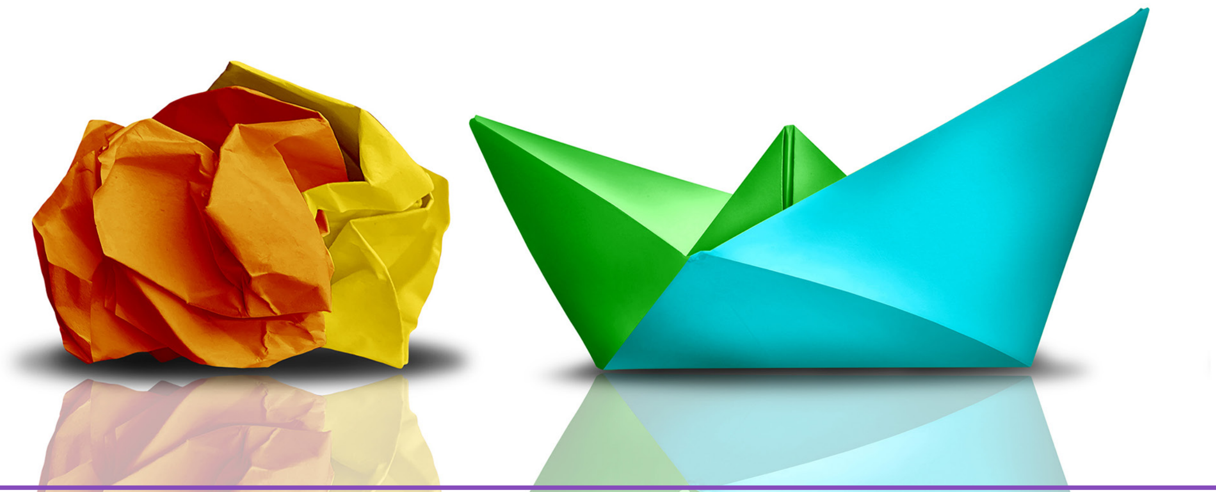
THE TRANSFORMATIONAL STRENGTH OF CATALYST TECHNOLOGY



The success of commercial fluid catalytic cracking (FCC) applications depends on the selection of catalyst technology and the close collaboration between the refiner and the catalyst supplier. A working relationship such as this involves a consistent thread between the catalyst design, targeted performance, and the testing results, in order to ensure that the ultimate catalyst technology selection is the best fit.

This article will demonstrate the increased profitability of two of Marathon Petroleum Corp. (MPC)'s FCC units, as a result of switching the BASF catalyst technologies from the maximum conversion technology, Distributed Matrix Structures (DMS), to the maximum light olefins technology, Multiple Framework Topologies (MFT).

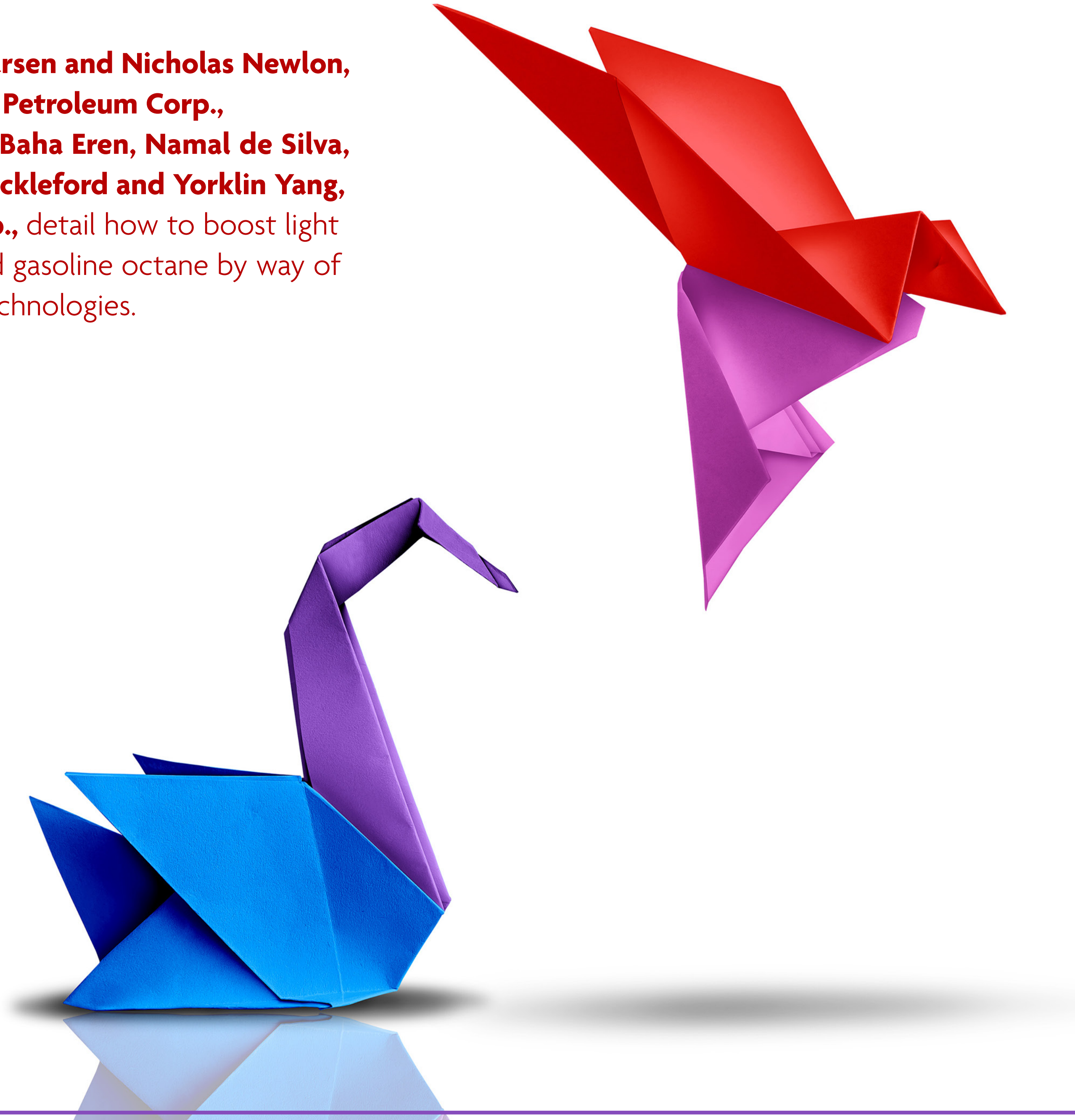
The challenge

For several years, the BASF catalyst NaphthaMax®, which is based off DMS technology, delivered value to these two FCC units in line with MPC's objective of maximising liquid volume yield of high-value products (gasoline and light olefins), while minimising low-value products such as dry gas, coke and slurry, while staying within applicable unit constraints. Unique FCC matrix structures in DMS catalysts, combined with optimised porosity, provide enhanced diffusion of heavy feed molecules, enabling the high conversion to valuable products. Today, further enhancement of butylenes and gasoline octane will boost profitability.

The traditional method of generating butylene selectivity by reducing hydride transfer via a rare-earth decrease of the ultra-stable Y zeolite (USY) was not a solution, as this also reduces the overall catalytic activity. In fact, this approach can negatively impact butylenes production as a result of lower conversion, despite the improved selectivity.

Another common method used to produce butylenes is ZSM-5 additives. The ZSM-5 zeolite is a shape-selective zeolite designed to crack light olefins into propylene and

Nikolas Larsen and Nicholas Newlon, Marathon Petroleum Corp., alongside Baha Eren, Namal de Silva, Alexis Shackleford and Yorklin Yang, BASF Corp., detail how to boost light olefins and gasoline octane by way of catalyst technologies.



butylenes. However, the use of ZSM-5 zeolite additives alone was not ideal, as it selectively produces more propylene than butylenes, thus deeming a strategy that solely involves ZSM-5 less profitable. As such, employing a new catalyst technology to deliver increased light olefins and octanes benefits, while minimising the adverse effects (such as loss of catalyst activity), was required.

The solution

BASF introduced the MFT catalyst technology to address the conventional challenges of butylene maximisation and octane enhancement in the FCC. MFT catalysts are designed by combining four key elements: multiple zeolite frameworks, active matrix, low acid site density, and higher activity. Since the commercial introduction of the first-generation MFT catalyst Fourte® in 2018, profitability improvements in numerous refineries across the globe have been observed.[1] In 2020, BASF introduced the second-generation MFT catalyst, Fourtune®, to provide enhanced butylene-to-propylene ratio attributed to the specialty zeolite framework that yields selective cracking of (predominantly gasoline range) olefins to butylenes.[2]

The MFT catalyst selection process for two MPC units (1 and 2) involved pilot plant testing, modelling, and sensitivity studies. Unit 1 runs a severely hydrotreated feed, and this process identified the economic potential of the Fourte catalyst to increase butylenes and octane. Unit 2 (which runs a mixture of hydrotreated and residue feed and adds a ZSM-5 additive) also wanted to increase butylenes and octane. Due to constraints, unit 2 also needed to further improve the butylene-to-propylene ratio, and identified Fourtune as a solution, based on economical factors. Overall, the predicted economic benefit of using Fourte for unit 1 was US$0.36/bbl, and Fourtune for unit 2 was US$0.42/bbl, showing significant profitability generation for the respective refineries.

The trials were evaluated by operating data analysis, kinetic modelling, and laboratory studies. The post-audit studies were carried out at the MPC facility by drawing equilibrium catalysts from the units during each catalyst trial at close to the full catalyst turnover in the unit. In the case of unit 2, which utilises a ZSM-5 additive, the equilibrium catalysts were selected at a time that the ZSM-5 contents were similar in both the incumbent catalyst and the MFT catalyst.

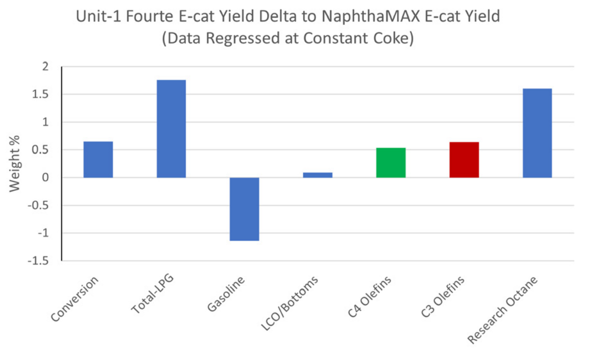


Figure 1a. DCR testing analysis comparing equilibrium catalyst, Fourte, against NaphthaMax, drawn from unit 1. Fourte produces higher C4 and C3 olefins, and higher gasoline research octane.

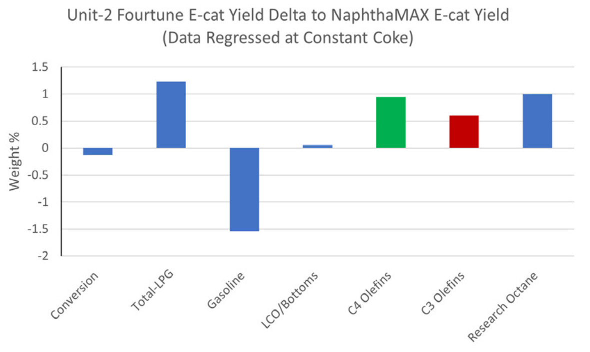


Figure 1b. DCR testing analysis comparing equilibrium catalyst, Fourtune, against NaphthaMax, drawn from unit 2. Fourtune yields higher light olefins, and increased C4=:C3= ratio, along with higher gasoline.

MPC utilises a DCR^{TM} FCC pilot unit, complemented by ACE Technology® (Advanced Cracking Evaluation Technology utilising a fixed fluidised bed micro-testing unit), along with accumulated analytical expertise. These testing capabilities are part of MPC's Refining Analytical and Development (RAD) facility located adjacent to the Catlettsburg refinery in Kentucky, US. MPC's testing philosophy is to run lab units with commercially-collected materials and adjust the pilot plant's operating parameters in a way that generates lab yields that match the commercial units. By minimising offsets between the lab and commercial units, a high degree of confidence is placed on the measured results. The testing results are used within an FCC process model (KBC's Petro-SIM®) to determine expected yields and optimised unit conditions for each catalyst candidate.

Results

MPC's post-audits yield shifts are summarised in Figures 1a and 1b. BASF's Fourte and Fourtune MFT catalysts delivered increased C4 olefins yields (the green bar), and octane benefits (the far-right blue bar) compared to the incumbent catalyst in units 1 and 2, respectively. It is important to point out that the MFT catalyst delivered the olefin and octane benefits without compromising the catalyst's activity. For unit 1, Fourtune delivered a C4= olefins increase of 0.5 vol%, and a C3 olefins increase of 0.6 vol% (coming from the gasoline decrease of 1.1 vol%), with an over 1.5 number increase in gasoline research octane. In unit 2 (which also utilises ZSM-5), Fourtune delivered almost 1 vol% more in C4= olefins, and 0.6 vol% more in propylene, along with a 1 number increase in gasoline research octane. This is a significant increase in butylene to propylene ratio.

The results obtained in pilot testing were further validated using operating data. Operational data from units 1 and 2 were gathered throughout the equilibrated period of NaphthaMax catalysts, followed by the transition to new catalysts, Fourte and Fourtune, respectively. Unit 1 operation data (Figure 2a) shows C4 olefin yield increase for Fourte compared to the incumbent catalyst. Fourte also gave a boost to the gasoline olefin pool, which was a major objective of the unit. In addition to olefin benefits, operation data shows Fourte maintaining bottoms destruction at equivalent conversion levels.

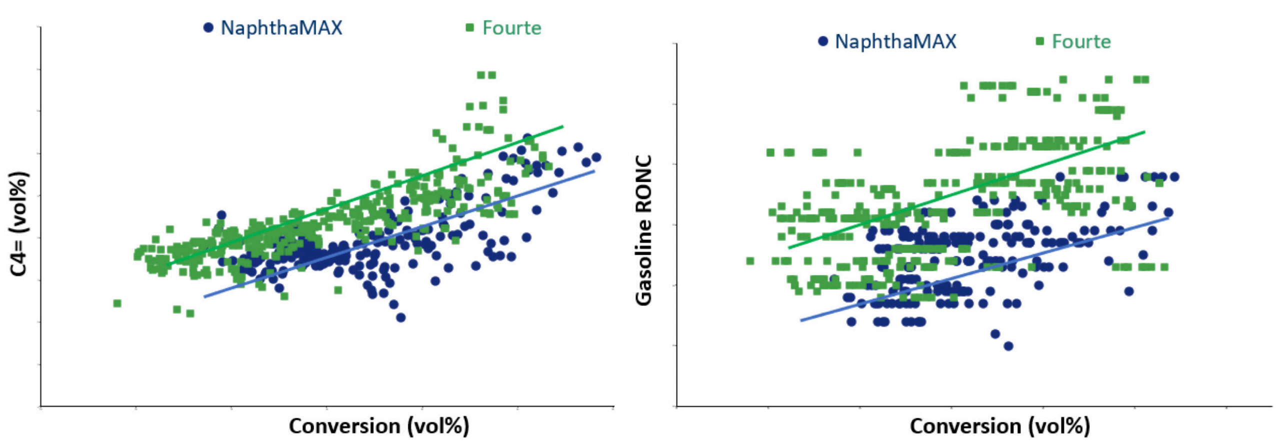


Figure 2a. Operational data analysis from unit 1 showing C4= olefins and octane advantage for Fourte.

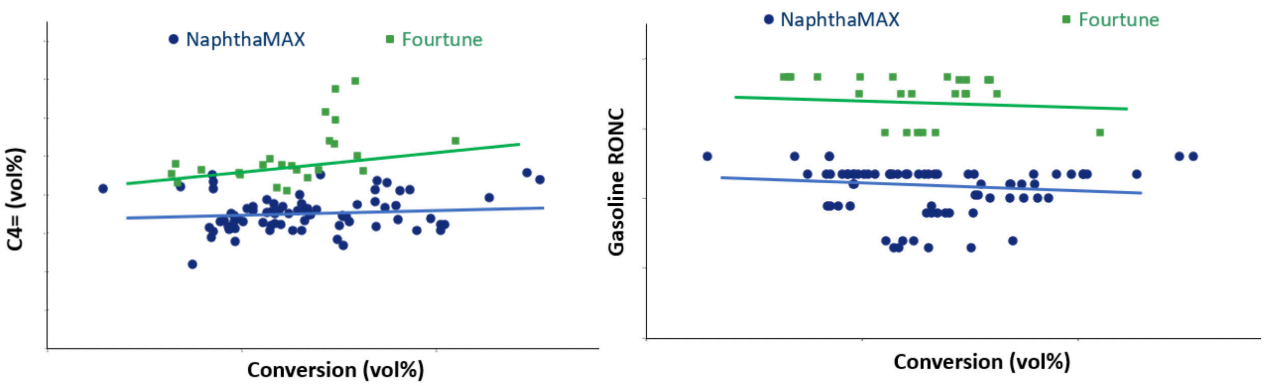


Figure 2b. Operational data analysis from unit 2 showing C4= olefins and octane advantage for Fourtune.

Table 1. Delta yield shifts based on operating data and heat-balanced modelling for units 1 and 2

Delta yield	Unit 1 (Fourte-NaphthaMax)	Unit 2 (Fourtune-NaphthaMax)
Propylene (vol%)	+ 0.7	+ 3.5
Butylene (vol%)	+ 0.2	+ 2.5
Total LPG (vol%)	+ 1.8	+ 4.1
Gasoline (vol%)	- 0.8	- 2.8
Gasoline RON	+ 0.4	+2.4

Several factors affected the analysis of catalyst performance in unit 2. When comparing the two periods of NaphthaMax and Fourtune, the unit had increased feed rate along with declining feed quality due to increased residue oil processing. Additionally, throughout the trial campaign, ZSM-5 additive was added at different times and at different concentrations, and this impacted the propylene yield and selectivity. Along with the ZSM-5 additions, this unit employed the use of flushing equilibrium catalyst. The changing properties of the flushing equilibrium catalyst, such as lower activity and varying levels of ZSM-5, meant that analysis was much more complex. By accounting for these variations, a time period was chosen where Fourtune and NaphthaMax had equally high levels of ZSM-5 in the unit for an even comparison of light olefin yields and selectivity.

Despite the complexity of data analysis, unit 2's operating data shows higher butylene and propylene yield for the Fourtune period, as seen in Figure 2b. FCC gasoline octane improves, as an increase in Research Octane Number Clear (RONC) of greater than 2 was observed. This shows that even with units that use high amounts of ZSM-5, Fourtune is able to deliver higher butylene selectivity, decreased saturates, and improved gasoline octane.

To further validate the results, kinetic modelling and statistical multiple regression analysis was carried out to evaluate the improved performance of the MFT catalysts, compared with the DMS catalysts. Table 1 summarises the kinetic model predictions of yields, which are consistent with the regression modelling results. Overall, Fourte delivered an economic improvement of US$0.55/bbl to unit 1 through the expected yield shifts. Kinetic modelling along with operational data analysis concluded that Fourtune delivered US$0.67/bbl yield benefits to unit 2.

Conclusion

In a collaborative effort, the refiner, MPC, and the catalyst vendor, BASF, demonstrated significant profitability improvement for two FCC units by switching catalyst technologies to target the latest economics. BASF's latest technology, MFT, offers improved butylenes and octane when compared against prior technologies. The two products, Fourte and Fourtune, both improve butylenes and octane, with Fourtune further improving on the butylenes-to-propylene ratio.

Based on prior competitive lab evaluations by MPC, and modelling by BASF, unit 1 selected Fourte and unit 2 selected Fourtune. The commercial trial evaluation based on operating data analysis, kinetic modelling, and lab studies demonstrated that MFT catalysts deliver increased butylene yields and octane boost, while maintaining high activity. Overall, kinetic modelling results showed unit profitability improvements of US$0.55/bbl and US$0.67/bbl by Fourte and Fourtune catalysts, respectively. HE

References

1. LARSEN, N., CLARK, T., CLOUGH MASTRY, M., and DE SILVA, N., 'Boosting profitability with butylenes', *Hydrocarbon Engineering*, (June 2020), pp. 43 - 46.
2. LARSEN, N., CLARK, T., DE SILVA, N., YANG, Y., and NEUMAN, D., 'Boosting profitability with butylenes to propylene ratio', *Hydrocarbon Engineering*, (September 2020). pp. 53 - 58.

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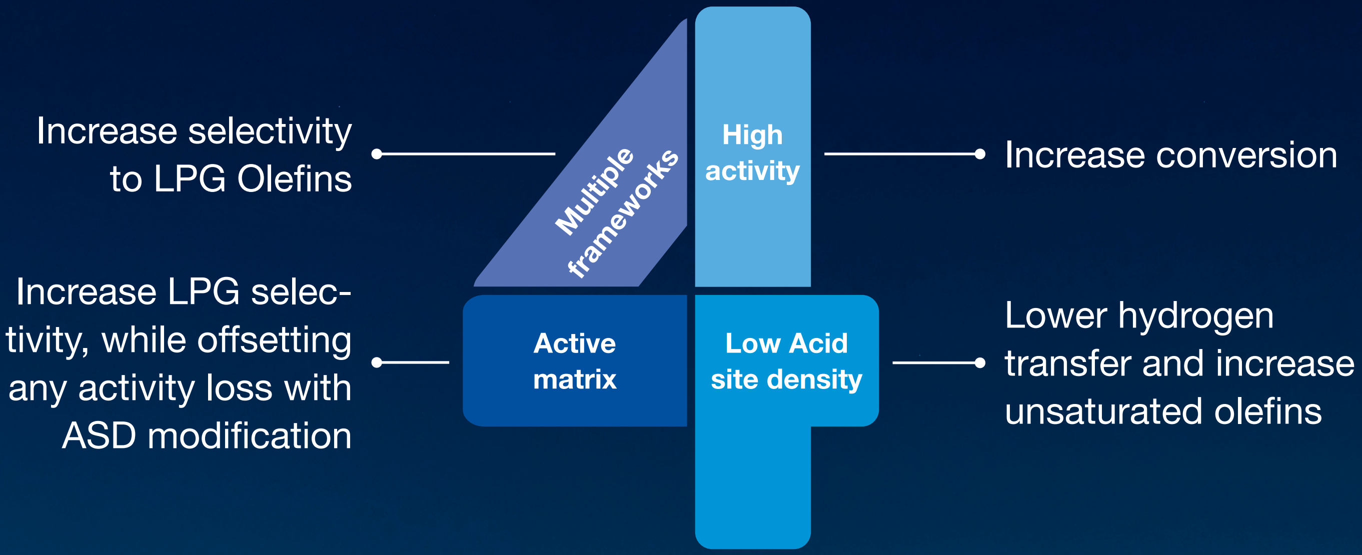

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