Xylenes

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Report Abstract
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INTRODUCTION

The xylene isomers, meta-xylene, ortho-xylene and in particular para-xylene, are important chemical intermediates. ortho-Xylene is oxidized to make phthalic anhydride which is used to make phthalate plasticizers among other things. meta-Xylene is oxidized to make isophthalic acid, which is used in unsaturated polyester resins (UPR). However, para-xylene has by far the largest market of the three isomers. The largest use of para-xylene is in its oxidation to make purified terephthalic acid (PTA). PTA is used in turn to make polymers such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). PET is one of the largest volume polymers in the world. As such, the demand for para-xylene is several times that for meta- and ortho-xylene.

Xylenes are normally obtained from various sources within a refinery or steam cracker including reformate, pyrolysis gasoline, toluene disproportionation and transalkylation. Globally, reformate accounts for over 75 percent of the mixed xylenes (see Figure 1). These sources usually produce a mixture of isomers from which the individual isomer is recovered.

Figure 1 Mixed Xylene Technology
COMMERCIAL TECHNOLOGY

Aromatics are produced as co-products in refinery catalytic reformers, olefins plants, coal tar processing, and toluene disproportionation (TDP) units. However, as seen in Table 1, the production distribution doesn’t necessarily match the demand.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Xylene Demand versus Production (Percent)</th>
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<tbody>
<tr>
<td></td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Distribution in reformate</td>
<td>18</td>
</tr>
<tr>
<td>Distribution in pygas</td>
<td>52</td>
</tr>
<tr>
<td>Isomer demand</td>
<td>1</td>
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</tbody>
</table>

Reformate is formed in the catalytic reforming of naphtha, a technology primarily directed at the production of high octane gasoline components. Pygas is a liquid byproduct formed in the production of olefins by steam cracking liquid feeds, such as naphtha or gas oil. Ethylene plants typically operate near full capacity, but the feedstock slate may vary depending on market conditions. However, the xylenes content of pygas is much less than that of reformate and the xylenes portion can contain up to 40 percent ethylbenzene. As a result, pygas is usually used as a source of benzene and not xylene. Xylene recovery is not usually recovered from pygas unless the steam cracker is associated with a larger aromatics complex.

Small amounts of aromatic rich streams are extracted from coal in the production of coke, which is a fuel and chemical feedstock for steel blast furnaces. It is very low in xylenes content (four to eight percent). Extraction from coal tar operations is not expected to grow, with the exception of production in China. Coke production is expensive and can be polluting, and steel producers continue to make investments to reduce their coke consumption, favoring direct coal injection technology. Coke oven light oil accounts for less than five percent of the total global supply of aromatics.

The recovered aromatics stream from extraction of reformate consists of benzene, toluene, mixed xylenes, and C9+ materials. Each of these can be separated by conventional distillation, although it is difficult to separate the individual xylenes isomers due to the closeness of their boiling points. It is possible; however, to separate ethylbenzene and ortho-xylene from the mixed xylenes feed by conventional distillation.

A xylenes splitter, which ordinarily would separate the C9+ aromatics from the xylenes, can be redesigned to remove ortho-xylene as well. This option is practiced by about 60 percent of United States xylenes producers. A few companies also recover ethylbenzene from the overheads product of the xylenes splitter. However, an ethylbenzene fractionator is an even more costly undertaking than an ortho-xylene column. Few, if any, ethylbenzene fractionators have been built in the past 25 years.

A typical process scheme for separation of the mixed xylenes obtained by extraction from reformate is shown in Figure 2. The usual objective of such a process scheme is to maximize the production of para-xylene, which is in high demand for the production of terephthalic acid.
**ortho**-Xylene is also recovered for use as feedstock to phthalic anhydride production. **meta**-Xylene may optionally be recovered to feed an isophthalic acid plant. In an alternative arrangement mixed xylenes are fed to the xylenes splitter; however, this results in the feed to **meta**-xylene recovery being devoid of ethylbenzene.

**Figure 2** Xylenes Recovery Processes
Commercial xylenes production is discussed in detail in the report, including catalytic reforming, pyrolysis gasoline, toluene disproportionation, transalkylation and dealkylation; also included is a detailed review of commercial recovery technology for para-xylene, ortho-xylene, meta-xylene, and ethylbenzene. Xylene isomerization technology is briefly discussed.

DEVELOPING TECHNOLOGY

Research in the area of xylenes is prolific, as exemplified by the fact that only considering the U.S., there have been 130 patents awarded and applied for between 2006 and the end of 2009. A brief description of some of the more interesting patents by the companies listed below are given in this section of the report.

- Conoco Phillips
- ExxonMobil
- IFP
- Johnson Matthey
- Nippon Oil Research Institute and King Fahd University of Petroleum and Minerals
- SABIC
- Samsung Petrochemicals
- UOP

PROCESS ECONOMICS

Cost estimates have been evaluated for para-xylene production via the following processes utilizing adsorption or Crystallization with isomerization:

- Adsorption/isomerization of mixed xylenes with isomerization of the ethylbenzene
- Two cases have been evaluated, with and without ortho-xylene recovery as a by-product
- Adsorption/isomerization of mixed xylenes with dealkylation of the ethylbenzene
- Crystallization/isomerization of mixed xylenes with dealkylation of the ethylbenzene (conventional technology)
- Crystallization technology with ammonia absorption refrigeration/isomerization of mixed xylenes and dealkylation of the ethylbenzene (new BP technology)

Cost estimates have been evaluated for para-xylene production via the following processes utilizing toluene disproportionation and transalkylation:
Selective toluene disproportionation process (STDP) with toluene feed and a one-stage crystallization recovery step at the back-end

PxMax\textsuperscript{SM} (toluene feed) with ExxonMobil Crystallization

Conventional TDP (toluene feed) followed by Adsorption/Isomerization

TDP (toluene/C9 aromatics feeds) followed by Adsorption/Isomerization

C9 Transalkylation followed by Adsorption/Isomerization

Cost estimates have been evaluated for \textit{para}-xylene production via the following processes utilizing an overall aromatics complex:

Integrated naphtha to \textit{para}-xylene route incorporating Hydrotreating / Reforming / Extraction / Disproportionation / Transalkylation / Adsorption / Isomerization / Distillation

Cost estimates have been evaluated for \textit{para}-xylene production utilizing the UOP proprietary Cyclar\textsuperscript{TM} process for converting LPG to BTX:

Cyclar\textsuperscript{TM} / adsorption / isomerization

Cost estimates have been evaluated for \textit{meta}-xylene production utilizing:

UOP’s MX Sorbex\textsuperscript{TM} process with mixed xylenes feed

The above cost estimates highlight the different process performances as they are all compared on a same capacity and location basis. However, other regions reflect to a greater extent the developing industry based on planned new projects. Therefore, Nexant has also developed and compared the economics of production of \textit{para}-xylene for a fully integrated aromatics complex for the following regions as well: South Korea, Middle East, Southeast Asia, Western Europe and Japan.

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included).

\textbf{COMMERCIAL ANALYSIS}

The main applications for mixed xylenes are shown in Figure 3.
Global supply, demand and trade data are given and discussed in the report.

In addition, supply, demand and trade data is given and discussed according to key regions (i.e., United States, Western European, and Asia Pacific).

A list of plants in each of the key regions above is given showing specific plant capacities, owning company, location and annual tonnage produced.