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## Maximizing existing xylene loop profitability

Paraxylene (PX) separation is an energy-intensive process, as are most industrial chemical separations.<sup>1,2</sup> In an aromatics complex, the PX separation process and the largest fractionation columns<sup>3</sup> are part of the xylene loop, making it the highest energy consumer in the plant. Therefore, maximizing the loop's efficiency is critical.

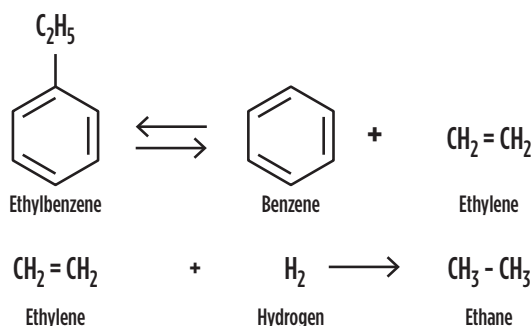
The xylene loop operates as follows:

1. Reformate C<sub>8</sub> aromatics containing approximately 20% PX are separated from heavier hydrocarbons in the xylene splitter
2. PX is recovered via adsorption or crystallization, while the remaining C<sub>8</sub> aromatics stream is processed in the vapor phase isomerization (VPI) unit, which converts ethylbenzene (EB) to benzene and para-depleted xylenes to equilibrium xylenes
3. After separation of benzene and trace toluene by fractionation, C<sub>8</sub> aromatics and heavier byproducts are redirected to the xylene splitter.

This process results in recycle C<sub>8</sub> aromatics constituting 75% of the total feed to the PX separation unit, vs. only 25% fresh reformate C<sub>8</sub> aromatics, making PX recovery a very inefficient process. Therefore, minimizing C<sub>8</sub> aromatics circulation and maximizing PX production from an existing xylene loop are highly desirable goals.

In the VPI unit, it is essential to achieve high EB conversion per pass while minimizing xylene loss.<sup>4</sup> EB conversion to benzene is illustrated in **FIG. 1**, while examples of side reactions leading to xylene loss are illustrated in **FIG. 2**.

High EB conversion per pass is desirable because it reduces EB traffic in the xylene loop, thereby maximizing xylene concentration and associated PX recovery. Low xylene loss is desirable



**FIG. 1.** EB conversion to benzene with subsequent hydrogenation of ethylene to ethane.

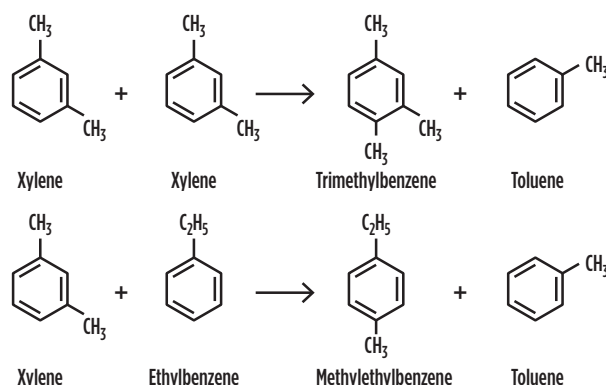
because resulting toluene and C<sub>9</sub>/C<sub>10</sub> aromatics must either be reprocessed in a transalkylation unit to recover the lost xylenes at substantial additional energy costs or be downgraded to gasoline value in plants where no transalkylation process is available.

**FIG. 3** illustrates VPI process performance evolution over 40 yr of catalyst/process improvements.

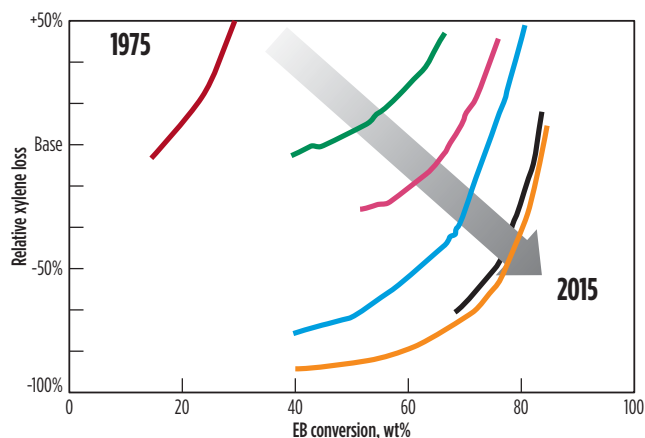
While incremental advances have led to processes with lower xylene loss, it can be seen that for any given technology, xylene loss increases with EB conversion. This stems from the fact that catalyst activity improvements for the EB dealkylation reaction invariably result in higher activity for transalkylation reactions, leading to xylene loss. The technical challenge, therefore, is to selectively increase catalyst activity for EB dealkylation without promoting undesirable side reactions.<sup>5</sup>

**Recent advances in xylenes isomerization.** Xylenes isomerization can be achieved by using a unique, dual-bed catalyst system that separates VPI chemistries—EB dealkylation and xylenes isomerization. The first catalyst (top bed in a downflow reactor, outer bed in a radial-flow reactor) is designed to primarily catalyze EB conversion to benzene and non-aromatics cracking. The first catalyst bed is operated as illustrated in **FIG. 4**. An amorphous selectivation agent is applied during the manufacturing process of the first catalyst.<sup>6</sup> The impact of this selectivation is twofold:

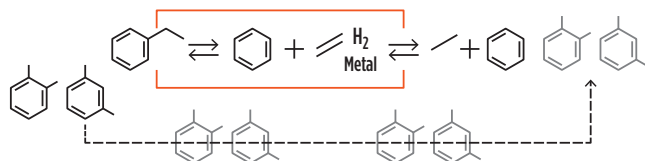
1. It reduces zeolite pore opening, thereby restricting access of larger-size molecules to zeolite pores. Since EB has a smaller kinetic diameter,<sup>7,8</sup> EB diffusion through zeolite channels is not hindered. On the other hand, the larger C<sub>8</sub> molecules (ortho-xylene and meta-xylene) will mostly bypass zeolite pores in the selectivated



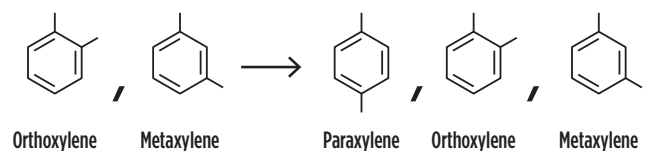
**FIG. 2.** Examples of side reactions leading to xylene loss.



**FIG. 3.** Evolution of VPI performance over four decades of VPI catalyst/process development.



**FIG. 4.** Illustration of the shape-selective mechanism used in the VPI first catalyst bed.



**FIG. 5.** Xylenes isomerization in the VPI second catalyst bed.

catalyst, and therefore will not transalkylate on active centers inside the pores. Catalytic activity within zeolite channels can be adjusted to the desired EB dealkylation per pass without increasing undesirable side reactions involving xylene molecules.

- It passivates the external surface acidity of the zeolite catalyst without impacting the inner pore system;<sup>9</sup> orthoxylene and metaxylene are not exposed to active sites while bypassing zeolitic channels.

The second catalyst (bottom bed in a downflow reactor, inner bed in a radial-flow reactor) is designed to primarily catalyze xylenes isomerization. The second catalyst bed is operated as shown in **FIG. 5**.

Orthoxylene and metaxylene are isomerized to equilibrium xylenes in the second catalyst bed. The second catalyst is less active<sup>10</sup> because the xylenes isomerization reaction requires significantly less activity than the EB dealkylation reaction. Also, since catalyst activity is low, benzene product from EB dealkylation in the first catalyst bed remains unreacted in the second catalyst bed.

### Xylenes isomerization retrofit in an existing facility.

For a high-performance xylenes isomerization process retrofit to be successful, the following must be achieved in the existing xylene loop facility:

- Economic benefits must be significant and justify catalyst changeout. In xylenes isomerization, cycles usually exceed 10 yr, because (a) incremental improvements in catalyst formulations have enabled longer cycles, and (b) the service is not challenging since coke precursors or contaminants are mostly trapped in the adsorption unit upstream from the VPI unit. Consequently, opportunities for catalyst changeouts due to end-of-cycle/end-of-life are scarce, but higher EB conversion per pass and reduced xylene loss can economically justify substitution with an improved catalyst and associated costs, even if the catalyst load in service has several years of remaining life.
- The proposed retrofitted catalyst/process must be a good fit for the existing unit in terms of catalyst quantity (weight hourly space velocity), reactor operating temperature and pressure, allowable reactor pressure drop, hydrogen-to-hydrocarbon molar ratio, and general operating constraints and feed specifications, as well as all potential specific requirements for a new process prior to and during unit startup. Usually, unit modifications to accommodate a new catalytic technology should be limited, as they impact the economic benefits of the process replacement and the timing of the unit turnaround. As the design operating conditions for an existing unit will always differ from the ideal conditions for the process to be retrofitted, such retrofit benefits must be relatively insensitive to changes in operating conditions, otherwise economic benefits may be impacted by the existing operating constraints.
- In addition to providing the expected economic benefits, the catalyst/process proposed for retrofit should not negatively impact plant constraints external to the VPI unit but critical to aromatics production, for example:
  - C<sub>8</sub> and C<sub>9</sub> non-aromatics molecules are generated in the reforming unit at varying rates depending on the reformer feed, type, operating conditions and reforming catalyst in use. Such molecules can be xylenes coboilers and may be difficult to fractionate out after entering the xylene loop. To avoid non-aromatics accumulation that would reduce the loop capacity for processing xylenes, it is important that a replacement VPI technology provides a C<sub>8</sub> and C<sub>9</sub> non-aromatics cracking rate equivalent to, or better than, the technology to be replaced.
  - In a VPI unit, ethylbenzene is converted to benzene, which adds to the plant benzene production mostly originating from reformat benzene and, when applicable, transalkylation benzene. Although isomerization benzene is a small stream compared to other benzene sources in the aromatics complex, it is still important to minimize the quantity of benzene coboilers generated in the VPI unit, especially in aromatics facilities that have been debottlenecked multiple times and where extraction capacity may be limited. A replacement VPI technology should generate as little (or even less) benzene coboilers than the incumbent technology.

**Commercial retrofit and associated benefits.** Idemitsu Kosan Co. Ltd. retrofitted its xylenes isomerization unit in

**TABLE 1.** Benefits achieved by upgrading the VPI process in Idemitsu Kosan's xylene loop at the aromatics complex in Chiba

Parameter	Prior process	New VPI process*
EB conversion per pass	Base	+8%
Capacity debottleneck for the adsorption unit	Base	+0.3%
Xylene loss per pass	Base	-19%
Reactor inlet temperature	Base	-2%
Non-aromatics conversion per pass	Base	+80%
Potential additional PX production	Base	+2%

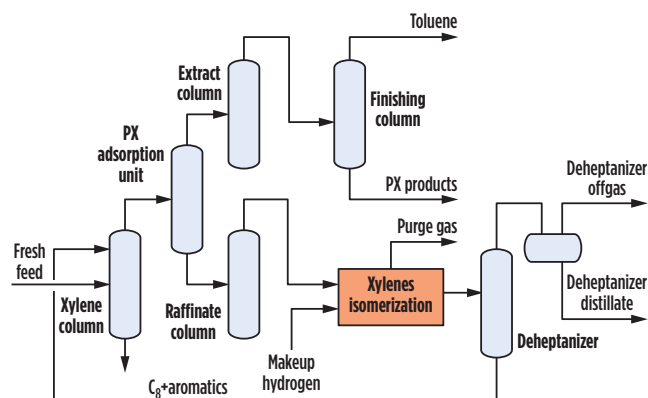
\* All data are provided in relative % value = [(New VPI process - Prior process) ÷ Prior process] × 100

Chiba, Japan in August 2017, using a proprietary<sup>a</sup> VPI process. **FIG. 6** shows the process flow scheme at the facility in Chiba.

Reducing xylene loss was one of the main drivers for a VPI process upgrade at the facility in Chiba. Idemitsu Kosan and ExxonMobil technical teams collaborated for months to evaluate the impact of the planned retrofit on the VPI unit performance under different situations (aromatics complex changes triggering variations in feed composition, turndown operation, high throughput operation, etc.) and the associated consequences on plant production. Existing pilot and commercial data were thoroughly analyzed, and new pilot studies were carried out where available data were not sufficiently close to the scenarios under assessment. Catalyst loading took place in July 2017, and alignment between technical teams on startup and initial operating procedures was gained prior to oil-in.

The new catalytic system is entirely compatible with Idemitsu Kosan's existing facilities in Chiba. No issues have been identified with respect to operating constraints or feed specifications. Furthermore, no plant requirements (such as non-aromatics destruction in the VPI unit or benzene purity from the isomerization process) have been negatively impacted by the catalyst changeout. The obtained benefits are listed in **TABLE 1** and detailed in the following section:

- **Increased EB conversion per pass.** The VPI unit operates at 8% relative higher EB conversion per pass vs. prior to catalyst changeout, which represents a capacity debottleneck of 0.3% for the adsorption unit. Alternatively, the adsorption unit can operate at a lower rate for the same PX output. The potential energy gain associated with a lower-rate operation has not been estimated.
- **Reduced xylene loss.** Relative xylene loss reduction per pass vs. prior operation amounts to 19%, resulting in incremental PX production. Due to declining domestic demand for oil products in Japan, maximizing the production of chemicals with higher added value is essential.
- **Lower operating temperature.** Reactor inlet temperature under operation has been reduced by 2%. The energy gain associated with reactor inlet temperature operation has not been estimated.
- **Increased non-aromatics conversion per pass.** The VPI unit operates at 80% relative higher non-aromatics conversion per pass vs. prior to catalyst changeout, a significant increase that results in reduced non-aromatics

**FIG. 6.** Schematic representation of IKC's xylene loop at the aromatics complex in Chiba, Japan.

traffic in the xylene loop and associated lower energy consumption at constant PX production.

- **Additional PX production.** The combination of lower xylene loss per pass in the loop at constant fresh feedrate and the opportunity to bring additional fresh feed due to operations improvements (higher EB conversion, higher non-aromatics conversion per pass) result in an overall potential additional PX production of 2%, which is significant, from an aromatics complex perspective, for a catalyst replacement that required no hardware addition or modification.
- **Enhanced operating flexibility.** Due to the high stability of the catalytic process in use, the Chiba plant has the flexibility to operate at higher-severity/EB and non-aromatics conversion per pass, or to operate at higher rates without significantly impacting the catalyst aging rate or expected cycle length.
- **Continued effort for unit operation improvement.** While the unit has been in operation for almost 1 yr, technical teams at Idemitsu Kosan and ExxonMobil continue to collaborate to optimize unit production, minimize utilities consumption, and address plant changes and associated technical queries. **HP**

#### NOTES

<sup>a</sup> Refers to ExxonMobil Catalysts and Licensing's vapor phase isomerization technology

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