

Reaching new heights



**Nikolas Larsen and
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present a case study in which
a novel catalyst technology
was used to improve the
profitability of fluid catalytic
cracking units at refineries.

While the petroleum refining industry is well established and highly optimised, significant opportunity still exists to improve performance and profitability for refiners in an increasingly competitive landscape. This article highlights how close collaboration between a refiner and a fluid catalytic cracking (FCC) catalyst supplier results in rapid development and deployment of a novel catalyst technology to improve refining margins. Through open cooperation between the two companies, catalyst design knowledge was integrated with detailed understanding of individual refinery operating limits and overall market drivers.

This article shares three case studies where Marathon Petroleum Corp. (MPC) increased the profitability of its FCC units after upgrading to BASF's newest iteration of its maximum butylenes (C4=) catalysts, Fourtiva™, from BASF's current butylenes catalysts, Fourte® and Fourtune™. These new catalysts synergistically combine BASF's Multiple Framework Topologies (MFT) with a new Advanced Innovative Matrix (AIM). Together, MFT and AIM target increased butylenes yield and selectivity, which deliver excellent total LPG olefinicity, higher butylene over propylene selectivity, and higher FCC naphtha octane with improved coke selectivity than the incumbent catalysts.

The history

Since being commercialised, BASF catalysts Fourte and Fourtune have delivered value to multiple MPC FCC units. These catalysts use BASF's MFT technology, which utilises multiple zeolite frameworks and an active matrix to produce a unique balance of low acid site density and high activity to maximise high value product yields. Globally, and especially in North America, market trends continue to show larger spreads for premium high-octane gasoline as motor vehicle engines have been designed for higher fuel efficiencies. FCCs are perfectly suited to take advantage of these market drivers by yielding more butylenes for alkylation units and increasing FCC naphtha octane for gasoline blending. These trends are supported by BASF's FCC catalyst technology R&D programmes which focus on delivering maximum value to refiners.

Olefin additives (e.g., those containing ZSM-5 zeolite) are available for refiners to increase light olefins from the FCC unit and fill their alkylation capacity. While olefin additives containing ZSM-5 zeolite are highly effective at producing LPG olefins, they more selectively crack light gasoline range molecules into propylene (C3=) and to a lesser extent, butylenes (C4=). In general, C4= alkylate has higher road octane value than C3= alkylate, and C4= alkylate is also less

cost intensive to produce. Alkylate made from C3= and isobutane can have a road octane of up to 91, whereas alkylate from C4= can have a road octane of up to 95. Therefore, C4= alkylation is preferred for most refiners operating alkylation units. BASF's MFT catalysts, and now AIM+MFT catalysts, use holistic catalyst design to increase C4=/C3= selectivity and overcome the existing C4=/C3= limitations of ZSM-5 and other olefin additives.

The path forward

To meet the market demand for light olefins for alkylate production and higher FCC naphtha octane for gasoline blending, BASF delivered the next improvement of its MFT catalysts to MPC to further improve its technology. Fourniva incorporates an AIM with improved porosity and optimal matrix activity to lower delta coke and minimise saturation reactions. This is combined with the MFT pillars of using multiple zeolite frameworks which have resulted in lower acid site density while maintaining high activity.

Three units are highlighted in this article. All three units historically have used an olefins additive with the objective of maximising light olefins production up to the sites' alkylation capacities.

Comprehensive trial evaluations incorporating operating data analysis, kinetic modelling, and laboratory studies were executed independently by both BASF and MPC. The laboratory studies used equilibrium catalyst (E-cat) samples collected before Fourniva was introduced to the unit and after the unit's circulating inventory was fully turned over to Fourniva. MPC utilises a Davison circulating riser unit (DCR) as a Pilot FCC unit, complimented by an advanced cracking evaluation (ACE) technology® unit with significant accumulated analytical expertise. The overall goal of MPC's pilot testing programme is to generate measured yield data from commercial materials to minimise the uncertainty surrounding key commercial decisions for each specific application. Pilot unit results have been validated with commercial experience. In addition to predicting commercial FCC performance with the pilot unit, kinetic modelling allows evaluation of product pricing and operational sensitivities to further increase confidence that the trial catalyst will deliver maximum value across multiple scenarios.

The commercial trial results

Based on the comprehensive pilot plant testing and

kinetic modelling results of both companies, Fourniva was selected to be trialed across eight MPC FCC units. Three of those trials are shared in this article. Operating data from trials on units 1, 2, and 3 were gathered throughout the equilibrated period of the incumbent Fourte or Fourniva catalyst and the equilibrated period of the Fourniva catalyst. The conclusions from the operating and pilot plant data showed excellent agreement with each other. Further, agreement in the observed yield shifts across multiple analysis methods (operations data, E-cat testing, kinetic modelling, and pilot plant post audits) increases confidence that the shifts in operations data are a result of the catalyst technology change and are not due to normal operating variability within the unit.

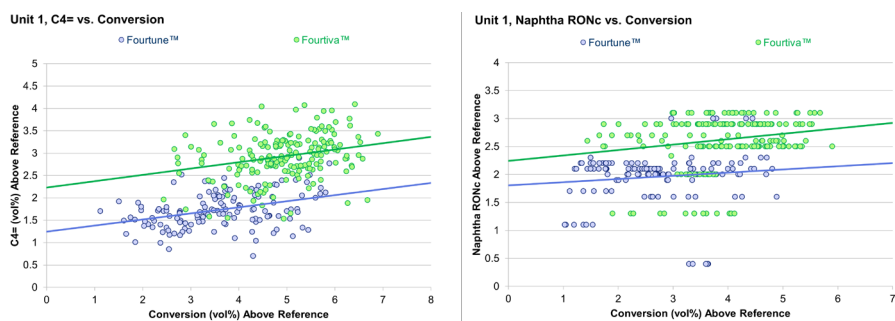


Figure 1. Unit 1 operating data showing improved C4= yield and FCC naphtha RONc for Fourniva over the incumbent Fourniva catalyst when filtered for similar unit feed rate and conversion to exclude abnormal operating data. The two time periods had similar average LPG olefin additive concentrations in the circulating inventory.

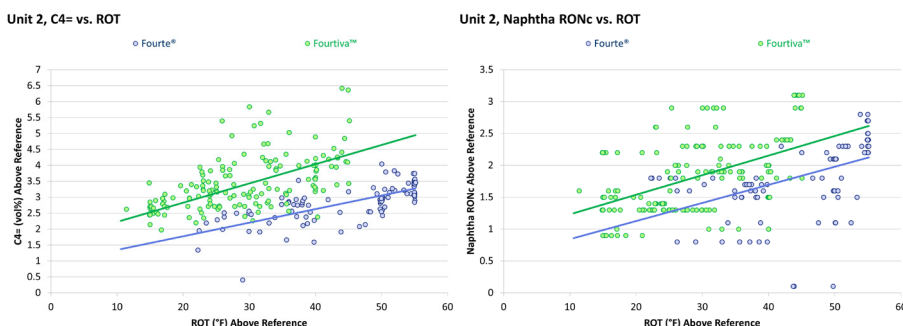


Figure 2. Unit 2 operating data showing improved C4= yield and FCC naphtha RONc for Fourniva over the incumbent Fourte catalyst when filtering for similar feed qualities to exclude abnormal operating data. The trial period also had lower average LPG olefin additive concentration in the circulating inventory.

Unit 1 commercial trial synopsis

The first trial was conducted on a unit that was using the Fourniva catalyst. The objectives were to further improve C4= yield and selectivity, along with increased

naphtha octane and improved coke selectivity. The unit uses an olefin additive to increase total LPG olefin production. To accurately analyse the trial performance of Fourtiva, BASF and MPC normalised the olefin additive influence by comparing operating data with the same additive concentration. In Figure 1, the C4= yields

and gasoline RONc data for unit 1 is plotted against unit conversion to normalise the effect of the operational differences between the two time periods. At the same olefin additive concentration, Fourtiva demonstrated significant C4= yield (+1 vol%) and gasoline octane (+0.5 RONc) improvement. The new technology also

delivered a 9% improvement in delta coke, resulting in a drop in regenerator dense bed temperature of 15°F. Overall, kinetic modelling showed an average economic uplift of US\$0.87/bbl for unit 1 across multiple shadow price set sensitivities at optimised conditions.

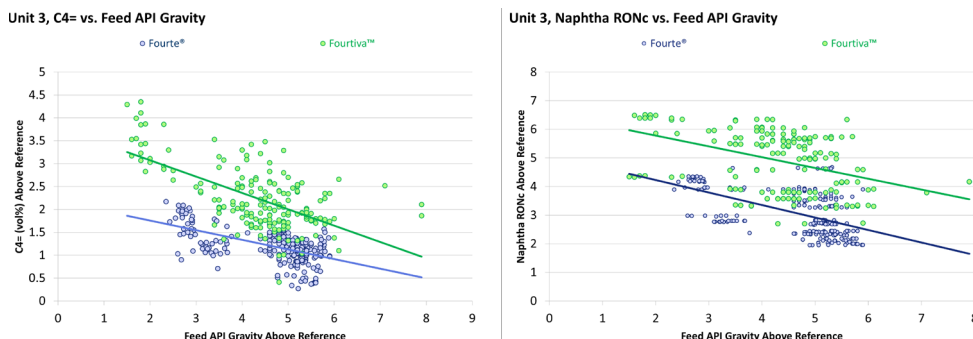


Figure 3. Unit 3 operating data showing improved C4= yield and FCC naphtha RONc for Fourtiva over the incumbent Fource catalyst. Both periods had similar average LPG olefin additive concentrations in the circulating inventory.

Unit 2 commercial trial synopsis

On unit 2, MPC was using BASF's maximum C4= catalyst, Fource, with an LPG olefin additive. Again, market drivers indicated that increased C4= yield and selectivity over C3= along with increased naphtha octane would be extremely advantageous for the refinery, so Fourtiva was selected as a suitable catalyst. As the unit transitioned to the new catalyst technology, more total feed was being processed by the FCC, which meant it was constrained by mixed C3+C4 product being sent to the alkylation unit. As a result, reactor severity was reduced to the minimum limit and the LPG olefin additive was discontinued. At the higher FCC feed rate, the alkylation unit was maintained at full capacity despite the FCC wet gas compressor operating at its maximum limit. Without using an LPG olefin additive, Fourtiva was able to fill the alkylation

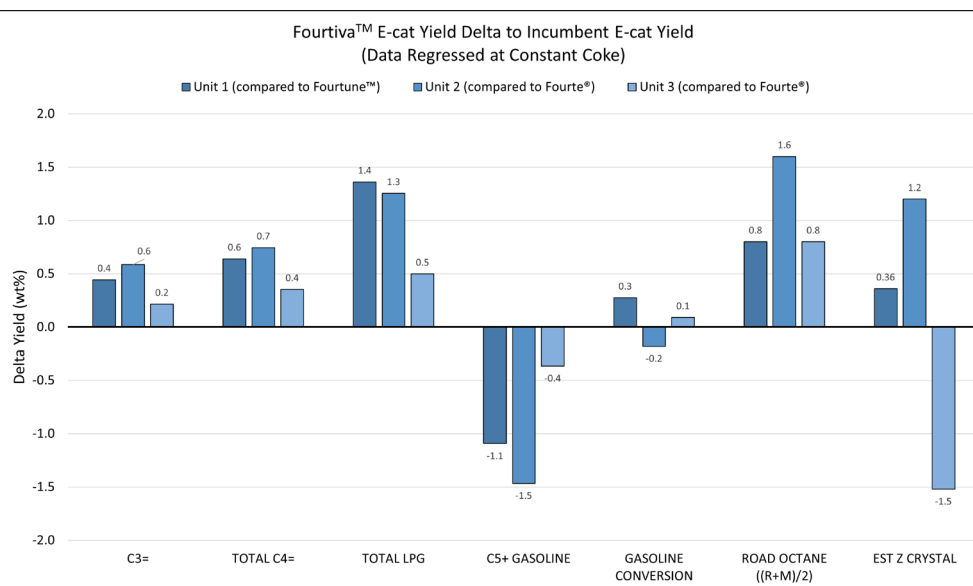


Figure 4. Pilot plant testing analysis comparing Fourtiva against Fourtune or Fource E-cat samples. In all cases, Fourtiva produced higher C4= and C3= yields, higher gasoline road octane, and lower delta coke than the incumbents.

Table 1. Delta yield shifts and profitability uplift at optimised conditions for Fourtiva over the incumbent Fource or Fourtune catalysts based on kinetic modelling for units 1, 2, and 3

Delta yield	Unit 1 (Fourtiva) - (Fourtune)	Unit 2 (Fourtiva) - (Fource)	Unit 3 (Fourtiva) - (Fource)
Propylene (vol%)	+0.9	+0.3	+0.5
Total C4= (vol%)	+0.6	+0.9	+1.0
Total LPG (vol%)	+1.5	+1.1	+1.6
C5+ gasoline (vol%)	-0.3	-1.0	-0.1
Gasoline RON	+1.00	+1.25	+1.15
Profit (US\$/bbl)	+0.87	+1.40	+0.71

unit with more favourable C4=’s due to the LPG selectivity of the new catalyst. The FCC was also able to fill its alkylation capacity while operating at minimum slurry product rundown rates, with minimum riser outlet temperature (ROT). To account for these operational differences, the C4= yields and gasoline RONc data shown in Figure 2 for unit 2 is plotted against reactor severity. The unit was able to achieve increased C4= yield (+1 vol%) and increased naphtha octane (+0.5 RONc) (shown in Figure 2), despite the lower LPG olefin additive in the circulating inventory. Kinetic modelling showed similar yield shifts and an average economic uplift of US\$1.40/bbl for unit 2 across multiple shadow price set sensitivities at optimised conditions.

Unit 3 commercial trial synopsis

On unit 3, MPC was also using BASF’s maximum C4= catalyst, Fourte, with an LPG olefin additive. Strong economic incentives for C4=’s, improved LPG olefinicity, and naphtha octane meant that Fourtiva was a suitable fit. For unit 3, the feed properties vary significantly between the summer and winter operating modes, affecting the product yields and selectivities. At lower feed API gravity, the unit observes increased C4= yields and higher naphtha RONc due to the lower hydrogen content in the feed. The C4= yields and naphtha RONc data in Figure 3 is plotted against FCC feed API gravity to normalise some of the differences in feed properties between the two time periods. Like unit 2, olefin additive concentration was lower in favour of Fourtiva C4= selectivity advantages observed during the trial. At constant feed API gravity, Fourtiva provided an increase in C4= yields (+1 vol%) and higher naphtha octane (+1 RONc) compared to the incumbent, Fourte, despite lower olefin additive use. These yield shifts were confirmed with kinetic modelling and showed an average economic uplift of US\$0.71/bbl for unit 3 across multiple shadow price set sensitivities at optimised conditions.

The pilot plant testing results

MPC’s pilot plant post audit yield shifts are summarised in Figure 4. For all units shown, BASF’s Fourtiva delivered increased butylenes and propylene yields, lower delta coke, and improved FCC naphtha road octane compared to the incumbent Fourte or Fourtune catalysts. Compared to Fourtune in unit 1 testing, the new catalyst technology shows increased LPG= yields and olefinicity, with improved selectivity to butylenes. Compared to Fourte in unit 2 and 3 testing, the new catalyst delivered increased butylenes and propylene yields with improved LPG olefinicity and higher butylenes to propylene selectivity.

It is important to note that the Fourtiva E-cat samples for units 1 and 2 had more estimated LPG olefin additive crystal concentration compared to the incumbent E-cat sample when they were pulled for the pilot plant post audit study. At similar LPG olefin additive crystal concentration, the magnitude of the

LPG olefin yield increases would have been lower while being even more C4=/C3= selective.

Conversely, the Fourtiva E-cat sample for unit 3 had less estimated LPG olefin additive crystal concentration compared to the incumbent E-cat sample when they were pulled for the pilot plant post audit study. The LPG olefin yields would have been further increased (although less C4= to C3= selectively) if the unit 3 E-cat samples had the same olefin additive concentration. Even so, the pilot plant data from unit 3 shows an extremely profitable incremental C4= to C3= yield increase of 0.4 wt% to 0.2 wt%, respectively. The incremental total LPG olefins yield increase is coming from a small reduction in gasoline yield, and an even larger reduction in LPG saturate yields.

The kinetic modelling results

To further validate the commercial unit and pilot plant results, kinetic modelling using KBC’s Petro-Sim® was completed to evaluate the improved performance of the Fourtiva catalyst over the incumbent Fourte or Fourtune catalyst. The kinetic modelling results are shown in Table 1. These results, corroborated by the yield shifts observed in the operating and pilot plant data, showed an average economic uplift of US\$0.87/bbl, US\$1.40/bbl, and US\$0.71/bbl for units 1, 2, and 3, respectively for the new catalyst technology across multiple shadow price set sensitivities. Combining commercial unit data, pilot plant testing, and kinetic modelling in the trial post-audit analysis demonstrates tremendous economic uplift across multiple units and highlights the robustness of MPC’s catalyst selection process.

Conclusion

Continued success of commercial fluid catalytic cracking (FCC) catalyst applications depends on open communication between the refiner and catalyst supplier to understand how to optimise the needs of individual refineries as they interact with overall market demands. The refiner, MPC, and the catalyst supplier, BASF, rapidly rolled out the next iteration of maximum butylenes catalyst technology to capture significant value for multiple refineries and meet market demands for selective butylenes yield and high FCC naphtha octane for gasoline blending. The new catalyst technology delivered improved total butylenes yields, butylene to propylene selectivity, coke selectivity, and FCC naphtha octane corroborated by both pilot plant testing and commercial unit data. Kinetic modelling showed profitability improvements of US\$0.87/bbl, US\$1.40/bbl, and US\$0.71/bbl for the new catalyst technology over the incumbent C4= selective catalysts for the units described in this article. 