MAXIMISING VALUE WITH C5 OLEFINS

Nikolas Larsen and Nicholas Newlon, Marathon Petroleum Corp., alongside Namal de Silva, Daniel Neuman, Yorklin Yang and Brian Killeen, BASF Corp., detail the companies' collaborative investigation to demonstrate that C5 olefin maximisation can be delivered through FCC catalysts.

C5 olefins pose an interesting challenge for refiners in North America.[1] Ever since methyl tert-butyl ether (MTBE) was banned from use in gasoline blending in the early years of the millennium, refiners have faced the challenge of utilising C5 olefins. The high Reid vapor pressure (RVP) of C5 olefins limits the amount that can be blended into the gasoline pool, particularly during the summer. One option for increasing the value of C5 olefins is alkylation. Existing alkylation units with feed segregation capabilities can process C5 olefins as a feedstock for alkylate production. While the quality of alkylate created from C5 olefins is not as good as that obtained from the alkylation of butylenes, the product is a significantly-improved gasoline blending component (higher octane; lower RVP) vs the feed.

C5 olefin alkylation is not without its challenges. As with the butadienes present in C4 feeds, di-olefins present in C5 olefin feeds will increase acid consumption. However, refiners with the ability to segregate C3 olefin and C5 olefin feeds in the alky unit have found increased flexibility on where to put the C5s produced in the fluid catalytic cracking (FCC), increasing the value of this stream as a result. Recently, it has been observed that C5 olefin values are in line with butylene value at refineries that have sufficient alkylation capacity and the capability to alkylate C5 olefins. As such, these refiners have significant incentives to promote C5 olefin production. Utilising an FCC catalyst that increases the ratio of butylenes-to-propylene may also show significant benefits with respect to C5 olefins production that is unlikely to be captured in current kinetic modelling data. As such, a catalyst that provides improved C5 olefin selectivity will add additional value to refineries with the capability to alkylate this stream in the summer, while still allowing for use as a gasoline blending component in the winter when RVP constraints are not as onerous.

While there are no dedicated efforts to develop C5 olefin maximisation catalysts, refiners have shown interest in employing FCC catalysts that have the upper hand of increased C5 olefin yields, in order to take advantage of local refinery economics, along with FCC and alkylation unit capacities and constraints. As a catalyst vendor, BASF has explored catalyst design to help refiners with these specific needs.

This article highlights the collaborative investigation between BASF and Marathon Petroleum Corp. (MPC) to demonstrate that C5 olefin maximisation is delivered by BASF's olefin catalysts: Fourte™ and Fourtune™. Both catalysts belong to the company's Multiple Framework Topology (MFT) technology family of catalysts.[2,3]

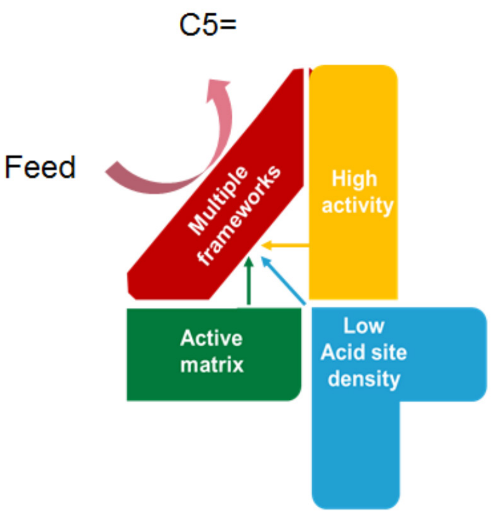

Figure 1. MFT has the appropriate zeolitic pore size and optimum acidity to generate and preserve C5 olefins.

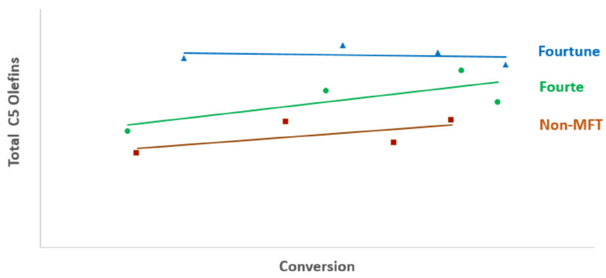

Figure 2. CRU testing data for lab-deactivated fresh catalysts of BASF's non-MFT catalyst and MFT catalysts – Fourte and Fourtune.

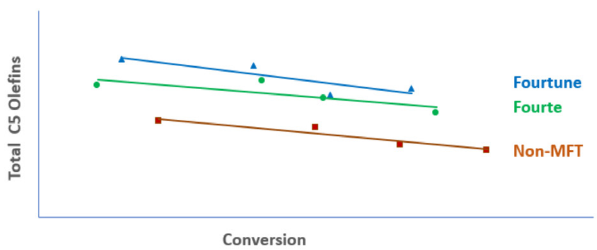

Figure 3. CRU testing data for equilibrium catalysts drawn for back-to-back trials of BASF's non-MFT incumbent with Fourte and Fourtune MFT catalysts in MPC unit 1.

A collaborative investigation

In MPC's circulating pilot plant, both fresh and equilibrium catalysts belonging to the MFT family were tested against conventional catalysts lacking the MFT technology, in order to determine whether the olefin enhancements observed for MFT catalysts extend to C5 olefin selectivity improvements. The results obtained in pilot testing were further validated using operating data from multiple MPC units.

In 2018, BASF introduced MFT to address the challenge of butylene maximisation and octane enhancement in the FCC. The catalysts are created 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, the technology has delivered profitability improvements in numerous refineries across the globe.[2] BASF introduced the second-generation Fourtune catalyst in 2020.[3] This catalyst provides enhanced butylene selectivity through enhancements to the specialty zeolite framework that yields selective cracking of (predominantly gasoline range) olefins to butylenes. In principle, the key elements utilised in MFT should facilitate the generation and preservation of C5 olefins.

Literature indicates that phosphorous-modified microporous and mesoporous ZSM-5 crack C5 olefins into lighter olefins (propylene and ethylene) where both conversion of C5 and the yield into lighter olefins show volcano shaped curves, with respect to strong acidity.[4] Zeolitic frameworks used in MFT catalysts have appropriate pore size to C5 generation. Most importantly, the acidity of these frameworks is optimised by the key elements of MFT to minimise C5 olefins from further cracking into lighter olefins (Figure 1).

Over the years, BASF's partnership with MPC has helped to design the right catalyst for its units and to ensure successful catalyst trials.

Catalyst selection

MPC's FCC catalyst selection philosophy is to thoroughly evaluate competitive catalyst products for a given application prior to using them commercially. The programme testing history has revealed that some proposed catalyst formulations would have a large negative economic impact if utilised in a commercial unit. As such, catalyst testing is employed to validate catalyst performance for a given application. Testing is especially important when evaluating emerging catalyst technology that has limited commercial experience.

MPC utilises a Davison Circulating Riser (DCR) FCC pilot unit, complemented by an Advanced Catalyst Evaluation (ACE) fixed fluidised bed micro-testing unit, along with accumulated

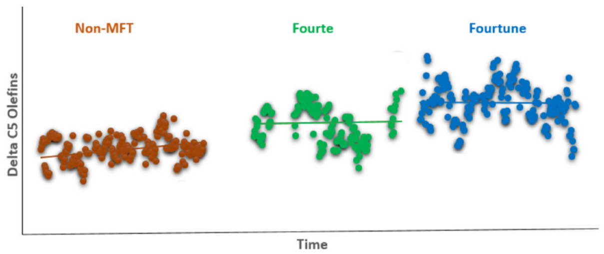

Figure 4. Operation data analysis with regression analysis model on Delta C5= (actual - predict) for unit 1.

Table 1. Regression modelling results for MFT catalyst transitions in MPC units

Unit	Catalyst	Delta C5= (wt%)
1	Fourte	0.24
1	Fourtune	0.53
2	Fourte	0.55
3	Fourte	0.33
4	Fourtune	0.10
5	Fourte	0.50

Table 2. KBC kinetic modelling results for MFT catalyst transitions in MPC unit 1

Catalyst	Non-MFT	Fourte	Fourtune
Delta C5= (vol%)	Base	+0.19	+0.36
Gasoline (vol%)	Base	-1.35	-0.19

analytical expertise. These testing capabilities are part of the company'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 operating parameters to generate lab yields that match the commercial units. By minimising offsets between the lab and commercial units, a high degree of confidence can be placed in the measured results. The testing results are used within an FCC process model (KBC's FCC-SIM) to determine expected yields and optimised unit conditions for each catalyst candidate. Pilot unit results have been validated with post-audits of unit data from numerous commercial catalyst changes.

Another important part of the catalyst selection philosophy is the close working relationship that the company establishes with each of the participating FCC catalyst suppliers. This collaboration is needed to select catalyst candidates formulated to have the highest likelihood of success, and to ultimately support the commercial FCC application for the selected catalyst. MPC strives to understand the technology behind the catalyst formulations so that the technology advantages for a given catalyst can be recognised in the test results. A consistent thread between catalyst design, intended performance, and the test results ensures that final catalyst selection is correct for the operating FCC unit.

Testing results

Figures 2 and 3 show Circulating Riser Unit (CRU) testing results for back-to-back commercial trials from BASF's non-MFT incumbent catalyst to the Fourte and Fourtune MFT catalysts in an MPC unit 1. MFT catalysts were qualified based on CRU testing results carried out at MPC for lab-deactivated fresh catalysts. As shown is Figure 2, MFT catalysts Fourte and Fourtune demonstrated increased C5 olefins compared to the non-MFT catalyst. Ultimately, the refinery performed commercial trials with both Fourte and Fourtune formulations. In the post-audit study carried out at an MPC facility, equilibrium catalysts were drawn from the unit during each catalyst trial at close to the full catalyst turnover in the unit. These catalysts were then tested in CRU to evaluate C5 olefin production. As shown in Figure 3, the results clearly demonstrated that BASF's Fourte and Fourtune MFT catalysts delivered increased C5 olefin yields compared to the non-MFT catalyst.

To further validate the results obtained in the circulating riser evaluations, the companies examined unit 1 operating data (Figure 4). Multivariable regression analysis was employed to determine olefin yield deltas observed in the FCC unit. The strongest operating variables found to impact C5 olefin yield shifts include riser outlet temperature, equilibrium catalyst activity, feed API, unit conversion, and ZSM-5 zeolite crystal content of the circulating inventory. The regression results showed that C5 olefin yields increased by an average of over 0.24 wt% for Fourte and 0.53 wt% for Fourtune.

Similarly, regression analyses of several MPC units where MFT catalysts were employed were carried out. In each case, it was observed that C5 olefin gain with the catalyst transitions to MFT catalysts (Table 1). Furthermore, heat-balanced KBC FCC-SIM modelling studies were carried out based on MPC CRU testing results for unit 1, with non-MFT, Fourte and Fourtune. The modelling results at optimised conditions showed a C5 olefin increase for MFT catalysts in both optimised cases (Table 2).

Conclusion

In summary, the benefits that MFT-based catalysts provide with respect to delivering profitability through butylene maximisation and octane enhancement can be further magnified for refineries that have the capability to alkylate C5 olefins or otherwise profitably handle additional C5 olefin products. Both Fourte and Fourtune delivered enhanced C5 olefin production to further increase FCC profitability in a number of MPC's units. HE

References

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