Shell Refinery Accelerates Bottoms Upgrading into Gasoline and Diesel Using a Novel FCC Catalyst Solution

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Maximizing diffusion of feed into and products out of an FCC catalyst is critical to unlocking the full value potential of an FCC unit in which the riser residence time is only a few seconds. RIVE® FCC catalysts incorporate Molecular Highway® Y-zeolite (MHY™) technology, which engineers a precise series of mesopores into the Y-zeolite framework, the primary active component of all FCC catalysts. This technology enhances diffusion of molecules into and out of the catalyst.

Building on the continued success of Rive Technology (Rive) and W. R. Grace & Co. (Grace) at a Shell U.S. Gulf Coast (USGC) refinery in 2016 [1], a customized catalyst solution incorporating MHY™ zeolite was designed and trialed at a second North American Shell refinery. The primary objective of this trial was to increase FCC bottoms upgrading into valuable gasoline and diesel products.

The trial results again demonstrated the significant value that this technology can provide to an FCC unit. During the trial, Shell was able to realize uplift in the range of \$1.45 to \$1.80 /BBL_{FF} (within the boundary of the FCC unit) depending on the market economics.

This article will further investigate Molecular Highway® Y-zeolite technology and how it was successfully used to improve performance at this refinery.

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Molecular Highway® Y-Zeolite Technology

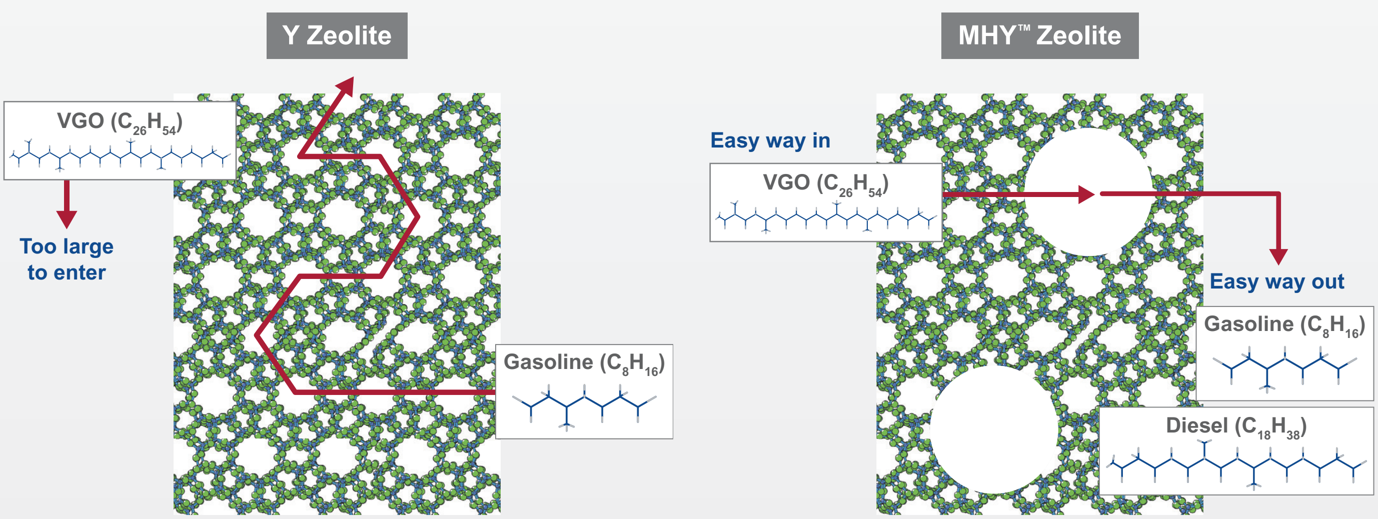
Since 2010, Rive and Grace have jointly developed and commercialized Molecular Highway® Y-zeolite (MHY™) technology for use in FCC units throughout the world. The MHY™ zeolite has a vast network of intermediate-sized (~40 Å) mesopores, which significantly enhances diffusion of the feed and cracked products.

The interconnected network of mesopores permits access for larger feed molecules that vaporize in the FCC unit at temperatures above 950°F to the strong acid sites in the zeolite framework. These acid sites are able to crack the larger feed molecules much more selectively than conventional active matrix materials. The improved diffusion within the zeolite drives bottoms upgrading into LPG olefins, gasoline, and LCO, without coke or gas penalties that are often associated with alternate technologies. Additionally, the MHY™ zeolite helps to channel the valuable cracked products out of the catalyst before the products succumb to potentially undesirable reactions such as over-cracking into dry gas, olefin saturation via hydrogen transfer, or coke formation via condensation reactions. These concepts are illustrated in Figure 1.

In June 2019 (after conclusion of this trial), Grace acquired the assets of Rive, including its patented MHY™ zeolite technology. This strengthened Grace's catalyst portfolio by enabling more rapid deployment of the technology across new catalyst frameworks. Through our flexible manufacturing technology, Grace can control the amount of mesoporosity in MHY™ zeolite to help refiners optimize their profitability. Alternative catalyst technologies claiming high mesoporosity lack the ability to engineer controlled, ordered, and interconnected mesoporosity **in the zeolite itself**.

Grace's MHY™ zeolite technology is protected by more than 40 patents around the world and has been applied successfully to more than 10 FCC units globally since 2011. Catalysts containing MHY™ zeolites typically provide the highest value in FCC units processing heavier feedstocks, particularly if the refinery is challenged by unit constraints such as maximum regenerator temperature, wet gas compressor rate, or air blower rate. However, refineries processing lighter feeds have still gained substantial uplift (>$0.50/BBL) from the diffusional improvements facilitated by MHY™ zeolite technology.

Molecular Highway® Y-zeolite (MHY™) Technology



Small pores in conventional Y zeolites work well with molecules that boil up to 950ºF (510ºC).

MHY™ zeolite technology creates larger pores, allowing zeolites to crack larger molecules that boil in the 950-1100ºF (510-593ºC) range.

Figure 1: Overview of MHY™ Zeolite Technology

The mesopores engineered into MHY™ zeolite allow larger feed molecules access to zeolite active sites for more selective catalytic cracking, while allowing the valuable cracked products to quickly exit.

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The catalyst used at this Shell refinery was customized to meet the specific objectives and constraints – namely, using improved diffusion to upgrade slurry into valuable gasoline plus distillate.

In Figure 2, the picture on the left shows a Scanning Electron Microscope (SEM) image of a conventional Y-zeolite. Each crystal face contains ~106 micropores of 7.5 Å diameter, which cannot be observed even at 100,000x magnification. The picture on the right shows a micrograph of MHY™ zeolite at similar magnification. While the micropores still cannot be seen at this magnification, the extensive network of MHY™ mesopores is clearly visible.

Mesopores in MHY™ zeolites are homogeneously distributed and interconnected within the zeolite. Researchers at Stockholm University used novel imaging techniques to investigate the internal architecture of MHY™ zeolite.

Electron tomography and rotational electron diffraction were utilized to provide an unprecedented, three-dimensional view inside the zeolite crystal, as shown in Figure 3. These images show clear evidence that MHY™ mesopores are homogeneously distributed and interconnected within the zeolite crystal, enabling enhanced diffusion of molecules into and out of the zeolite, thereby improving catalytic performance.[2]

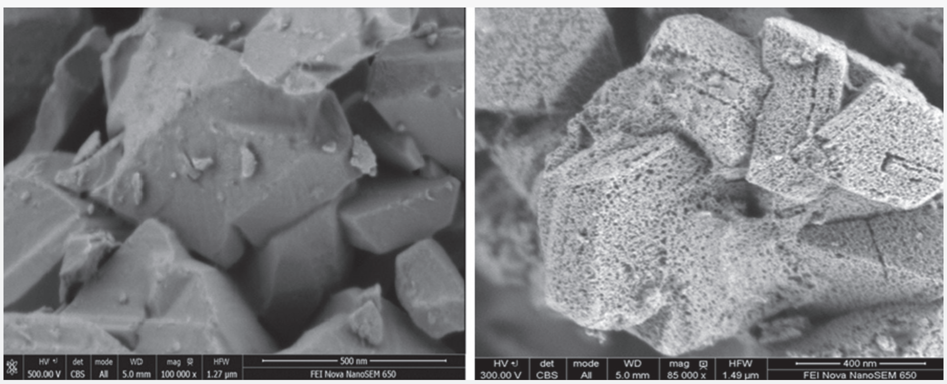

Figure 2: Micrographs of Conventional Zeolite (left) and MHY™ Zeolite (right)
At similar magnifications, micropores in conventional zeolite are not viewable (left image), while the 40 angstrom network of mesopores within MHY™ zeolite are viewable (right image).

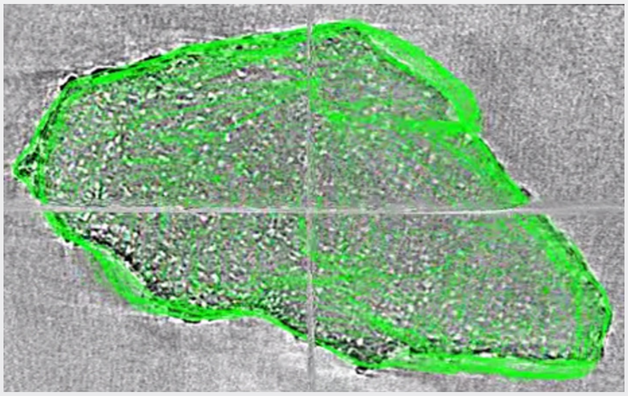

Figure 3: Molecular Highways in MHY™ Zeolite [2]
Electron tomography and rotational electron diffraction by Stockholm University show the network of mesopores are interconnected and extend throughout the MHY™ zeolite.

Shell North American FCC Unit

The FCC unit is a Shell revamped Kellogg design which typically processes low sulfur VGO. The regenerator operates in partial burn, and the unit typically maximizes feed rate to the air blower limit. The primary product objectives are to maximize gasoline + diesel. Catalyst circulation rate and LPG production are usually near their maximum rates. Mixed C_4's has a minimum olefinicity specification. No purchased Ecat or other catalyst additives are used at this refinery.

Catalyst Trial Objectives

Grace and Rive together were awarded a trial at the refinery based on excellent pilot testing results from a competitive RFP and proven success at another Shell refinery using a RIVE® FCC catalyst. While some of the objectives and constraints differed between these Shell FCCs, both units were able to benefit from improved hydrocarbon diffusion through the catalyst. The primary objective of this trial was to increase product revenue while maintaining excellent physical properties of the catalyst. Avenues to increasing FCC revenue included:

- Increase conversion and liquid volume
- Decrease slurry yield
- Increase gasoline + diesel yield
- Reduce dry gas yield
- Maintain LPG yield
- Maintain or reduce catalyst addition rate

Through a comprehensive ACE™ testing program and subsequent modeling and optimization, Grace and Rive designed a catalyst to meet the refinery's objectives. Value uplift was predicted to be approximately \$0.92/BBL_{FF} using RFP pricing. Catalyst improvement projections were independently confirmed via laboratory testing at Shell's Technology Center (Houston) and modeling with Shell's proprietary SHARC® model.

Trial analysis and evaluation was a joint team effort by Rive, Grace, Shell's technology group, and the refinery personnel. Several different methods were used to analyze the trial and determine the catalyst's uplift, including:

- Operating Data Evaluation (cross-plots; comparing similar time periods)
- Ecat Data Evaluation (cross-plots; ACE™ testing at before and after Ecat turn-over to the RIVE® FCC catalyst)
- FCC Kinetic Modeling

Risk Mitigation and Technical Service

Prior to the trial, the combined team worked closely to create a risk management plan. Key risk management items included:

- Ensuring C_4 olefinicity remained above minimum specifications
- No increase to catalyst attrition/losses
- Regenerator bed temperature would remain within specified limits

For each risk, the team created a detailed monitoring plan and mitigation plan. Near the start of each review throughout the trial, each of these risk management items was discussed. With the high level of attention and review frequency, each item was maintained or improved during the trial.

Collaboration between Rive, Grace, Shell's technology group, and the refinery personnel ensured a successful trial. The entire team worked to push the unit to significantly improved profitability, by leveraging the catalyst's benefits at optimized operating conditions. Grace was also able to utilize the technical expertise from its Global Customer Technology group to assist with fine tuning operating variables during the trial.

Evaluating Operating Data

The combined team monitored daily operating data throughout the trial to evaluate the effects of the catalyst change. Updated process data was shared by the refinery on a weekly basis. The following graphs provide operating data comparisons between the incumbent catalyst and RIVE® FCC catalyst at > 30% T/O in unit inventory and normal partial burn operation.

It was important to the refinery that the catalyst addition rate did not increase during the trial. The box plot in Figure 4 shows that the catalyst addition rate during the trial decreased by approximately 0.03 lb/BBL_{FF}.

Figure 5 shows a comparison of Feed API, which indicates the feed was slightly heavier during the RIVE® FCC catalyst trial compared to pre-trial operation. This degradation of feed quality typically makes slurry upgrading into valuable products more challenging.

Catalyst Addition Rate, lb/BBL

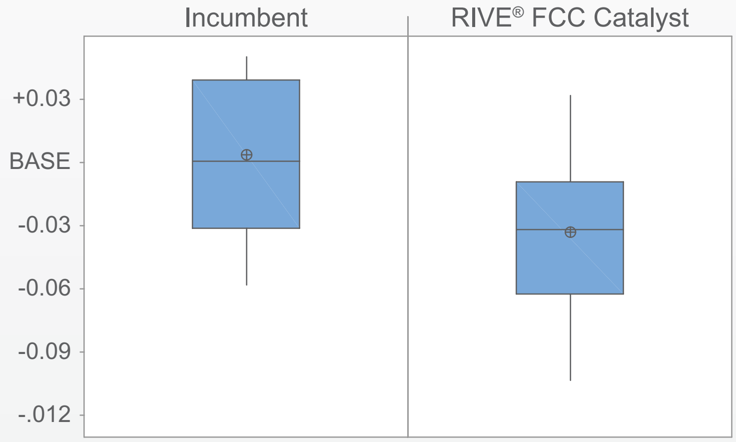

Figure 4: Catalyst Addition Rate

A box plot comparison of catalyst addition rate (lb/BBL_{FF}) indicates a 0.03 lb/BBL reduction in catalyst usage with RIVE® FCC catalyst.

Feed Gravity (°API)

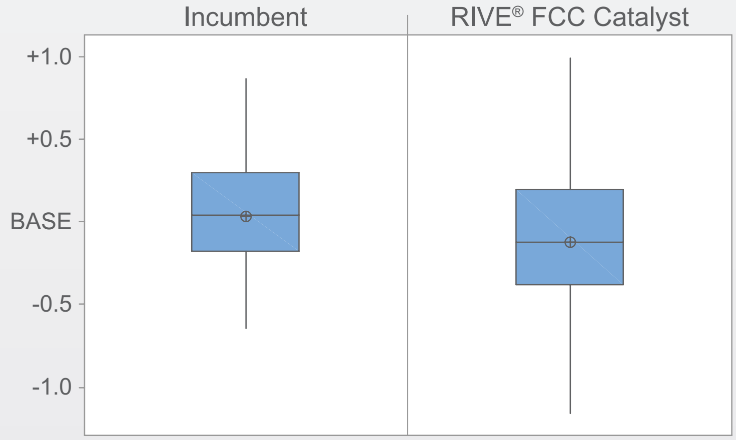

Figure 5: Feed API

A box-plot comparison of feed gravity indicates the feed quality was slightly heavier (worse) during the RIVE® FCC catalyst trial.

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Because of the reduced fresh catalyst addition rate and heavier feed quality, the metals on Ecat increased. Compared to pre-trial operation, nickel on Ecat was 300 mg/kg higher and vanadium on Ecat was 500 mg/kg higher. Also, the refiner reduced the ratio of Sb/Ni by approximately 20% intentionally, as lower gas factors were observed during the trial.

Despite the higher Ecat Ni and V and lower Sb/Ni ratio, the dry gas selectivity (Figure 6) was only slightly higher for the RIVE® FCC catalyst. Had the unit maintained Ecat metals and Sb in a similar range to the pre-trial period, reduced dry gas production would have been expected.

Based on economics and unit constraints, it was desirable for LPG production to be near the same levels as pre-trial operation. As shown in Figure 7, LPG selectivity was approximately the same as the incumbent catalyst.

The most valuable products at the refinery, on a per bbl of product basis, were Gasoline and LGO (Light Gas Oil, similar to the lighter range of typical Light Cycle Oil), and the main trial objective was to maximize slurry upgrading into these products. As the Gasoline cut-point changed frequently, Figure 8 shows the selectivity of the combined 'Gasoline + LGO' product. At a given conversion, the RIVE® FCC catalyst provided approximately 2.0 $vol\%_{FF}$ higher yield.

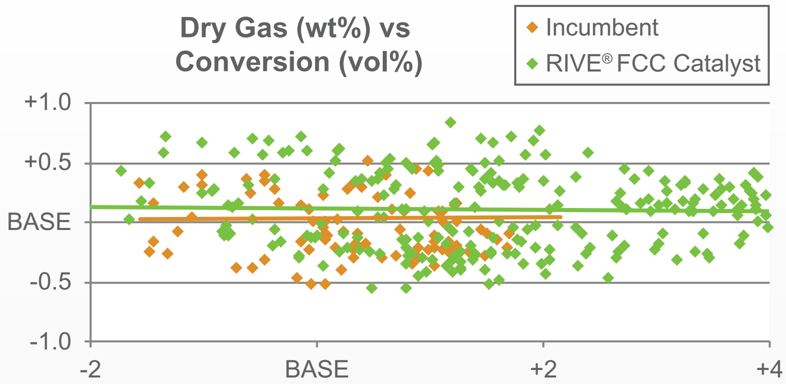

Figure 6: Dry Gas Selectivity

With +300mg/kg Ni on Ecat, +500mg/kg V on Ecat, and a 20% reduction in Sb/Ni, the RIVE® FCC catalyst showed only slightly higher dry gas selectivity than the incumbent.

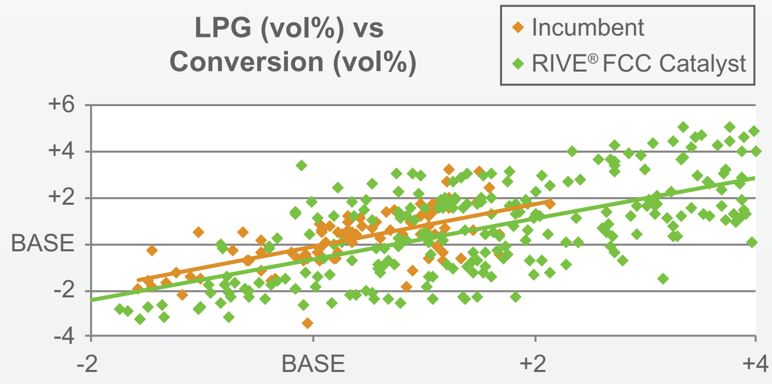

Figure 7: LPG Selectivity

As desired, LPG selectivity was approximately the same as the incumbent.

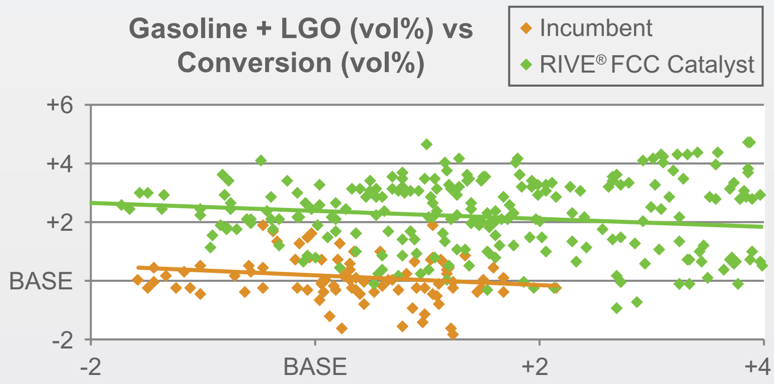

Figure 8: Gasoline + LGO Selectivity

RIVE® FCC catalyst provided approximately 2.0 $vol\%_{FF}$ higher Gasoline + LGO yield (most valuable products), compared to the incumbent.

Figure 9 shows the Slurry product selectivity. For a given conversion, the RIVE® FCC catalyst provided approximately 0.6 vol%$_{FF}$ lower Slurry yield.

The box plot in Figure 10 compares the slurry gravity of pre-trial operation to the operation with RIVE® FCC catalyst. Consistent with the improved slurry selectivity shown in Figure 9, the slurry gravity decreased during the trial by about 2.5 °API, which was the lowest historical slurry gravity noted by this Shell site during periods of normal operation. Slurry upgrading was so improved that during the trial, when lighter feed was processed, Shell altered cut-points to ensure slurry gravity did not fall below their minimum requirement.

Evaluating Similar Periods of Operation

To better understand the effects of the catalyst change, similar Summer periods of operation were compared between the catalysts. Figure 11 provides a comparison of Ecat metals during these periods. As noted previously, Ni and V were significantly higher during the RIVE® FCC Catalyst period, while the ratio of Sb/Ni on Ecat was notably lower.

Figure 12 provides the yields (vol%FF) at these two similar periods of operation. Despite having higher Ecat metals, bottoms upgrading improved dramatically, resulting in an additional 2.0 vol%FF of gasoline and diesel-range products.

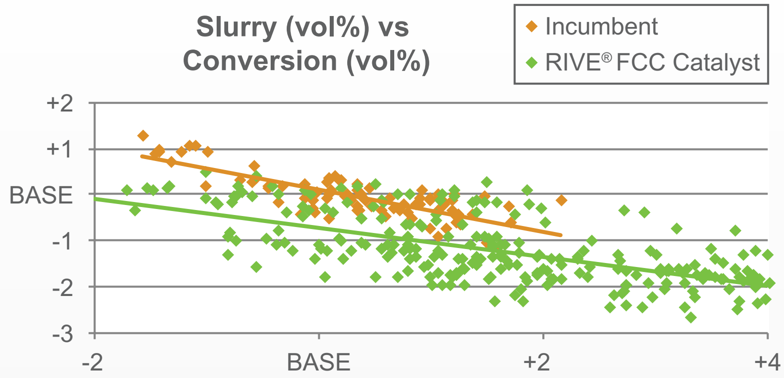

Figure 9: Slurry Selectivity

RIVE® FCC catalyst upgraded approximately 0.6 vol%$_{FF}$ more slurry than the incumbent.

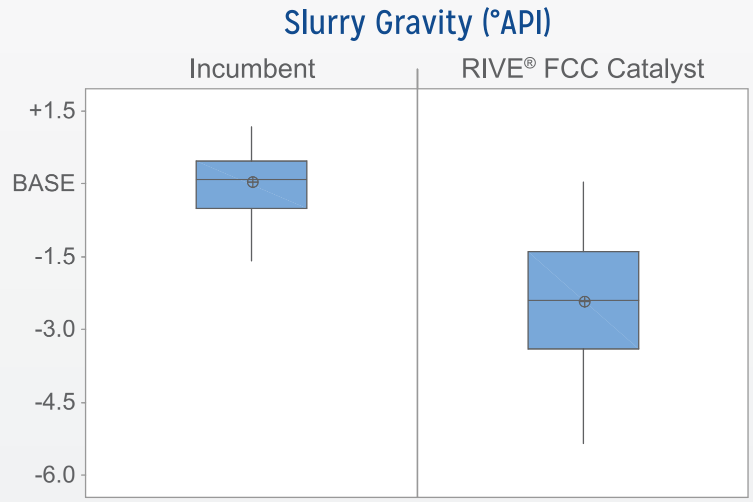

Figure 10: Slurry Gravity

The slurry gravity decreased by about 2.5 °API during the RIVE® FCC catalyst trial.

	May - June 2017 Incumbent Catalyst	June 15 - August 8, 2018 RIVE® FCC Catalyst
Ecat Ni, mg/kg	Base	+ 290
Ecat V, mg/kg	Base	+ 550
Ecat Sb/Ni	Base	- 0.04

Figure 11: Ecat Metals Comparison between Summer 2017 and Summer 2018

Ecat Ni and V was significantly higher during the RIVE® FCC catalyst period, while Sb/Ni was lower.

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	May - June 2017 Incumbent Catalyst	June 15 - August 8, 2018 RIVE® FCC Catalyst
C_3's, vol%	Base	- 0.15 vol%
C_4's, vol%	Base	- 0.05 vol%
Gasoline, vol%	Base	+ 0.90 vol%
LGO/HGO, vol%	Base	+ 1.10 vol%
Slurry, vol%	Base	- 0.65 vol%
Total C_3+ Liquid Volume, vol%	Base	+ 1.15 vol%

Figure 12: Yields Comparison between Summer 2017 and Summer 2018
The RIVE® FCC catalyst demonstrated improved bottoms upgrading into gasoline and diesel products.

	Incumbent Ecat	RIVE® FCC Catalyst (80% T/O)	Comments
Activity			
Cat-to-Oil Ratio, wt%/wt%	Base	- 0.17	Increased Activity
Ecat Metals, mg/kg			
Ecat Ni	Base	+ 62	Increased
Ecat V	Base	+ 126	Increased
Ecat ACE™ Yields, wt%			
Coke	Base	No change	Constant Coke
Total Dry Gas	Base	No change	Same, despite higher Ecat Ni and V
LPG	Base	- 0.2	Slightly lower
Gasoline	Base	+ 0.6	**Increased Significantly**
LCO	Base	+ 0.1	Slightly higher
Bottoms	Base	- 0.5	**Decreased Significantly**
LPG Olefinicity	Base	No change	Same

Figure 13: Ecat Benchmark ACE™ Study
An ACE™ study was performed using Shell feed on pre-trial and 80% T/O RIVE® FCC catalyst Ecat. The results agreed that slurry was significantly improved, resulting in increased gasoline + diesel yields.

Evaluating Ecat Data

Grace performed ACE™ testing to benchmark the trial Ecat against the incumbent Ecat using Shell feed collected just prior to the trial. Testing Ecat samples on this feed removes variation in commercial feed and operational impacts and isolates the effects of the catalyst change. However, differences in Ecat metals and test unit residence time still affect the ACE™ testing results.

The ACE™ study evaluated the following Ecat samples:

- Pre-trial incumbent Ecat
- 80% turn-over (T/O) RIVE® FCC Catalyst Ecat

Consistent with observations previously noted in operating data, slurry upgrading improved, driving yields of Gasoline + LCO, at constant coke. Dry gas yield was the same, despite higher Ecat metals. LPG yield and LPG olefinicity were similar to the incumbent, as desired. The results of this ACE™ study are provided below in Figure 13.

The ability to maintain LPG olefins is a particularly notable point in this application. In other applications of MHY™ zeolite technology, an increase in LPG olefinicity is often noted. However, due to the unique catalyst design employed in the Shell trial, the RIVE® FCC catalyst was able to hold LPG olefins at a constant level. This demonstrates the flexibility inherent in the MHY™ zeolite technology and RIVE® FCC catalyst systems.

Modeling Highlights

Using a variety of test run cases, Rive Technology and Grace used kinetic modeling to estimate more accurate yield/uplift comparison, while Shell independently used their SHARC® kinetic model to evaluate the results.

Both models agreed that the RIVE® FCC catalyst provided significant value improvement for Shell. Contributors to value improvement included (a) increased C_3+ total liquid volume, (b) increased slurry upgrading into gasoline and diesel products, and (c) decreased dry gas at a given Ecat metals level. Modeling results were aligned on an uplift improvement of \$1.45 to \$1.80 /BBL_{FF} (within the boundary of the FCC unit), depending on the market economics. This uplift range was consistent with the results gathered from comparing similar periods of summer operating data. The value uplift realized at the refinery exceeded the initially predicted $0.92/ BBL_{FF}, since Shell realized more bottoms upgrading than initially projected.

Looking Forward

Based on the positive results observed at the unit and through the evaluation above, Shell continues to use a RIVE® FCC Catalyst. Based on mutual learnings from our combined team, as well as predicted changes to feed quality and product pricing, an optimized RIVE® FCC catalyst formulation was developed for the refinery, which is projected to further increase uplift by >$0.40/ BBL_{FF}.

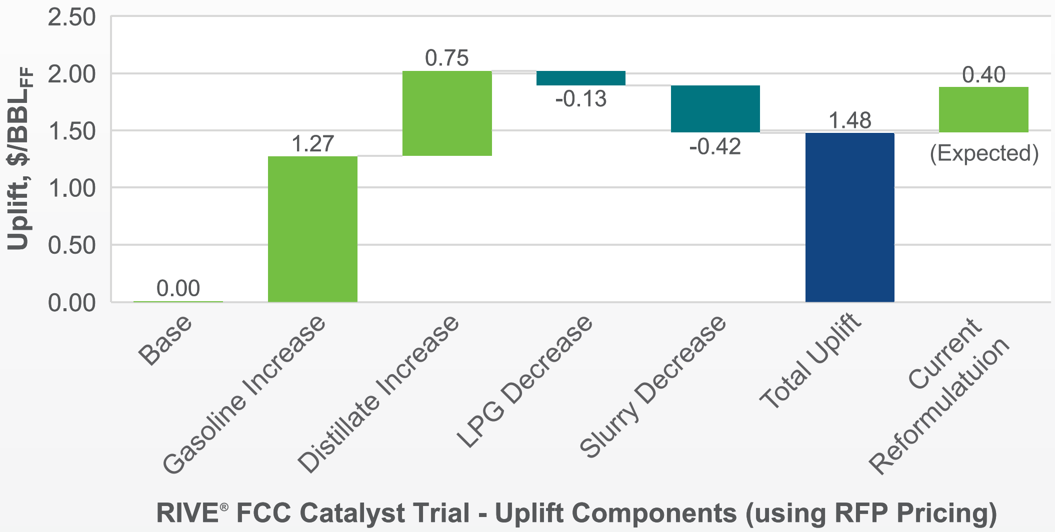

Figure 14: RIVE® FCC Catalyst Continues to Drive Value at the Shell Refinery

Conclusions

1. The results from this commercial FCC catalyst trial support the fundamental principle that improving diffusion of feed into and product molecules out of active zeolite crystals is critical to unlocking the full value potential of an FCC unit, in which the riser residence time is only a few seconds.
2. In line with the refinery's objectives, the following FCC performance improvements were documented at normal operating conditions, relative to pre-trial conditions comparing the RIVE® FCC catalyst to the incumbent base catalyst.
   a. Total C_3+ liquid volume increased by 1.15 vol%
   b. Slurry yield decreased by 0.65 vol%
   c. Gasoline yield increased by 0.90 vol%
   d. LGO/HGO yield increased by 1.10 vol%
   e. Dry gas remained approximately the same with significantly higher Ni and V and reduced Sb on Ecat.
3. Extensive FCC modeling with multiple kinetic models, Ecat benchmark ACE™ testing, and operating data comparison between periods of similar operating conditions, confirmed uplift in the range of $1.45 to $1.80 /$BBL_{FF}$ (within the boundary of the FCC unit), depending on feed quality and market economics.
4. Performance improvements, strong technical service, and collaborative relationship between Shell, Grace, and Rive Technology resulted in a continued use of the RIVE® FCC catalyst after the trial, and an enhancement to the catalyst which is expected to drive even more value from the FCC.

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