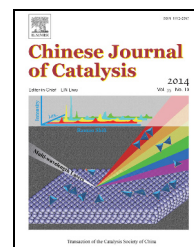


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## Review

# A brief review of *para*-xylene oxidation to terephthalic acid as a model of primary C–H bond activation



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## ABSTRACT

The oxidation of *para*-xylene to terephthalic acid has been commercialised as the AMOCO process (Co/Mn/Br) that uses a homogeneous catalyst of cobalt and manganese together with a corrosive bromide compound as a promoter. This process is conducted in acidic medium at a high temperature (175–225 °C). Concerns over environmental and safety issues have driven studies to find milder oxidation reactions of *para*-xylene. This review discussed past and current progress in the oxidation of *para*-xylene process. The discussion concentrates on the approach of green chemistry including (1) using heterogeneous catalysts with promising high selectivity and mild reaction condition, (2) application of carbon dioxide as a co-oxidant, and (3) application of alternative promoters. The optimisation of *para*-xylene oxidation was also outlined.

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## 1. Introduction

Terephthalic acid is a main component in the polyester industry, and is used in polyester terephthalate (PET) and polyester fibre manufacturing. About 70% of terephthalic acid used in PET manufacturing is produced from the oxidation process of *para*-xylene [1,2]. Besides its use in the manufacturing of plastic ware and drinking bottles, terephthalic acid can also be used in other applications such as in textiles, as a carrier in paints, and as a coating resin (Fig. 1).

The largest producers of terephthalic acid in commercial production are British Petroleum (BP), BP Zhuhai Chemical Company (Ltd.) and JBF Petrochemicals Ltd. (JBF), with an annual production of terephthalic acid of more than 10 Mt. All the plants are located in Europe and North America, China and India (<http://www.technip.com>; accessed on 25 June 2014).

The other main license holders for terephthalic acid production are DuPont, Dow Chemical, Mitsubishi Chemical, Eastman Chemical, Hitachi, Mitsui Chemicals, Interquisa, and Grupo Petromex. Currently, the market price of terephthalic acid is about 1100–1200 USD/t ([bp.com/annualreport](http://bp.com/annualreport); accessed 31 Jan. 2014). It is worthwhile to mention that the largest application of PET is in textiles (Fig. 2) [3].

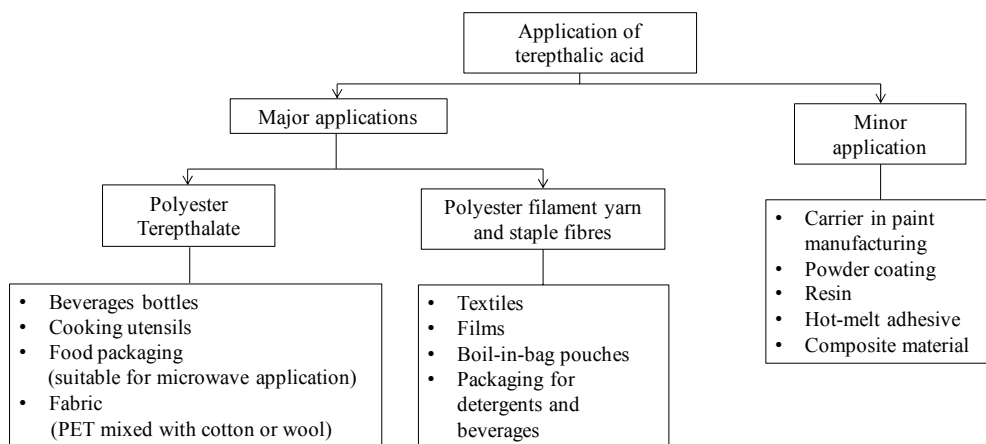
### 1.1. Initial development of *para*-xylene oxidation

The first oxidation of *para*-xylene was recorded in 1912 by Ciamician and Silber [4]. They studied the effect of light on the oxidation of some benzene derivatives including *para*-xylene. Molecular oxygen was used as the oxidant, and these derivatives were exposed to sunlight for a year. As a result, terephthalic acid was produced as one of the products besides *p*-toluic

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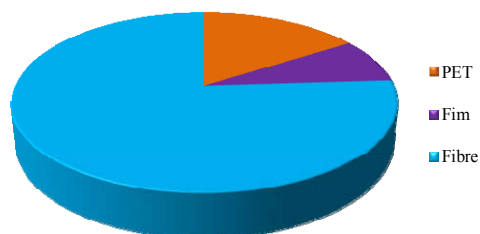
**Fig. 1.** Application of terephthalic acid in the polyester industry. [http://www.bp.com/liveassets/bp\\_internet/belgium/belgium\\_geel/STAGING/local\\_assets/downloads\\_pdfs/G\\_3\\_08\\_3\\_06\\_PTA\\_UK.pdf](http://www.bp.com/liveassets/bp_internet/belgium/belgium_geel/STAGING/local_assets/downloads_pdfs/G_3_08_3_06_PTA_UK.pdf) (accessed on 12 February 2014); [http://www.ril.com/html/business/polyester\\_inter\\_pta.html](http://www.ril.com/html/business/polyester_inter_pta.html) (accessed on 18 March 2014); [5] <http://www.iocl.com/Products/PurifiedTerephthalicAcid.aspx> (accessed on 18 March 2014); [6] <http://www.eastman.com/Products/Pages/ProductHome.aspx?Product=71001808> (accessed on 18 March 2014).

acid [5].

A decade after Ciamician and Silber's study, Stephens (1926) modified the oxidation process by changing the sunlight exposure to the use of dimmed light. The study was conducted at 100 °C, and the reaction time was 24–60 d with the major product of xylenes and monoaldehydes. Stephens's study contributed to the study of the oxidation mechanism by revealing that the reactants (hydrocarbon and alkane) undergo stepwise oxidation and gave aldehydes and ketones as the intermediates. Besides that, Stephens also showed the inhibiting effect of water in the oxidation process [6]. However, these studies by Ciamician and Silber and Stephens were not practical for industrial application due to the long reaction time. Therefore, the use of a catalyst, either a homogeneous or heterogeneous catalyst, for the oxidation of *para*-xylene to terephthalic acid has received a warm welcome.

## 1.2. AMOCO commercial process

Before the AMOCO process was commercialised in the late 1970s, a few processes were used to produce high quality terephthalic acid. One of these processes was conducted with the hazardous condition of nitric acid as the oxidant at high temperature 200 °C and 1.35 MPa of oxygen pressure. A precipitate of terephthalic acid was formed that was separated and purified to give the high quality compound. A high quality terephthalic acid is defined as the purified product with an impurity content of 4-carboxybenzaldehyde (4-CBA) less than 25 ppm.



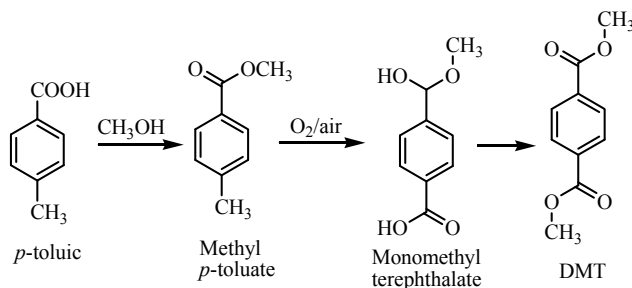
**Fig. 2.** Terephthalic acid consumption (2011–2012) around the world.

However, many steps are required for the purification process [7,8] and the purified yield was still contaminated with coloured impurities. These impurities subsequently contributed to the deteriorated quality of the product. Therefore, esterification with methanol to dimethyl terephthalate (DMT) was introduced as an alternative route to avoid inconveniences in the purification process.

In addition, DMT was used as a replacement for terephthalic acid. In the DMT route, the oxidation of *para*-xylene is conducted with a cobalt catalyst in the absence of a solvent, and the temperature and pressure are 180 °C and 0.8 MPa of air, respectively. The *p*-toluic acid produced is esterified with methanol to methyl *p*-toluate followed by autoxidation to monomethyl terephthalate. Monomethyl terephthalate is then esterified by methanol again to form DMT. The complete steps of the esterification of *p*-toluic acid to DMT is shown in Scheme 1 [9].

PET was patented by John Rex Whinfield in 1946 [10]. As *p*-toluic acid is resistant to oxidation by the cobalt catalyst, the process relies on the oxidation of methyl *p*-toluate (produced as a result of esterification by methanol) to monomethyl terephthalate [7]. This situation constrained the production of terephthalic acid as it increased the operation cost due to the many steps required in the esterification by methanol.

The solution to the resistance of *p*-toluic acid to oxidation was solved by the discovery of bromide-controlled air oxidation in 1955. This discovery led to the implementation of the



**Scheme 1.** Esterification of *p*-toluic acid to DMT [9].

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