BOOSTING PROFITABILITY WITH BUTYLENES TO PROPYLENE RATIO

Nik Larsen and Tiffany Clark, Marathon Petroleum Corp., alongside Namal de Silva, Yorklin Yang and Daniel Neuman, BASF Corp., introduce a new catalyst that can boost butylene selectivity over propylene in FCC units.

In 2017, 46 million t of butylenes were produced worldwide, with an expected annual growth rate of nearly 1% per year through 2022. Fluid catalytic cracking (FCC) units around the world account for 48% of global butylenes production. BASF has reviewed the objectives of hundreds of global FCC operations during a one-year period and observed that 50% identified increased LPG olefins yields as one of their top objectives.[1] In North America, FCC objectives clearly display a preference for butylenes over other LPG components. Butylenes need continues to grow, influenced by the expanding alkylation demands.[2]

Driven by this demand, refiners utilise alkylation of olefins from the FCC unit as one method to achieve the octane specifications. Increased butylenes demand presents catalyst vendors with a new challenge and opportunity to design FCC catalysts tailored towards butylene maximisation. BASF's multiple framework topology (MFT) technology addresses this challenge with the design of novel catalysts created by integrating four key elements: multiple frameworks, active matrix, low acid site density, and higher activity.[3] Since the commercial introduction of the first generation MFT catalyst Fourte™, it has demonstrated profitability boost in several refineries. Following its success, BASF's R&D efforts to design new butylene maximisation catalysts with additional features to deliver unique performance have continued. This article introduces the second generation MFT catalyst: Fourtune™.

This catalyst delivers excellent butylenes selectivity over propylene (i.e., higher butylene/propylene ratio), providing additional flexibility for refiners requiring higher value butylene yields and with a need for less propylene due to specific refinery constraints or economics. The catalyst builds upon the key elements of MFT technology, such as increased porosity and diffusion characteristics, enhanced matrix cracking, and modification of zeolite acid site density to reduce olefin saturation reactions while still maintaining activity. It employs a specialty zeolite framework that is more selective to cracking small olefins into butylenes.

Figure 1 shows the key steps of the Fourtune catalyst development. In the first step, a number of zeolitic frameworks are evaluated using rapid ACE screening to identify candidates that demonstrate improved butylene selectivity. Selected candidates are then further optimised in the second step, by modifying the chemical and physical properties to further enhance butylenes yield. Figure 1 shows the effect of one such property (i.e., framework acidity) on butylene yields. In the third step, advance multiple frameworks are integrated in the final catalyst. The catalyst's excellent butylene/propylene ratio has been proven in extensive laboratory and pilot scale testing prior to commercial production, and has now been demonstrated in commercial operations.

Fourtune has delivered profitability with preferential selectivity towards butylenes in two initial refinery trials conducted in FCC units operated by Marathon Petroleum Corp. (MPC). MPC's objective for FCC catalyst vendors is to maximise FCC profit for the given product economics (i.e., supplied pricing) by maximising liquid volume yield of higher value products (LPG olefins, gasoline), while minimising low value products such as dry gas and slurry, within the limits of applicable unit constraints. BASF's partnership with MPC over the years has enabled the design of the right catalyst for the company's units and ensured smooth catalyst trials. In each of these trials, close interaction with the central technical organisation from MPC as well as the refinery, via performance testing and modelling optimisation studies, made it possible to demonstrate improved yield benefits and increased profitability to the FCC units.

During the refinery trials, both BASF and MPC worked closely to monitor the trial via multiple methods: weekly equilibrium catalyst data analysis, refinery operating data evaluation, heat-balanced KBC FCC-SIM modelling, and multi-variable regression analysis models to monitor the effects of operational/feed changes. The high-quality, objective, and state-of the-art testing and modelling approach of MPC was a major strength in these collaborative efforts. Both BASF and MPC also utilised a Circulating Riser Unit (CRU) for pilot plant testing, checking refinery feed and equilibrium catalyst samples before and after the trial to validate that the catalyst provided the expected yield shifts. In these evaluations, CRU was benchmarked to the commercial unit performance and then subsequent equilibrium catalysts were tested at the same conditions.

Table 1. Yield delta values for Fourtune compared to Fourte based on operating data and heat balanced modelling for Trial 1

	Yield delta for Fourtune
Propylene (vol.%)	-0.79
Butylenes (vol.%)	0.55
Gasoline (C5-450˚F/232˚C) (vol.%)	0.01
LCO (450 – 680˚F/360˚C) (vol.%)	-0.10
Slurry (680˚F/360˚C+) (vol.%)	-0.10
Delta Coke (wt%)	0.00
Gasoline RON	1.00

Commercial trial 1

The first application for the catalyst was at a US refinery seeking increased FCC profitability through increased butylenes production vs the improvements already observed with BASF's first generation MFT catalyst. The refinery placed substantial value on FCC gasoline octane, and highly valued an increase in butylenes production to fill the alkylation unit. The catalyst selection process involved

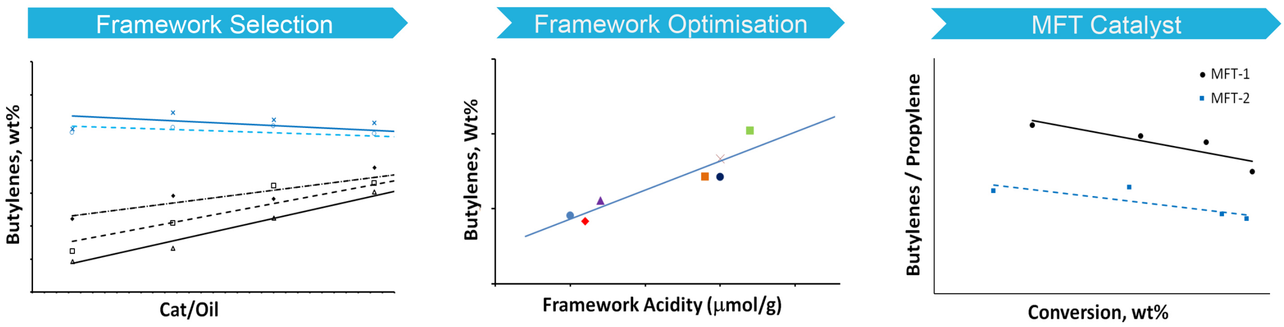

Figure 1. Key steps in the second generation MFT catalyst development.

CRU pilot plant testing followed by modelling, and sensitivity studies. In this evaluation, Fourtune demonstrated the economic potential to deliver even more profitability.

During the trial, the refinery reduced the amount of unconverted oil from the hydrocracker in the FCC feed and also showed unexpectedly large variations in deasphalted oil in the FCC feed. Both of these changes had a major impact on feed quality during the Fourtune trial; the fluid activity (FACT) of the circulating inventory was about 2 wt% higher than during the Fourte trial due to marginally higher catalyst additions. Supplemental ZSM-5 usage also showed significant rate variations. In order to best post-audit the impact of the switch between catalysts, MPC undertook an additional circulating riser pilot plant study utilising refinery feed

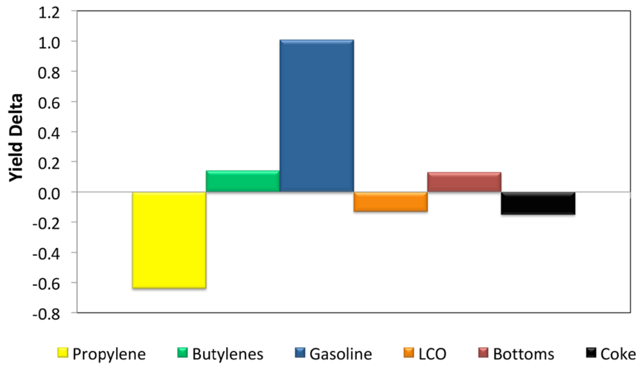

Figure 2. Delta yield shifts (Fourtune minus incumbent Fourte) based on CRU post audit of equilibrium catalysts from Trial 1.

and equilibrium catalyst samples during each catalyst trial. The testing confirmed that the new catalyst provided the expected yield shifts. A summary of the delta yield shifts observed in the post-audit CRU study are shown in Figure 2. The results showed that Fourtune provided 0.7 wt% incremental yields of butylenes at a nominal 0.1% propylene increase. As expected, there were no significant shifts in bottoms upgrading or coke selectivity observed in the post audit. Octane results showed a I > 1 number increase in road octane for Fourtune over Fourte. It is important to point out that there was no change in REO level. Therefore, increased butylene benefits could be attributed to the new catalyst technology. Also of note is the higher butylenes/propylene ratio observed for the new catalyst despite the presence of ZSM5 additive, which is known to make more propylene over butylenes. Utilising the results from the pilot plant post audit, heat-balance modelling of the results, MPC observed that the new catalyst provided a US$0.30/bbl benefit over the first generation catalyst.

Commercial trial 2

The second commercial application of the new catalyst occurred at another MPC refinery whose aim was also to maximise the value of the FCC product yields with a severely hydrotreated gasoil feed. This unit has a considerable active catalyst inventory (and relatively low make-up rate) such that a typical transition would have required more than six months to turn over the unit inventory. Kinetic modelling of the unit's operation suggested that the new catalyst would provide strong economic benefits and the refinery chose to proceed with this evaluation. In addition, during the recommissioning of the unit, the majority of the unit inventory was replaced with the equilibrium catalyst from the first trial described previously.

In this refinery, maximising olefin yields were of paramount importance to fully utilise the refinery's alkylation capacity. FCC gasoline octane was also valued, but not as dramatically as in the first trial. During a major FCC turnaround, the

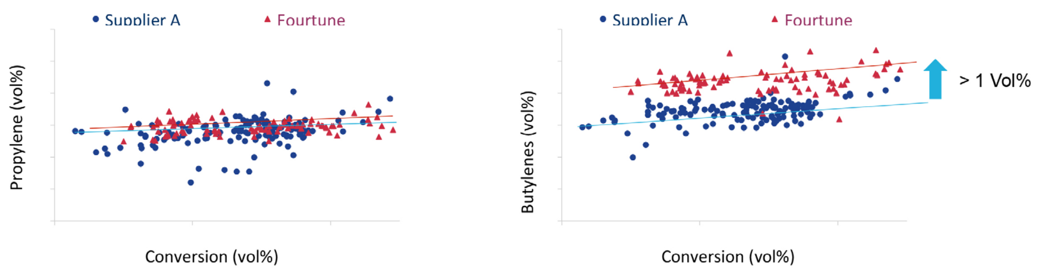

Figure 3. Operation data analysis for trial 2: propylene maintained, butylene increased (i.e., higher butylene/propylene ratio).

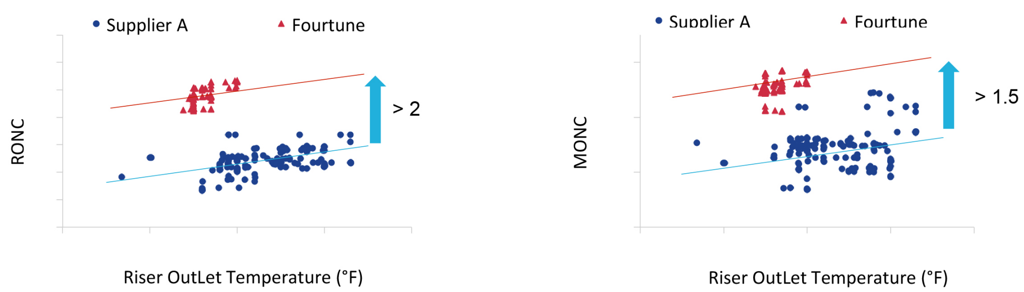

Figure 4. Operation data analysis for trial 2: 3 number higher RONC and 2 number higher MONC.

concept of restarting the unit with equilibrium catalyst that had been accumulated from the first trial was evaluated.

In contrast to the first trial, the second trial proceeded with very steady feed quality. Catalyst activity was also largely unchanged. The presence of ZSM-5 additive in the ecat from the first trial certainly impacted the initial results, but since no further ZSM-5 was added to the unit, the incremental propylene yields observed immediately after start-up declined rapidly thereafter. Riser outlet temperature was reduced by 8˚F, which made the observed octane increase all the more impressive.

As a result of the decision to restart the unit with the equilibrium catalyst from the previous trial and immediately commence with fresh Fourtune catalyst, a sharp change in the unit yields were observed immediately upon lining out of the restarted unit. Refinery operating data showed significantly higher butylene yields while propylene yield was largely unchanged (Figure 3). FCC naphtha octane response was also dramatic with > 2 number improvement in road octane (Figure 4). A post audit of the trial using operating data analysis, and kinetic modelling clearly concluded that the new catalyst exceeded the predicted yield benefits by significant margins. The final operating data confirmed an improvement to FCC margins of > US$2/bbl.

Conclusion

Following commercial success of the first MFT catalyst, R&D efforts continued in order to introduce the second-generation catalyst within a rapid timeframe. This catalyst, which contains speciality zeolite framework, is designed to deliver preferential butylene increases over propylene. The step out yield response of Fourtune with respect to butylene/propylene ratio has enabled BASF and MPC to demonstrate that this new catalyst can be highly profitable for refineries that prefer butylenes over propylene. In its first two commercial FCC trials, the new catalyst has successfully demonstrated where significant profitability improvement was achieved. In these trials, profitability improvements ranging between US$0.30 and US$2/bbl were achieved. Following commercial success of the first two trials, the catalyst has entered additional MPC FCC units. Collaboration between BASF and MPC led to significant improvements in the FCC product performance delivered to MPC.

References

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Note

Juan Hurtado, Vasileios Komvokis and Bilge Yilmaz, BASF Corp., also contributed as authors of this article.