We don’t just make FCC catalysts, we make FCC catalysts for YOU.

Grace Davison is the global leader for FCC catalysts and additives, offering solutions-oriented approaches backed by a broad, highly differentiated portfolio and industry-leading technical service. Grace Davison’s research leadership and flexible manufacturing system support value-added technology tailored to meet customer’s current and future needs.

Technology | Support | Experience
Investing in Innovation

It's a fact that many companies slash research and development during difficult economic times. But, in keeping with our value of putting our customers first, Grace Davison has held R&D expenditures and increased capital budgets to support investment in new technologies.

So why invest in innovation? One of our core principles emphasizes building strong customer relationships by meeting current needs while anticipating future challenges. And investment in research pays for Grace Davison and our refining customers on a daily basis with optimized operations.

What does investment in innovation look like?

Anticipating future challenges—Zeolite performance underlies FCC technology. Accessibility and activity are key. That's why we're excited to join with Rive Technology on the revolutionary "Molecular Highway" technology to deliver FCC catalysts that extend the possibility of catalyst performance in ways we can only anticipate. You are invited to get a first glimpse at this process inside. We look forward to working with you and Rive to develop the catalysts that not only meet, but exceed your future challenges. Let us know how you think this innovation will help you.

Meeting current customer needs—We don't need to restate the current rare-earth situation. You already know all about it, but what you don't know is that Grace Davison's Research scientists never lost focus on the importance of low and zero rare-earth catalysts and additives. We continue to examine the role of rare-earth in catalyst performance and how to not only use less rare earth but to maximize its efficiency and minimize, or even eliminate, its use.

Our world-class Technical Service engineers support you so that you realize the maximum value from our commitment to the future of refining. We've included an update on equilibrium catalyst trends from the last decade to help you benchmark your operation and catalyst performance. And Grace Davison and ART Tech Service engineers have collaborated on an article inside detailing the optimization of FCC feed hydrotreater and FCC unit performance to drive the combined operation for maximum product value.

Grace Davison restates our pledge to invest in innovation to make you, our customers, successful.

We welcome your comments.

Sincerely,

Rosann K. Schiller
Senior Marketing Manager
Grace Davison Refining Technologies
03 Jointly Developed FCC Catalysts with Novel Mesoporous Zeolite Deliver Higher Yields and Economic Value to Refiners
By Barry Speronello, Javier Garcia-Martinez, Allen Hansen, Rive Technology and Ruizhong Hu, Grace Davison Refining Technologies

17 The Development of Rare-Earth Free FCC Catalysts
By Colin Baillie and Rosann K. Schiller, Grace Davison Refining Technologies

23 A New Generation of Super DESOX® Additive
By Eric Griesinger, Marketing Manager, Grace Davison Refining Technologies

24 ResidUltra™: Low RE Catalyst Technology for Resid Processing Applications
By Sudhakar Jale and Ruizhong Hu, Grace Davison Refining Technologies

27 Worldwide FCC Equilibrium Catalyst Trends
By Olivia A. Topete, Grace Davison Refining Technologies

33 GDNOX™ 1 Additive - Grace Davison’s Next Generation NOx Reduction Additive
By Eric Griesinger, Grace Davison Refining Technologies

34 Improving FCC Economics with Light Olefins Additives
By Kristen Wagner, Grace Davison Refining Technologies

35 Higher Profits from Higher Sulfur
By Kristen Wagner, Grace Davison Refining Technologies

37 Grace Davison’s EZ™ Loader Additive Injection System
By Kelly Stafford, Grace Davison Refining Technologies

38 Balancing the Need for Low Sulfur FCC Products and Increasing FCC LCO Yields by Applying Advanced Technology for Cat Feed Hydrotreating
By Brian Watkins and Charles Olsen, Advanced Refining Technologies and David Hunt, Grace Davison Refining Technologies
Jointly Developed FCC Catalysts with Novel Mesoporous Zeolite Deliver Higher Yields and Economic Value to Refiners

Background

Rive Technology and Grace Davison are commercializing advanced fluid catalytic cracking (FCC) catalyst technology that dramatically increases the yield of transportation fuels per barrel of crude oil. Rive’s Molecular Highway™ technology makes traditional zeolite catalysts more capable of cracking large hydrocarbon molecules, and allows valuable primary cracked products, like gasoline and diesel molecules, to more readily escape the catalyst before they are overcracked to less valuable light gases and coke. This new catalyst is a drop-in replacement for current catalysts and will enable refiners to increase throughput and profitability without capital investment. In this paper we explain Rive™ zeolite technology, describe its incorporation into a Grace proprietary catalyst matrix formulation, and discuss preparations for a first refinery trial later this spring.
Rive’s Molecular Highway™ Technology

Since the introduction of zeolite-based catalytic cracking in the 1960’s, zeolite Y has been the active ingredient of choice. It’s relatively stable at the high temperatures within the FCC unit (up to about 1400˚F) and very efficient at catalyzing the cracking of smaller FCC feed molecules that can enter through its micropores, with pore mouths of about 0.7 nm. However, as illustrated in Figure 1, many feed molecules are too large to enter Y zeolite micropores and must first pre-crack less selectively either thermally or outside of the zeolite before entering the zeolite crystals. Similarly, larger gasoline and LCO product molecules are a tight fit within zeolite pores and can take a relatively long time to leave the zeolite crystal. During that relatively long stay within the micropores, such valuable products can be re-cracked (overcracked) to less valuable gases and coke.

Rive™ zeolite technology was invented at MIT in the early 2000’s by Garcia-Martinez and Ying. It improves on zeolite Y by creating a network of intermediate sized (2 - 6 nm.) mesoporous “molecular highways” throughout the crystals of zeolite Y. These “molecular highways” admit and pre-crack even the largest feed molecules, while also channeling product gasoline and diesel molecules safely out of the zeolite.

Mesopores in Rive™ zeolite can be clearly seen in transmission electron microscope (TEM) images, such as those shown in Figure 2. Figure 2a is a TEM image of a conventional Y zeolite crystal showing its rows of lattice reflection lines resulting from the regular atomic structure within the crystal (a few are highlighted in red for clarity). Figure 2b of a mesoporous Rive™ zeolite crystal similarly shows the crystal lattice lines, but in addition one can see the larger, lighter colored spots corresponding to the mesopores in the Rive™ zeolite (a few of which are circled in red).

The size and volume of mesopores created in Y zeolite can be controlled over a fairly wide range with Rive’s Molecular Highway™ technology. Figure 3, below, shows a pore size distribution typical of that used for catalytic cracking. The graph compares the cumulative pore volumes of both Rive™ Y zeolite and conventional Y zeolite as a function of pore diameter, and it shows that both types contain a large volume of micropores at <20 Å. (<2 nm.) diameter. In addition, however, Rive™
Both types contain catalytic micropores. 

<table>
<thead>
<tr>
<th>Pore Width, Å</th>
<th>Cumulative Pore Volume, cc/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td>0.45</td>
<td>0.40</td>
</tr>
<tr>
<td>0.40</td>
<td>0.35</td>
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<tr>
<td>0.35</td>
<td>0.30</td>
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<tr>
<td>0.30</td>
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<tr>
<td>0.25</td>
<td>0.20</td>
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<tr>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Rive™ zeolite also contains larger, “Meso” pores.

Both types contain catalytic micropores.

Rive™ Technology can control the amount and size of the mesopores.

---

**Figure 2a**
TEM Photomicrograph of Standard Y Zeolite

**Figure 2b**
TEM Photomicrograph of Mesoporous Rive™ Y Zeolite

**Figure 3**
Argon Adsorption Showing 40 Angstrom Mesopores Created in Y Zeolite by Rive’s Molecular Highway™ Technology
zeolite also contains about 0.15 cc/gm of larger pores in a very narrow range at about 40 Å in size. These 40 Å (4 nm), "meso" sized pores are unique to Rive™ zeolite and are the key to achieving the superior cracking yields described below. The catalytic impact of these zeolite mesopores complements matrix porosity that has been fine-tuned by FCC catalyst manufacturers over the past 50 years of zeolite based FCC catalysts.

**Catalytic Properties of Rive™ Zeolites and Catalysts**

Initial screening experiments for catalytic cracking of VGO were done by Dr. Garcia-Martinez to compare the cracking yields of powdered pure mesoporous ultrastable Y zeolite (USY) with pure conventional USY in a fluid bed micro-activity test unit at the National Center for Upgrading Technology (NCUT) in Devon, Alberta, Canada, and the results showed greatly improved yields with the mesoporous material.

Figure 4, shows a yield comparison of zeolites steamed for 4 hours at 1450°F and 100% steam. At equal 70 wt.% conversion, mesoporous USY increased gasoline yield 10% relative from 42% to 47%, increased distillate (LCO) yield by 20% relative, and decreased coke yield by 20% relative! These selectivity improvements were a dramatic confirmation of the benefits of zeolite mesoporosity for improving large-molecule cracking and reducing loss of gasoline to coke and gases.

Since that time Rive Technology has focused its efforts on capturing that magnitude of improved performance (i.e., uplift) in formulated FCC catalysts. In mid-2010 Rive and Grace Davison entered a joint development and marketing agreement for products that combine Rive’s Molecular Highway™ technology with Grace’s market leading knowledge of catalyst formulation and manufacturing. The program’s goal is to develop revolutionary new FCC catalysts based on the two technologies. Progress has been rapid, and a first refinery trial is planned for late spring of 2011.

Initial work focused on formulations using relatively inert silica sol matrices with testing being done at the Chemical Processing Engineering Research Institute (CPERI), Thessaloniki, Greece. A range of formulations was tested, and Figure 5, below,
shows ACE testing results for a preferred formulation after steaming for 4 hrs at 1450°F and 100% steam.

Table I lists the feed properties. While the feed used for this study had a relatively low CCR and 90% boiling point, its low API gravity and high Ca show that it is relatively aromatic and difficult to crack.

Figure 5a is a plot of gasoline yield vs. conversion comparing a catalyst containing Rive™ zeolite (in Red) to a catalyst containing conventional zeolite. The zeolites were processed to have the same steamed crystal unit cell size and the catalysts had the same zeolite contents and matrix formulations.

Figure 5a shows that the benefits of Rive™ zeolite mesoporosity translate well from pure zeolite powders to catalysts. In this case the uplift was about 3 percentage points (about 6% relative) compared to the catalyst made using conventional zeolite.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPERI Feedstock Properties</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td><strong>°API</strong></td>
</tr>
<tr>
<td><strong>CCR</strong></td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
</tr>
<tr>
<td><strong>IBP</strong></td>
</tr>
<tr>
<td><strong>50%</strong></td>
</tr>
<tr>
<td><strong>95%</strong></td>
</tr>
<tr>
<td><strong>Kwatson</strong></td>
</tr>
<tr>
<td><strong>Ca</strong></td>
</tr>
</tbody>
</table>
Similarly, Figure 5b compares the coke yields of the two catalysts and shows that the catalyst having Rive™ zeolite made about 1 percentage point (15% relative) less coke than the catalyst containing conventional zeolite.

LCO yields (Figure 5c) were similar for the two catalysts, though, so the advantage in bottoms cracking seen with the pure powders was diminished when mesoporous zeolite was formulated into a silica sol matrix and used to crack this relatively challenging feedstock.

The first commercial catalyst formulations containing Rive™ mesoporous zeolite were developed based on ACE testing using paraffinic vacuum gasoil. Controls for these tests were alumina-matrix commercial catalysts A (moderate
rare earth) and B (high rare earth). Both equilibrium catalyst and lab deactivated fresh catalysts were used in the comparisons.

Figure 6 contains graphs of conversion vs. cat/oil ratio, and selectivities vs. conversion for the equilibrium and lab deactivated versions of commercial catalyst A. It shows that the deactivation conditions used for this test (8 hrs/1450°F/100% steam) were somewhat less severe than that experienced in the FCCU, but the selectivity matches were excellent.

Figure 7, below, is a comparison of a steamed GRX™ catalyst formulation containing a moderate rare earth mesoporous Rive™ zeolite with lab steamed commercial catalyst A. The two catalysts were substantially equal in activity, yielding similar conversions at equal cat/oil ratios. There was also little difference in gasoline selectivity between the two. There was, however, a significant benefit in bottoms upgrading and coke selectivity for the GRX™ catalyst containing mesoporous Rive™ zeolite, and those benefits are particularly evident in the graph of bottoms
yield vs. coke. At constant 3% coke, the GRX™ catalyst produced 1/3 lower bottoms relative to the catalyst containing conventional zeolite (5% vs. nearly 8%).

Figure 8 below shows a similar comparison for GRX™ and conventional zeolite-containing alumina matrix catalysts at higher rare earth content. Again catalyst activities were equal, but at higher rare earth level there was a significant gasoline yield advantage for the GRX™ catalyst with mesoporous Rive™ zeolite, along with improved bottoms cracking and coke selectivity.

Overall, Rive™ mesoporous zeolites in different catalyst formulations tested to-date have consistently showed selectivity benefits in one form or another in all tests. The degree of benefit has varied depending upon the overall formulation, and the feedstock used for the test, but directionally performance benefits in bottoms upgrading, gasoline yield, coke selectivity and/or olefinicity have consistently been demonstrated.

Catalyst formulation work is continuing with the objective of achieving the level of selectivity improvement seen with pure zeolite powders. As of today, comparing the catalytic results achieved with pure powdered zeolites with those from formulated catalysts, we estimate that these excellent first improvements have the potential to double when the full potential of the technology is realized.
Economic Value – Creating $0.79 per Barrel in the Refinery

Because of the complex inter-relationship between different units in a refinery and with economic factors like crude pricing and the value spread between feed and cracked products, it is challenging to relate catalyst performance to refinery value. Rive Technology has used industry-standard AspenTech PIMS and KBC Profimatics modeling tools to bridge the gap between lab test results and economic value to the refiner.

The analytical process is shown in Figure 9, below. ACE testing data measured at either CPERI or Grace Davison is processed using either Profimatics FCC-SIMSTM process simulation software, or a proprietary kinetic model developed by Rive Technology to produce catalyst performance factors that, in turn, are converted to Profimatics catalyst factors. Shift vectors generated with Profimatics are then input to a PIMS model of a standard reference refinery and the operation is optimized. Sensitivity analyses have been run on variables such as crude or product pricing, the value spread between feedstocks and products, and different operating limits.
To ensure that crude costs and refinery product pricing data are input into the PIMS model in a consistent manner, correlations were developed based on historic data. We found that the historic cost of each crude and the price for each refinery product could be predicted well using linear functions of the prevailing 3-2-1 Crack Spread and the cost of West Texas Intermediate crude (WTI). Therefore, for any projected WTI cost and crack spread, the price of each crude and each product could be setup systematically in the model.

The hypothetical reference refinery for this process has a 150,000 bpd crude capacity with a 42,000 bpd FCC unit. It has both sour and sweet crude stills. Refinery constraints are listed below:

1. Sweet crude is at rate limit (sour crude rate is usually not a limit, but can be set if desired)
2. Naphtha hydrotreater is feed limited (i.e. reformer naphtha feed treater)
3. FCC is coke limited
4. Hydrocracker is at rate limit
5. Coker is at rate limit
6. Product blending specs

Catalyst factors and shift vectors for the example analysis are based on the GRX/Commercial catalyst comparison summarized in Figure 7. Crude price is set at $75/bbl of West Texas Intermediate (WTI) based on the 2 year average spot price March 2009 thru February 2011. The crack spread is assumed to be $10/bbl; which is consistent with long range projections from the Energy Information Administration (EIA). Later we will show the impact of changes in crude price and crack spread on the economics.

Table II show the PIMS estimates for 2 operating cases. In Case 1 crude rates were allowed to float within the unit constraints of the reference refinery. In Case 2 crude rates were constrained to the levels optimized for the base catalyst case.

Case 1 shows that increased economic value results from the following factors:

1. The combination of improved coke selectivity and reduced gas selectivity for the GRX catalyst with Rive™ mesoporous zeolite allows both the quality of the feed to the FCC unit to be reduced and reactor top temperature to be increased 17°F while keeping within the FCCU coke limit.
   a. Coker Distillate is rerouted from the FCC to the distillate hydrotreater, which augments and improves diesel blending stock and makes the FCCU feed heavier.
   b. Sweet crude train is limited, but to make up diverted FCCU feed and to provide more blend stock for higher quality products coming from the FCCU, more sour crude is run. Naphtha cut point is decreased to
stay within the reformer naphtha pretreater feed limit, thereby swinging more material to kero (jet).

c. FCCU feed rate decreases 1.8%, and feed quality is reduced.

d. Increased riser top temperature results in increased FCCU conversion and also increases the octane and olefin content of the cracked products. Negative value bottoms fall 15%.

2. Feed to the alkylation unit increases as a result of greater olefins from the FCCU and together with the increased octane from the FCCU, total octane barrels is sustained.

3. Added jet from crude allows more FCC hydrotreated heavy naphtha to be blended into diesel instead of jet.

4. Hydrocracker is at its maximum feedrate, but the unit is able to shift yields to more naphtha and less distillate due to increased diesel from both FCC hydrotreated heavy naphtha and coker distillate.

5. Reformer pretreater is limited, but 2.1%

---

### Table II
**Incremental Value of Improved Catalytic Selectivity from GRX™ FCC Catalyst**
All data shown are relative to base case (not shown)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1: Optimized Crude Rates</th>
<th>Case 2: Crude Rates Constrained to Base Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery Throughput</td>
<td>+5.3 vol.%</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Refinery Profitability</strong></td>
<td><strong>+0.79 $/bbl crude</strong></td>
<td><strong>+0.47 $/bbl crude</strong></td>
</tr>
<tr>
<td>Refinery Products:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPG</td>
<td>+0.3 vol.% of crude</td>
<td>+0.2 vol.% of crude</td>
</tr>
<tr>
<td>Gasoline</td>
<td>+1.0 vol.% of crude</td>
<td>+0.3 vol.% of crude</td>
</tr>
<tr>
<td>Distillates</td>
<td>+3.8 vol.% of crude</td>
<td>+2.7 vol.% of crude</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>+0.3 vol.% of crude</td>
<td>-2.6 vol.% of crude</td>
</tr>
<tr>
<td>FCC Riser Temperature</td>
<td>+17˚F</td>
<td>+11˚F</td>
</tr>
<tr>
<td>FCC Rate</td>
<td>-1.8 vol.% of crude</td>
<td>-2.0 vol.% of crude</td>
</tr>
<tr>
<td><strong>FCC Yields:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>+3.8 wt.%</td>
<td>+4.4 wt.%</td>
</tr>
<tr>
<td>Gas</td>
<td>+0.6 wt.%</td>
<td>+0.6 wt.%</td>
</tr>
<tr>
<td>C$_3$+$C_4$ Olefins</td>
<td>+1.2 wt.%</td>
<td>+1.2 wt.%</td>
</tr>
<tr>
<td>C$_3$+$C_4$ Non-Olefins</td>
<td>+1.6 wt.%</td>
<td>+1.7 wt.%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>+0.2 wt.%</td>
<td>+0.8 wt.%</td>
</tr>
<tr>
<td>Distillate</td>
<td>-2.2 wt.%</td>
<td>-2.4 wt.%</td>
</tr>
<tr>
<td>Bottoms</td>
<td>-1.6 wt.%</td>
<td>-2.0 wt.%</td>
</tr>
<tr>
<td>Coke (constant max coke rate constraint)</td>
<td>+0.2 wt.%</td>
<td>+0.1 wt.%</td>
</tr>
</tbody>
</table>
more reformate is produced due to more Hydrocracker naphtha production (which does not need to go through the constrained pretreater).

The net result of these changes, shown in Table II, is a 5.3% increase in refinery throughput with 1.0% coming in gasoline and 3.8% in distillates. The net value of these improvements is $0.79/bbl ($118,000/day, or $43,000,000/yr).

Case 2 in Table II focuses on the value to the FCCU alone by constraining the refinery feed rate to base case levels. Consequently the spillover value to other units is diminished, but there is still an increase in overall distillate and gasoline yields of 3.0% of the crude rate, and the FCCU experiences a 2 wt% drop in bottoms yield. Increased gasoline octane and olefins yields also help sustain octane-barrels.

The values in Table II are based upon a crude price of $75/bbl and a crack spread of $10/bbl. Figure 10, below, shows the impact of changes to these values on the increased profitability of Case 1. It plots the value uplift in $/bbl of crude vs. crack spread ($5/bbl to $15/bbl), and it displays three lines representing WTI crude prices of $63/bbl, $75/bbl, and $87/bbl. This range represents the 10% and 90% points in the distribution of monthly running average WTI prices since March 2009 (see reference viii).

The graph shows that value uplift due to the improved selectivity of GRX™ catalyst containing mesoporous Rive™ zeolite increases nearly linearly with crack spread and roughly the same with increases in crude price. It is highly profitable in all combinations within the explored range. Even under the least favorable condition of $63/bbl crude price and $5/bbl crack spread, the uplift is worth $0.52/bbl crude (ca. $28,000,000/yr). At the most favorable conditions the value uplift is $1.04/bbl crude, or ca. $57,000,000/yr. While it is not shown, sensitivity analysis also indicates that the value uplift due to improved FCC catalyst selectivity is approximately linear with refinery size.

Figure 10
Improved Profitability from FCC Catalyst Containing Rive™ Mesoporous Zeolite as a Function of Crude Cost and Crack Spread
Commercialization

Manufacturing of the first FCC catalyst from this joint program between Grace Davison and Rive Technology is now moving from the pilot scale to full commercial production. Thousands of pounds of Rive™ Y zeolite have been produced at the pilot plant of Grace’s Curtis Bay, MD manufacturing facility, and, as you can see from Figure 11, below, its performance matches that of smaller scale materials made in Rive's Princeton NJ laboratory. Figure 11 compares two catalysts made using the same formulation and rare earth level, but one catalyst contained Rive™ zeolite that was processed in the laboratory and the other contained Rive™ zeolite that was produced in the pilot plant.

Figure 11 shows that catalyst made with pilot plant Rive™ zeolite was more active and had equal selectivity compared to catalyst made using lab-produced Rive™ zeolite. Continuous calcination at the tech center allowed for more uniform stabilization of the zeolite which, in turn, produced a more crystalline and more hydrothermally stable product. At equal zeolite content the pilot plant catalyst had a steamed zeolite surface area of 190 m2/gm compared to 160 m2/gm for the catalyst with lab produced zeolite. Consequently, the pilot plant catalyst had about 25% higher activity (i.e., pilot plant zeolite catalyst achieved 75% conversion at 5.5 cat/oil vs. 7 cat/oil for the lab catalyst).

![Figure 11: Scale-up of Rive™ Zeolite Manufacturing Process at the Grace Davison Technical Center Produced Excellent Quality](image)
Otherwise, the two catalysts were identical. Figure 10 shows that there were no differences in either the gasoline, LCO, or coke selectivities of the two catalysts.

Based on these excellent results, plant modifications to accommodate the Rive process are in progress, and a first refinery trial is scheduled for later in the spring of 2011.

What’s Next?

Along with FCC catalysts based upon Y zeolite, Rive and Grace Davison plan to introduce mesoporous ZSM-5 based catalysts and additives for cracking. Laboratory progress is well along on these materials, and, if things go as expected, first results should be ready for publication by late this year or early in 2012.

References

1. barry.speronello@rivetechnology.com
2. Javier Garcia-Martinez is also a Professor of Inorganic Chemistry at the University of Alicante (Spain): javier@rivetechnology.com
3. allen.hansen@clinchain.com
4. ruizhong.hu@grace.com
6. Product of KBC Advanced Technology, Houston, Texas
7. Product of Aspen Technology, Inc., Burlington, Massachusetts
The Development of Rare-Earth Free FCC Catalysts

Colin Baillie
Marketing Manager
Grace Davison
Refining Technologies
Worms, Germany

Rosann K. Schiller
Senior Marketing Manager
Grace Davison
Refining Technologies
Columbia, MD USA

Rare-earth metals are an important component of FCC catalysts, as well as being a key raw material for many strategic industries with applications ranging from military devices to electronic components. In addition, they are essential constituents in newly evolving green technologies, such as hybrid cars and wind turbines. Rather ironically, rare-earth metals are not so rare, however they tend to be concentrated in hard to extract ore deposits. As a result, the world’s supply comes from only a few sources; China alone accounts for 95% of the world’s rare-earth metal output. Recent export quota restrictions on rare-earth metals from China have caused the price of rare-earth metals to rapidly rise. Because of these new market forces, we present here our progress in the development of rare-earth free FCC catalysts.

Grace Davison has a long history of providing innovation in the development of FCC catalysts, including the addition of rare-earth metals to stabilize the zeolite Y component of the FCC catalyst, which was revolutionary for catalytic cracking. Grace
also has a successful history of developing rare-earth free FCC catalysts as shown in Figure 1. We introduced new catalysts and zeolite components that enhanced gasoline octane in the 1980’s and 1990’s, delivering activity and stability without the use of rare earth. The RE free zeolites were used in over 85% of our catalysts in North America at the time. Later in the 1990’s Grace developed Z-21, a rare-earth free stabilized zeolite Y. Based on this new technology the NEXUS® catalyst family was commercialized in 1997, as a rare-earth free catalyst family for low-metal feed applications. NEXUS® catalyst has since been used in 10 applications.

This article will describe commercial experience of the NEXUS® catalyst family, as well as introduce several new rare-earth free catalyst families. These include REsolution™ and REBEL™ catalysts based on the existing Z-21 zeolite, as well as REactoR™, REplaceR™ and REDuceR™ catalysts based on the Z-22 zeolite, which is a newly developed rare-earth free zeolite.

### Commercial Experience Using NEXUS® Catalysts

In 2008, a refiner conducted back-to-back catalyst evaluations comparing NEXUS® catalyst to a competitive rare-earth based FCC catalyst. The feed properties and operating parameters for both periods were similar. The Ecat Gas and Hydrogen Factors during the back-to-back testing are shown in Figures 2 and 3, respectively. As can be clearly seen, NEXUS® catalyst is more selective at constant nickel equivalents than the competitive offering.

The FCC product yields obtained during back-to-back testing are shown in Table I. NEXUS® catalyst provided higher conversion (2.8 wt.%), lower hydrogen yield (0.04 wt.%), a lower dry gas yield (0.5 wt.%) and a higher gasoline yield (5 wt.%). To summarise, the refiner considered the NEXUS® catalyst trial to be a complete success, realizing a benefit of approximately 1 million €/year. The refinery remains on NEXUS® catalyst to this day.

### New REsolution™ and REBEL™ Catalyst Families Based on Z-21 Zeolite

Recently, Grace Davison has renewed efforts to develop new rare-earth free catalysts. This has involved further formulation development by combining the rare-earth free Z-21 zeolite with new matrices, resulting in the new families of REsolution™ catalysts and REBEL™ catalysts.

Rare-earth free REsolution™ catalysts are intended for low-metal feed applications, and represent a further improvement on NEXUS® catalyst performance.
Within each family of REsolution™ catalysts, the ability to independently adjust the activity and selectivities of zeolite and the matrix, as well as the ratio of zeolite/matrix activity allow for a tremendous degree of formulation flexibility. For low-metal applications REsolution™ will match/improve the performance of standard rare-earth based catalysts. Table II, shows ACE pilot plant testing (CPS-3 deactivation, no metals) comparing REsolution™ and NEXUS catalysts. It can be seen that REsolution™ provides higher conversion and LPG olefins yield, as well as similar gasoline yield, bottoms upgrading and coke. Several trials of REsolution™ catalysts are currently taking place in Europe.

Further R&D work has provided a new rare-earth free high matrix catalyst system for FCC applications. REBEL™ catalyst, formulated with Z-21, demonstrates similar activity and selectivity as Midas® 100 catalyst, and is now under development (Table III).

**Grace’s Latest Zeolite Innovation – Rare-Earth Free Z-22 Zeolite**

Most recently, Grace Davison has achieved a breakthrough with a proprietary stabilization process and a unique treatment step to boost acidity, resulting in Z-22, a state-of-the-art rare-earth free zeolite. Relative to REUSY, Z-22 provides equivalent activity, higher LPG olefins and gasoline octane, at constant bottoms and coke make, as shown in Table IV.
Z-22 zeolite has been successfully produced in our manufacturing plants. Several new catalyst families utilizing Z-22 are now being introduced for hydrotreated or low to moderate feed-metal applications, with one commercial trial currently underway in North America.

The introduction of rare-earth free catalysts that utilize the Z-22 zeolite is also being planned in Europe. For example, REactoR™ catalyst utilizes the Z-22 zeolite, but also incorporates the processing technologies used in NADIUS™ catalyst (a rare-earth based catalyst for low-metal feed applications). ACE pilot plant testing (CPS-3 deactivation, metals free) demonstrates that both catalysts show similar selectivities in terms of dry gas, coke and bottoms upgrading, whilst REactoR™ catalyst provides higher yields of LPG olefins at the expense of some gasoline yield (Table V).

REplaceR™ catalyst is another new rare-earth free catalyst family that is based on the Z-22 zeolite, but this catalyst incorporates the processing technologies used in NaceR™ catalyst (another rare-earth based catalyst for low-metal feed applications). ACE pilot plant testing (CPS-3 deactivation, metals free) comparing REplaceR™ with NaceR™ show that REplaceR™ provides similarly high activity, slightly higher LPG olefin yields and similar bottoms upgrading and coke yield.

These ACE pilot plant results demonstrate that for low-metal applications REactoR™ and REplaceR™ catalyst are suitable rare-earth free alternatives to

---

**Table I**

<table>
<thead>
<tr>
<th>Product Yields</th>
<th>NEXUS®-346</th>
<th>Competitor</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.03</td>
<td>0.07</td>
<td>-0.04</td>
</tr>
<tr>
<td>Dry Gas (+H₂S)</td>
<td>3.60</td>
<td>4.12</td>
<td>-0.52</td>
</tr>
<tr>
<td>LPG</td>
<td>16.25</td>
<td>18.19</td>
<td>-1.94</td>
</tr>
<tr>
<td>Gasoline C₃-210°C</td>
<td>50.16</td>
<td>45.20</td>
<td>4.96</td>
</tr>
<tr>
<td>LCO 210-360°C</td>
<td>15.62</td>
<td>18.72</td>
<td>-3.10</td>
</tr>
<tr>
<td>MCB 360+ °C</td>
<td>7.98</td>
<td>7.68</td>
<td>0.30</td>
</tr>
<tr>
<td>Coke</td>
<td>4.72</td>
<td>4.56</td>
<td>0.16</td>
</tr>
<tr>
<td>Conversion</td>
<td>76.39</td>
<td>73.60</td>
<td>2.79</td>
</tr>
</tbody>
</table>

**Table II**

<table>
<thead>
<tr>
<th>ACE Yields at Constant Conversion (CPS-3 deactivation, metals free)</th>
<th>NEXUS® Catalyst</th>
<th>REsolution™ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-oil</td>
<td>4.9</td>
<td>4.5</td>
</tr>
<tr>
<td>LPG olefins, wt. %</td>
<td>13.7</td>
<td>14.2</td>
</tr>
<tr>
<td>Gasoline, wt. %</td>
<td>49.4</td>
<td>49.4</td>
</tr>
<tr>
<td>HCO, wt. %</td>
<td>10.0</td>
<td>9.8</td>
</tr>
<tr>
<td>Coke, wt. %</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Table III**

<table>
<thead>
<tr>
<th>ACE Yields at Constant Conversion (CPS-3 deactivation, 3000 ppm Ni+V)</th>
<th>REBEL™ Catalyst</th>
<th>MIDAS®-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-oil</td>
<td>5.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Dry Gas, wt. %</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Propylene, wt. %</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Butylenes, wt. %</td>
<td>5.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Gasoline, wt. %</td>
<td>46.6</td>
<td>46.8</td>
</tr>
<tr>
<td>Bottoms, wt. %</td>
<td>9.6</td>
<td>9.5</td>
</tr>
<tr>
<td>Coke, wt. %</td>
<td>4.2</td>
<td>4.3</td>
</tr>
</tbody>
</table>
established rare-earth based catalysts. Within these catalyst families the matrix type as well as the zeolite/matrix ratio can be varied. Additional formulation flexibility is possible, enabling fine tuning of the catalyst to suit FCCU-specific requirements regarding activity and selectivity. REactoR™ and REplaceR™ catalysts are also manufactured with the proprietary Grace Davison alumina-sol binder system, which ensures low particulate emissions due to its excellent attrition resistance.

A Rare-Earth Free Catalyst for Resid Feed Applications

Due to the additional demands placed on zeolite stability, the development of rare-earth free catalysts for the resid feed sector is much more challenging than for the low-metal feed sector. Rare-earth metals remain the most effective vanadium trap. However, processing technology involving metals resistance functionality has now been successfully applied to catalyst systems containing the Z-21 and Z-22 zeolites, resulting in the REduceR™ catalyst family. Although not fully equivalent to the performance of benchmark pure rare-earth based resid catalysts, REduceR™ catalyst can be used as a blending component with a rare-earth based resid catalyst, thus reducing the overall rare-earth requirement. ACE pilot plant testing (CPS-3 deactivation, 5,000 ppm Ni+V) comparing a rare-earth based NEKTOR™ resid catalyst and the same catalyst containing 30% of REduceR™ catalyst are shown in Table VII. To summarise, REduceR™ catalyst, a rare-earth free resid catalyst can be blended with a rare-earth based resid catalyst to provide

---

**Table IV**

Z-22 Delivers the Same Equivalent Activity and Selectivity Without Rare Earth

<table>
<thead>
<tr>
<th>Component</th>
<th>Z-22</th>
<th>REUSY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-oil</td>
<td>6.6</td>
<td>6.8</td>
</tr>
<tr>
<td>Dry Gas, wt.%</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>4.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Butylenes, wt.%</td>
<td>11.0</td>
<td>10.4</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>52.0</td>
<td>53.0</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

---

**Table V**

ACE Testing Comparing NADIUS with ReactoR™ Catalyst

<table>
<thead>
<tr>
<th>Component</th>
<th>NADIUS Catalyst</th>
<th>ReactoR™ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, wt.%</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>LPG Olefins, wt.%</td>
<td>14.6</td>
<td>15.3</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>51.0</td>
<td>50.3</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>1.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

---

**Table VI**

ACE Testing Comparing NaceR™ Catalyst with ReplaceR™ Catalyst

<table>
<thead>
<tr>
<th>Component</th>
<th>NaceR™ Catalyst</th>
<th>ReplaceR™ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, wt.%</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>LPG Olefins, wt.%</td>
<td>13.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>50.4</td>
<td>50.0</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>10.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>2.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>
similar performance in the key areas of activity, bottoms upgrading and coke yield. Grace is continuing R&D work to develop a rare-earth free catalyst with the stability and performance to allow the complete elimination of rare-earth based grades in resid applications.

**Summary**

Grace has a long history of innovation in rare earth free catalysis. In the 1980’s and 1990’s, a large proportion of Grace’s customers in North America utilized RE free zeolite in their catalyst formulations to maximize FCC gasoline octane. In 1997, NEXUS® catalyst, formulated with Z-21, a rare-earth free zeolite, was introduced for low-metal feeds. In 2008, R&D activities were intensified to develop new rare-earth free catalysts. This has resulted in several new catalyst families for the low-metal feed sector as well as several promising leads for resid cracking:

- **REsolution™** catalyst: contains rare-earth free Z-21 zeolite in combination with a new matrix.
- **REactoR™** catalyst: contains the newly developed rare-earth free Z-22 zeolite with the application of the processing technologies used in NADIUS™ catalyst.
- **REplaceR™** catalyst: contains the newly developed rare-earth free Z-22 zeolite with the application of the processing technologies used in NaceR™.
- **REduceR™** catalyst, a rare-earth free resid catalyst, which can be blended at a 30% level into rare-earth based resid catalysts without significant performance deterioration in resid applications.
- **REBEL™** catalyst, a high matrix catalyst formulated with Z-21, yields similar performance as Midas® 100 catalyst after deactivation with metals.

Grace Davison Refining Technologies has responded quickly to the issues of rare-earth price and availability by developing these new rare-earth free catalysts, in order to relieve the cost pressure on customers without incurring performance penalties. The developments involving the new Z-22 zeolite will require modifications to our manufacturing plants, which will limit the short-term availability of some rare-earth free catalyst families. If you are interested in these new rare-earth free catalyst families we suggest that you contact your Grace technical sales and services representatives to find out which catalyst is most suitable for your operation.

**References**

2. Grace Davison Catalagram, European Edition 1999

---

**Table VII**

ACE Yields at Constant Conversion (CPS-3 deactivation, 2500/4500 ppm V/Ni)

<table>
<thead>
<tr>
<th></th>
<th>NEKTOR™ Catalyst</th>
<th>70% NEKTOR™ 30% ReduceR™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-oil</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>LPG Olefins, wt.%</td>
<td>13.8</td>
<td>13.9</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>51.0</td>
<td>50.9</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>7.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>5.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Grace introduces two new SOx additives to mitigate the dramatic price escalation in rare-earth.

These products build upon the proven effectiveness of Super DESOX® additive. Super DESOX® OCI additive is the first generation of low RE SOx additive from Grace. Super DESOX® OCI additive has proven in commercial scale trial to be as effective as the Super DESOX® additive, resulting in on par pick-up factor efficiency.

Additionally, Grace has since developed Super DESOX® MCD additive, a second generation of SOx additive with even lower rare earth. Lab testing suggests that it is possible to attain a suitable and cost effective balance between SOX transfer ability and additions. Super DESOX® MCD additive will be in multiple commercial trials in the second quarter of 2011.

Finally, Grace is actively researching rare earth free SOx additive, Super DESOX® CeRO additive. We will keep you apprised of our progress towards commercialization.
Rare earth oxide is one of the key components of FCC catalysts improving the stability of faujasite zeolite, scavenging feedstock metals and enhancing the selectivity towards desired products. The prices of rare-earth compounds continue to skyrocket due to China’s restricted export quota system and pending environmental regulations, causing a rise in catalyst prices by more than 50%. The catalyst market accounts for about 20% of global rare earth supply in 2010. Even though this share is expected to drop to about 15% due to the growth in other markets, particularly magnets, the demand for rare-earth by volume will increase by about
15% in next 5 years due to the overall growth in catalyst industry. Although several companies in other countries are planning to reopen their rare earth mining and processing facilities, there is expected to be a tight supply of rare earths in the near future.

**ResidUltra™: Catalyst Technology**

The refineries using resid feedstocks need a catalyst to crack larger molecules and deliver optimal coke selectivity. These catalysts typically have higher amounts of rare earth (RE) to trap contaminants in the feed, protecting activity and selectivity. Grace introduced a breakthrough resid catalyst called, IMPACT® catalyst in 2003. IMPACT® catalyst contained a proprietary Integral Vanadium Trap (IVT) technology and has demonstrated step-out improvements in coke selectivity and bottoms cracking in over 70 units worldwide.

Grace has been actively pursuing the development of RE-free and low RE catalysts for various feedstocks. By careful re-optimization of matrix functionalities for bottoms cracking and metals trapping, we have developed a novel catalyst technology called ResidUltra™ catalyst. ResidUltra™ catalyst reduces the RE content by about 40% relative to IMPACT® catalyst and retains the same activity and selectivity with all the benefits of Al-sol binding technology.

ResidUltra™ and IMPACT® catalyst samples from commercial production were deactivated via Cyclic Propylene Steaming (CPS) at 1450°F with 3,000 ppm vanadium and 2,000 ppm nickel and tested side by side in the ACE over resid feedstock. The constant conversion data is summarized in Table 1. Relative to IMPACT® catalyst, ResidUltra™ catalyst has:

- Similar catalytic activity
- Same hydrogen selectivity
- Slightly better coke selectivity
- Similar gasoline, LCO, and bottoms yields
- Slightly higher octane number and LPG olefins yields

Conversion effects for cat-to-oil ratio, coke, hydrogen, and gasoline yields are plotted in Figure 1 and 2. In general, the performance of both of these catalysts can be considered to be equivalent even though ResidUltra™ has about 40% lower RE content. ResidUltra™ is currently in commercial trial at two locations.

### Table I

**The Activity and Selectivity of ResidUltra™ Catalyst vs. State-of-the-Art Resid Benchmark Catalyst**

<table>
<thead>
<tr>
<th></th>
<th>IMPACT® Catalyst</th>
<th>ResidUltra™ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-oil, wt.%</td>
<td>6.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Hydrogen, wt.%</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>Dry Gas, wt.%</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Total C₃’s, wt.%</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Total C₄=’s, wt.%</td>
<td>5.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>50.2</td>
<td>50.8</td>
</tr>
<tr>
<td>LCO, wt.%</td>
<td>18.0</td>
<td>18.1</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>6.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>7.7</td>
<td>7.2</td>
</tr>
<tr>
<td>RON</td>
<td>90.9</td>
<td>91.2</td>
</tr>
</tbody>
</table>
Summary

The ACE results clearly demonstrate that ResidUltra™ has equivalent or better performance than IMPACT® catalyst when tested over resid feed. The 40% reduction in RE content is an excellent economic incentive for refiners processing resid to switch to this novel catalyst technology.

References

1. Chegwidden, J. and Kingsnorth, D.J., “Rare Earths: Facing the Uncertainties of Supply” 6th International Rare Earths Conference, Hong Kong, November 2010.


Worldwide FCC Equilibrium Catalyst Trends
Assessing the First Decade of the 21st Century

The Analytical Services Center (ASC) Tech Service group at Grace Davison receives equilibrium fluid cracking catalyst (Ecat) samples from refineries spanning the globe. On average, Grace receives over 200 Ecat samples each week from the world’s FCCU’s. The resulting information is of critical importance for the FCC unit engineer, who is responsible for continuous optimization and troubleshooting of his/her operation.

The subsequent discussion highlights the trends observed in Ecat properties over the last ten years. The data reflected is not exclusive to Grace Davison products. Samples containing competitive catalyst, additives, and products are also included.

As the refining industry as a whole is challenged by the supply constraints of rare earth, it is interesting to see the trends in properties over the last ten years. Ecat contaminant levels maintain their upward trend as the world
moves to more and more resid processing. Rare-earth remains the most effective means to maintain activity and selectivity in severe operations. However, we are working diligently to reduce the rare-earth content of the catalyst, and maintain performance. At the same time, refiners need to consider the economic tradeoffs associated with rare-earth reductions and assess what process changes can be made in the unit operation to offset any resultant performance differences.

Vanadium

Figure 1 illustrates the trend in vanadium over the first decade of the 21st century. With the exception of 2000 to 2001, the Asia Pacific market unfailingly maintains the highest levels of contaminant vanadium. Interestingly, while all other markets have experienced an increase in average vanadium levels in the latter part of the decade, the Asia Pacific market average has experienced a sudden drop of almost 20% from 2009 to 2010. In its entirety, the averaged FCC world contaminant level has been consistent in a band centered around 2,000 wppm. The North American market continues to demonstrate the lowest levels of vanadium in the world (1,626 ppm).

Nickel

Falling for the first time below 3500 wppm, the Asia Pacific market reliably maintains the top ranking spot for average nickel level in Ecat. As shown in Figure 2, there is a
tremendous differential between Asia Pacific and the rest of the world. The gap never closes to less than 1,600 wppm. The growth in resid processing in Asia will continue this trend in years to come. As with vanadium, the Asia Pacific market has demonstrated a decrease over the past few years while all other markets have shown a small increase. Similar to vanadium, the North American market maintains the lowest average nickel levels (1,363 ppm).

**Iron**

The movement in average iron level on industry Ecat, shown in Figure 3, can best be explained as diverse. The North American market has consistently maintained the highest average levels of iron overall increasing from 0.52 wt.% to 0.6 wt..% Beginning in 2002, the European average iron level began a steady descent from 0.52 wt.% to 0.46 wt.% and has remained at this level since 2007. The worldwide average indicates a downward trend overall for the last three years.

**Calcium**

In 2004, most of the industry Ecat averages faced a steady 4 to 5 year climb in calcium. Asia Pacific led the pack when average levels rose from 0.09 wt.% to 0.2 wt.%.

Figure 4 shows that during the past year, the worldwide trends have tilted downward and will likely continue in that direction.
Sodium

With few exceptions, sodium (Figure 5) has been steadily trending down for over ten years. Latin America continues to maintain the highest values with a median value over the past three years of 0.35 wt.%. North America dropped to a decade average low of 0.26 wt.%. The average vanadium and nickel levels that characterize the Asia Pacific market indicate that this region continues to process feeds that are vastly different from the rest of the world. As alluded to earlier, the average Ecatal results from this territory continue to report the highest average levels for 80% of the primary FCC catalyst contaminants. Up until 2008, most worldwide contaminant trends were directionally consistent. The coming years will be exciting as the industry is challenged to process higher amounts of discounted feedstocks to maintain profitability.

Activity

Until 2004, most of the industry saw a steady climb in Ecatal activity. As indicated by Figure 6, over the next four years, activity trends flattened with slight periodic increases. In 2009, activity numbers regained momentum to reach decade highs in all but the European market. With the highest numbers amongst all four regions, North America experienced an average 3.4 number increase from 69.9 to 73.3 over the last decade. The world wide average
gained 2.9 activity numbers from 68.7 to 71.6 over the same time period.

The continued upward trend in catalyst activity occurred despite a parallel upward trend in contaminants such as vanadium and nickel to decade high levels. Grace’s advanced metals trapping technologies have enabled many refiners to retain activity despite increasing contaminant levels.

### Rare Earth

As shown in Figure 7, worldwide rare earth averages are characterized by a steady upward slope from 1.9 wt.% to 2.9 wt.% \( \text{Re}_2\text{O}_3 \) over the 2000 to 2010 time period. Reaching a high of 3.0 wt.% \( \text{Re}_2\text{O}_3 \) in 2008, the North American average upheld the highest values for the last six years. Consequently, as shown in Figure 6, activity levels also increased with rare earth.

After the price of rare earth increased nearly twenty times in eight months, the topic of rare-earth has quickly become the focal point of many reformulation and new technology efforts. Although market trends have yet to show a significant response, the debut of low and zero rare earth catalysts from Grace will produce a significant shift in Ecatal rare-earth levels from here on out.

### Unit Cell Size

Figure 8 illustrates the trend in unit cell size. Between the years of 2000 and 2005, there was significant variability and
disparity amongst regions. In 2005, the difference between the Latin American and European regions averaged 0.04 Å. The European region also registered an average unit cell size decade high for all regions at 24.32 Å. During the latter part of the decade, market unit cell size began to converge to an average 24.31 Å. The exception, the Latin American region, remains slightly lower at 24.30 Å but the overall regional divergence is significantly reduced in comparison to years prior to 2005.

**Particle Distribution (0 to 40 microns)**

In November 2009, Grace’s routine Ecat particle size test was changed to new instrumentation. The new particle size properties no longer have the micro-mesh factors applied and the results are directly from the equivalent spherical analysis model of the measurement data. As a result, a significant shift in the 2010 data can be seen in Figure 9.

Nonetheless, previous years’ data tells that while there is little variance over time within each region, there is substantial offset amid regions. The worldwide average for 0-40 particle size is 6%. High average catalyst age or low catalyst additions per volume of inventory will decrease the 0-40 fraction and increase average particle size.

Grace remains committed to providing Ecater analyses as a key component of our technical service package for customers. The historical results for any unit can provide an invaluable reference point for troubleshooting activities or assessment of performance deltas after major turn-arounds. Ecater results are available 24/7 on our customer website, www.e-catalysts.com. Contact your sales representative to gain access to your unit’s sample results as well as a host of other technical literature and information.

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**Figure 9**

**Average 0-40 µ wt.% by Region for 2000 to 2010**

![Graph showing average 0-40 µ wt.% by region for 2000 to 2010 with data points for Asia Pacific, Europe, Latin America, North America, and World Wide.]
GDNOX™ 1 Additive - Grace Davison’s Next Generation NOx Reduction Additive

Eric Griesinger  
Marketing Manager, Grace Davison Refining Technologies, Columbia, MD

GDNOX™ 1 additive is the next generation NOx reduction additive for the FCC regenerator unit. Unlike traditional NOx reduction additives, GDNOX™ 1 additive utilizes a new technology platform that builds on the success of DENOX®, while allowing refiners the ability to achieve greater NOx reduction. And, unlike earlier generation NOx reduction additives, GDNOX™ 1 additive greatly mitigates H2 and/or dry gas penalties. GDNOX™ 1 additive is formulated to reduce exposure from inflation in rare earth pricing.

As extensive pilot plant testing shows in Figure 1, refiners have the ability to incrementally improve NOx reduction, by upwards to 80%, with increased GDNOX™ 1 additive dosing rates. To achieve targeted NOx reduction, the recommended dosing rate for GDNOX™ 1 additive typically ranges between 2.5 wt.% and 7.5 wt.% of catalyst inventory.

GDNOX™ 1 additive allows refiners to:

- Meet local/federal NOx regulations,
- Meet EPA constraints without the cost of capital,
- Process feeds high in nitrogen with greater economic flexibility,
- Balance refinery wide NOx emissions, and
- Maintain FCC throughput

Ask your Grace sales representative for more information.

<table>
<thead>
<tr>
<th>GDNOX™ 1 Additive Addition Rate% of Inventory</th>
<th>Base Line NOx (ppm)</th>
<th>NOx After GDNOX™ 1 Additive Addition (ppm)</th>
<th>Percentage NOx Reduction/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% GDNOX 1</td>
<td>292</td>
<td>139</td>
<td>50</td>
</tr>
<tr>
<td>5.0% GDNOX 1</td>
<td>287</td>
<td>110</td>
<td>60</td>
</tr>
<tr>
<td>10.0% GDNOX 1</td>
<td>287</td>
<td>62</td>
<td>80</td>
</tr>
</tbody>
</table>
Improving FCC Economics with Light Olefins Additives

Kristen Wagner
Marketing Manager, Grace Davison Refining Technologies, Columbia, MD

The refining industry is well versed in the use of ZSM-5 light olefins additives for the incremental production of propylene for chemical and polymer applications and butylenes for alkylation unit feedstock. However, light olefins additives are also capable of providing significant flexibility in operating the FCC unit, providing additional economic benefits for the refiner.

Grace delivered incremental profitability to a refiner who took an early turnaround on a catalytic reformer. The refinery was octave short and there was no opportunity to increase riser temperature. Grace recommended the use of a light olefins additive to boost the overall octane from the FCC complex. The use of ZSM-5 increases the yield of C3 and C4 olefins to feed the alkylation unit and any other units designed to create gasoline range material from FCC olefins. The effect of ZSM-5 on the conversion of gasoline olefins to LPG olefins can be seen in Figure 1.

As a result of ZSM-5 cracking, the incremental light olefins production from the FCC results in higher alkylate yields. Alkylate is a refinery blending stream that is high in both motor and research octane. At the same time, the yield of FCC gasoline generally drops at constant riser temperature, but the octane is increased, with general increases ranging from 0.3 to 0.7 numbers.

When the total octane properties of the FCC gasoline and alkylate are added together, there is an increase in the octane of the total gasoline pool from the FCC complex. This is a valuable economic option when the FCC unit is running at reduced feed rates and there is available capacity in the alkylation unit. By varying the concentration of light olefin additive in circulating catalyst inventory, the refiner can take advantage of available capacity in the alkylation unit while independently optimizing the riser outlet temperature. This option may be especially helpful in the fall and winter, when higher LCO yields are generally desirable but a loss in volume gain across the FCC is not.

Grace Davison is the leading supplier of high activity, high stability light olefins FCC additives. OlefinsMax®, OlefinsUltra®, and OlefinsUltra® HZ additives are being used in over 70 FCC units worldwide. They continue to provide economic value for the refiner by generating incremental propylene, additional feed for alkylation and an increase in gasoline octane.
Introduction

The use of GSR® (Grace Sulfur Reduction) technology in the FCC unit can reduce the desulfurization required by the FCC feed hydrotreater, resulting in longer hydrotreater catalyst life and a lower severity operation. GSR® products are used in both short term and long term applications to preserve hydrotreater catalyst life and postpone hydrotreater outages.

Proper management of FCC feed hydrotreater outages is increasingly important as refiners rely heavily on hydrotreating to meet gasoline sulfur limits, while trying to minimize operating costs. Unfortunately, tighter sulfur regulations are forcing refiners to either expand FCC feed hydrotreating capacity or increase severity on their existing hydrotreaters and hydrocrackers, resulting in more frequent turnarounds and higher expenses.

Some methods to manage gasoline pool sulfur limits during a hydrotreater turnaround include purchasing low sulfur FCC feed or reducing FCC throughput. Both options place a greater financial burden on the refiner. Other approaches have been to find outlets for higher sulfur gasoline during a turnaround, but with continued global implementation of sulfur regulations, this option is becoming less viable.

GSR® Technologies

Grace has provided GSR® technologies to the industry for over 17 years to reduce FCC gasoline sulfur by up to 35%. These technologies include D-PriSM® additive, SuRCA® catalyst, GSR® 5 additive, and NEPTUNE™ catalyst. Grace GSR® products are currently being used in all regions of the world today. Aside from reduced hydrotreater severity, other commercial benefits of using GSR® technologies include, FCC feedstock blending flexibility and improved gasoline octane (reduced naphtha post treater severity).

Commercial Performance: GSR® 5 During Hydrotreater Turnaround

Figure 1 is a commercial example of GSR® 5 usage during and after an FCC feed hydrotreater turnaround. Coordinated efforts with Grace allowed the refiner to baseload their inventory and achieve target sulfur reduction levels within three weeks. The

Higher Profits with Higher Sulfur

Kristen Wagner
Marketing Manager,
Grace Davison Refining Technologies,
Columbia, MD
use of GSR® 5 allowed them to process higher sulfur feed yet remain in gasoline pool sulfur compliance. The refiner estimated that GSR® 5 provided a cost savings of over $1.5M during the HDT turnaround by eliminating the need for additional downstream gasoline post treating and therefore maintaining the value in their gasoline stream blending.

Conclusion

Grace holds over 20 GSR® patents and has been the leader in GSR® additives and catalysts since 1996 with D-PriSM®, SuRCA®, GSR® 5, and NEPTUNE™ product options. These catalysts and additives have been used in over 85 FCC units worldwide, with and without hydrotreating hardware, to provide 20%-35% sulfur reduction in the FCC gasoline streams. GSR® technologies reduce sulfur species present in the FCC gasoline boiling range. This advantage allows the refiner to reduce gasoline undercutting, process higher sulfur feeds, reduce CFHDT severity or prevent serve octane requirement during post treatment. These products create economic advantages around FCC feedstock blending, operating flexibility during hydrotreater outages, gasoline stream blending options and advantages with naphtha post treating. In-unit reduction of FCC gasoline sulfur continues to create opportunities and options for refiners to drive profitability.

<table>
<thead>
<tr>
<th>Commercial Experience</th>
<th>D-PriSM®</th>
<th>GSR® 5</th>
<th>SuRCA®</th>
<th>NEPTUNE™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical sulfur reduction levels</td>
<td>15-25%</td>
<td>20-35%</td>
<td>20-35%</td>
<td>40-45%</td>
</tr>
<tr>
<td>Desired unit operation</td>
<td>FB or PB</td>
<td>FB</td>
<td>FB</td>
<td>FB</td>
</tr>
<tr>
<td>Range of application lengths</td>
<td>4-48 months</td>
<td>3-72 months</td>
<td>1-8 years</td>
<td>1 year</td>
</tr>
<tr>
<td>Usage rates (% of inventory)</td>
<td>10-15%</td>
<td>25%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
It has long been understood that optimum additive performance and unit stability in an FCCU are greatly assisted by continuous and steady injection of FCC additives. The challenge has been further complicated in recent years as refiners must now comply with multiple environmental regulations and depend upon stable operation and product addition rates to do so. Grace Davison's newest loader, designed specifically for additive use, combines functionality and reliability with ease of use. The EZ™ Additive Loader’s compact design and ability to load two additives simultaneously offers an EZ™ solution to meet FCCU objectives.

The benefits of an EZ™ Additive Loader system:

- Consistent control of additive injections
- Reliability with low maintenance requirements
- Robust range of injection rates
- Accurate injection weight and record keeping ability
- Advanced Touch Screen control for user-friendly operation
- Compact pre-assembled skid mounted design for simple installation
- Fugitive dust containment (no environmental impact)
- Injection of two materials independently
- Direct connection to additive tote bins

More than just a loader:

- Every EZ™ Additive Loader is tested prior to shipment in our test facility
- Pre-installation training available at our test facility
- Extensive on-site start-up assistance and operating/maintenance instruction
- On-line loader operations manual
- Interactive web-based troubleshooting guide
- Critical spare parts inventory maintained

Stable additive additions to the FCCU are an important part of achieving maximum FCCU profitability. As refiners move to meet more stringent product and environmental regulations, addition systems will become an essential part of the unit control. Grace Davison’s EZ™ Additive Loader system provides a cost effective and reliable means of adding additives on a continuous basis.

Kelly Stafford
Technical Sales Support Coordinator, Grace Davison Refining Technologies, Columbia, MD
Balancing the Need for Low Sulfur FCC Products and Increasing FCC LCO Yields by Applying Advanced Technology for Cat Feed Hydrotreating

The benefits that hydrotreating fluidized catalytic cracking Unit (FCC) feed has on product yields and sulfur content were recognized some time ago and described in many earlier publications\(^2-5\). Recent regulatory demands and the drive towards clean fuels resulted in a renewed interest in FCC feed hydrotreating to facilitate compliance and satisfy the need for improved yields. To address these needs, Advanced Refining Technologies LLC (ART) introduced the ApART\(^\circledR\) Catalyst System for FCC pretreatment \(^6\). This technology was developed to provide significant increases in HDS conversion while at the same time providing significant upgrading of FCC feedstock quality and has been described in detail previously\(^7\).

In essence, an ApART\(^\circledR\) Catalyst System is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each catalyst can be optimized to meet individual refiner’s goals and constraints. ART has continued to develop a better understanding of the reac-
tions and kinetics involved in FCC pretreating, and through its relationship with Grace Davison Refining Technologies, a detailed understanding of the effects of hydrotreating on FCC unit performance. The complexity of combinations of catalyst design and operating conditions for both the FCC feed hydrotreater and the FCC unit continues to present a significant optimization opportunity for refiners to drive the combined operation to maximum product value.

It has been shown that both the hydrotreating catalyst system and the operating strategy for the FCC pretreater are critical to providing the highest quality feed for the FCC. In general, NiMo based catalysts produce FCC feed with lower nitrogen and Poly Nuclear Aromatic (PNA) content than CoMo based catalysts. This shifts the FCC yields towards higher conversion at the expense of LCO production. The operating mode of the hydrotreater can also be used to improve the FCC feed. Driving the hydrotreater to remove more nitrogen and PNA’s (so-called PNA mode of operation) results in an FCC feed which again shifts the FCC products toward more gasoline and LPG production. This is shown in Figure 1, which summarizes the delta FCC yield at constant coke yields from an Advanced Catalytic Cracking (ACE) pilot plant study comparing the effects of hydrotreating FCC feed over a CoMo and NiMo catalyst. The data clearly show that using a NiMo catalyst results in higher FCC conversion along with higher gasoline yield compared to a CoMo catalyst for both low and high FCC pretreat severity. (Higher dry gas noted at higher conversion and constant reactor temperature is an artifact of pilot testing and is not observed commercially.) The data also show the impact of pretreater operating severity. At high severity or PNA mode, there is a large increase in FCC conversion and corresponding increase in gasoline yield.

Of course, there are also significant differences in hydrogen consumption and pretreater cycle length for the different modes of operation, and these costs need to be balanced against the benefits of increased FCC conversion. This is described in more detail in other work.

The FCC catalyst formulation is also an important factor that can be tailored to shift FCC yields and help maximize profitability. Figure 2 summarizes pilot plant data demonstrating the impact on yields of different FCC catalysts using a constant FCC feed that was hydrotreated over a NiMo catalyst with the pretreater operating in PNA versus HDS modes. The data show that significant differences in FCC conversion and FCC product yields at constant coke yield can be affected by changes in FCC catalyst technologies.

Much of the work investigating the effects of FCC pretreating on FCC performance has emphasized gasoline pro-
duction due to the prevailing economics of the time. The governmental mandate for ultra low sulfur diesel (ULSD) and the resulting increase in demand for these cleaner fuels prompted many refiners to increase LCO production from the FCC unit to maximize the mid-distillate pool. Several papers have explored ways to increase FCC LCO by adjusting FCC catalyst formulations and modifying FCC operation. Understanding the effects that this increased LCO production has on downstream ULSD operation and options for dealing with it have been explored in detail. Given the impact FCC pretreating has on the FCC performance just described, the pretreater clearly has a role to play in modifying the FCC product slate to meet increasing distillate demand.

In addition to changing economics, refiners are also looking at more stringent regulations on fuels which often serve as an outlet for FCC LCO. LCO is blended into wide variety of mid-distillate streams as summarized in Figure 3. It can be sent to a hydrocracker to make high quality jet and kerosene products, and if the refiner has the hydrotreating capacity available, it can be sent to a diesel hydrotreater to produce ULSD or sent to higher sulfur products like fuel oil. A portion of the LCO may also be used as cutter stock or blended for marine diesel. Sulfur specifications on many mid-distillate streams are expected to get more stringent, and Figure 4

![Figure 2 Impact of FCC Catalysts on Performance](image-url)

![Figure 3 Outlets for FCC LCO](image-url)
summarizes expectations for one such stream, marine diesel.

It is clear that FCC pretreating plays an important part in reducing the sulfur content of FCC products like gasoline and LCO. ART has completed many studies looking into the effects of hydrotreating on FCC performance and the quality of the FCC products. The work demonstrates that reducing the sulfur in FCC gasoline and LCO simply requires a reduction in the sulfur of the FCC feed by increasing the severity of the pretreater. Figure 5 shows the relationship between FCC feed sulfur and the resulting sulfur of the FCC gasoline. This data was generated using a variety of FCC feeds that had been hydrotreated over several types of catalysts and catalyst systems. As can be seen in the chart, there is a good correlation between FCC feed sulfur and the corresponding FCC gasoline sulfur. In this case, the sulfur content in the FCC gasoline is roughly 100 times less than the sulfur in the feed to the FCC.

As might be expected, a similar relationship exists between the sulfur in the FCC LCO and the FCC feed sulfur. An example of this relationship is shown in Figure 6. This chart shows that the LCO sulfur is roughly the same as the FCC feed sulfur. These rules of thumb are helpful when trying to estimate the impact of a change in the FCC pretreater and its effect on the FCC product sulfur levels.
The balance of operating the FCC pretreater to meet increasing HDS requirements and increase LCO yield, requires an optimized catalyst system and changes to the pretreater operating strategy in order to provide lower sulfur FCC products and higher LCO yields when the market demands it.

As discussed previously, removing PNA’s and nitrogen from the FCC feed improves FCC performance in terms of increased conversion and higher gasoline yield. Figure 7 summarizes FCC pilot plant data for several hydrotreated FCC feeds. The left axis shows the FCC conversion and the right axis shows the FCC feed quality depicted as a ratio of either product nitrogen content to feed nitrogen content or product PNA content to feed PNA content. Clearly, the PNA and nitrogen content of the FCC feed have a strong effect on FCC performance. At the highest pretreater severity, the FCC conversion actually decreases by about 1 wt.% relative to the previous severity in the chart. The decrease in FCC conversion coincides with an increase in PNA content from 0.48 to 0.55. Notice also that the conversion decreases despite the fact that the FCC feed nitrogen content is at the lowest level suggesting the PNA feed content has the larger impact on FCC conversion.

Figure 8 summarizes data from this same study which shows that as FCC conversion increases as a result of increasing pretreater severity, the gasoline yield increases
and the LCO yield decreases. Can this effect be mitigated somewhat by the proper choice of catalyst system in the pretreater?

Another study was completed which investigated the impacts of the pretreater catalyst system on FCC performance. A range of catalyst systems were investigated ranging from 100% NiMo to a system which was predominantly CoMo catalyst. Figure 9 compares the gasoline and LCO yields as a function of the catalyst system at constant pretreater severity. The data indicate that adjusting the catalyst system does result in a shift in the FCC product yields. In this example, increasing the amount of CoMo catalyst tends to result in higher LCO yields and correspondingly lower gasoline yield. The data also suggests that there is an optimum catalyst system which can result in a maximum LCO yield.

As expected, the quality of the FCC products is also impacted by the catalyst system. Figure 10 shows the FCC gasoline and LCO product sulfur observed in the same study. As mentioned previously, there is a good correlation between FCC feed sulfur and the FCC product sulfur.

This same work also looked at the sulfur speciation for the FCC gasoline and LCO products. This is useful information if the LCO is subsequently fed to a hydrotreater. Figure 11 compares the yield of LCO and the amount of substituted dibenzothiophenes (hard sul-
remaining in the LCO as a function of the pretreater catalyst system. The total sulfur in the LCO decreases at a significantly faster rate than the hard sulfur concentration, but the amount of hard sulfur as a fraction of the total sulfur decreases at an even faster rate. Decreasing the total LCO sulfur by 25% lowers the hard sulfur concentration by over 35%. It also shows that as LCO sulfur decreases, the yields of LCO can shift assuming constant FCC operation. Simply cutting the LCO sulfur in half with additional pretreater severity can decreases the quantity of LCO by almost one percent in this case. Again, the data suggests there may be an optimum catalyst system which can provide the right balance between LCO yield and LCO sulfur content.

The LCO API gravity was also estimated from correlations using FCC feed gravity and FCC conversion since not enough LCO product is produced to measure density. The LCO API gravity gives a rough indication of the aromatic content and can also be useful for estimating hydrogen consumption if the LCO is being sent to a hydrotreating or hydrocracking operation. Figure 12 shows some general trends in LCO gravity as a function of FCC conversion and FCC feed API. There is a strong correlation between LCO API and the FCC severity. As FCC conversion increases to produce more gasoline, there is a negative impact on the LCO API indicating the LCO is becoming more aromatic. By increasing
pretreater severity, the quality of the feed to the FCC improves (API gravity increases) and at constant FCC conversion levels on the chart, it is apparent that the LCO API increases along with FCC feed API, indicating that a better quality LCO can be produced.

Directionally decreasing the FCC to increase LCO production can increase the LCO API by as much as 5 numbers. This indicates there is an interesting interaction between the FCC pretreater operation and the quality of the FCC LCO. Increasing the severity of the pretreater will increase the FCC feed API and decrease the FCC feed sulfur and nitrogen. This can result in a higher quality LCO in terms of lower sulfur and higher API (higher cetane), but as alluded to earlier, this requires between 200-400 SCFB higher hydrogen consumption at the pretreater. The higher cost may be justified depending upon the margin of the finished product that contains the LCO.

These correlations were also used to assess the product quality in terms of aromatics or API in the study above. As a general rule when the FCC feed sulfur is decreased there is a corresponding decrease in LCO yield and a decrease in LCO API gravity. However, having to operate the pretreater at higher temperatures in order to lower the sulfur and improve the FCC feed API is not the only solution to improving product properties. Figure 13 compares several pretreater catalyst systems, and shows how an optimized
loading can not only produce a higher yield of LCO, but also one with the highest possible API gravity. In this case, there is a maximum LCO yield which is about one wt.% higher, and there is almost a one number improvement in the API of the LCO.

Figure 14 shows another example demonstrating the effects of FCC pretreater catalyst type on LCO quality. The chart compares how a CoMo and NiMo catalyst system can change the feed quality to the FCC and ultimately the LCO API gravity. Although the all CoMo system is producing the highest quality LCO in terms of API gravity, it is apparent that the all NiMo system is capable of nearly achieving the same quality at high pretreater severity. This is comparable to the PNA mode of operation mentioned above, and as indicated the pretreater cycle length will be shorter operating that way. This suggests that the tailoring of the FCC pretreater is important in order to gain the maximum flexibility.

Making changes to the FCC pretreater to operate in a different mode (HDS or PNA mode) also influences the resulting LCO product. Switching between HDS and PNA modes of operation can result in changes in the LCO API gravity. Figure 15 compares the same three FCC feedstocks as in Figure 12 but this time the data is plotted against FCC coke yield to represent changes in the FCC operation. So, both the pretreat catalyst system and the pretreater operation can influence LCO yield and quality.
In addition, the operation of the FCC changes the LCO yield and quality. This indicates that re-optimization of both the FCC and pretreater operation is required to ensure high yields of LCO and an overall profitable FCC yield slate.

Different pretreat catalyst systems can result in higher FCC bottoms yields if the FCC is not re-optimized as it shifts from maximum conversion to maximum LCO operations. Figure 16 is an example of comparing the LCO yield generated from two different FCC catalysts processing the same FCC feedstock. Switching FCC catalyst from A to B provides several percent higher LCO yield at the same FCC feed quality. This provides a means to offset higher bottoms yield which may occur from changes in the operation of the upstream pretreater to focus on increasing LCO yields. Hu et al. showed that Grace Davison’s MIDAS® catalysts and Olefins® Ultra ZSM-5 technologies are a profitable approach to minimize bottoms yield during maximum LCO operation.9

**Conclusion**

If the refiner’s objective is to maximize the distillate pool it is important to understand the key relationships between FCC pretreat and FCCU operations and their corresponding catalyst systems. Both processes must be re-optimized as the refiner moves from gasoline to distillate production to ensure maximum profitability. All of the combinations presented show the need for refiners to follow an integrated approach to managing the catalysts and operation of the FCC pretreater and FCC units. Both FCC and hydroprocessing unit operations can be continuously optimized throughout the course of the hydrotreater run, to significantly increase refiner revenue.

Results from a variety of ACE studies using many different feeds and a variety of FCC pretreat catalyst systems indicate that the amount of sulfur in the FCC products is dictated primarily by the FCC feed sulfur. Furthermore, for hydrotreated FCC feeds, the distribution of sulfur in FCC products is independent of the type of FCC pretreat catalyst system employed and depends solely upon the amount of sulfur in the FCC feed. This work demonstrates that the ability to make a major impact on FCC yields is strongly influenced by the type of FCC pretreater catalyst system used in conjunction with the appropriate FCC catalyst. Simply making a change to one operation without consideration for the other can result in unexpected results and limited flexibility to produce the fuels needed for downstream blending or use.

Both the hydrotreating catalyst system and the operating strategy for the pretreater are critical to providing the highest quality feed for the FCC. Driving the hydrotreater to remove nitrogen and PNA’s improves FCC product value when targeting gasoline production, but this needs to be balanced against the...
increased costs of higher hydrogen consumption and shorter cycle length that result from this mode of operation. Use of tailored ApART® catalyst systems can optimize the FCC in order to produce not only high quality feeds to the FCC but also low sulfur products resulting in less impact on downstream hydrotreating. This tailoring can also be beneficial if the FCC products are used directly without hydrotreating, as they can be driven towards lower sulfur and higher gravity products allowing the refiner to be able to blend these fuels directly. This creates a fuel pool that can also have higher cetane values due to the higher gravity.

The complex relationship between the FCC pretreater and the FCCU underscores the importance of working with a catalyst technology supplier that has the capabilities to understand the interplay between the hydrotreating performance of the FCC pretreater and the performance, yield structure and product sulfur distributions of the FCC. ART, and through its relationship with Grace Davison Refining Technologies, offers just such capabilities and delivers them through tailored ApART® catalyst systems to meet the refiner’s specific FCC feed slate needs and FCC pretreat operation constraints.

References

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  - Feedstock contaminant removal
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  - Upgrading and stabilization
- **1st Generation Biofuels:**
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Susan Ehrlich, Business Director
Grace Davison
Renewable Technologies
+1 410.531.4197

www.gracebiofuels.com