

J. SEXTON, J. HIGHFIELD and N. LARSEN,  
Marathon Petroleum Company, LP, Catlettsburg,  
Kentucky; and S. ISMAIL and D. NEUMAN,  
BASF Corp., Florham Park, New Jersey

## Innovative catalyst solution mitigates FCC operational issue

Marathon Petroleum Co.'s (MPC's) Catlettsburg fluid catalytic cracking unit (FCCU) experienced a catalyst circulation constraint due to partial blockage of an intra-regenerator standpipe. The unit was initially debottlenecked by introducing torch oil, along with increased catalyst addition, to maintain unit activity. The refinery then introduced a high-activity co-catalyst into the FCCU.<sup>1</sup> The co-catalyst solution allowed removing the torch oil while maintaining catalyst activity, thus optimizing the FCCU's profitability within the catalyst circulation limit. The cost of the co-catalyst is minor, while the direct measured value creation at the Catlettsburg refinery was over \$1/bbl.

**Background.** The Catlettsburg FCCU was originally commissioned in 1983 as the world's first reduced crude conversion (RCC) process unit.<sup>2</sup> The process unit had a nominal capacity of 43,000 bpd (43 Mbpd). The reactor/riser system operated at low pressure to minimize the hydrocarbon partial pressures and to promote full and rapid vaporization of the resid feedstock.

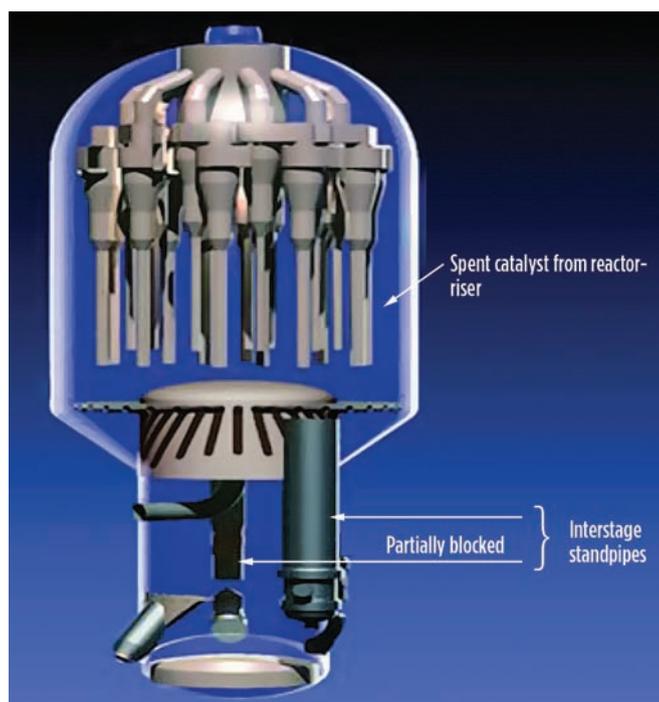
A unique feature of the design was a two-stage regenerator with a common flue-gas header. The two-stage design operated in partial-burn mode, with a typical carbon dioxide (CO<sub>2</sub>)/carbon monoxide (CO) ratio of 4. The regenerator used two catalyst coolers that generated 450-psig steam for heat-balance management. The regenerator flue gas was processed by limestone fluidized bed CO boilers, followed by a pair of baghouses for particulate capture. The regenerator pressure was controlled through a pair of flue-gas slide valves.

The RCC unit was converted to an FCCU in 2003 as part of an overall refinery re-positioning project. By feeding hydrotreated vacuum gasoil (VGO), the result was a nominal 95-Mbpd FCC capacity. The unit pressure was increased, and the two-stage regenerator was converted to full-burn operation. The catalyst coolers were decommissioned with one converted to an intra-regeneration standpipe to facilitate improved catalyst distribution. All of the existing equipment was reused with the exception of a new main air blower.

**FIG. 1** shows the present regenerator configuration. Catalyst exiting the riser is directed via the catalyst stripper to the upper section of the regenerator. In this section, the catalyst is burned relatively clean, with over 90% reduction in catalytic coke, which is deposited on the catalyst during the cracking process

in the riser. The remaining coke on the catalyst is burned in the lower, hotter section of the regenerator. The catalyst is then transferred from the upper regenerator to the lower regenerator via two standpipes. The catalyst leaves the bottom of the lower regenerator and is sent to the riser for the next cracking cycle.

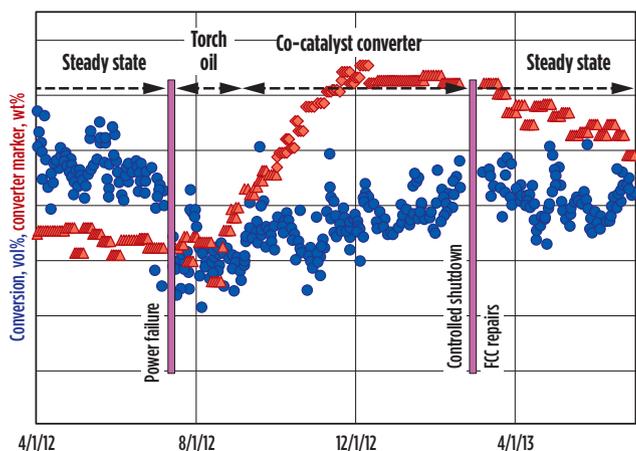
**Situation.** Upon re-starting the unit, following an unplanned refinery shutdown due to a power failure, the unit experienced a catalyst flow restriction in one of the intra-regeneration standpipes. The reduced catalyst flow to the lower section compromised the heat balance, which was brought into an operable range by injecting torch oil. The FCCU was allowed to resume operations at the desired feedrate. The high localized temperature generated by the torch oil combustion was detrimental to



**FIG. 1.** A schematic of the two-stage regenerator; the standpipe on the back end was partially blocked.

**TABLE 1.** Comparison of total catalyst and heating costs during the three cases

| Case number                                   | 1                           | 2                          | 3                                |
|---|-----------------------------|----------------------------|----------------------------------|
| <b>Operational mode</b>                       | <b>Low ROT steady state</b> | <b>Torch oil emergency</b> | <b>Co-catalyst under control</b> |
| <b>Riser/reactor operation</b>                |                             |                            |                                  |
| Combined feedrate, bpd                        | Base                        | Base                       | Base                             |
| API gravity, °API                             | Base                        | Base                       | Base                             |
| Feed temperature, °F                          | Base                        | Base                       | Base                             |
| Riser outlet temperature, °F                  | Base                        | Base                       | Base                             |
| C/O ratio, wt/wt                              | Base                        | Base - 2.10                | Base - 0.66                      |
| <b>Regenerator conditions</b>                 |                             |                            |                                  |
| Regen bed temperature, °F                     | Base                        | Base + 91                  | Base + 22                        |
| <b>Fresh catalyst and torch oil</b>           |                             |                            |                                  |
| Fresh cat + co-catalyst makeup, tpd           | Base (Fresh cat only)       | 2.3* Base (Fresh cat only) | 1.5* Base (1:1 ratio)            |
| Torch oil costs                               | Zero                        | High                       | Zero                             |
| <b>Total cost of heating the unit, \$/bbl</b> | <b>Base</b>                 | <b>Base + \$1.20</b>       | <b>Base + \$0.10</b>             |
| <b>Equilibrium catalyst</b>                   |                             |                            |                                  |
| Activity, FACT%                               | Base                        | Base + 1.0                 | Base + 1.0                       |
| Nickel, ppmw                                  | Base                        | Base - 33                  | Base - 21                        |
| Vanadium, ppmw                                | Base                        | Base - 336                 | Base - 210                       |
| <b>Conversion</b>                             |                             |                            |                                  |
| Standard fresh feed conversion, vol%          | Base                        | Base - 1.40                | Base + 0.35                      |
| Cutpoint temperature, °F                      | Base                        | Base                       | Base                             |



**FIG. 2.** Actual operating data at the Catlettsburg refinery during the three cases.

catalyst activity. Consequently, catalyst addition was increased to maintain catalytic activity.

Because the unit processes very clean feed, the metal deposition on the catalyst is low, and the activity of its equilibrium catalyst (e-cat) is typically well maintained. Under normal steady-state operations, this unit uses very low levels of fresh catalyst. With the injection of torch oil, catalyst deactivation accelerated, and the catalyst addition rate more than doubled the typical usage to sustain activity at a desired level.

MPC worked with its catalyst supplier to identify possible options to optimize the FCCU's profitability. A co-catalyst was quickly identified as a viable solution for Catlettsburg.<sup>1</sup>

**Co-catalyst.** The co-catalyst selected provides high activity and porosity with a large total surface area at 410 m<sup>2</sup>/g. It has a high Z/M ratio with maximum rare earth on the zeolite, thus the catalyst is stable even at high regenerator temperatures. The matrix provides a tailored porosity to allow the diffusion of heavy hydrocarbons into the particle, resulting in selective cracking.

The co-catalyst is designed to fundamentally change unit performance faster than what can be achieved via a base catalyst change-out and, to a greater extent, than conventional operational changes. The flexibility provided by co-catalysts allows refiners to quickly respond to changes in operational issues, take advantage of changing economics, address feedstock changes, or simply improve the conversion of the existing base catalyst to maximize profitability.

The use of a co-catalyst as a torch-oil replacement strategy at Catlettsburg was the first application of its kind. MPC understood that the co-catalysts' high activity would provide consistent additional Δ coke, based on previous experiences. A risk assessment determined that there was little downside exposure by using the co-catalyst system.

**Results.** The FCCU at Catlettsburg has a large catalyst inventory compared to other units with similar feedrates. Therefore, the co-catalyst was used at the high end of the usage rates. MPC chose to utilize the co-catalyst at a 1:1 ratio with the existing fresh catalyst formulation. Notwithstanding the high ratio of co-catalyst to fresh catalyst, the actual addition of the co-catalyst to the unit reached 30% of the inventory just before the planned shutdown to repair the unit. The co-cata-

**TABLE 2.** Comparison of operating conditions during the three cases

| Case number                                   | 1                     | 2                           | 3                         |
|---|-----------------------|-----------------------------|---------------------------|
| Operational mode                              | Low ROT steady state  | Torch oil emergency         | Co-catalyst under control |
| <b>Riser/reactor operation</b>                |                       |                             |                           |
| Combined feedrate, bpd                        | Base                  | Base                        | Base                      |
| API gravity, °API                             | Base                  | Base                        | Base                      |
| Feed temperature, °F                          | Base                  | Base                        | Base                      |
| Riser outlet temperature, °F                  | Base                  | Base                        | Base                      |
| C/O ratio, wt/wt                              | Base                  | Base - 2.1                  | Base - 0.66               |
| <b>Regenerator conditions</b>                 |                       |                             |                           |
| Regen pressure, psig                          | Base                  | Base                        | Base                      |
| Regen bed temperature, °F                     | Base                  | Base + 91                   | Base + 22                 |
| Total air rate (dry), MSCFll                  | Base                  | Base + 423                  | Base + 28                 |
| Flue gas CO <sub>2</sub> , vol%               | Base                  | Base + 0.2                  | Base + 0.1                |
| Flue gas CO, vol%                             | Base                  | Base                        | Base                      |
| Flue gas O <sub>2</sub> , vol%                | Base                  | Base + 0.01                 | Base                      |
| <b>Fresh catalyst and torch oil</b>           |                       |                             |                           |
| Surface area                                  | Base                  | Base                        | Base + 19                 |
| Fresh cat + co-catalyst makeup, tpd           | Base (Fresh cat only) | 2.3 * Base (Fresh cat only) | 1.5 * Base (1:1 ratio)    |
| <b>Total cost of heating the unit, \$/bbl</b> | <b>Base</b>           | <b>Base + \$1.20</b>        | <b>Base + \$0.10</b>      |
| <b>Equilibrium catalyst</b>                   |                       |                             |                           |
| Activity, FACT%                               | Base                  | Base +1.0                   | Base + 1.0                |
| Nickel, ppmw                                  | Base                  | Base - 33                   | Base - 21                 |
| Vanadium, ppmw                                | Base                  | Base - 336                  | Base - 210                |
| CRC, wt%                                      | Base                  | Base                        | Base                      |
| ZSM-5 additive content, wt%                   | Base                  | Base                        | Base                      |
| Rare-earth oxides, wt%                        | Base                  | Base                        | Base                      |
| <b>Conversion</b>                             |                       |                             |                           |
| Standard fresh feed conversion, vol%          | Base                  | Base - 1.34                 | Base + 0.35               |
| C <sub>3</sub> <sup>+</sup> Liquid, vol%      | Base                  | Base - 0.10                 | Base + 0.17               |

lyst was introduced to the FCCU in the third week of August 2012, and, as shown in **FIG. 2**, conversion began to recover.

During the torch oil injection period, even at increased catalyst addition rates, the conversion dropped substantially by about 3 vol%. Soon after the incident on the standpipes, the refinery's production plan changed due to market demands, and the riser outlet temperature (ROT) was reduced to maximize light cycle oil (LCO) production. This move further exacerbated the situation, as a lower ROT means lower catalytic-coke generation and, therefore, lower regenerator temperature. During this time, the refinery experienced three economic burdens placed on the FCCU:

- The increased operating cost of expensive torch oil
- The value creation loss through the conversion drop
- The increased catalyst usage to maintain process activity.

The blockage in the interstage standpipe substantially reduced catalyst flow from the cooler section to the hotter section of the regenerator. This, in turn, compromised the catalyst circulation from the regenerator to the reactor. To maintain the regenerator temperature, a combination of high preheat, torch

oil and lower feedrate stabilized the FCCU operation but at a lower catalyst-to-oil (C/O) ratio.

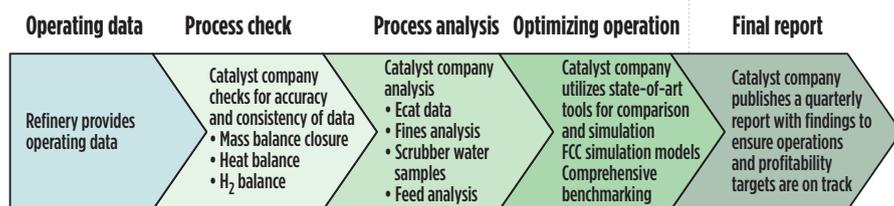
The FCC simulations, based on steady-state conditions, are used to eliminate the effects of extraneous variables in the evaluation.<sup>3</sup> It is well known that catalytic conversion is the most profitable conversion process, as it increases the total liquid yield of high-valued products. This is also valid for the co-catalyst, as it has the highest activity per unit of catalytic coke make. As summarized in **TABLE 1**, the C/O ratio during the torch oil campaign dropped 25%. As expected, there was a corresponding decrease in conversion loss, as oil feed did not "see" sufficient catalyst for cracking to occur.

When comparing the torch oil, Case 2, with the co-catalyst, Case 3, it is apparent that the C/O ratio with co-catalyst increased 23% over the torch oil period. The increase in C/O accompanied with co-catalyst's higher activity made it possible for the conversion to increase 1.75 vol% above the torch oil (Case 2) or 0.35 vol% above the Base Case.

Co-catalyst not only increased volume conversion, but, more importantly, the high activity of the product generated

**TABLE 3.** Comparison of yield slates during the three cases

| Case number  | 1                           | 2                           | 3                                |
|--|-----------------------------|-----------------------------|----------------------------------|
| <b>Operational mode</b>  | <b>Low ROT steady state</b> | <b>Torch oil emergency</b>  | <b>Co-catalyst under control</b> |
| Unit net profit, \$/bbl  | Base                        | Base - \$0.83               | Base - \$0.52                    |
| <b>Riser/reactor operation</b>   |                             |                             |                                  |
| Combined feedrate, bpd   | Base                        | Base                        | Base                             |
| Riser outlet temperature, °F   | Base                        | Base                        | Base                             |
| C/O ratio, wt/wt   | Base                        | Base - 2.1                  | Base - 0.66                      |
| <b>Fresh catalyst</b>  |                             |                             |                                  |
| Fresh cat + co-catalyst makeup, tpd  | Base (Fresh cat only)       | 2.3 * Base (Fresh cat only) | 1.5 * Base (1:1 ratio)           |
| <b>Total cost of heating the unit, \$/bbl</b>  | <b>Base</b>                 | <b>Base + \$1.20</b>        | <b>Base + \$0.10</b>             |
| <b>Equilibrium catalyst</b>  |                             |                             |                                  |
| Activity, FACT%  | Base                        | Base +1.0                   | Base + 1.0                       |
| Nickel, ppmw   | Base                        | Base - 33                   | Base - 21                        |
| Vanadium, ppmw   | Base                        | Base - 336                  | Base - 210                       |
| CRC, wt%   | Base                        | Base                        | Base                             |
| ZSM-5 additive content, wt%  | Base                        | Base                        | Base                             |
| Rare-earth oxides, wt%   | Base                        | Base                        | Base                             |
| <b>Volume percent basis</b>  |                             |                             |                                  |
| Dry gas (H <sub>2</sub> + H <sub>2</sub> S + C <sub>1</sub> + C <sub>2</sub> + C <sub>2</sub> <sup>-</sup> ), vol% | Base                        | Base + 0.52                 | Base + 0.03                      |
| Propane, vol%  | Base                        | Base + 0.01                 | Base + 0.16                      |
| Propylene, vol%  | Base                        | Base - 0.26                 | Base + 0.03                      |
| n-Butane, vol%   | Base                        | Base - 0.07                 | Base - 0.02                      |
| Isobutane, vol%  | Base                        | Base - 0.45                 | Base + 0.33                      |
| Total butenes, vol%  | Base                        | Base - 0.04                 | Base - 0.11                      |
| Total C <sub>3</sub> + C <sub>4</sub> , vol%   | Base                        | Base - 0.10                 | Base +0.61                       |
| C <sub>5</sub> <sup>+</sup> gasoline (450°F cutpoint), vol%  | Base                        | Base - 0.64                 | Base - 0.09                      |
| LCO (450°F to 680°F), vol%   | Base                        | Base + 1.00                 | Base - 0.50                      |
| Decant (680°F +), vol%   | Base                        | Base + 0.34                 | Base + 0.15                      |
| C <sub>3</sub> <sup>+</sup> liquid, vol%   | Base                        | Base - 0.10                 | Base + 0.17                      |

**FIG. 3.** Information flow to support refinery operations to create maximum value.

sufficient catalytic coke that the refinery could reduce the torch oil injection rate. The transition from torch oil to co-catalyst converter was rapid. By the end of September, the torch oil injection was reduced to virtually zero. Additionally, total catalyst additions (base catalyst plus co-catalyst) were reduced by over 30%. Finally, application of the co-catalyst provided operating flexibility and allowed MPC to schedule a controlled shutdown.

**Post-audit results.** As part of its relationship with its catalyst supplier, MPC Catlettsburg regularly provided the catalyst sup-

plier with operating data and economics of the Catlettsburg refinery. This partnership and sharing of data creates an opportunity for the catalyst company to provide technical support reports that detail an ongoing systematic evaluation of the FCCU. The reports are a framework for conversations regarding the matching of an optimal catalyst solution to meet the changing needs of the refinery. **FIG. 3** gives a graphical summary of the work flow or activities involved in ensuring that quality discussions are possible.

MPC's Catlettsburg refinery personnel worked with the catalyst company to evaluate the benefits of co-catalyst vs. torch-oil injection. An FCC simulation using a commercially available FCC model was done.<sup>4</sup> Using the data from a period in which the refinery was running well under steady-state conditions, a Base Case model was constructed. It is well known that there are many interacting variables affecting the performance of the FCCU. An analysis was undertaken to answer questions such as

the impact of co-catalyst on the constant feed, ROT and other operating conditions. All comparisons were done on the basis of constant ROT and matched the actual operating conditions such as regenerator temperature, C/O ratio, and the yield slate. Case 1 or steady state is the Base Case, as shown in **TABLE 2**.

Case 2, denoted by the *torch-oil case*, simulated the operating conditions when the refinery was experiencing the problems when one of the interstage standpipes between the two sections of the regenerator was partially blocked. In this case, the sustained unit operation was achieved by injecting torch oil and increasing catalyst addition. An empirical method was agreed upon to simulate the torch oil injection, and it was utilized to match the actual catalyst-addition rates and refinery operating conditions. The empirical approach was a heuristic method to simulate lowering of catalyst activity by artificially increasing the sodium in the feed to match the activity. As torch oil was not a regular feature of the operation, it was not included in the economics calculation performed by the simulation model.

Finally, the co-catalyst, or Case 3, was a simulation where there was no torch oil in the unit and the FCCU was running smoothly with the base catalyst and co-catalyst alone.

From the simulation output of **TABLE 2**, the major constraint is the heat balance management. Initially, this necessitated using torch oil to overcome the constraint. But, the torch oil also severely deactivated the FCC catalyst and required increasing the catalyst-addition rate to maintain the equilibrium activity of the circulating catalyst.

To maintain the equilibrium activity at the desired level, the refinery initially used increased catalyst during the torch-oil period. Then, when the co-catalyst was introduced, conditions changed. The volume of torch oil was reduced initially and finally eliminated while still maintaining the equilibrium activity.

The dense-bed regenerator in Case 3 is about 70°F lower than Case 2 as operations were optimized to increase the catalyst circulation rates closer to the restricted limit. The unit ran smoothly at C/O that was approximately 25% higher than Case 2. The end result during the co-catalyst campaign was a liquid volume increase of 0.3 vol% higher than Case 2.

At the same time, liquid volume expansion improved and the yield slate improved as well. The activity of the co-catalyst was able to generate sufficient catalytic coke to enable removing the torch oil, and the refinery was able to harvest a higher selectivity of desired products. Dry gas was significantly lower by 0.5 vol%, while propylene and butylene yields matched or exceeded the Base Case. The gap created in gasoline yield, between Cases 1 and 2, with torch oil, was closed when the co-catalyst replaced the torch oil in Case 3. Decant oil (bottoms) was also reduced. However, LCO yield was lower because of the high activity of the cracking of the primary intermediates into gasoline and light olefin products.

From **TABLE 3**, the unit net profit decrease with the co-catalyst was \$0.31 better than the case with torch oil. Again, the simulation model does not take into account the costs for torch oil into its economic valuation, which nonetheless, is still a real cost and valued at over \$1.20/bbl.

**Lessons learned.** As a result of the partial blockage of the interstage standpipes, the FCC unit was seriously challenged in circulating catalyst between the regenerator and the reactor. While the partial plug could only be remedied by a shutdown, the most economical option was to search for ways to keep the FCCU in operation and to take a planned shutdown when it best suited the refinery's schedule. Surveying the field of options, the best possible solution was boosting activity with a highly selective co-catalyst capable of providing the heat to sustain the regenerator, while at the same time providing excellent product selectivity.

The flexibility provided by the co-catalyst system allowed MPC Catlettsburg refinery to quickly respond to changes in operational issues. The reduction in operating cost and improved yields provided MPC well over \$1/bbl in benefits. In addition, the co-catalyst positively affected the yield slate, but the greatest benefit to the refinery was that it allowed the refinery management to bring the unit under control and to take a planned shutdown at a time of their own choosing. **HP**

#### NOTES

<sup>1</sup> BASF's high-activity Converter.

<sup>2</sup> The RCC process was jointly developed by UOP and Ashland.

<sup>3</sup> The tables presented in this study are based on KBC Profimatics runs.

<sup>4</sup> KBC's FCC-SIM simulation model was used.

**JEFFREY SEXTON** is the refining technology manager for Marathon Petroleum Co., located in Findlay, Ohio. He directs the efforts of 22 process-subject-matter experts to provide technical and operational expertise and to support Marathon's downstream organization. He previously worked for UOP in a variety of FCC assignments and has worked on over 40 different FCC units around the world. Mr. Sexton was previously the cat-cracking subject-matter expert for Marathon responsible for FCC technical and operating performance. He has authored over 25 technical papers, holds multiple patents and made several presentations at the NPRA (now AFPM) and other industry forums. Mr. Sexton is currently the chairman of the US EPA Consent Decree FCC Technical Team and PSRI Technical Advisory Committee. He holds a BS degree in chemical engineering from Rose-Hulman Institute of Technology.

**NIKOLAS LARSEN** is a cat-cracking subject-matter expert for Marathon Petroleum Co., located in Findlay, Ohio. As a corporate technologist, he provides technical/operational expertise and support for Marathon's eight FCC units. Mr. Larsen has also held a variety of other technical and supervisory positions within Marathon at different locations. He holds a BS degree in chemical engineering from the University of Notre Dame.

**JOHNNY HIGHFIELD, JR.** is the operations coordinator at Marathon Petroleum Co.'s (MPC) Catlettsburg, Kentucky refinery. In this position, he coordinates plantwide operations activities including policies, procedures and training. Mr. Highfield serves as the operations sulfur recovery advisory group leader for MPC's seven refineries. He has 17 years of experience in a variety of technical and operations positions at the Catlettsburg refinery and has one pending patent. Mr. Highfield holds a BS degree in chemical engineering from the University of Kentucky.

**SOPLY ISMAIL** is the FCC modeling and additives technical service specialist for BASF located in Iselin, New Jersey. Before joining BASF, he worked at major South African refineries where he received numerous awards. Mr. Ismail holds an MS degree from Lehigh University and an MBA from the University of South Africa.

**DANIEL NEUMAN** is a senior account manager for BASF located in Owings Mills, Maryland. He has considerable experience in FCC technology and earned BS and MS degrees in chemical engineering from Tufts University in Medford, Massachusetts. He is the holder of several patents, and has authored many papers for the refining catalysts industry.

We create  
chemistry  
that makes  
speed love  
flexibility.



BASF Co-Catalysts quickly provide fundamental change in an FCCU's performance. These high powered products allow refiners to quickly respond to changes in operational issues, take advantage of changing economics, address feedstock changes, or simply improve the conversion of its existing base catalyst. When Co-Catalysts help meet the ever-changing needs of the refiner, it's because at BASF, we create chemistry.

[www.catalysts.basf.com/refining](http://www.catalysts.basf.com/refining)

 **BASF**

The Chemical Company