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HP Special Focus | Catalysts

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Flexibility in catalyst technology for improved bottoms upgrading

Bottoms product from fluidized catalytic cracking (FCC) is typically one of the least valuable products from a refinery. As a result, strong bottoms cracking in the FCC process is needed by refiners. While maximization of bottoms upgrading might be desired, FCC feed, unit constraints, operation decisions and catalyst selection all determine the ability of an FCC unit (FCCU) to upgrade bottoms into more valuable products. Due to the wide variability in these factors, there is not a one-size-fits-all catalyst solution to improve bottoms upgrading in every FCCU. This work details three separate case studies of back-to-back catalyst trials in FCCUs around the world. In each case, the specific characteristics of the FCCU were considered to select a catalyst technology that improved bottoms upgrading.

The first study describes how a catalyst technology and zeolite-to-matrix surface area (Z/M) were optimized to improve bottoms destruction in a North American FCCU. In this case, the lowest Z/M option was not optimal, and a more moderate Z/M provided the best upgrading route for the FCCU. In contrast, the second case study details how a low Z/M catalyst provided the best bottoms upgrading in a European FCCU. The third case study occurred at a heavy resid unit in Asia. The bottoms upgrading optimization was realized using a high Z/M catalyst that improved coke selectivity. From these three cases, it can clearly be seen that the optimum FCC catalyst for upgrading bottoms will vary depending on the FCCU's specific requirements, operations and constraints.

Case Study 1. The first example is from a North American FCCU. This example shows that changing catalyst technology and tuning Z/M to an optimum level can result in improved bottoms upgrading in an FCCU. This FCCU processed vacuum gasoil with mild-to-moderate metals levels and used BASF Catalyst A, a high Z/M [equilibrium catalyst (Ecat) Z/M = 2] proprietary catalyst[a] to achieve high conversion. The objectives of the FCCU shifted to incentivize further bottoms destruction. As a result, two new catalysts were trialed in the FCCU to meet the objective of improving bottoms upgrading without sacrificing conversion. One catalyst was not from the authors' company and contained a much lower Z/M level (Ecat Z/M = 0.8) vs. Catalyst A. The new catalyst aimed to use higher matrix content to achieve bottoms destruction. The authors' company proposed a different FCC catalyst[b] (Catalyst B) with a more moderate Z/M (Ecat Z/M = 1.4). The new BASF FCC Catalyst B[b] uses the authors' company's improved zeolite-Y technology and was chosen due to its superior mesoporosity, which allows for better bottoms upgrading without sacrificing conversion to liquid products.

TABLE 1 provides a summary of key yields at constant conversion during the trials. There are several notable outcomes. First, BASF Catalyst B resulted in lower bottoms and higher light cycle oil (LCO) yields than either of the other two catalysts, despite experiencing elevated contaminant metals levels during the trial. The LPG + gasoline yields also increased vs. the other catalysts. Similarly, the dry gas yield was lower than the other catalysts despite having > 500 ppm more contaminant metals on the Ecat—an indication of more selective cracking.

However, examining the yield shifts at constant conversion only told part of the story, as a key goal of the new BASF Catalyst B was to improve bottoms upgrading without sacrificing conversion. **FIG. 1** shows the bottoms vs. conversion and LCO vs. conversion results from the trial of the three different catalysts. The low Z/M, non-BASF catalyst had lower activity than the incumbent BASF Catalyst A, and this can be seen in the consistently lower conversion levels. Any potential benefit of improved or increased matrix amount could not be

TABLE 1. Summary of yields from each trial period

	Incumbent Catalyst A[a]	Non-BASF catalyst	New Catalyst B[b]
Ecat Z/M	2	0.8	1.4
Ecat, nickel (Ni) + vanadium (V)	3,617	3,645	4,185
Conversion	73.5	73.5	73.5
Dry gas	2.8	3	2.9
Gasoline + LPG	66.7	66.1	66.3
LCO	16.8	16.7	17.2
BOT	9.7	9.8	9.3

realized due to the loss in conversion. As a result, there was no improvement in bottoms upgrading compared to the incumbent Catalyst A.

The benefit of both the improved zeolite-Y technology and the more moderate Z/M level Catalyst B can be seen in **FIG. 1.** The FCC proprietary catalyst[b] imparted more activity than the low-Z/M, other catalyst, resulting in higher conversion levels. While the conversion levels were lower than the incumbent Catalyst A, the impact of the improved porosity and matrix technology are seen as the bottoms upgrading noticeably improved vs. the other two catalysts—shown by the higher LCO and lower bottoms yields. This trial provides an example where the catalyst technology must be balanced with optimization of other catalyst parameters (in this case, Z/M) to achieve bottoms upgrading goals.

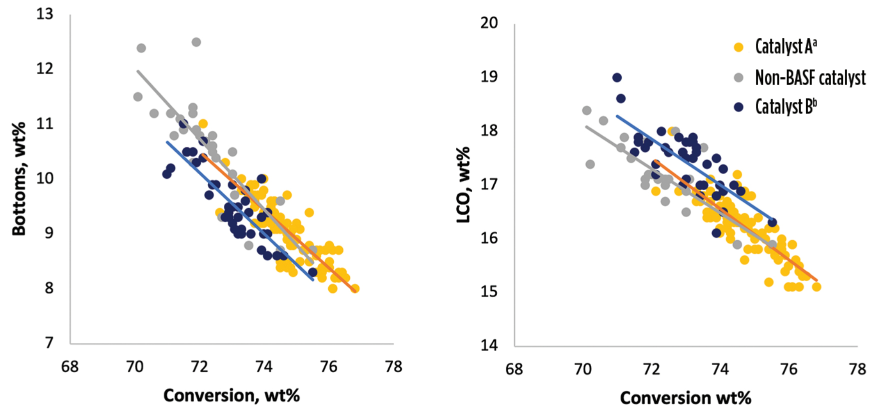

FIG. 1. Bottoms upgrading vs. conversion in Case Study 1's trials at a North American FCCU.

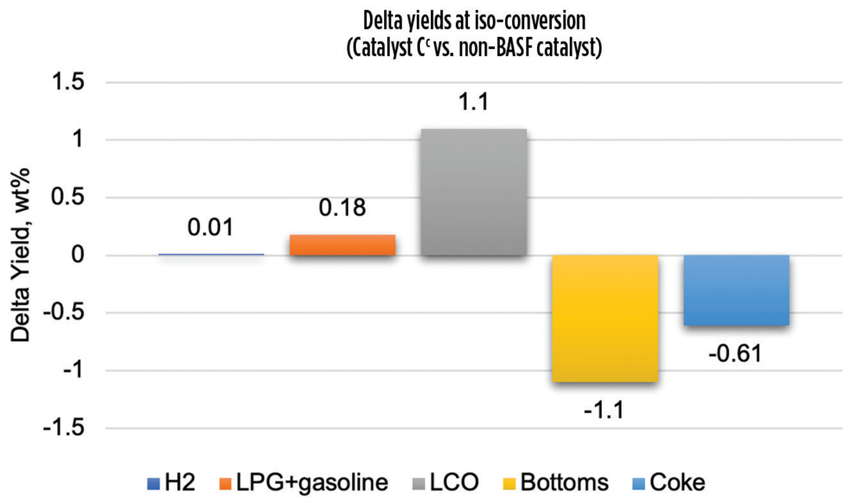

FIG. 2. Post-audit yield results from Case Study 2.

TABLE 2. Yield selectivities at iso-coke (8.5 wt%)

Yield, wt%	Non-BASF catalyst	Catalyst E[e]
Hydrogen	0.61	0.56
Dry gas	3.2	3.3
Total LPG	20.4	21.1
Gasoline	39.1	41.3
LCO	15.6	14.7
Bottoms	13.3	11
Conversion	71.2	74.3
LCO/BOT	1.2	1.3

Case Study 2. This case study involved a European refinery whose main objectives were to improve coke selectivity and minimize bottoms product and dry gas yields. The incumbent catalyst[c] (Catalyst C) was a moderate-to-low Z/M catalyst designed to minimize bottoms and maximize fuels without increasing dry gas and coke. It is a precursor to the authors' company's newer, enhanced Catalyst D[d], which improves upon the incumbent catalyst to meet the same objectives. The refinery commissioned a catalyst evaluation and tested various catalysts. A non-BASF catalyst showed very favorable testing outcomes, promising lower bottoms yields among other benefits. The refinery decided to change from the incumbent Catalyst C and trial the other catalyst in the FCCU.

After a few months of the industrial trial, the refinery—after having tracked the chemical markers and the catalyst turnover—decided that the performance seen in the unit was not in alignment with expectations based on testing. Furthermore, the regenerator temperature was higher due to delta coke, the wet gas compressor was constrained due to an increase in dry gas and slurry yields were noticeably higher. The refinery decided to change back to BASF Catalyst C and perform a post audit to determine the industrial yield shifts.

Ecat samples from the non-BASF catalyst's trial period and Catalyst C's periods were chosen for post-audit analysis. The ECAT metals levels between the two time periods were comparable (both samples had > 4,500 ppm Ni + V), but nearly twice as much ZSM-5 was used during Catalyst C's period; therefore, the anlaysis was done on LPG + gasoline to eliminate additive effects on selectivity.

The post-audit results are shown in **FIG. 2.** These results reveal large differences in bottoms upgrading and overall liquid yields between the two catalyst trials. The non-BASF catalyst resulted in lower LPG + gasoline and LCO yields. Furthermore, the LCO/bottoms ratio was worse with the other catalyst, going from 1.3 wt%/wt to 1.1 wt%/wt. These changes were not captured in pre-trial testing, went against unit objectives and were detrimental to unit profitability.

Case Study 3. The final case study of tailoring catalyst technology and design to meet the bottoms upgrading objectives of an FCCU was at an Asian refinery. The refinery wanted to increase FCC profitability by improving bottoms upgrading, while maintaining high conversion and coke selectivity despite sporadic metals poisoning episodes and maintaining Ecat metals levels greater than 7,500 ppm of Ni + V. The unit was often limited in bottoms upgrading ability due to reaching regenerator temperature limits.

Using an activity model fine-tuned to the FCCU's operation, a catalyst was proposed (BASF Catalyst E[e]) to maximize conversion in a heavy resid environment. The objective for this catalyst was to offer improvements to the incumbent catalyst through enhanced pore architecture and metals passivation. Catalyst E was evaluated—along with other candidates—through pilot plant testing, modeling and sensitivity studies and was eventually selected for trial.

TABLE 2 details the post-audit results using both catalysts at iso-coke conditions. BASF Catalyst E demonstrated improved coke selectivity by showing significantly higher conversion at iso-coke levels. As a result, LPG and gasoline yields were also higher. Additionally, the hydrogen yield of Catalyst E was lower despite the higher conversion, a result of the strong metals passivation of the catalyst. Finally, LCO/BOT and overall bottoms yield were both improved, demonstrating that this catalyst was the right fit for optimizing bottoms upgrading in this unit.

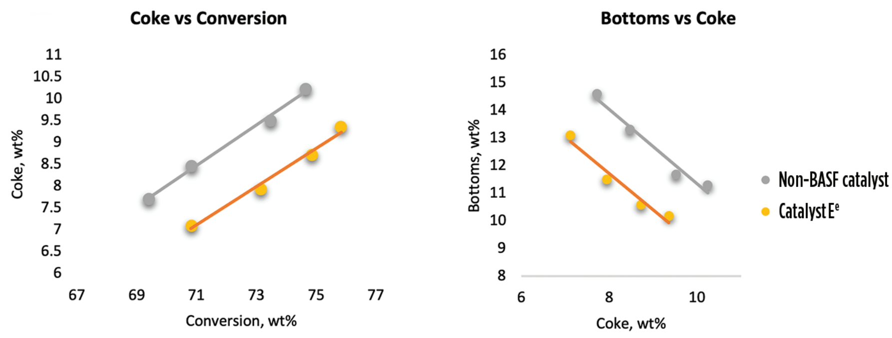

FIG. 3. Selected yield plots from Case Study 3's post-audit study.

FIG. 3 shows two cross plots from the post-audit study of this catalyst trial. The strong coke selectivity and improved bottoms upgrading provided by Catalyst E can further be seen in this analysis. Catalyst E demonstrated slightly higher conversion yet consistently lower coke make. Similarly, Catalyst E was also able to crack significantly more bottoms at comparable coke levels. Once again, despite being a different technology than the catalysts seen in the previous two trials, consideration of the specific requirements of this unit led to an improvement in bottoms upgrading through catalyst selection.

Takeaway. As one of the least valuable FCC products, the need to minimize bottoms is expected to increase as pressure on refiners to get the most out of every barrel of feed intensifies. The three trials detailed in this article illustrate that understanding the needs and constraints of each unit is critical to maximizing bottoms upgrading through FCC catalyst selection, as the strategy for the appropriate catalyst technology used in each trial is different. Three different catalysts were used across the three trials. Despite the three catalysts being different, bottoms upgrading was improved significantly in each case because close collaboration between the refinery and the FCC catalyst supplier ensured that the catalyst provided met the precise needs of the unit and delivered maximum profitability. HP

NOTES

[a] BASF's NaphthaMax® catalyst
[b] BASF's Luminate® catalyst
[c] BASF's Aegis® catalyst
[d] BASF's Altrium® catalyst
[e] BASF's Fortress® NXT catalyst

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