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Terephthalic Acid

PERP 09/10-6

Report Abstract
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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 main 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 carboxybenzaldehyde (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.

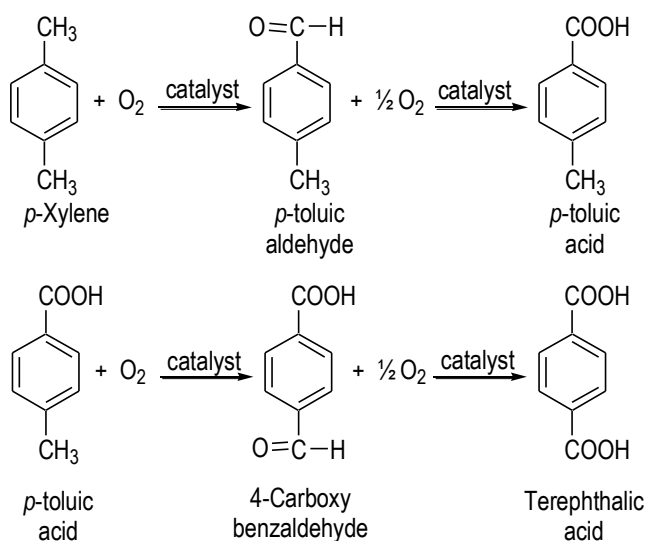
The outline of this report is as follows.

- 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 *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 *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 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, *p*-toluic acid, which is much easier to remove by physical means.

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

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 R²R 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.

Medium Quality Terephthalic Acid (MTA)

For completeness of the report, this section on MTA has been included in the report, although Nexant has not learnt of any significant change to the medium quality terephthalic acid production technology in recent years. The major new fact is that Eastman-Lurgi are not licensing their MTA technology on its own anymore but offer the process in their IntegRex™ process which combines PET to MTA manufacture.

- The Eastman/Lurgi EPTA process technology is described in detail as well as its advantages.
- A brief overview of Mitsubishi Chemical's QTA Process is given, highlighting their experience in this technology.

As alluded to earlier in this report, Terephthalic acid has different grades as set by certain specifications. The typical grades are Technical-Grade Terephthalic Acid (TGTA), Medium-purity Terephthalic Acid (MTA) and highly-Pure Terephthalic Acid (PTA). TGTA can contain as much as several thousand parts per million 4-carboxybenzaldehyde (4-CBA); MTA as much as several hundred ppm; and PTA as much as 50 ppm. TGTA use is severely limited in most polyester applications, while the use of MTA had been growing.

- This section of the report compares MTA and PTA in terms of Quality and Potential Color Formation, as well as Commercial Application.

The section is concluded with a discussion on Usage and Cost Issues as well as Market Issues facing MTA.

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.

This section starts by giving brief reviews of the main improvements brought to the terephthalic process as described in Section 3 and 4 which concern:

- Liquid oxidation (mixing improvement, alternative solvent and process conditions)
- Purification step
- Innovative catalyst composition for both oxidation and hydrogenation steps
- Innovative oxidation promoter
- Energy savings by recovery of heat, reactant and catalyst
- Alternative feedstock and raw materials sourcing

In the last part of the section, Nexant explores what the future could be for PTA manufacture, optimization and green routes.

ECONOMICS

In this sub-section, Nexant develops and compares cost of production estimates for different commercial processes using the same location basis, the U.S. Gulf Coast (USGC).

Economic estimates for the production of purified terephthalic acid are given via the following routes:

- Oxidation followed by hydrogenation as characterized by the conventional process (former Dow process).
- Oxidation followed by hydrogenation as characterized by the COMPRESS™ PTA process.
- Oxidation followed by hydrogenation as characterized by INVISTA.
- Oxidation followed by hydrogenation as characterized by BP.
- Oxidation followed by solvent purification as characterized by GTC Technology.

Economic estimates for the production of medium terephthalic acid are given via the EPTA process characterized by Eastman/Lurgi on a USGC also.

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.

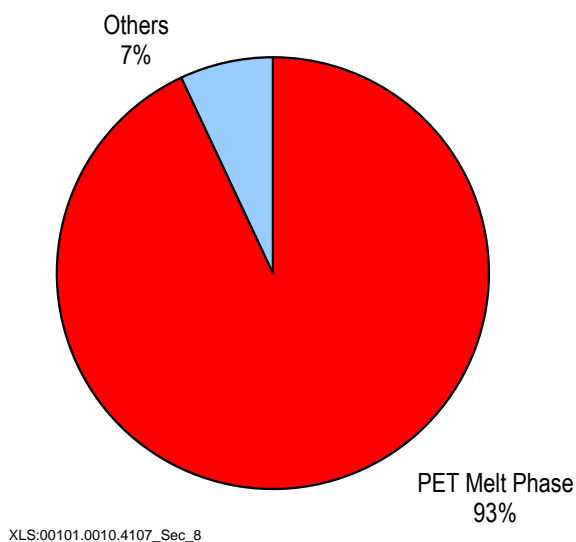
A cost of production estimate has been outlined for the following plants to be:

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

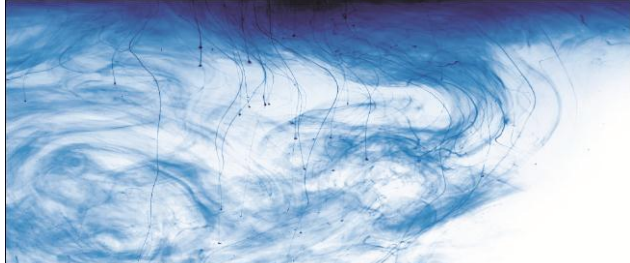
COMMERCIAL APPLICATIONS & REGIONAL MARKET REVIEW

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.



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