

# HYDROCARBON PROCESSING®

## OPTIMIZATION

ADVANCING PROCESSING TECHNOLOGIES,  
OPERATIONS AND SUSTAINABILITY

Analyzing the latest  
CO<sub>2</sub> capture technologies

Catalyst case studies: Improving  
operations and profitability

How can the petrochemical industry  
compete for global talent?

G. LIU, Tianjin Dagu Chemical Co., Ltd.,  
Tianjin, China; R. SUNDARARAMAN,  
ExxonMobil Chemical Co., Spring, Texas; and J. CAO,  
ExxonMobil Catalysts and Licensing, Spring, Texas

## Ethylbenzene plant debottleneck with a high-activity transalkylation catalyst

Modern commercial ethylbenzene (EB) plants use liquid-phase alkylation processes with zeolite catalysts to achieve high product yields. The desired primary reaction is the alkylation of benzene with ethylene. However, successive undesired reactions also occur in the alkylator, producing polyalkylated compounds such as diethylbenzene (DEB) and triethylbenzene (TEB). To maximize EB yield, these polyethylbenzenes (PEBs) are separated in the fractionation section and recycled into a transalkylation reactor in which the ethyl groups are transferred onto the benzene ring to produce additional ethylbenzene. FIG. 1 shows the schematic of the alkylation reactions and the transalkylation reactions in EB production.

At the heart of the technology is the shape-selective MWW family of zeolite catalysts that enables EB production in high purity and yields. The MCM family of alkylation zeolite catalysts revolutionized EB production. Tailored to the molecular diffusion rate of the different reactants, the MWW family zeolite pocket structure is designed to achieve high selectivity to EB. This high-activity catalyst enables the process to be operated in liquid phase at low temperatures, which dramatically lowers capital expenditures and operational expenditures (OPEX). This proprietary EB alkylation process<sup>a</sup> was first commercialized at the Chiba Styrene Monomer Co., Chiba, Japan, in 1995.<sup>1-3</sup>

The MCM family of zeolite catalysts is more EB or monoalkylate selective than large-pore zeolites, including zeolites beta and Y.<sup>3</sup> This enables the process to use low feed ratios of benzene to ethylene. The lower benzene-to-ethylene (B/E)

ratio reduces the benzene circulation rate, which, in turn, improves operational efficiency and reduces the throughput to the benzene recovery column.<sup>4</sup> The monoalkylating selectivity to EB is measured by the once-through production rate of PEB, which decreases with the increase of the B/E ratio (FIG. 2).

The transalkylation reactor in the proprietary EB alkylation process is designed to match the alkylation reactor performance. Because of the high mono-selectivity of the alkylation catalyst, the production rate of PEB in the alkylator

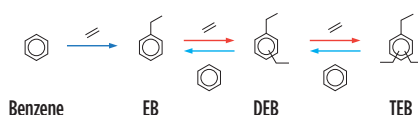


FIG. 1. EB production via alkylation and transalkylation reactions.

is small. Therefore, the size of a transalkylator in the EB alkylation process tends to be small. At a constant EB production rate, the amount of activity of transalkylation catalyst required to maximize the PEB conversion, while minimizing the low-value heavy residue purge, is determined by the amount of PEB pro-

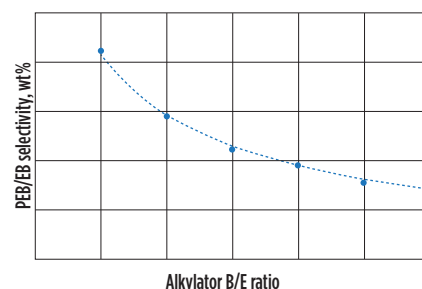


FIG. 2. Impact of B/E ratio on catalyst selectivity.

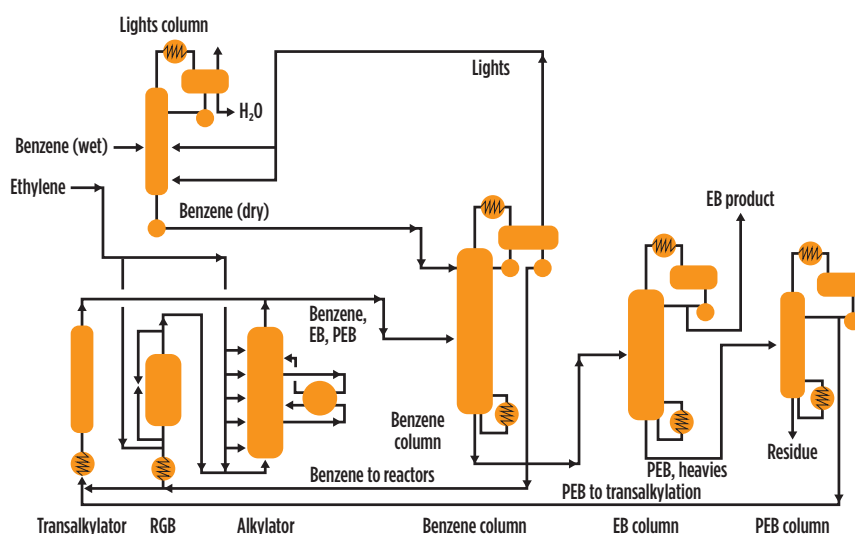


FIG. 3. Process flow scheme of the proprietary EB alkylation process<sup>a</sup> at TDCC's facility.

duced in the alkylator. Increasing the EB production rate will directionally lead to high PEB production, which increases the weight hourly space velocity (WHSV) of the transalkylator. To maintain constant conversion to reduce PEB recycle, the reactor temperature must be increased. However, high-temperature operation results in higher heavies yield and fast catalyst deactivation.

The other mitigation steps include increasing the B/E ratio in the alkylator operation. As shown in FIG. 2, the selectivity to PEB decreases with the increase of B/E. However, high B/E operation increases benzene recycle and results in high energy consumption. In such a case when the operation flexibility in the alkylation section is limited, the transalkylator becomes a bottleneck in the EB process unit. Therefore, a higher-activity transalkylation catalyst is required to convert more PEB

at increased EB production rates, while minimizing residue production.

**Overview of Tianjin Dagu Chemical Co.'s EB alkylation operation and constraints.** Tianjin Dagu Chemical Co.'s (TDCC's) EB alkylation<sup>a</sup> unit was first commissioned in January 2010 with a production rate of 500,000 metric tpy of styrene monomer. The unit was originally designed to use a proprietary catalyst<sup>b</sup> in the reactor guard bed (RGB) and six-bed alkylator, along with a proprietary transalkylation catalyst<sup>c</sup> in the transalkylator. FIG. 3 shows the process flow scheme of the proprietary EB alkylation process at TDCC's facility.

During the booming period of the styrene market, TDCC's primary objective was to increase the plant's capacity. TDCC and the co-authors' companies' technical teams collaborated for months to evalu-

ate the proprietary EB alkylation performance and identify the bottleneck in the transalkylation section at increased capacity. It was found that the unit was unable to maintain the designed PEB conversion at design temperature and WHSV when higher PEB was made in the alkylator; therefore, the operation needed to increase the reactor temperature, which inevitably led to high heavies yield and catalyst aging.

Plant operation optimization was attempted to achieve a high EB production rate while minimizing residue purge. While the results showed improvement, they did not meet TDCC's operational expectations (i.e., high production rate and low residue make at low OPEX). Measures were then taken that included increasing the alkylation section's B/E ratio. The increased B/E ratio did reduce PEB yield, but resulted in high OPEX due to high benzene recirculation. As a second option, TDCC reluctantly shut down the unit temporarily to load additional proprietary transalkylation catalyst<sup>c</sup> in the remaining limited space of the reactor. Unfortunately, the additional catalyst was still unable to bring adequate activity for the required PEB conversion. Eventually, there were essentially two remaining options:

1. Invest in a new larger reactor to load more catalyst
2. Deploy a higher-activity transalkylation catalyst.

Option 1 was not economical in terms of capital and schedule. To support TDCC's objective to increase EB production, and to enable increased plant capacity and address the transalkylation section bottleneck, the technical teams started an accelerated catalyst development program to identify a higher-activity transalkylation catalyst for potential deployment at TDCC.

**High-activity transalkylation catalyst development: Pilot plant experience.**

With an extensive catalog of active materials, the technical teams quickly identified 10 catalysts with varying zeolite types, compositions and treatment methods to address TDCC's constraints. These materials were screened in a lab-scale batch reactor with commercially representative feed specifications and conditions. A normalized catalyst activity plot from this testing (FIG. 4) illustrates that six out of the 10 catalysts tested showed two times the activity vs. the proprietary transalkylation

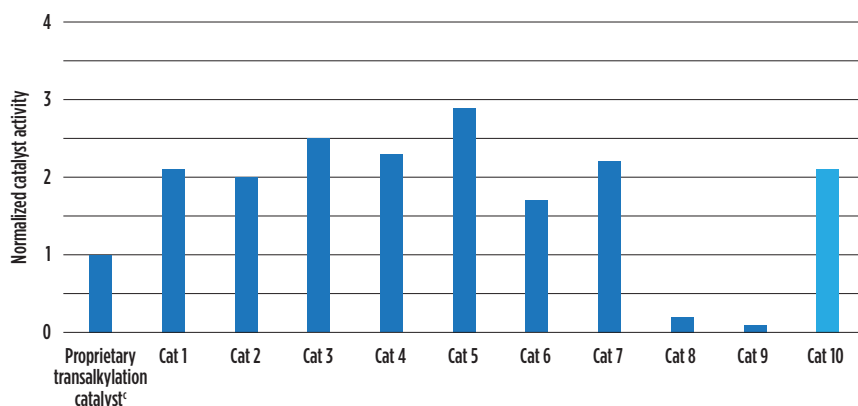


FIG. 4. Catalyst screening for a higher-activity transalkylation catalyst.

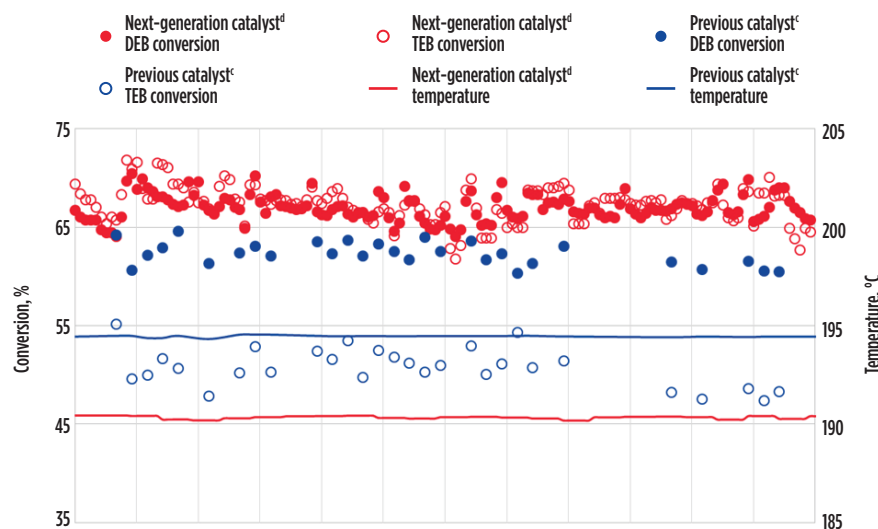


FIG. 5. Next-generation transalkylation catalyst<sup>d</sup> (2017 cycle) vs. the previous catalyst<sup>c</sup> (2013 cycle) at a PEB WHSV of 1.2 h<sup>-1</sup>.

catalyst<sup>c</sup>. In addition to being two times more active than the proprietary transalkylation catalyst, Cat 10 was selected for further testing and qualification, since it had the shortest lead time for commercial manufacturing, which would enable faster deployment to TDCC.

The selected catalyst from this lab testing was designated as the next-generation, higher-activity transalkylation catalyst<sup>d</sup>. For detailed product yields, pilot plant testing of the next-generation transalkylation catalyst<sup>d</sup> and its predecessor<sup>c</sup> were conducted using a commercial PEB recycle feed and conditions that would best simulate TDCC conditions. Data obtained showed the next-generation transalkylation catalyst to be 15°C more active vs. its predecessor under similar DEB conversion. If operated at the same temperature, the next-generation transalkylation catalyst showed significantly higher DEB conversion vs. its predecessor. The results of the pilot plant testing are shown in **TABLE 1**.

The combination of lab and pilot plant testing data showed that the next-generation transalkylation catalyst could overcome TDCC bottlenecks in the transalkylation section.

constraints or feed specifications.

TDCC eventually became the first adopter of the novel, high-activity transalkylation catalyst. Catalyst loading took place in May 2017, and alignment between technical teams on startup and initial operating procedures was gained prior to oil-in. The plots in **FIG. 5** show the start of cycle performance of the next-generation transalkylation catalyst (2017 cycle) and its predecessor (2013 cycle) under similar PEB WHSV of 1.2 h<sup>-1</sup> for both cycles.

The performance of the next-generation catalyst for transalkylation to EB showed significantly better performance over the previously used catalyst under similar conditions at TDCC. As shown in **FIG. 5**, the next-generation transalkylation catalyst had a 3°C lower reactor temperature vs. the previously used catalyst. The next-generation catalyst also had a higher average DEB conversion of 67% vs. 62%. At the start of cycle-fresh catalyst conditions, TEB conversion averaged 67% for the new catalyst vs. 51% for the previously used one. This start-of-run benefit of lower cycle temperature and higher conversion is consistent with the pilot plant data shown in **TABLE 1**, demonstrating the high-

in the transalkylation section, resulting in up to a 9% increase in EB production vs. the previous cycle. At the time of the publication of this article, the next-generation transalkylation catalyst load has been on stream for nearly 4 yr. The new catalyst has shown exceptional stability, with a very low aging rate, and it continues to meet TDCC's expectations.

**Takeaway.** Rapid deployment of a next-generation, high-activity transalkylation catalyst<sup>d</sup> has provided TDCC a fit-for-purpose technology solution for debottlenecking its EB transalkylation plant. The site was able to achieve 109% of design capacity to allow market value capture of \$5.5 MM/yr. The novel transalkylation catalyst presents higher activity than its prior version. With the same load size, higher single-pass PEB conversion was achieved at a lower reactor temperature. The next-generation transalkylation catalyst has been in stable operation—with negligible aging—at TDCC's facility since May 2017.

Overall, the high-activity transalkylation catalyst provides operating flexibility to achieve the following benefits:

**TABLE 1.** Pilot plant testing of the next-generation transalkylation catalyst vs. its predecessor

Catalyst	Target DEB conversion		Target temperature	
	Transalkylation catalyst <sup>c</sup>	Next-generation transalkylation catalyst <sup>d</sup>	Transalkylation catalyst <sup>c</sup>	Next-generation transalkylation catalyst <sup>d</sup>
Bz/PEB wt ratio	2	2	2	2
PEB WHSV, h <sup>-1</sup>	1.1	1.1	1.1	1.1
Temperature, °C	194	177	190	190
DEB conversion	65%	65%	60%	72%
TEB conversion	56%	60%	42%	83%
Heavies/EB, wt/wt	0.59%	0.62%	0.63%	0.85%

### High-activity transalkylation catalyst deployment: Commercial experience.

TDCC technical and management teams and the co-authors' company evaluated the impact of the drop-in, next-generation transalkylation catalyst upgrade on the proprietary EB alkylation process<sup>a</sup> unit's performance and associated risks. Based on lab and pilot plant data, risk matrix and mitigation steps were developed. The new catalyst was fully compatible with TDCC's existing EB alkylation facilities. No issues were identified with respect to operating

er activity of the next-generation transalkylation catalyst. More importantly, with the change in transalkylation catalyst to the higher-activity catalyst, TDCC did not see additional residue make from the plant.

TDCC's primary objective was to increase plant capacity to capture the booming styrene market. The higher activity of the next-generation transalkylation catalyst enabled TDCC to meet this objective. As shown in **FIG. 6**, higher PEB conversion with the new catalyst cycle enabled TDCC to overcome the bottleneck

- Debottleneck a transalkylation/PEB loop to achieve higher overall unit capacity
- Lower PEB recycle to save PEB loop energy consumption
- Lower start-of-run temperature slows catalyst aging rate, providing a larger operating temperature window and increasing the cycle length
- Low-temperature operation reduces heavies production to minimize fuel value downgrading

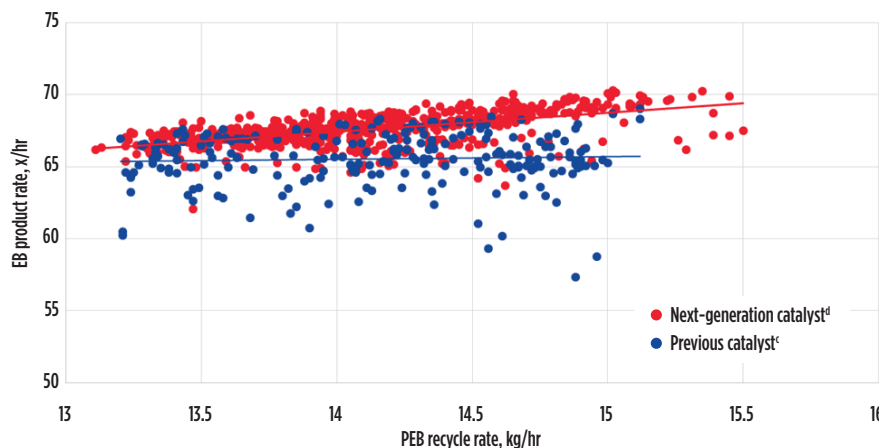


FIG. 6. EB production rate vs. PEB recycle rate: Next-generation transalkylation catalyst<sup>d</sup> and the previously used catalyst<sup>c</sup>.

- Lower initial catalyst fill cost, with reduced load size for constant unit capacity. **HP**

NOTES

- <sup>a</sup> Badger Licensing's EBMax<sup>SM</sup> technology
- <sup>b</sup> ExxonMobil's EM-3300 catalyst
- <sup>c</sup> ExxonMobil's EM-3700 transalkylation catalyst
- <sup>d</sup> ExxonMobil's EM-3750 transalkylation catalyst

LITERATURE CITED

- <sup>1</sup> Maerz, B. R., C. R. Venkat, S. S. Chen and D. N. Mazzone, "EBMax<sup>SM</sup>: Leading-edge ethylbenzene technology from Mobil/Badger," DeWitt & Co. Inc.'s 1996 Petrochemical Review, Houston, Texas, March 1996.
- <sup>2</sup> Mazzone, D. N., P. J. Lewis, C. R. Venkat and B. R. Maerz, "Mobil/Badger into the future," *Hydrocarbon Asia*, April 1997.

<sup>3</sup> Cheng, J. C., T. F. Degnan, J. S. Beck, Y. Y. Huang, M. Kalyanaraman, J. A. Kowalski, C. A. Loehr and D. N. Mazzone, "A comparison of zeolites MCM-22, beta, and usy for liquid phase alkylation of benzene with ethylene," *Studies in Surface Science and Catalysis*, Volume 121, 1999.

<sup>4</sup> Degnan Jr., T. F., C. M. Smith and C. R. Venkat, "Alkylation of aromatics with ethylene and propylene: Recent developments in commercial processes," *Applied Catalysis A: General*, November 2001.

<sup>5</sup> ExxonMobil Catalysts and Licensing LLC, Fact Sheet: "Cutting-edge catalysts for ethylbenzene production ExxonMobil zeolite catalysts: Producing the majority of the world's ethylbenzene."



**GEHONG LIU** is the General Manager of Tianjin Dagu Chemical Co. Ltd. He has been working in chemicals manufacturing for 18 yr and has extensive management experience in chloralkali chemicals and the petrochemical industry.

Mr. Liu holds six patents and has published 12 peer-reviewed technical papers. He graduated from the Wuhan Institute of Technology with a degree in chemical engineering. He obtained a post-graduate degree from Tianjin University.



**RAM SUNDARARAMAN** is a Staff Engineer with ExxonMobil Chemical Co. Dr. Sundararaman has 15 yr of experience in catalyst and refining technology development and holds several U.S. patents. He earned a PhD in fuel science from Penn State.



**JAMES CAO** is the Senior Technical Sales Manager for aromatics licensing with ExxonMobil Catalysts and Licensing LLC. He has more than 25 yr of experience in heterogeneous catalysis and its commercial applications and holds 25 U.S. patents and various international filings. Dr. Cao has been responsible for technology licensing and catalyst sales of xylenes, EB and cumene processes. He earned his MS and BS degrees in chemical engineering from Tsinghua University, and his PhD in chemical engineering from the City University of New York.

Electronic permissions to ExxonMobil from *Hydrocarbon Processing* magazine / Gulf Publishing.  
June © 2021 Gulf Publishing Company