounts of unreacted *para*-xylene, and reaction water. Air can be supplied to this crystallizer to facilitate further reaction of *para*-xylene and intermediates. The crude terephthalic acid is crystallized, centrifuged or filtered, and dried before further purification to fiber grade PTA.

Hydrogenation is used to remove impurities from the PTA that would result in discoloration of the eventual polyester. The major impurity, 4-carboxybenzaldehyde (4-CBA), is hydrogenated (typically over a palladium-on-charcoal fixed bed catalyst) to *para*-toluic acid, which is more soluble in water and thus readily separated from terephthalic acid. Crude terephthalic acid is fed to a slurry vessel where it is contacted with hot water, heated, and fed to the reactor. The aqueous solution of CTA containing impurities is contacted with hydrogen in the hydrogenation reactor. The reactor effluent is sent to a series of crystallizers. PTA recovery is typically done in two steps: high pressure centrifuging followed by atmospheric centrifuging or vacuum filtration. The mother liquor, which contains the impurities, can be processed to recover terephthalic acid and intermediates prior to being sent to disposal. After a wash with hot water (reslurry stage between the two recovery steps), the wet crystals are dried and the final fiber grade PTA is conveyed to storage.

Process and catalyst improvements have boosted PTA purity to 99.8 percent or better. PTA uniformity is also important in maintaining long production runs in subsequent polyester manufacture.

The scale of PTA plants has increased from 60 thousand metric tons per year in the 1960s to over 700 thousand tons per year today (single reactor). Machine development has also been a significant factor in minimizing the requirements for the use of parallel equipment, particularly with solids/liquid separation and drying equipment. With increased scale and improved technology, capital cost per metric ton of PTA for the latest plants can be less than half that of plants constructed only five years ago.

Medium Quality Terephthalic Acid (MTA)

Over the last ten years or so, several terephthalic acid producers have found that while thousands of ppm of 4-CBA in the terephthalic acid will not produce good PET, the 4-CBA levels do not necessarily have to be as low as less than the 25 ppm found in PTA. This finding has stimulated the development of so-called medium quality terephthalic acid (MTA) that contains 4-CBA levels intermediate to that of PTA and CTA, generally in the range of 170-300 ppm. The major technology developers of MTA are Eastman Chemical/Lurgi, who call their version EPTA, and Mitsubishi Chemical, who call their version Qualified Terephthalic Acid (QTA).

Medium quality terephthalic acid is generally produced via a post or secondary oxidation step, where the majority of the *para*-toluic acid and 4-CBA impurities are converted to additional terephthalic acid. This step negates the need for the final purification step needed in the production of PTA, where the 4-CBA is reduced to *para*-toluic acid. The post-oxidation essentially is a series of reactors that operate at higher temperature and pressure than the first oxidation reaction. The TPA is slurried in acetic acid and is oxidized in the presence of a catalyst. The post-oxidation step does not remove/convert as much of the organic impurities as does the hydrogenation. The resulting "medium quality" TPA contains higher levels of impurities than PTA, but at levels low enough to allow use in the fast growing PET bottle market.

Both the Eastman/Lurgi EPTA process and the Mitsubishi Chemical QTA process are discussed in the report.

Comparison of MTA and PTA

The apparent and claimed advantage of medium quality terephthalic acid (MTA) is the lower cost to build the plant and lower cost of production. Lower production costs provide a competitive edge for producers employing MTA processes. However, a disadvantage, or at least a perceived disadvantage, of MTA is the lower quality, in terms of impurity level, compared to conventional PTA

The most significant differences between PTA and MTA are in 4-carboxybenzaldehyde and *para*-toluic acid concentrations. These impurities are thought, at least by "conventional wisdom", to have a large impact on final product color and appearance. Contained acetic acid level is also much higher for the medium quality terephthalic acid and can be a corrosion problem in the polyester plant.

Most medium-purity and high-purity technologies reduce 4-CBA to sub-300 or 50 ppm levels, respectively, and there is no evidence that further reduction has any great influence on the downstream process. The question is - does reducing the 4-CBA level to 10-25 ppm, as is the case for leading PTA producers, more beneficial, in a demonstrable way, than at the higher levels of MTA? While anecdotal information usually ascribes 4-CBA impurity in terephthalic acid as the bad actor regarding yellowing in PET production, this is not necessarily the case. The many issues surrounding the roles of the various terephthalic acid impurities on PET quality has been investigated and our findings described in the report. PTA, MTA, and PET producers in the United States, Western Europe, and Asia were interviewed as to their take on this important issue.

Economics and Supply/Demand

Detailed cost of production estimates, including the effects of fixed costs such as labor-related and investment-related costs, are provided in the report for both MTA and PTA. With lower investment costs for MTA, the cost advantage improves when considering full production cost and investment return.

The report includes supply, demand (by country), and trade estimates (2000-2015) for the United States and Asia/Pacific for PTA and DMT. Parallel data are provided for Western Europe, except that demand is not detailed by country.

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