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A new liquid-phase isomerization process for xylene loop debottleneck and energy savings

In a typical xylene loop, C_8 aromatics are fractionated out of a heavy reformate C_8+ aromatics stream and collected in the xylene column overhead. Then, paraxylene (PX) from the C_8 aromatics stream is recovered as product—usually by an adsorption or crystallization process—in the PX recovery section. The remaining PX-depleted C_8 aromatics stream is processed in a vapor phase isomerization (VPI) unit, where ethylbenzene (EB) is converted to benzene and PX-depleted xylenes are isomerized to equilibrium xylenes. VPI invariably yields traces of C_9 and C_{10} aromatics due to undesirable side reactions—hence, the VPI C_8+ aromatics effluent is returned to the xylene column for fractionation. C_8 aromatics loop circulation continues until all xylenes are converted to and recovered as PX. The process energy consumption is significant.¹ Four phase changes occur in the xylene loop, as illustrated in FIG. 1. These changes include:

1. C_8 aromatics from the C_8+ aromatics stream are vaporized in the xylene column, while C_9+ aromatics are collected as liquid in the xylene column bottoms.
2. C_8 aromatics are then condensed prior to PX separation, because the PX separation process—adsorption or crystallization—requires a liquid feed.
3. PX-depleted C_8 aromatics from the PX separation raffinate are vaporized, since xylene isomerization/EB conversion to benzene occurs in the gas phase.
4. C_8 aromatics isomerate is condensed in the deheptanizer bottoms downstream of the VPI unit, while benzene (from EB conversion) and trace toluene (from side reactions) are collected in the deheptanizer overhead.

PX separated from the C_8 aromatics stream in the PX recovery section represents approximately 20 wt% of the total inlet stream,² meaning that most hydrocarbons entering the xylene loop will undergo the four phase transformations shown in FIG. 1, making PX production via xylene loop a highly energy-intensive process.

Liquid phase isomerization. Research efforts in liquid phase isomerization (LPI) span several decades,^{3,4,5,6} with the primary objective of reducing xylene loop energy consumption. The main challenges are the following:

- Selective EB conversion is difficult to achieve in the liquid phase. Furthermore, EB conversion to benzene would require benzene post fractionation, while the objective is to route the LPI effluent directly to the xylene column

without any reboiling step.

This means that LPI must be operated in addition to a VPI unit—rather than instead of this unit—to avoid EB accumulation in the xylene loop.

- While EB conversion to benzene takes place in a VPI unit (FIG. 2), side reactions leading to benzene or toluene formation in the LPI process must be minimized for the LPI effluent to meet the feed specifications of the PX separation process, thereby allowing for its direct routing to the xylene column.
- PX selectivity must be close to that obtained with VPI processes—meaning that equilibrium PX at a given process temperature must be obtained—to maintain similar PX concentration in the C_8 aromatics stream feeding the PX recovery section.
- Gas formation in the LPI process (e.g., by non-aromatics cracking reactions) must be minimized, and any trace light gas make must be vented out through the existing xylene loop fractionation system.⁷
- LPI catalyst changeouts must be compatible with the requirements of modern aromatics complexes, meaning that cycles of 5 yr–6 yr aligned with aromatics plant turnarounds must be achievable to avoid unplanned shutdowns.

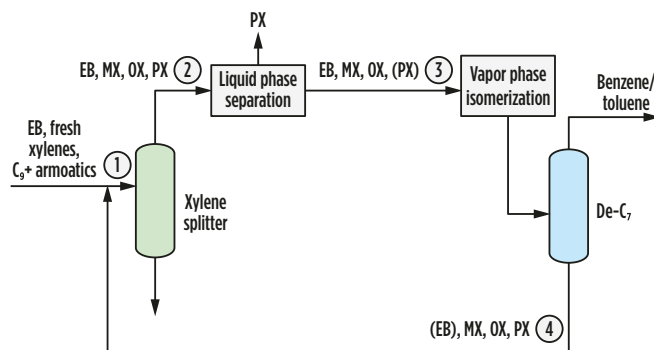


FIG. 1. C_8 aromatics undergoing four phase changes via traffic through the xylene loop.

Commercialization of a new liquid phase xylene isomerization process.

A liquid phase xylene isomerization process using ZSM-5 catalyst was commercially available in the 1980s,⁷ requiring frequent unit shutdowns for catalyst regeneration. Owing to short cycles and an inability to convert EB, this and other liquid processes were progressively phased out and replaced with vapor phase processes. However, a new LPI process^a has been commercially operated since 2015, meeting all the requirements listed above, namely:

- Negligible light aromatics make allows LPI effluent to be routed directly to the xylene column.
- Equilibrium PX is obtained at process operating temperature.
- Gas make is extremely low and manageable through available hardware when the LPI process is added to an existing facility.
- Catalyst cycles are compatible with modern aromatics complexes' turnaround requirements.

Furthermore:

- The addition of the LPI process to an existing or grassroots facility can be achieved at minimum cost. The process implementation requires a vessel, a heat exchanger, a feed heater (usually a hot oil or high-pressure steam heater) and a pump. Moreover, the low-temperature process can be conveniently retrofitted in a carbon steel vessel, such as a spare clay treater.
- Xylene losses per pass are extremely low—significantly lower than the xylene losses per pass reported in any commercial VPI process.
- Energy savings are not only achieved through the bypass of two-phase transformation steps in the xylene loop, but also because the LPI process operates at a much lower temperature than the VPI process; furthermore, reduced

traffic also means a lower energy requirement for the VPI process.

- When the LPI process is operated at certain conditions or with a PX recovery unit with less stringent C_9/C_{10} aromatics specifications than the typical adsorption processes, then part or all of the LPI process effluent may even bypass the xylene column (see dashed line in **FIG. 2**).
- When combined with a xylene production process yielding little to no EB (such as toluene methylation⁸, toluene disproportionation or aromatics transalkylation⁹), xylene isomerization can be achieved via the LPI process only; therefore, there is no need for a VPI unit to operate in parallel in the same xylene loop.

Case Study 1: Commercial deployment at Reliance Industries Ltd.'s (RIL's) Jamnagar, India facility.

RIL started utilizing the new LPI process at its Jamnagar facility in April 2018. The flow scheme is shown in **FIG. 3**. An increase in PX recovery was the main driver for the addition of an LPI process unit at this plant in Asia. RIL and the LPI process technical teams evaluated yields and impact on the existing complex, considering three potentially available vessels at different sets of operating conditions. Finally, RIL decided to retrofit the LPI process in a former feed treater. The project was implemented within a few months. Catalyst loading took place in March 2018, and alignment between technical teams on startup and initial target performance was gained prior to oil-in.

The LPI process was entirely compatible with RIL's existing facilities. No issues were identified after several months on stream. RIL's target PX recovery increase has been successfully achieved, as shown in **TABLE 1**. The following benefits were noted:

- **PX recovery increase.** The addition of the LPI unit resulted in a substantial PX concentration rise in the feed to the PX separation unit, which consequently increased PX recovery by more than 15% when isomerization feed was processed through both the VPI and LPI units vs. the base case through the VPI unit only. This represents a substantial PX production increase for RIL's Jamnagar facility.
- **Reduced xylene loss.** Processing a portion of the C_8 aromatics stream through the LPI unit resulted in lower xylene loss per pass vs. processing all C_8 aromatics through the VPI unit. While xylene loss reactions primarily produce toluene, C_9 and C_{10} aromatics, which can be recombined in a transalkylation unit to yield benzene and xylenes, recirculating these molecules through various fractionation steps adds significant energy consumption—thus, energy savings are associated with the lower xylene loss per pass inherent to the LPI process.
- **Lower operating temperature.** Reactor inlet temperature for the LPI process is substantially lower than the reactor inlet temperature for the VPI process. This represents an additional energy gain vs. processing the entire C_8 aromatics stream through the VPI unit.

Case Study 2: Commercial deployment at ExxonMobil Chemical's Rotterdam facility.

ExxonMobil Chemical Holland (EMCH) started operating the LPI process at its facility in Rotterdam, Netherlands in January 2015. The facility's process flow scheme is shown in **FIG. 4**. Energy consumption reduction was the primary goal for the addition of the LPI unit in Rotterdam. As illus-

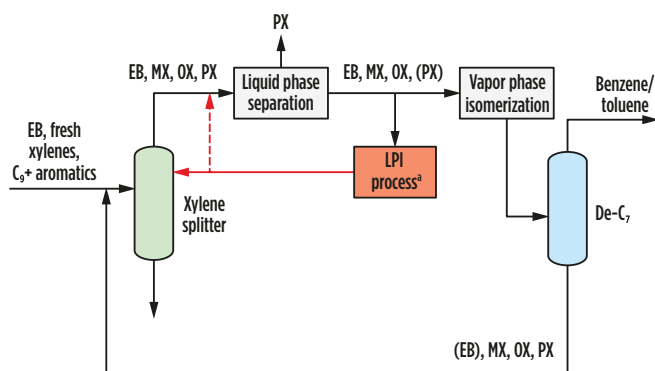


FIG. 2. LPI in parallel with the VPI process.

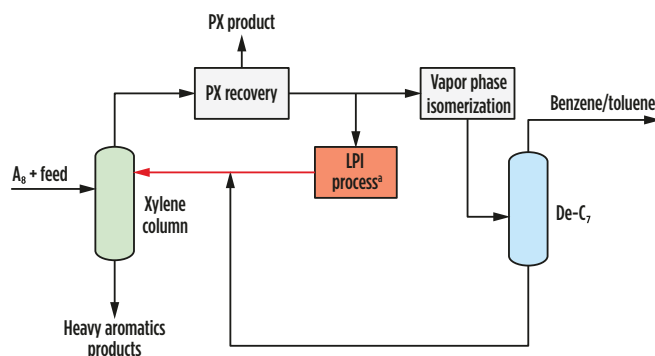


FIG. 3. Schematic representation of the LPI process addition in the Jamnagar aromatics complex.

trated in **FIG. 4**, the PX-depleted C₈ aromatics raffinate from the adsorption unit is routed through the VPI and LPI processes operating in series. Equilibrium xylenes effluent from the VPI process moves through a PX recovery step by crystallization, and the PX-depleted crystallizer filtrate is re-isomerized via the LPI process prior to PX recovery by adsorption. The resulting benefits are listed in **TABLE 2**. These benefits included:

- **Xylene loop energy consumption.** Prior to the LPI process deployment, crystallizer filtrate with low PX content would mix with fresh mixed xylenes. This reduced the overall PX concentration in the feed to the adsorption unit. Following the addition of the LPI unit, equilibrium xylenes are combined with fresh mixed xylenes in the adsorption unit feed, thereby considerably reducing traffic in the adsorption unit and overall xylene loop at constant PX production. This results in a very significant reduction in energy consumption of 9% for the overall loop operation. Such energy savings were sufficient to justify the LPI process implementation, not taking into consideration additional benefits.
- **Feed consumption.** Xylenes are isomerized in the LPI process at extremely low xylene loss per pass (0.2 wt%, see **FIG. 5**). Furthermore, higher PX concentration in the feed to the adsorption unit means reduced traffic—and, therefore, lower xylene loss—in the VPI process. These combined improvements yield a 4% feed consumption reduction for the Rotterdam site at constant PX production.
- **Xylene loop debottleneck.** Although not initially taken advantage of, the LPI unit addition allows for future PX production increases at the Rotterdam facility.

Case Study 3: Commercial deployment at ExxonMobil Chemical Asia-Pacific’s (EMCAP’s) facility in Singapore. In June 2017, EMCAP started operating the LPI process at its facility in Singapore. **FIG. 6** shows the process flow scheme at the Singapore facility. A reduction in energy consumption was the primary goal for the addition of an LPI unit in Singapore. The existing PX-depleted C₈ aromatics stream had to be routed through the VPI and LPI units operating in parallel. Process simulations were used to assess the split between the VPI and LPI, and to evaluate the impact on the overall complex operation. The following factors were optimized:

- Higher EB conversion per pass in the VPI unit, which was required to avoid EB accumulation in the xylene loop, but

TABLE 1. PX recovery increase achieved by adding the LPI process at RIL’s facility

Parameter	VPI at the design complex’s feedrate	VPI + LPI at the design complex’s feedrate
PX recovery	Base	Base + > 15%

TABLE 2. Benefits achieved by the LPI process implementation at EMCH’s facility in Rotterdam

Parameter	VPI only in operation	VPI + LPI operating in series
Xylene loop energy consumption at constant PX production	Base	-9%
Feed consumption at constant PX production	Base	-4%

which directionally increased operating temperature and xylene loss per pass in the VPI unit

- Reduced traffic in the VPI unit, as a result of the stream being partly diverted to the LPI unit, and directionally lowering operating temperature and xylene loss per pass in the VPI unit
- The LPI operating conditions minimizing benzene and toluene formation to allow LPI effluent to be routed to the xylene column.

The LPI process implementation design allowed the split of the C₈ aromatics stream, with 50% to the VPI unit and 50% to the LPI unit, while adjusting respective operating conditions to achieve the energy savings target and to maintain and/or increase PX production. The resulting benefits are listed in **TABLE 3**. These benefits included:

- **Xylene loop energy consumption.** The bypass of loop energy-intensive steps, processing of xylenes through the low-temperature LPI process and reduced traffic through the high-temperature VPI process resulted in a significant reduction in energy consumption of 10% at constant PX production. These energy savings alone justified the implementation

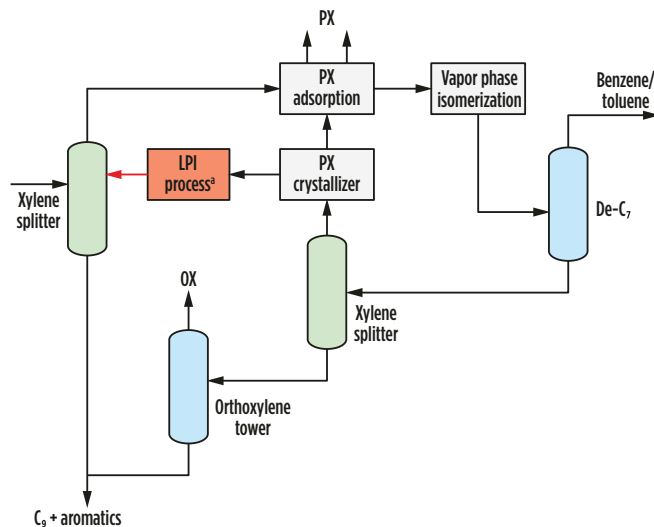


FIG. 4. Schematic representation of the liquid phase isomerization process addition at EMCH’s aromatics complex in Rotterdam, Netherlands.

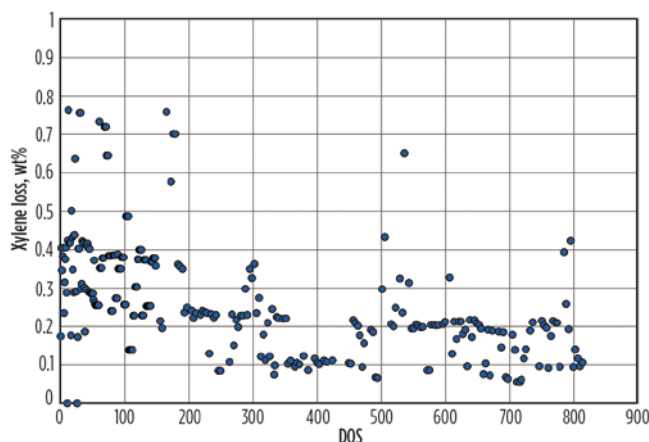


FIG. 5. An extremely low xylene loss level was achieved in EMCH’s liquid phase isomerization unit in Rotterdam.

of the LPI process.

- **Reduced xylene loss.** Diverting part of the C₈ aromatics stream through the LPI unit resulted in lower xylene loss per pass (relative 25%) vs. processing the full C₈ aromatics stream through the VPI unit. For EMCAP's site, this resulted in a reduced fresh aromatics complex feed rate by 1.5%–2% at constant PX production.
- **Xylene loop debottleneck.** Although not initially taken advantage of, the LPI unit addition allows for future PX production increases at the Singapore facility.^{1P}

TABLE 3. Benefits achieved by adding the LPI process at EMCAP's facility in Singapore

Parameter	VPI only in operation	VPI + LPI operating in parallel
Xylene loop energy consumption	Base	-10%
Xylene loss per pass	Base	-25%

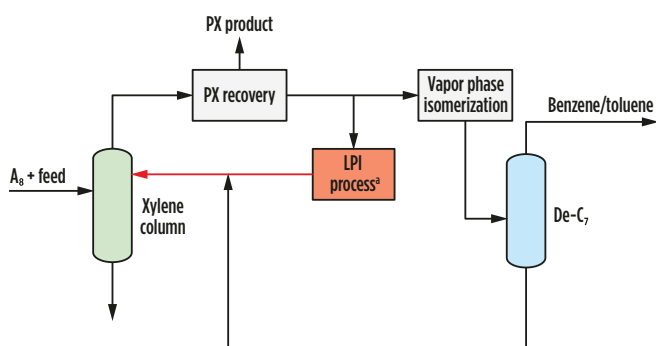


FIG. 6. Schematic representation of the liquid phase isomerization process addition at the aromatics complex in Singapore.

NOTES

^{1P} Refers to ExxonMobil Chemical's Liquid Phase Xylene Isomerization process

LITERATURE CITED

¹ Sakaguchi, T. and M. Molinier, "Maximizing existing xylene loop profitability," *Hydrocarbon Processing*, January 2019.
² Bambal, A. S., G. B. Kuzmanich and P. C. Whitchurch, US2017/0297977, "Liquid phase xylene isomerization in the absence of hydrogen," 2017.
³ Sen Sarma, P. K. and S. Bhatia, "Liquid phase xylene isomerization over nickel hydrogen mordenite catalyst," *Zeolites*, 1987.
⁴ Amelse, J. A., J. A. Donohue, N. A. Kutz, J. B. Melville and B. L. Slusar, US4962258, "Liquid-phase xylene isomerization," 1990.
⁵ Gonçalves, J. C. and A. E. Rodrigues, "Xylene isomerization in the liquid phase using large-pore zeolites," *Chemical Engineering & Technology*, 2016.
⁶ Shi, Q., J. C. Gonçalves, A. F. P. Ferreira, M. G. Plaza and A. E. Rodrigues, "Xylene

isomerization over beta zeolites in liquid phase," *Industrial & Engineering Chemistry Research*, 2018.

⁷ Molinier, M., J. S. Abichandani, J. L. Andrews, T. P. Bender, R. G. Tinger, D. J. Stanley and G. J. Wagner, US9302953, "Process for the production of xylenes," 2016.
⁸ Chauvel, A. and G. Lefebvre, *Petrochemical Processes—Technical and Economic Characteristics*, Institut Français du Pétrole Publications, 1989.
⁹ Tsai, T. C., S. B. Liu and I. Wang, "Disproportionation and transalkylation of alkyl-benzenes over zeolite catalysts," *Applied Catalysis A: General*, Elsevier, 1999.



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