Terephthalic Acid “PTA”

INTRODUCTION

Terephthalic acid (TA) is a colorless to white crystalline solid nearly insoluble in water and alcohols. It is also known as para-phthalic acid and almost all of its production is consumed in processing polyethylene terephthalate (PET), a polymer used essentially in the production of plastic bottle and clothing.

The two most common grades of terephthalic acid commercially available are:

- Purified Terephthalic Acid (PTA) which contains over 99.99 weight percent TA and less than 25 ppm 4 carboxibenzaldehyde (4-CBA) - see Section 3 for further details.
- Medium Quality Terephthalic Acid (MTA) which also contains over 99.90 weight percent TA but with up to 400 ppm 4-CBA. 4-CBA is responsible for giving a yellow color to the produced PET, which is not widely accepted in this industry. Therefore dyes have to be added to the MTA to obscure this color and this allows its use in some notable applications.

PTA is prepared via oxidation of para-xylene and purification of the crude intermediate terephthalic acid (CTA). MTA is obtained through staged-oxidation of para-xylene. PTA technology is available through licenses and joint ventures with many internationally renowned players. Significant developments have occurred in terephthalic acid technology in recent years and this is one of the key focuses of this report.

The outline of this report is as follows:

- An overview of the licensing technology status is given.
- Current production technology is discussed.
- A patent review has been carried out and developing technologies and improvements are discussed.
- Nexant’s view on “what the next step” for terephthalic acid production technology will be, e.g., Process Intensification concept applied to achieve PTA quality in a single oxidative step as well as emerging “green” routes to PTA.
- Comparative economics for the commercial PTA technologies offered by Davy Process Technology and Dow, BP, Invista, and GTC Technology, as well as the economics for Lurgis’ MTA technology are given and compared for the same region (namely USGC).
- Regional economics for plants being built in the next five years in various regions of the world are given.
- Commercial end-use applications, global and regional market overview analysis is given.

CURRENT TECHNOLOGY
Purified Terephthalic Acid (PTA)

The oxidation of \textit{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 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 \textit{para}-xylene are not shown):

\[
\begin{array}{c}
\text{p-Xylene} + \text{O}_2 \xrightarrow{\text{catalyst}} \text{p-toluic aldehyde} \\
\text{p-toluic acid} + \text{O}_2 \xrightarrow{\text{catalyst}} \text{4-Carboxybenzaldehyde} \\
\text{4-Carboxybenzaldehyde} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{catalyst}} \text{Terephthalic acid}
\end{array}
\]

Purification of CTA requires at least one chemical step in addition to the physical procedures (e.g. crystallization, washing). One of the major impurities is one of the intermediates in the reaction sequence, namely 4-carboxybenzaldehyde (4-CBA), and it is quite difficult to remove by physical means but can be reverted by catalytic hydrogenation in an aqueous solution to the intermediate from which it is formed, \textit{p}-toluic acid, which is much easier to remove by physical means.

The technology consists of the following major processing steps:

- \textit{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
This conventional process technology developed by Dow (Inca) is discussed in some detail in the report.

Processes offered by various licensors are also discussed including:

- COMPRESS PTA Process from Davy Process Technology and Dow

The origin of the purified terephthalic acid (PTA) technology licensed by Dow Italia s.r.l. goes back to 1968, when a 60 000 ton per year PTA plant was implemented in Porto Marghera (Venice) Italy, followed in 1974 by the Ottana plant in Italy, with a design capacity of 80 000 tons per year. Since then, significant process improvements were implemented.

In 2008, Dow signed a technology development program with Davy Process Technology (DPT) and together they are offering to license (from 2010) an improved process known as COMPRESS™ PTA. The COMPRESS™ PTA process is apparently aimed at a technically streamlined process. Nexant understands this has been achieved by combining conventional unit operations adapted from other chemical processes where Davy/Dow have historical know-how and this has allowed a reduction in total equipment count while seemingly still achieving a high process efficiency.

COMPRESS PTA process chemistry, technology and key distinguishing features are discussed.

- INVISTA PTA Process

The INVISTA PTA production process comprises the oxidation plant in which para-xylene is converted to crude terephthalic acid (CTA) by oxidation, the purification plant in which CTA is purified by hydrogenation, and the R^2R unit in which byproducts are recovered from the oxidation plant residues.

The reliability of these process units is such that they effectively operate as a single plant with many advantages.

INVISTA process chemistry, technology and key distinguishing features are discussed

- BP (AMOCO) Process

BP is the world’s largest PTA producer, having maintained its leadership notably thanks to the acquisition of AMOCO and its proprietary technology in 1998. The technology patented in the early sixties, conventional oxidation followed by purification process, has seen many incremental improvements over the decades. With conserving their global leadership and patents expiration in mind, BP took a step forward and brought major changes to a forty year old mature terephthalic process in the early part of this decade. BP owns most of the plants using its innovative process and does not license its technology, however the technology is accessible through joint ventures.

The PTA technology is still based on the oxidation of para-xylene followed by purification through hydrogenation of CTA. Progress has been made by removing many steps of the conventional process.
BP chemistry technology and key distinguishing features are discussed.

- **GTC TECHNOLOGY Process**

The GTC Technology process for purified terephthalic acid differs from conventional processes as it involves a purification step by selective solvent crystallization and dismisses hydrogenation totally.

GTC claims their patented technology can use lower quality para-xylene feedstock, meaning the process can cope with mixed xylenes conversion resulting in terephthalic acid (TA) as well as isophthalic acid (IPA) because the purification system is able to separate the isomers. In conventional routes using hydrogenation, the system can only manage a small amount of impurities and therefore not only requires costly high purity para-xylene feed but also an efficient oxidation step. Although this report details the purification of both TA and IPA, a simplified version of the process is available for production and purification of TA from para-xylene as well.

GTC TECHNOLOGY process chemistry, technology and key distinguishing features are discussed.

**PATENT REVIEW**

Over the last five years, many patents have been published and applied for with regard to aromatic carboxylic acids and in particular terephthalic acid and its production. Although most patents are still pending, there have been many developments made to improve the conventional process as described in the previous sections. There are also a few patent applications relating to alternative ways to para-xylene use to produce terephthalic acid.

The above cost estimates highlight the different process performances as they are all compared on a same capacity and location basis, having the same raw materials, utility and labor costs basis. However, the USGC location is not reflective of the developing industry as no new project is planned to be built in this region. Therefore, Nexant has also developed and compared the economics of production for the major global capacity additions planned in the next five years.

A cost of production estimate has been outlined for the following plants to be:

- North-East Asia (China)
- South Asia (India)
- South America (Brazil)
- Central Europe (Poland)
- Middle East (Oman)

**COMMERCIAL APPLICATIONS & REGIONAL MARKET REVIEW**
PTA (and its methyl ester DMT) is primarily used to produce polyester (PET), as exemplified in the figure below.

West European PTA Consumption

- Commercial applications are outlined in the report.
- Global supply and demand data are given and discussed.
- North American, Western European and Asia Pacific supply, demand and trade data are given and discussed, including a listing of specific plant capacities in these regions denoted by company, location and annual tonnage produced.

Purified terephthalic acid (PTA)

1 tonne of PTA will make around 19,000 sleeveless polyester shirts

PTA is the key raw material for the manufacture of polyester fiber, resin, and film. PTA is used to produce polyethylene terephthalate (PET), which flows into the production of goods that we use in our everyday lives and enhances the quality of life around the world.

It can be found in plastic containers for beverages, food and electronics, apparel, home textiles, carpets and industrial fibre products, and audio and video recording tapes, photographic
Dragon Group purified terephthalic acid (PTA) process has two stages: in the first stage PX is oxidized to form crude terephthalic acid (CTA), and in the second stage CTA is refined to purified terephthalic acid (PTA).

**To produce one ton of PET needs about 0.85-0.86 ton of PTA**

Worldwide around 65% of PTA goes into polyester fibre, 27% to PET bottle resin and the remaining 8% to film and other plastic end uses.

BP has a major global PTA business with around one fifth of global production capacity. Now, it will continue to concentrate on its PTA strategy into high-growth markets such as China and in OECD markets,