Let’s do the math.

Grace custom catalyst solutions, co-developed with you, are about more than performance—and more than chemistry. They’re designed to add to your bottom line.

In some cases, the difference between our refinery customers’ financial return on Grace technologies versus the alternative has reached into eight figures.

If you’re ready to put Grace chemistry to work to strengthen your business, we’re ready to show you how we can help. Call us to get started with the calculations.


At Grace, value is all about our customers’ financial success.

Learn more at grace.com/value.
A 75-Year Commitment to Innovation

*Scott Purnell, Vice President, Marketing, Refining Technologies, W. R. Grace & Co.*

This year marked the 75th anniversary of Grace’s shipment of the very first FCC catalyst to the first FCC unit in Baton Rouge, LA, USA in May 1942. While there have been many changes since then, much has stayed the same. One of those constants is the need for ever-improving technology in the refining industry.

Another is Grace’s commitment to innovation. It was this commitment that led Grace to be the first company to supply commercial FCC catalyst in 1942, the first to supply a spray-dried, microspheroidal catalyst, and the first to supply a zeolite-based catalyst to the world’s refiners. In addition, Grace is an innovator in FCC additives applications, commercializing the first Pt-based CO promoter, the first SOx transfer additive, the first additive for reduction of NOx, and the first technologies for reduction of gasoline sulfur.

This focus on innovation has allowed us to continue to deliver proven value to our customers. As we’ve said before, we don’t just sell products, we sell solutions. And these solutions, custom-formulated and often developed collaboratively with our customers, combined with industry-leading technical service allow our customers to improve their bottom lines. That’s really the bottom line. It is the ultimate measure by which we judge our success. We aren’t successful unless our customers are successful.

You can read the history of our FCC innovations on grace.com/fcchistory. However, we can’t rest on our laurels. We must and will continue to innovate and deliver value to our customers by addressing new challenges as they arise. In this issue of *Catalagram*, you will find some recent examples of our talent, technology, and the trust we earn from our customers on display. Explore options to drive octane while complying with ultra-low sulfur gasoline regulations on Page 8. Understand how utilizing state-of-the-art zeolite technology unlocked value at a U.S. Gulf Coast RFCC on Page 20, and see how employing the matrix technology of our MIDAS® catalyst improved profitability at a refinery in Greece on Page 38.

Also, in this issue we spotlight solutions for increasing middle distillate yields from Advanced Refining Technologies (ART), our joint venture with Chevron. The ART partnership builds upon a long history of innovation from both Grace and Chevron to offer a complete portfolio of hydrosprocessing catalysts, making ART the world leader in these types of solutions for refiners.

As always we welcome your feedback and look forward to more ways in which we can work together to *Deliver Value* now and into the future.

“We aren’t successful unless our customers are successful.”

*Scott Purnell*
Vice President, Marketing, Refining Technologies
WHAT’S INSIDE

IN THIS ISSUE of Catalagram®, our experts demonstrate the value of doing business with Grace. From improved product performance to increased profitability, Grace’s FCC catalysts and additives and ART’s hydroprocessing catalysts and catalysts systems deliver significant value in today’s challenging refining environment.

What’s Inside

GRACE IN THE NEWS

4 GRACE LEADS GLOBAL TECHNICAL WORKSHOPS FOR REFINERS

5 UPDATES FROM THE MIDDLE EAST

6 CELEBRATING 75 YEARS OF FLUID CATALYTIC CRACKING (FCC) TECHNOLOGY

6 DEMONSTRATING VALUE IN VIETNAM

SUCCESS STORIES

8 DRIVING OCTANE IN AN ULTRA-LOW SULFUR GASOLINE MARKET

20 MOTIVA UNLOCKS VALUE WITH AN INNOVATIVE CATALYST SOLUTION FROM RIVE AND GRACE

30 UNDERSTANDING CATALYTIC SOLUTIONS FOR INCREASING MIDDLE DISTILLATE YIELDS

38 IMPROVING FCC UNIT PROFITABILITY
GRACE IN THE NEWS
Grace Leads Global Technical Workshops for Refiners

From May through September, Grace’s FCC experts have been hosting technical workshops for refiners at our headquarters in Columbia, MD, USA and sites in Germany and Italy.

In May, 29 customer representatives from the United States, Latin America, and Asia Pacific regions visited our U.S. headquarters. Workshops were designed for engineers and operations managers who sought to learn more about FCC, including basic principles and operations, equipment technology, catalyst fundamentals, and troubleshooting.

Ann Benoit, our Technical Service Leader for the Americas, organized and facilitated the U.S. course, which was led by Grace R&D scientists and FCC technical personnel. Throughout, attendees participated in interactive presentations and discussions on a number of technical topics, including heat balance, feedstock impacts, troubleshooting, optimization, and fundamentals. The workshops concluded with a tour of Grace’s Curtis Bay FCC manufacturing plant and Process Innovation Center, and Columbia R&D facilities.

Also in May, Grace hosted the first edition of its EMEA FCC Technology Symposium in Sardinia, Italy. This event was designed to discuss and share between participants key aspects of FCC including unit operation, process troubleshooting, revamp experience, spent catalyst classification, and catalyst trials.

Thirty participants from southern Europe were present for technical presentations combined with social activities and the opportunity to network. Each participant was given the opportunity to present a case study from their own experience and have open discussions with all the participants. A refinery visit to the Sarlux site was included.

As this issue of Catalagram® goes to press in September, Grace plans to host similar workshops in what has become a regular series of global opportunities to share knowledge and expertise. 😊
Updates from the Middle East

Grace and Sohar University signed a unique, long-term agreement to establish four world-class, fully licensed Material Characterization Labs (E-cat) in Oman to eliminate the need to send samples abroad for testing. Grace is investing in equipment and technology including materials analysis devices and absorption technology while the university is providing laboratory space and utilities. These labs will serve the refining and petrochemical industry throughout the Cooperation Council for the Arab States of the Gulf (GCC). This industrial-academic collaboration is the first of its kind for the region, and signifies Grace’s ongoing investment in and commitment to the people and the economy of the region.

Omani Professionals Trained in Worms, Germany

In connection with the commissioning of the E-cat Lab in the Middle East at Sohar University, Oman, the new lab team has been undergoing intensive training at the Grace Lab facilities in Worms, Germany. The new Grace team consists of a group of four professional Omani women – two chemists from the Sultan Qaboos University, a chemist from the Petroleum Institute, Abu Dhabi, and a chemical engineer from Sohar University. Under the mentorship of Grace’s Catalyst Evaluation Services team, the new employees have been trained in microactivity testing, the evaluation of physical catalyst properties, and elemental analysis techniques, among other skills.

Up-to-date E-cat analyses are a valuable, key requirement for assessing the operation of FCC units. The first-of-its-kind Grace E-cat lab at Sohar University will provide more rapid support to the refineries in the Middle East.

Grace Presents at MERTC in Bahrain

Earlier this year, the Middle East Refining Technology Conference was held in Bahrain. Grace spoke on “Maximizing FCC Profitability in a Challenging Market” using two successful industrial case studies to highlight the superior value delivered by Grace catalysts.

Delivering Value in Abu Dhabi

Grace has commissioned the construction of a new catalyst logistics silo terminal and the first FCC catalysts manufacturing facility in the Middle East, located in the Kizad Industrial Zone approximately 70 km outside of Abu Dhabi. The silo hub is operational, while detailed engineering for the catalysts manufacturing plant is underway, with operations expected to be aligned with growth in Middle East catalyst demand. This investment will deliver on Grace’s commitment to serving refineries throughout the Middle East.

Our investment in the region maximizes value for FCC operations while managing risk to the refinery. You can find out more about the high-performing technology and demonstrated expertise that makes us the preferred supplier of FCC catalysts and additives to the Middle East at grace.com/middleeast.

Omani professionals receive training at Grace in Worms, Germany.
Celebrating 75 Years of Fluid Catalytic Cracking (FCC) Technology

Seventy-five years ago, Grace shipped the world’s first synthetic FCC catalysts from Curtis Bay, MD to the first cat cracker in Baton Rouge, LA. The synthetic Fluid Cracking Catalyst and the FCC process played a large role during World War II in supplying the Allied forces with necessary fuel. Post war demand for motor fuel gave rise to significant growth of the FCC process and FCC catalyst production and resulted in a need to improve the FCC catalyst performance.

The FCC process remains the preferred process for global fuel production today and Grace remains an innovator in the field as the leading supplier of best-in-class FCC catalyst and additive technology. Grace’s catalyst technology has been continually improved to meet changing needs. The Curtis Bay plant produced 18 tons/day of FCC catalyst in 1942. Modern plants produce at rates ranging from 150 to 350 tons/day. As the need to produce cleaner burning fuels increases, Grace continues to lead the way with new and better solutions for the industry.

To mark this anniversary, we have compiled a fascinating history of FCC catalysts, the role Grace played in the beginning, and Grace’s continued innovation in the global fuel refining market today.

Demonstrating Value in Vietnam

At the 12th FCC Forum April 23-26 in Vietnam, Grace experts presented strategies to maximize LPG olefins and bottoms upgrading in the FCCU. Our case study, “Improving Commercial R2R FCC Performance with Custom Solutions”, was developed in collaboration with one of our customers to demonstrate how we can deliver the broadest selection of catalysts and additives products in the industry. We’re a proud partner with our FCC catalyst customers in Southeast Asia and around the world.

This technical case study presented in Vietnam along with several others such as "Maximizing Propylene in the FCC Unit" and "Generating Value with FCC Catalyst Innovation at Placid Refining" can be found on grace.com/vietnam.

The genesis of the FCC technology that today provides for approximately half of all motor gasoline produced goes as far back as March of 1919. Professor Walter Patrick of the Johns Hopkins University in Baltimore, MD was granted a U. S. Patent for the development of a novel method of producing silica gel with high surface area and pore volume. Believe it or not, the first batches of silica gel prepared at the Hopkins Laboratories were dried on the radiator in the winter and on a tin roof in the summer.

Read more at grace.com/fcchistory.
SUCCESS STORIES
Driving Octane in an Ultra-Low Sulfur Gasoline Market

Andy Huang

Ann Benoit
Technical Service Leader, FCC, W. R. Grace & Co.

Gary Cheng
Technical Sales Manager, FCC, W. R. Grace & Co.

Bob Riley

Over the last two decades the refining industry has weathered a storm of volatile market conditions and increasingly stringent fuels regulations. These events and other variables have created a market environment that requires flexibility. The most flexible unit in a refinery is the FCC. Refiners need flexibility to operate with a dynamic feed slate of varying quality as well as flexibility to produce a wide range of products to meet market demand. In North America refiners are now, or will soon be, tasked with meeting challenging ultra-low sulfur gasoline regulations (Tier 3).

For many refineries meeting the sulfur limits will require operating adjustments, catalyst formulation changes, and/or capital investment. For others, the ABT credit trading program can provide a measure of relief for a brief period of time. Many operating strategies that reduce sulfur may reduce gasoline octane, which is often undesirable due to refinery octane requirements. Incremental production from the alkylation complex can accomplish various goals; high octane value and low sulfur gasoline blend stock that compensates for octane loss due to more severe gasoline hydrotreating.
In this article we will discuss octane fundamentals, the specifics of the Tier 3 regulations, and visit a number of refinery case studies and operating strategies for preserving octane, maximizing alkylation rates, and reducing sulfur to maintain regulatory compliance. Also, we will illustrate the value in each operational or catalytic route discussed using an example of a 50kbpd refinery against recent U.S. economics.

Octane Drivers

The demand for high octane premium gasoline is increasing in North America. Data published by U.S. Energy Information Administration\(^1\) indicates that the share of premium gasoline has steadily risen since 2008 and recently has reached its highest share in more than a decade (see Figure 1).

While this trend is linked to lower gasoline prices driven by cheap crude oil and a surplus of petroleum products, another major contributing factor is likely a stricter fuel economy standard and a recent shift in engine designs. Fuel economy for the total U.S. fleet has increased from 19.9 to 31.5 miles per gallon (mpg) from 1978 to 2014 since the Corporate Average Fuel Economy Standards (CAFE) were first enacted by Congress in 1975 (see Figure 2)\(^2\).

The latest CAFE regulations finalized in October 2012 set the fleet-wide fuel economy for model years 2017-2021 in the range of 40.3-41.0 mpg and increasing to 48.7 mpg for model years 2022-2025\(^3\). Automakers are responding to these new standards with weight reduction, improved aerodynamics, new transmission design, hybrid technology, and electric vehicles. One particular strategy to meet these new standards, which are driving demand for premium gasoline, is the use of smaller turbocharged engines. In 2009 model year cars, turbocharged engines accounted for only 3.3% of all new gasoline-powered light duty vehicles. This number grew to 17.6% by 2014. Turbocharged vehicles are expected to account for 83.3% of the light duty vehicles market by 2025\(^4\).

As more turbocharged vehicles saturate the market, the demand for premium gasoline with a higher octane number will also increase as automakers start recommending or requiring the use of higher-octane gasoline.

Notes:

All economic cases in this paper are cast against the same set of refinery economics. These economics show a slight preference for LCO over gasoline, strong alkylation (C\(_4\))\(^\sim\) economics, and a reasonably strong octane-bbl value. Value potential for specific refiners should be evaluated using refinery specific economics.

NHTSA, EPA, and CARB are currently in the mid-term evaluation process for CAFE and GHG emissions standards for model year 2022-2025.
The "true" method for measuring octane number is to use an octane engine at constant speed with varying compression ratios to achieve standard knock intensity of reference fuel. Research Octane Number (RON) is measured at 600 RPM with 60°F air/fuel mix to mimic city driving and Motor Octane Number (MON) is measured at 900 RPM with 300°F air/fuel mix to mimic highway driving. The downsides of this method are the lower reproducibility and the high cost associated with testing since this method requires a large fuel sample. Other methods that measure the molecular types in the gasoline include NMR analysis, Fluorescent Indicator Absorption, Near-Infrared Spectroscopy, and Gas Chromatography.

The table and chart below illustrate the octane numbers for different hydrocarbon molecules. Aromatic and olefinic molecules both have high RON and MON values, followed by naphthenes, iso-paraffins, and then paraffins with the lowest octane value. Octane sensitivity, defined as the difference between RON and MON, can be high for olefins and aromatics, and responsible for the familiar "gap" between RON and MON of gasoline. Paraffins exhibit excellent sensitivities, but tend to have lower overall octane, which is especially true for long straight-chained paraffins as shown in Figure 3.

<table>
<thead>
<tr>
<th>Description</th>
<th>RON</th>
<th>MON</th>
<th>Octane Sensitivity (RONC-MONC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>100.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>62</td>
<td>63</td>
<td>-1.0</td>
</tr>
<tr>
<td>Olefins</td>
<td>103.5</td>
<td>86.2</td>
<td>17.3</td>
</tr>
<tr>
<td>89.8</td>
<td>79.3</td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>Aromatics</td>
<td>111.4</td>
<td>96.0</td>
<td>13.4</td>
</tr>
<tr>
<td>104.4</td>
<td>94.5</td>
<td></td>
<td>9.9</td>
</tr>
<tr>
<td>114.8</td>
<td>102.5</td>
<td></td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 1. Examples of structural effects

Maximizing Octane in a Conversion Refinery

The first step toward maximum octane operation is understanding the octane contribution of different streams to the refinery gasoline pool. The schematic in Figure 4 shows simplified refinery gasoline routings for a typical conversion refinery with several streams contributing to the overall gasoline blending pool. To maximize octane in the gasoline pool, refiners typically rely on models to optimize gasoline blending, while taking into consideration both physical and performance characteristics such as RVP, sulfur, benzene, olefins, aromatics, and octane. Maximizing the production of high octane streams such as alkylate and reformate and making incremental octane improvements on FCC naphtha are critical to maximizing octane in a conversion refinery. FCC naphtha is the largest volume stream in the gasoline pool, as shown in Figure 5.
Maximizing Octane in an Ultra-Low Sulfur Environment

Tier 3 regulations for lower gasoline sulfur will create challenges around maximizing octane, as many refiners will turn to higher gasoline post-treatment severity for increased desulfurization, which will negatively impact octane. Under the new Tier 3 regulations, refiners are required to produce gasoline with an annual average sulfur content of ≤ 10 ppm, with a maximum gasoline sulfur cap at the refinery gate of ≤ 80 ppm. FCC naphtha is the main “problem stream,” as it comprises 40-50 vol% of finished gasoline and contributes to 80-90% of the total sulfur in the refinery gasoline pool.

A recent survey illustrated in Figure 6 shows that some North American refiners are already compliant with Tier 3 regulations or have purchased credits to 2019-2020. Some refiners have switched to a light/sweet crude slate, but this limits feed flexibility and comes with a higher cost. Catalytic solutions such as Grace’s gasoline sulfur reduction technologies convert sulfur molecules to H₂S in the FCC reactor, thereby reducing the sulfur ending up in FCC naphtha. There are also post-treatment technologies designed to preserve octane by removing sulfur selectively or combining and concentrating sulfur molecules into a distillate stream. These post-treatment technologies often require additional capital investment by the refiners.

The majority of refiners are meeting the regulations by increasing hydrotreating severity with pre-treating FCC feed or post-treating FCC naphtha. This option increases the refinery H₂ consumption and reduces the run length of these hydrotreaters. For some refiners, pre-treating FCC feed is still not sufficient and can sometimes present a heat balance challenge for the FCCU. While post-treating is effective for reducing sulfur content, it saturates aromatics and olefins resulting in octane loss in the FCC naphtha.

This can be exacerbated at refineries that consume an increased diet of shale-derived crudes, which are naturally light and produce low sulfur, but also low octane, gasoline. If the majority of refiners are faced with octane loss due to increasing hydrotreating severity and refinery feed choices, what options are available in this ultra-low sulfur environment? The following case studies highlight different options for maximizing overall refinery octane:

A generic price set is applied to these case studies to illustrate the effectiveness and the profitability of each approach. This price set places a high value on LPG olefins (alky feed) and octane barrels, with a slight preference for LCO over gasoline.
Case 1: Feed and Operational Changes

The unique ability of FCC units to automatically adjust their operating conditions allows them to accommodate many feedstock types and qualities. While feed selection is typically not used for improving octane of FCC naphtha, feedstock selection does have an effect on octane. Processing feeds containing higher paraffins tends to lower gasoline octane. Processing feeds that contain higher aromatics and naphthenes increases gasoline octane as these feed molecules convert to aromatics and olefins in the gasoline range. As a rule of thumb, 0.2# decrease in UOP K factor (or Watson K factor) or 0.1# increase in Cn/Cp translates to 1# increase in RON. Table 2 compares the DCR yields of paraffinic and naphthenic feedstocks at constant operating conditions.

FCC operating conditions can be readily adjusted to meet market demand. Refiners can boost gasoline octane by increasing reactor temperature or conversion with higher cat-to-oil ratio. Increasing reactor temperature increases gasoline olefin content, and increasing conversion with higher cat-to-oil ratio increases aromatics. The incremental generation of these higher octane molecules results in higher gasoline octane.

As shown in Figure 7, for every 18°F increase in reactor temperature, RONC increases by 1#. As base RONC increases, octane response becomes less sensitive at increasing reactor temperature. For every 10 LV% increase in conversion with higher cat-to-oil, RONC increases by 1#.

<table>
<thead>
<tr>
<th>Feed Properties</th>
<th>Paraffinic Feed</th>
<th>Napthenic Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>27</td>
<td>22.5</td>
</tr>
<tr>
<td>Watson K factor</td>
<td>11.9</td>
<td>11.6</td>
</tr>
<tr>
<td>Cp</td>
<td>65.6</td>
<td>57.4</td>
</tr>
<tr>
<td>Cn</td>
<td>16.9</td>
<td>21.2</td>
</tr>
<tr>
<td>Ca</td>
<td>17.5</td>
<td>21.5</td>
</tr>
<tr>
<td>Cn/Cp</td>
<td>0.26</td>
<td>0.37</td>
</tr>
<tr>
<td>Gasoline Yield, 430°F E.P., vol%</td>
<td>59.8</td>
<td>54.0</td>
</tr>
<tr>
<td>API</td>
<td>59.7</td>
<td>58.3</td>
</tr>
<tr>
<td>RONC&lt;sub&gt;90&lt;/sub&gt;</td>
<td>90.7</td>
<td>91.8 (+1.1)</td>
</tr>
<tr>
<td>MONC</td>
<td>79.6</td>
<td>80.3 (+0.7)</td>
</tr>
</tbody>
</table>

Table 2. DCR yields of paraffinic vs. napthenic feedstocks

As shown in Table 3, the yield estimates for two different reactor outlet temperatures (ROT) are compared. With reactor temperature elevated to the point of over-cracking, the total gasoline and LCO yields become slightly lower. However, it is clear that the octane benefits from higher alky feed (C<sub>3</sub>= and C<sub>4</sub>=) and higher RON and MON still outweigh the over-cracking losses. For a 50 kbps FCC unit, the benefit from higher reactor outlet temperature is estimated to be $12MM/yr ($0.68/bbl) as shown in Figure 8. This assumes that there is available downstream handling capacity for the increased LPG generation.

<table>
<thead>
<tr>
<th></th>
<th>970°F ROT</th>
<th>1010°F ROT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas, wt%</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Total C&lt;sub&gt;4&lt;/sub&gt;, wt%</td>
<td>5.7</td>
<td>7.4</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;=, wt%</td>
<td>4.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Total C&lt;sub&gt;5&lt;/sub&gt;, wt%</td>
<td>10.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Total C&lt;sub&gt;6&lt;/sub&gt;=, wt%</td>
<td>7.0</td>
<td>8.7</td>
</tr>
<tr>
<td>Gasoline, wt%</td>
<td>51.9</td>
<td>51.0</td>
</tr>
<tr>
<td>Estimated RON</td>
<td>93.2</td>
<td>95.4</td>
</tr>
<tr>
<td>Estimated MON</td>
<td>80.9</td>
<td>82.1</td>
</tr>
<tr>
<td>LCO, wt%</td>
<td>17.8</td>
<td>15.3</td>
</tr>
<tr>
<td>Bottoms, wt%</td>
<td>8.3</td>
<td>6.8</td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>4.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 3. Driving octane with reactor temperature
Case 2: Undercutting FCC Naphtha

Changing the fractionator operation downstream of the FCCU is another way that refiners can operate in an ultra-low sulfur gasoline market. By undercutting FCC naphtha (reducing the end point), the gasoline sulfur content can be reduced while increasing octane value. The heavier fraction is dropped into the distillate cut and can be further processed to make diesel. Undercutting FCC naphtha gives refiners flexibility when processing sour feed, extending naphtha treater run length, or managing naphtha treater outage. However, refiners should consider:

1. Undercutting FCC naphtha will change the distillation range for the distillate cut. Refiners will need to ensure the IBP and 10% points specs can still be met for finished diesel when undercutting FCC naphtha.
2. Depending on the hydrocarbon makeup of the naphtha (feed dependent), the naphtha octane value may show no change or even a debit when undercutting FCC naphtha.
3. Main fractionator top temperature limitations will be a factor on how low a refinery can reduce the gasoline end point.

Figures 9 and 10 show the gasoline sulfur and octane distribution as a function of end point. In this example, reducing the end point from 430°F to 400°F reduces sulfur by ~30% with a slight debit on octane value.

Figures 11 and 12 illustrate another example of the impact undercutting naphtha has on octane. FCC naphtha octane increased by as much as 2# while shifting about 10% naphtha yield to LCO.

These examples illustrate that gasoline endpoint can have varying effects on octane. Because of the variability, test runs are recommended to understand the impact of undercutting FCC naphtha on octane for a given FCC unit, feed, and operation.

When applying a generic price set with a slight preference to LCO over gasoline to the example shown in Figure 13, this shift in operation is economically attractive. For a 50 kbpd FCC unit, the benefit from undercutting naphtha by 10°F for this refinery is estimated to be $6MM/yr (+$0.35/bbl).
Figures 11 and 12. Refinery data, FCC naphtha yield and octane shift from undercutting FCC naphtha

Figure 13. Driving octane by undercutting FCC naphtha

**Case 3: Catalytic Solutions**

In addition to operating changes, modifications can be made to the FCC catalyst itself to drive octane; however, each of these changes will impact the FCC yield profile and overall unit profitability.

Within traditional FCC technologies, refiners can pursue zeolite modifications to drive octane. Most commonly, a reduced zeolite unit cell size will favor olefin production, which will lead to higher gasoline octanes, as well as higher olefin production for the alkylation unit. However, reduced zeolite unit cell size is typically achieved by reducing zeolite rare earth stabilization, which reduces the acid site density of the zeolite, leading to lower activity per unit of zeolite. Catalyst suppliers can increase zeolite content up to a point, depending on the catalyst family, but beyond this point, the refiner will have to consider alternate catalyst formulations or higher catalyst additions if in-unit activity is not maintained. Figure 14 shows the relationship between FCC gasoline octane and zeolite unit cell size in traditional FCC catalysts.

In recent years, Grace has commercialized a new catalyst technology called ACHIEVE® 400. This solution excels at producing both high octane gasoline and high value alkylation feedstock, preferentially making $C_4$ = (when compared to a traditional light olefin additive). Since its launch in 2013, ACHIEVE® 400 catalyst has been used in over a dozen commercial applications.

ACHIEVE® 400 incorporates isomerization activity within the catalyst by using two different types of zeolite – a traditional Y zeolite and a specially tuned pentasil zeolite. Incorporation of isomerization activity into the catalyst particle itself results in a more desirable yield pattern than would be realized by use of a traditional octane boosting FCC additive. ACHIEVE® 400 catalyst yields both a higher octane FCC gasoline and an improved butylene-to-propylene ratio when compared to ZSM-5 additives. The zeolite isomerization activity in ACHIEVE® 400 catalyst increases the yield of FCC butylene and iso-butane, keeping the alkylation unit full and maintaining refinery pool octane. Figure 15
shows the commercial C₄= yield pattern from an application of ACHIEVE® 400 catalyst at a U.S. refiner, demonstrating the strong and preferential yield of butylene.⁵

When applying ACHIEVE® 400 in a typical case, gasoline octane and LPG olefins are driven at the expense of FCC gasoline volume. Figure 16 illustrates the economic value added by using ACHIEVE® 400 to drive octane in a typical 50 kbd refinery.

ACHIEVE® 400 technology is part of Grace’s broader ACHIEVE® catalyst technologies, which have been deployed in over 30 commercial applications to date. In commercial operations, product value uplifts in the range of $0.45-$0.95/bbl have been observed.

**Case 4: Additive Solution**

In addition to catalytic solutions like the ACHIEVE® 400 catalyst, many refiners have used light olefins (LO) additives as another way to boost LPG olefins as alky feed and increase FCC gasoline octane. Conventional LO additives, generally containing ZSM-5 zeolite, are designed to increase propylene and butylene yields at the expense of low octane gasoline range molecules. These incremental LPG olefins can be sent to the alkylation unit to produce higher octane alkylate for the refinery gasoline pool. Many conventional LO additives tend to be more propylene selective, providing an excellent source of propylene if the refinery is integrated with a chemical plant. These additives can also be modified to isomerize low value straight chain olefins in the FCC naphtha into higher octane branched components.

---

**Figure 15.** Higher C₄= yield with ACHIEVE® 400 technology at a U.S. refiner

**Figure 16.** Value derived from ACHIEVE® 400 catalyst in a 50 kbd refinery
Figures 17 and 18 illustrate the effect of conventional LO additives on LPG olefins yield. The extent of incremental LPG olefins depends on factors such as operating conditions, feedstock, base catalyst, and the additive itself. High activity additive and low hydrogen transfer base catalyst is the recipe to maximize LPG olefins at a constant additive usage. Conversely, low activity additive and high hydrogen transfer base catalyst will reduce the extent of improved LPG yields. The effect of conventional LO additives on gasoline RON is also shown here. As base RON increases, the incremental improvement diminishes; therefore, the starting or base octane must be considered when using LO additives.

Incremental LPG olefins and higher gasoline octane were achieved by adding conventional LO additive. For a 50 kbpd FCC unit, the benefit of using LO additive is estimated to be $17MM/yr (+$0.93/bbl). It is important to note that the potential value uplift in any specific refinery is often bound by unit constraints or refinery operations.

Due to increasing demand for higher octane gasoline in an ultra-low sulfur environment, many refiners are looking for ways to fill their alkylation unit. This creates a higher demand for butylenes, as they are better alky feed components than propylene. Grace is responding to this demand with a novel family of additives that are more butylenes-selective than conventional LO additives. These additives are formulated specifically to help refiners fill alkylation units with a preferred feedstock. In Figures 20 and 21, an ACE evaluation was performed to compare GBA additive (butylenes selective) to conventional LO additives from the OlefinsUltra® series. Increasing additive usage increases total LPG olefins. With GBA additive, higher butylenes-to-propylene ratio is achieved under the same testing conditions. GBA additive also provides a higher boost to RON due to improved isomerization activity.

Using GBA additive would provide an additional $2-3MM/yr. ($0.1-0.17/bbl) uplift over conventional LO additives when butylenes and octane barrel are more valuable. Selection of additive types will ultimately depend on unit objectives, market demand, and downstream unit integration. Regardless of the additive selection, using an additive approach allows refiners to quickly respond to market needs and changes without going through a catalyst reformulation. This approach helps refiners to maximize unit profitability and minimize risk of poor unit performance.

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>Base + ZSM-5 Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas, wt%</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Total C₃, wt%</td>
<td>6.4</td>
<td>7.9</td>
</tr>
<tr>
<td>C₃, wt%</td>
<td>5.5</td>
<td>6.8 (+1.3)</td>
</tr>
<tr>
<td>Total C₄, wt%</td>
<td>12.0</td>
<td>13.4</td>
</tr>
<tr>
<td>Total C₅, wt%</td>
<td>7.1</td>
<td>8.0 (+0.9)</td>
</tr>
<tr>
<td>Gasoline, wt%</td>
<td>48.6</td>
<td>45.8</td>
</tr>
<tr>
<td>Estimated RON</td>
<td>90.1</td>
<td>91.0 (+0.9)</td>
</tr>
<tr>
<td>Estimated MON</td>
<td>79.0</td>
<td>79.7 (+0.7)</td>
</tr>
</tbody>
</table>

Table 4 and Figure 19. Driving octane with light olefins additive
Case 5: GSR® Technology

One disadvantage of using a higher severity of gasoline post-treatment to achieve desulfurization is the subsequent decrease in post-treated octane. As a result, many refiners around the world, including North America\(^4\), have used FCC gasoline sulfur reduction technology to minimize this negative impact on octane. Many refiners in North America are currently evaluating the use of FCC gasoline sulfur reduction technology as part of their overall Tier 3 compliance strategy.

North America is not the first region to face the challenge of achieving 10 ppm gasoline sulfur. Japan was the first country to implement such a national limit. A reduction to 10 ppm gasoline sulfur was made compulsory in January 2008; however, the Japanese petroleum industry moved on a voluntary basis to this level at the beginning of 2005. The challenge was even bigger considering that a maximum of 10 ppm sulfur was imposed, rather than the weighted average of 10 ppm sulfur under the legislation. Grace’s GSR® technology has successfully been used by the majority of refineries in Japan, playing an important part in their environmental compliance strategy. Nine FCC units in Japan have used GSR® technology on an ongoing basis, with 50% of Japanese refiners currently using such technology.

The chemistry of sulfur reduction in the FCC has been heavily studied and documented. Sulfur reduction mechanisms and effectiveness vary depending on the technology employed and the feed and unit conditions. Figure 22 shows the general pathway for reduction of thiophenic sulfur species in FCC gasoline.

As part of its product development and research efforts, Grace’s R&D team undertook extensive efforts to analyze the exact mechanisms of sulfur reduction in the FCC. The reaction mechanism for sulfur removal from the FCC (Figure 23) for Grace’s D-PriSM® additive has been proposed based on that work.

Of importance in this mechanism is that sulfur in thiophenic species is catalytically converted to H\(_2\)S in the FCC unit, resulting in no incremental formation of regenerator SOx. In all commercial applications, the incremental H\(_2\)S created is so small that it is within the measurement error for detection in the FCC mass balance.

![Figure 22. Reduction pathway of thiophenic sulfur species to H\(_2\)S](image)
Figures 24 and 25 show data from two Japanese refining operations. In the first graph, D-PriSM® additive technology reduced sulfur by 25%. In the second application, a 35% reduction in gasoline sulfur was achieved using Grace’s SuRCA® catalyst.

In both cases, and in many others, one of the motivations to reduce FCC gasoline sulfur is to preserve octane in post-treating units. Figure 26 shows an estimate of the value created in a typical 50kbbpd application, achieving 25% sulfur reduction in the FCC, cast against recent U.S. economics. It is critical to note that the value drivers include both an octane benefit and, in this case, a savings in hydrogen consumption. This hydrogen benefit is often overlooked, and can be a significant factor depending on the specific refinery situation.

There are over 100 commercial applications of Grace’s GSR® products, which have been successfully applied for all feed types, typically providing between 20-40% reduction in FCC gasoline sulfur.
**Case 6: Combining Strategies for Sulfur Reduction**

In most cases, a catalytic solution for sulfur reduction will be one piece of a gasoline sulfur management strategy. In many cases, value can be maximized by combining complementary operating and catalyst strategies. Figure 27 shows an example of this from a commercial application in the United States.

In this application, the refiner utilized Grace’s ACHIEVE® 400 catalyst to maximize FCC naphtha octane and butylene production. The catalyst added substantial value, but produced a lower gasoline volume. Properly accounting for these pros and cons with the standard economics used throughout this paper, the ACHIEVE® 400 catalyst was able to add approximately $0.74/bbl to the product yields. However, this refiner was further constrained on gasoline pool octane and decided to utilize Grace’s SuRCA® catalyst to reduce gasoline sulfur, primarily to save octane in the post-treater. Adding those benefits to the benefits from the ACHIEVE® 400 catalyst, the refinery was able to realize $0.86/bbl in value just around gasoline octane optimization.

Many combinations of the above examples are possible. A critical part of optimal long-term operating strategy around octane economics should include consultation with key equipment, catalyst, and chemicals suppliers.

Tier 3 gasoline regulations, and other low sulfur gasoline regulations, will put increasing pressure on refiners to maintain octane pool levels while meeting ever lower levels of sulfur content in refinery gasoline. Refiners have a variety of options to manage pool sulfur, depending on their configuration and local markets. Operating strategies include selection of FCC cut points and reactor temperature. Feedstock selection can also play an important role in octane production; shale and other paraffinic feedstocks can be detractors to octane, and naphthenic and aromatic feedstocks can be contributors. Catalysts and additives specifically designed to either produce higher octanes, higher LPG olefins (especially C4=), or both, can add significant value to refiners’ operations. Finally, catalytic gasoline sulfur reduction can play a role in minimizing octane loss in gasoline post-treaters. Many refiners will consider and ultimately employ several of these strategies in parallel to maximize refinery octane.

**References**


[Figure 26: Octane preservation and H2 savings with GSR® technology](#)

[Figure 27: Combining different strategies to maximize octane in an ultra-low sulfur gasoline market](#)

grace.com | 19
Motiva Unlocks Value with an Innovative Catalyst Solution from Rive and Grace

Karthik Rajasekaran  
Project Engineer, Motiva

Raul Adarme  
Energy, Catalysts, and Chemicals Manager, Motiva

Clint Cooper  
Technical Account Manager, Rive Technology

Nathaniel Faulkenberry  
Technical Sales Manager, FCC, W. R. Grace & Co.

Through a unique collaborative effort between Motiva, Grace, and Rive Technology, an innovative catalyst solution incorporating Rive’s mesoporous zeolite was designed and trialed at a Motiva U.S. Gulf Coast (USGC) refinery in 2016. Rive’s zeolite technology imparts a precise series of mesopores into Y zeolite framework, the primary active component of all FCC catalysts, which enhances diffusion of molecules into and out of the catalyst.

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. The trial results reviewed in this article demonstrated the significant value that this technology can bring to an FCC unit. During and since the trial, Motiva has been able to realize uplift in the range of $0.40 to $1.20 /BBL depending on the market economics.

As a result of these demonstrated performance improvements and strong technical service relationship between Motiva, Grace, and Rive, Motiva continued using a Grace FCC catalyst containing Rive’s MOLECULAR HIGHWAY® technology to realize exceptional value in their operation.
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. Through a collaborative effort between Motiva, W. R. Grace & Co. (Grace), and Rive Technology (Rive), an innovative catalyst solution incorporating Rive’s mesoporous zeolite was designed and trialed at a Motiva U.S. Gulf Coast (USGC) refinery. This technology engineers a precise series of mesopores into Y zeolite framework, the primary active component of all FCC catalysts, which consequently enhances diffusion of molecules into and out of the catalyst.

The trial results demonstrated the significant value that this technology can bring to an FCC unit. During and since the trial, Motiva has been able to realize uplift in the range of $0.40 to $1.20/BBBLFF (within the boundary of the FCC unit) depending on the market economics.

This paper will further investigate Rive’s MOLECULAR HIGHWAY® technology and how it was successfully used to improve performance at a USGC Motiva refinery.

Catalyst Trial Objectives

Based on the potential for high value improvement, Motiva trialed a catalyst designed with Rive’s mesoporous zeolite technology at one of their major USGC refineries. The primary objective of the trial was to increase product revenue while maintaining excellent physical properties of the catalyst. Avenues to improving FCC revenue included:

- Increase total C3+ liquid volume
- Increase LPG olefinicity (both C3 and C4)
- Decrease slurry, dry gas, and coke
- Increase gasoline octane
- Decrease hydrogen in coke

Through a comprehensive ACE testing program and subsequent FCC-SIM modeling and optimization, Grace and Rive developed a catalyst designed to meet the refinery’s objectives.

Predicted improvements to the FCC unit during the catalyst trial were:

- Improved coke selectivity, which would boost cat-to-oil by 10% (relative to base)
- Increased C3 and C4 olefinicity by 2% (relative to base)
- Decreased dry gas by 20% (relative to base)
- Similar/slight increase to gasoline octane
- Similar/slight decrease to hydrogen in coke
- No increase in catalyst losses despite higher catalyst circulation
- 2.3 vol% increase (absolute) of total C3+ liquid volume
- Value uplift of over $1.00/BBBLFF using base pricing

Motiva FCC Unit

The FCC unit processes a mix of VGO, heavy coker gas oils, and resid. The feed rate is typically pushed to a maximum air blower/supplemental oxygen limit. The catalyst circulation rate could be increased by approximately 10% over base levels before meeting the maximum allowable circulation rate. The FCC base catalyst addition is 50% fresh catalyst and 50% purchased E-cat. Purchased E-cat is used to assist with metals management.

Rive’s MOLECULAR HIGHWAY® Technology

Rive and Grace jointly developed and commercialized MOLECULAR HIGHWAY® technology for use in FCC units throughout North America and Europe. The Rive process introduces a vast network of intermediate-sized (~40 angstroms) mesopores into the zeolite, which significantly enhances diffusion of the feed and cracked products in the catalyst.

In Figure 1, the picture on the left shows a SEM photomicrograph of a conventional Y zeolite. Each crystal face contains millions of 7.5 angstrom diameter micropores, which are too small to see even at 100,000x magnification. The picture on the right shows a photomicrograph of Rive’s zeolite at similar magnification. While the micropores still cannot be seen at this magnification, the extensive network of Rive’s mesopores is clearly visible.

Importantly, the mesopores shown above in the Rive zeolites are homogeneously distributed and interconnected within the zeolite. Stockholm University recently used more novel imaging techniques to investigate the internal architecture of Rive’s zeolite.1

![Figure 1: Photomicrographs of Conventional Zeolite (left) and Rive Zeolite (right). At similar magnifications, micropores in conventional zeolite are not viewable (left photomicrograph), while the 40 angstrom network of mesopores within Rive zeolite are viewable (right photomicrograph).](image-url)
Electron tomography and rotational electron diffraction were utilized to provide an unprecedented look inside the zeolite crystal, as shown in Figure 2. These images show clear evidence that Rive’s mesopores are homogeneously distributed and interconnected within the zeolite, enabling enhanced diffusion of molecules into and out of the zeolite, thereby improving catalytic performance.¹

As a result of Rive’s interconnected network of mesopores, larger feed molecules which vaporize in the FCC unit at temperatures above 950°F are able to access the zeolite. The acid sites in the zeolite are able to crack the larger feed molecules much more selectively than conventional active matrix materials. Additionally, these Molecular Highways™ rapidly channel the valuable cracked products out of the zeolite before they 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 below in Figure 3.

FCC catalyst formulations containing Rive zeolite typically show several benefits compared to catalysts containing conventional zeolites. These benefits include improved bottoms upgrading, decreased delta coke, and decreased dry gas production. Rive has used these trademark benefits to increase FCC feed throughput by alleviating existing unit constraints such as air blower rate, wet gas compressor rate, and regenerator temperature.

Two previously documented Rive commercial operations have been captured in American Fuel & Petrochemical Manufacturers (AFPM) papers AM-13-03 and AM-12-.² ³

LPG olefins such as propylene and butylene are very reactive, particularly at high temperatures such as those present within the FCC riser and reactor. If these valuable molecules must travel across longer diffusion path lengths, they can become saturated through hydrogen transfer reactions into less-valuable LPG paraffins, over-crack into dry gas, or condense within the catalyst pores to form coke. Rive’s intermediate-size mesopores have been proven to allow rapid transport of these valuable LPG olefins out of the zeolite, thereby enhancing LPG olefinicity.

The Rive catalyst for this operation included 1% ZSM-5. The purchased E-cat (50% of total E-cat) contained a significant amount of ZSM-5.

Figure 2: MOLECULAR HIGHWAY® Technology in Rive Zeolite.¹
Electron tomography and rotational electron diffraction by Stockholm University show Rive’s network of mesopores are interconnected and extend throughout the zeolite.

Figure 3: Overview of Rive’s MOLECULAR HIGHWAY® Technology. The mesopores engineered into Rive’s zeolite allow access and more selective catalytic cracking to larger feed molecules, while allowing the valuable cracked products to quickly exit the zeolite.
Rive/Grace Catalyst Trial Data

In the following sections, the feed rate/quality, operating conditions, and E-cat data observed during the Rive/Grace catalyst trial will be discussed.

FCC Feed Data

The total FCC feed rate, relative to normal operation (base) throughput, is shown in Figure 4. Feed rate was decreased at times due to irregular refinery operation, such as during maintenance of other process units. Feed rate was pushed beyond base throughput when dictated by refinery economics. FCC operation was very stable at feed rates 10-15 KBPD above the base feed rate.

As shown in Figures 5A-D, fresh feed quality varied during the trial, particularly during periods of irregular operation. API and CCR generally remained in similar ranges as before the trial; however, basic nitrogen in the feed increased by approximately 50 ppm during the trial, which would typically lead to a loss of approximately 0.5 wt% conversion. The feed K factor, a measure of feed crackability, was generally lower during the trial, which indicated a more naphthenic feed, which is more difficult to crack.

**Figure 4: Total FCC Feed Rate.** Feed rate typically varied between +/- 10 KBPD of normal (base) operation.

**Figure 5A: Fresh Feed API.** The feed API averaged similar values for the incumbent and Rive/Grace catalysts.

**Figure 5B: Fresh Feed CCR.** The feed CCR averaged similar values for the incumbent and Rive/Grace catalysts.

**Figure 5C: Fresh Feed Basic Nitrogen.** Basic nitrogen during the trial was approximately 50 ppm higher than the base feed quality.

**Figure 5D: Fresh Feed K Factor.** The lower K factor during most of the trial was indicative of less crackable feed.

FCC Operating Data

Rive, Grace, and Motiva closely monitored daily operating data throughout the trial to evaluate the effects of the catalyst change.

Improvement to coke selectivity was observed early in the trial, as the catalyst circulation rate and cat-to-oil ratio (C/O) increased while the regenerator temperature decreased. Since the C/O
varied strongly with feed rate fluctuations, a cross-plot of C/O vs. total feed rate is provided in Figure 6. At the base feed rate, the Rive/Grace C/O was 12% higher than the incumbent catalyst.

Another effect of improved coke selectivity is decreased regenerator temperature. At the base riser temperature, the regenerator bed temperature was 20°F lower than with the incumbent catalyst (Figure 7). Lower regenerator temperature is beneficial for reducing dry gas, reducing deactivation of E-cat, reducing SOx emissions, and improving overall mechanical reliability in the regenerator.

As shown in Figure 8, dry gas yield decreased by 6% relative to the incumbent catalyst at the base riser outlet temperature. The Rive zeolite allowed the valuable, reactive LPG olefins to more easily exit the zeolite instead of over-cracking into dry gas.

As a result of the higher C/O and reduced dry gas production, \( C_3 \) total liquid volume increased during the trial, as shown in Figure 9. The following cross-plot helps to compare improvements to \( C_3 \) total liquid volume for a given feed rate. At the base feed throughput, the \( C_3 \) total liquid volume increased by 1.5 vol% on average.

The \( P_2O_5 \) contents measured on E-cat were similar (on average) for both the incumbent and Rive/Grace catalysts, so LPG olefinicity increases were not a result of changes in stabilized ZSM-5 additive usage. Additionally, the boost to butylenes was greater than the boost to propylene, which is an opposite trend than what is typically observed from increased ZSM-5 additive usage.

\( C_3 \) olefinicity was not affected by riser temperature as much as \( C_4 \) olefinicity due to the significant presence of ZSM-5 in the purchased E-cat.

Even with changes in operation that should have directionally increased hydrogen in coke (reduction in ratio of stripping steam usage to catalyst circulation), the hydrogen in coke decreased during the trial, as shown in Figure 12. For a constant ratio of stripping steam to catalyst circulation, the hydrogen in coke decreased by 15% (relative to base). This is a testament to the improved diffusional properties and strippability of the Rive/Grace catalyst.
Benefits to improved stripping include additional recovery of valuable hydrocarbons, lower regenerator temperature, higher cat-to-oil, and lower partial pressure of steam in regenerator (improved zeolite stability).

Another effect of the catalyst’s improved coke selectivity was reduction of carbon on regenerated catalyst (CRC) throughout the trial. Since the carbon deposited on the spent catalyst decreased, the E-cat was burned cleaner in the regenerator, which yielded a lower CRC. The CRC was reduced from approximately 0.25 wt% to 0.10 wt% during the trial, which increased the amount of available acid sites on the regenerated catalyst.

Although the catalyst circulation rate increased by more than 10% during the trial, ash in slurry (an indicator of catalyst attrition/loss) did not increase.

Figure 9: **C$_3$+ Total Liquid Volume vs. Total Feed Rate**. For the base feed rate, the Rive/Grace catalyst produced 1.5 vol% more valuable liquid product on average than the incumbent catalyst.

Figure 10: **C$_3$ Olefinicity vs. Riser Outlet Temperature**. C$_3$ olefinicity increased by approximately 2% (relative) with the Rive/Grace catalyst.

Figure 11: **C$_4$ Olefinicity vs. Riser Outlet Temperature**. C$_4$ olefinicity increased by approximately 4% (relative) with the Rive/Grace catalyst.

Figure 12: **Hydrogen in Coke vs. Steam/Circulation Ratio**. Despite reduced stripping steam and higher circulation, the hydrogen in coke decreased by 15% (relative) with the Rive/Grace catalyst, due to improved diffusional properties.

Figure 13: **Carbon on Regenerated Catalyst (CRC)**. The CRC decreased during the trial as another response to the catalyst’s improved coke selectivity. This provided cleaner regenerated catalyst to contact the fresh feed in the riser.

Continued on Page 26

grace.com | 25
Gas Factor

The gas factor is a measure of the E-cat’s tendency to produce hydrogen compared to methane. It is greatly affected by the metals level on the E-cat, particularly in regard to the concentration of nickel. During the trial, the ratio of antimony-to-nickel decreased from an average of 0.20 to 0.17. Still, the gas factor fell considerably with the Rive/Grace catalyst for a given ratio of Sb/Ni. Using 20% less antimony (Sb/Ni ratio of 0.17), the Rive/Grace E-cat achieved a similar gas factor (3.2) to the incumbent E-cat (Sb/Ni ratio of 0.21).

**Coke Factor**

The coke factor is a measure of the E-cat’s coke selectivity compared to a steam-deactivated reference catalyst at the same conversion. Lower coke factors translate commercially into lower delta coke, lower regenerator temperature, and higher cat-to-oil. The coke factor decreased from an average of 1.2 with the incumbent catalyst to 1.1 with the Rive/Grace catalyst. As demonstrated commercially, the delta coke and regenerator temperature decreased during the trial, while the cat-to-oil increased.

**Fluidization Factor**

The fluidization factor is a measure of the fluidization characteristics of the E-cat. An E-cat having a higher fluidization factor can typically provide more reliable catalyst circulation commercially, leading to improved operability in standpipes and slide valves. This can also provide improved diffusion/heat transfer between the catalyst and feed. The fluidization factor increased from an average of 3.08 with the incumbent catalyst to 3.20 with the Rive/Grace catalyst.
Benchmark ACE Testing

Rive/Grace performed an ACE study on E-cat samples using Motiva feed collected just prior to the trial. The study evaluated the following E-cats:

- Pre-trial incumbent E-cat
- 35% turn-over (T/O) Rive/Grace E-cat (Rive/Grace catalyst cannot surpass 50% unit T/O since fresh and purchased catalyst addition rates are equal)

E-cat properties are provided in Table 1. Green arrows for the 35% T/O E-cat sample represent advantaged metals compared to the pre-trial E-cat, while red arrows indicate disadvantaged metals compared to the pre-trial E-cat.

### Table 1: E-cat properties from Benchmark ACE Test

<table>
<thead>
<tr>
<th></th>
<th>Pre-trial E-cat</th>
<th>35% T/O E-cat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni, ppm</td>
<td>2663</td>
<td>3096</td>
</tr>
<tr>
<td>V, ppm</td>
<td>4189</td>
<td>3665</td>
</tr>
<tr>
<td>Sb, ppm</td>
<td>615</td>
<td>547</td>
</tr>
<tr>
<td>Sb/Ni</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>P₂O₅, ppm</td>
<td>8600</td>
<td>7100</td>
</tr>
</tbody>
</table>

Table 2 provides ACE results of the E-cat samples run at constant conversion of 70%. Highlights between the incumbent E-cat and the 35% T/O Grace/Rive E-cat are as follows:

- Total LPG yield increased from 17.1 wt% to 17.9 wt%.
- All LPG paraffin yields were lower, while all LPG olefin yields were higher. C₃ olefinicity increased by 3% (relative to base), while C₄ olefinicity increased by 4% (relative to base). The increased LPG olefinicities occurred with less P₂O₅ on E-cat, as noted in Table 1.
- Total Gasoline + LCO yield decreased by 0.5 wt%, which was converted predominantly into valuable LPG olefins.
- Coke yield decreased from 6.9 wt% to 6.5 wt%. Commercially, this translated into lower delta coke, lower regenerator temperature, and increased circulation.
- Gasoline octane increased slightly from 87.85 to 88.00 (R+M)/2.
- While dry gas yield increased slightly from 2.2 wt% to 2.3 wt%, Sb/Ni on E-cat was 15% lower for the Rive/Grace E-cat, as noted in Table 1. Commercially, the lower regenerator temperature further assisted in reducing dry gas.

### Table 2: Benchmark ACE Test Results

<table>
<thead>
<tr>
<th></th>
<th>Pre-trial Ecat</th>
<th>35% T/O Ecat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>CO</td>
<td>55</td>
<td>59</td>
</tr>
<tr>
<td>Total Dry Gas, wt%</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Propane, wt%</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Propylene, wt%</td>
<td>54.4</td>
<td>61.1</td>
</tr>
<tr>
<td>Iso-Butane, wt%</td>
<td>34.1</td>
<td>33.3</td>
</tr>
<tr>
<td>N-Butane, wt%</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Butylene, wt%</td>
<td>65.0</td>
<td>69.0</td>
</tr>
<tr>
<td>Total LPG, wt%</td>
<td>17.1</td>
<td>17.9</td>
</tr>
<tr>
<td>Gasoline, wt%</td>
<td>43.9</td>
<td>43.3</td>
</tr>
<tr>
<td>LCO, wt%</td>
<td>20.6</td>
<td>20.7</td>
</tr>
<tr>
<td>C3 Olefinicity</td>
<td>84.4</td>
<td>87.1</td>
</tr>
<tr>
<td>C4 Olefinicity</td>
<td>60.7</td>
<td>63.3</td>
</tr>
<tr>
<td>Total LPG Olefinicity</td>
<td>66.6</td>
<td>77.6</td>
</tr>
<tr>
<td>Total Gasoline Octane, (R+M)/2</td>
<td>87.85</td>
<td>88.00</td>
</tr>
</tbody>
</table>

Rive/Grace Trial Uplift

Uplift during the Rive/Grace catalyst trial was evaluated using several methods. These methods include:

- Shell proprietary SHARC® simulation
- Rive/Grace FCC-SIM simulation
- Rive/Grace benchmark ACE testing
- Motiva look-back tool

The SHARC® and FCC-SIM models were in agreement that the Rive/Grace catalyst provided significant value improvement for Motiva. Contributors to value improvement included (a) increased C₃+ total liquid volume, (b) increased LPG olefinicity (particularly C₄), (c) decreased dry gas, and (d) decreased hydrogen in coke. The Motiva refinery was able to realize uplift in the range of $0.40 to $1.20/BBL_ff (within the boundary of the FCC unit), depending on the market economics. The value uplift was slightly less than projected at the start of the trial due to unrealized limitations of total LPG production.

Uplift was further validated from modeling the results of the benchmark E-cat ACE results in Table 2, which compared the pre-trial E-cat against the Rive/Grace E-cat.

Continued on Page 28
Motiva created a unique look-back tool, which could evaluate FCC profitability for periods of similar operation between the incumbent catalyst and Grace/Rive catalyst. Profitability was evaluated for periods of time when the feed rate, fresh and purchased catalyst addition rates, feed quality, operating conditions, and LPG production were all similar. This evaluation tool was helpful to isolate and confirm the value realized by the refinery as a result of the catalyst change.

Technical Service

Collaboration between the Motiva refinery, Rive, and Grace was excellent throughout the trial. The objective of the entire team was to push the unit to maximum profitability, by leveraging the catalyst’s benefits at optimized operating conditions.

Weekly teleconferences, monthly data reviews at the refinery, active Action Item Logs, and a true dedication by all to refinery improvement were keys to the trial’s success.

Looking Forward

Based on mutual learnings from our combined team, as well as predicted changes to feed quality, product pricing, and unit constraints such as total LPG production, an optimized Rive/Grace catalyst formulation was developed for the refinery. The close relationship between all parties and the new custom catalyst formulation are expected to continue to drive unit improvement and product revenue for Motiva.

The results from this commercial FCC catalyst trial support Rive’s assertion that increasing 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.

Grace/Rive designed a catalyst for a trial at a major USGC Motiva refinery in 2016. In line with the refinery’s objectives, the following FCC performance improvements were documented at normal operating conditions, relative to pre-trial conditions.

- Cat-to-oil increased by 12%
- Total C3+ liquid volume increased by 1.5 vol%
- Regenerator temperature decreased by 20°F for a base riser temperature
- Dry gas decreased by 6% for a base riser temperature
- C3 olefinicity increased by 2% for a base riser temperature
- C4 olefinicity increased by 4% for a base riser temperature
- Hydrogen in coke decreased by 15%
- Carbon on regenerated catalyst (CRC) decreased by 60%

Extensive FCC modeling with both FCC-SIM and SHARC®, E-cat benchmark ACE testing, and operating data comparison between periods of similar operation confirmed that Motiva realized uplift in the range of $0.40 to $1.20 /BBLFF (within the boundary of the FCC unit), depending on feed quality and market economics.

As a result of these demonstrated performance improvements and strong technical service relationship between Motiva, Grace, and Rive, Motiva continued using a Grace FCC catalyst containing Rive’s MOLECULAR HIGHWAY® technology to realize exceptional value in their operation.

References:

Acknowledgments:
The authors wish to acknowledge with sincere appreciation and thank the entire team from Grace for their collaboration, expertise, and support of the research and development described in this paper.

We also express our sincere thanks to Ken Peccatiello, Natalie Petti, and the other advisors to Rive Technology for their contributions.

The work and support from Motiva is also greatly appreciated.
The Right Catalyst System for You

Are you getting the right hydroprocessing catalyst system to maximize your profits?

With Advanced Refining Technologies, you can count on our practical refinery expertise, state-of-the-art technology and R&D, strong technical service, and global manufacturing to improve your run lengths, product quality, and yields.

When you optimize unit profitability, you know you’ve found the right catalysts... and the right partner.

Let’s work together.

artcatalysts.com

The global leader in hydroprocessing catalysts
Understanding Catalytic Solutions for Increasing Middle Distillate Yields

Brian Watkins  
Manager, Technical Service  
Advanced Refining Technologies (ART)

Charles Olsen  
Global Technology Manager, DHT  
Advanced Refining Technologies (ART)

To take maximum advantage of domestic crude and opportunity feed sources, refiners are exploring ways to maximize their middle distillate production. In the process, they are discovering issues not previously considered. If a refiner’s objective is to maximize the distillate pool, it’s important to understand the key relationships between sulfur and nitrogen and the impact they have on designing a catalyst system to optimize unit performance.

Improvements in catalytic solutions and a detailed understanding of hydrotreater kinetics have provided avenues for significant advances. Advanced Refining Technologies (ART) has conducted extensive pilot plant work to better understand these potential options. This work has shown that a catalyst system design incorporating a new, ultra-high activity, self-supported catalyst series, ICR™ 1000, is a viable option for the production of higher yields of middle distillate.

This article demonstrates the need for refiners to follow an integrated approach to managing the catalyst and the operation in order to have a continuously optimized hydrotreater cycle, and to significantly increase refiner revenue. Both the hydrotreating catalyst system and the operating strategy are critical to providing the highest quality products. Driving the hydrotreater to remove nitrogen and PNA’s improves product value as well as product volume gain. Use of tailored SmART CATALYST SYSTEM® technology will optimize the ULSD hydrotreater. This creates a stable operating system that is flexible and allows the refiner to increase throughput and produce higher quality diesel.
With the continued interest in processing domestic crude sources as well as opportunity feed sources, refiners are exploring ways to maximize their middle distillate production. Several domestic feed sources have reduced the demand on the ULSD hydrotreater making it significantly easier to treat to ULSD however; other new feed sources are presenting processing issues that were not previously considered. A critical element in every approach to increasing diesel yield is the proper design and selection of a catalyst system for each specific hydrotreating unit. This approach to increasing diesel yields, requires a detailed understanding of feed and operating conditions such that the hydrotreater can be operated at optimum conditions for the unit cycle. Challenges in terms of understanding the species of sulfur and nitrogen present, hydrogen consumption, coupled with the chemistry required, will be discussed in order to provide some guidance and understanding in order to maintain product quality with existing assets and minimal investment.

Improvements in catalytic solutions and a detailed understanding of hydrotreater kinetics have provided avenues for significant advances in improved ULSD performance. Advanced Refining Technologies (ART) has conducted extensive pilot plant work to better understand these potential options. This work has shown that a catalyst system design incorporating a new, ultra-high activity, self-supported catalyst series, ICR™ 1000, is a viable option for the production of higher yields of middle distillate.

In order to assess the effectiveness of ICR™ 1000 series catalysts, it is important to understand the concentration of various species of sulfur and nitrogen present through the reactor. For an initial understanding, Table 1 shows a variety of sulfur, nitrogen and aromatic compounds and the corresponding change in boiling point that occurs upon removal of sulfur and nitrogen, and though saturation of aromatic rings. The table demonstrates that a fair amount of boiling point shift can occur through typical hydrotreating.

<table>
<thead>
<tr>
<th>Untreated Compound</th>
<th>Boiling Point, °F</th>
<th>Treated Compound</th>
<th>Boiling Point, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfur Containing Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butyl Mercaptan</td>
<td>209</td>
<td>Butane</td>
<td>31</td>
</tr>
<tr>
<td>Octane Mercaptan</td>
<td>390</td>
<td>n-Octane</td>
<td>258</td>
</tr>
<tr>
<td>Benzo thiophene</td>
<td>430</td>
<td>Ethyl Benzene</td>
<td>277</td>
</tr>
<tr>
<td>Decylmercaptan</td>
<td>465</td>
<td>n-Decane</td>
<td>345</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>630</td>
<td>Biphenyl</td>
<td>493</td>
</tr>
<tr>
<td>4,6 DMDBT</td>
<td>645</td>
<td>3,3'-Dimethyl-Biphenyl</td>
<td>536</td>
</tr>
<tr>
<td><strong>Nitrogen Containing Compounds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>240</td>
<td>Pentane</td>
<td>97</td>
</tr>
<tr>
<td>Indole</td>
<td>489</td>
<td>Ethyl Benzene</td>
<td>277</td>
</tr>
<tr>
<td>2-Methyl Indole</td>
<td>522</td>
<td>Propyl Benzene</td>
<td>319</td>
</tr>
<tr>
<td>Isoquinoline</td>
<td>468</td>
<td>2-Ethyl Toluene</td>
<td>329</td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>424</td>
<td>Tetralin</td>
<td>406</td>
</tr>
<tr>
<td>β-Ethyl Naphthalene</td>
<td>496</td>
<td>2-Ethyl Tetralin</td>
<td>459</td>
</tr>
<tr>
<td>Anthracene</td>
<td>644</td>
<td>Octahydro Anthracene</td>
<td>561</td>
</tr>
</tbody>
</table>

Table 1: Boiling point shifts achieved from hydrotreating

In addition, understanding the catalyst properties and their basic kinetic functions is critical in optimizing a catalyst loading. All hydrotreating catalysts have an acidic component combined with an active metals component. For typical hydrotreating catalysts these metals are either Cobalt-Molybdenum (CoMo) or Nickel-Molybdenum (NiMo) on an alumina or silica-alumina support. In order to increase measurable volume gain in a given hydrotreater, the kinetic response of the catalyst to the molecules in the oil must be changed in order to be much more active and efficient for aromatic saturation. The catalyst which controls this process is a self-supported catalyst designed with extremely high catalytic activity, which can be two or three times more active relative to current generation, conventional catalysts. However, to fully realize the benefits of this catalyst it requires properly balancing the amounts and types of catalysts used with ICR™ 1000 as well as proper placement of ICR™ 1000 in the system.

As a second step, it is useful to understand the chemistry involved in hydrotreating, and in particular, the chemistry required for maximizing product volume swell. Table 2 lists several different classes of hydrocarbon compounds that can be found in diesel range feeds. The data shows that as hydrogen is added to a molecule, the density of the compound decreases. This indicates that even some simple hydrotreating reactions result in a decrease in density of the product; or put another way, result in an increase in product volume.

Continued on Page 32
that dramatic shifts in boiling point and density can be realized by hydrogenating aromatic compounds, and it can be greater than simply removing sulfur and nitrogen. Density decreases by 20-25% with boiling points shifts anywhere from 50-150°F upon saturation of the aromatic rings.

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>°API</th>
<th>H/C Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso Paraffin</td>
<td>2,3-dimethyl-octane</td>
<td>C_{10}H_{22}</td>
<td>0.738</td>
<td>60.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Paraffin</td>
<td>n-decane</td>
<td>C_{10}H_{22}</td>
<td>0.730</td>
<td>62.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Olefin</td>
<td>1-decane</td>
<td>C_{10}H_{22}</td>
<td>0.741</td>
<td>59.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Naphthene</td>
<td>Decalin</td>
<td>C_{10}H_{18}</td>
<td>0.897</td>
<td>26.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Mono Aromatic</td>
<td>Tetratin</td>
<td>C_{10}H_{18}</td>
<td>0.970</td>
<td>14.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Poly Aromatic</td>
<td>Naphthalene</td>
<td>C_{10}H_{8}</td>
<td>1.140</td>
<td>-7.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 3 lists selected properties of several different aromatic compounds that are found in diesel-range feedstock, along with the corresponding fully saturated compound. It is apparent that dramatic shifts in boiling point and density can be realized by hydrogenating aromatic compounds, and it can be greater than simply removing sulfur and nitrogen. Density decreases by 20-25% with boiling points shifts anywhere from 50-150°F upon saturation of the aromatic rings.

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>°API</th>
<th>H/C Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>Decalin</td>
<td>C_{10}H_{18}</td>
<td>0.897</td>
<td>26.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Saturates</td>
<td>Perhydro Fluorene</td>
<td>C_{10}H_{18}</td>
<td>0.920</td>
<td>487</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Perhydro Phenanthrene</td>
<td>C_{10}H_{18}</td>
<td>0.944</td>
<td>518</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Perhydro Pyrene</td>
<td>C_{10}H_{18}</td>
<td>0.962</td>
<td>604</td>
<td></td>
</tr>
</tbody>
</table>

This suggests that in order to achieve a high degree of product volume swell in ULSD, a detailed understanding of aromatic and polynuclear aromatic (PNA) hydrogenation is required. It is well understood that hydrogenation of aromatic compounds is a reversible reaction, and that the equilibrium conversion is less than 100% under typical conditions. The conversion is highly dependent on temperature and hydrogen partial pressure as well as the catalyst type present. The figure compares the conversion observed for both a NiMo and a CoMo catalyst. The data clearly indicates that the NiMo catalyst has the greater aromatic saturation activity of the two catalysts shown, and both catalysts show there is a maximum amount of aromatic saturation that can be accomplished under a given set of operating parameters. The NiMo catalyst also has greater aromatic saturation activity, with product aromatics concentration over 4 vol% (absolute) lower compared to the CoMo catalyst. As expected, this difference in aromatic conversion accounts for the higher H2 consumption typically seen for a NiMo compared to a CoMo catalyst. The chart also shows the influence of equilibrium on aromatics conversion. As the temperature increases beyond about 670-680°F, the conversion begins to decrease as the rate of the dehydrogenation reaction starts to increase enough to compete with hydrogenation reactions. At high enough temperatures, both catalysts can give the same conversion since they are operating in the equilibrium-controlled regime.
One significant consequence of achieving a high level of saturation of multi-ring and mono-ring aromatic compounds is higher hydrogen consumption. However, not all aromatic species are created equal when it comes to hydrogen consumption. The hydrogenation occurs in a stepwise fashion where aromatic rings are saturated in succession, with each step along the pathway subject to equilibrium constraints. The rate limiting step to the fully saturated species is hydrogenation of the last aromatic ring (the mono aromatic), and this step consumes the most hydrogen of all the reactions in this pathway. Three moles of hydrogen are required to hydrogenate the mono-ring compared to two moles of hydrogen required to hydrogenate the rings in the poly aromatic compound.

Figure 2 summarizes pilot plant data demonstrating how the aromatic species change in ULSD product as a function of the residence time (i.e. 1/LHSV) (Liquid Hourly Space Velocity) in the reactor. For PNA saturation, the two-ring aromatic is converted to the mono-aromatic relatively quickly as shown by a steep decline in PNA concentration as a function of residence time below 0.5 hr. At longer residence times, which represent space velocities of about 2 hr⁻¹ or lower, there is very little change due to equilibrium constraints. For mono-ringed aromatic saturation, there is a steady increase in conversion as the residence time is increased, and eventually the mono-ringed concentration begins to decrease indicating that mono-ring saturation starts to increase as the LHSV is decreased. These data show that PNA saturation occurs fairly readily under typical hydrotreating conditions, but saturation of mono rings aromatics is much more difficult and is aided by lower LHSV, or improved catalyst kinetic ability.

Since conversion of the mono aromatic compounds provides the most significant boost in product volume, hydrotreaters with very short residence time (high LHSV) will have difficulty achieving higher volume swell due to the much slower rate of saturating the final aromatic ring. These units will require a higher temperature in order to drive the kinetic saturation portion of the reaction. This can have some negative effects on expected cycle time due to the higher start of run temperature and the increased fouling rate associated with higher temperature.

ART further explored aromatic saturation and the impact on product volume by completing some pilot plant work using a feedstock containing 30% cracked material. The work investigated the impacts of increasing LHSV and temperature compared to a base case resembling typical ULSD unit operation. Figure 3 shows the resulting product sulfur as the LHSV increases over the catalyst bed (i.e. decreasing the top bed volume).

The base LHSV is able to product ULSD around 640°F weighted average bed temperature (WABT), and increasing the LHSV by a factor of 1.8 increases the required temperature for ULSD by nearly 35°F. As expected, as the LHSV is increased further (decreased bed volume), a point is reached where the system is no longer capable to produce ULSD. This data can be used to model the sulfur and nitrogen removal as the feed moves through the catalyst bed. Figure 4 shows the simulation of how the nitrogen and sulfur conversions change through the catalyst bed.
It shows that the conversion is high in the top 40% of the reactor and dramatically decreases through the bottom 30-40% as the species of sulfur and nitrogen have become low in concentration, and remaining species are more complex and difficult to remove.

In an attempt to optimize performance, and capitalize on the synergetic effect of either a NiMo or a CoMo catalyst, the same work was completed using a 100% CoMo catalyst loading. In this case, the sulfur trends are similar in that 640°F is required to produce ULSD, but in this case the product nitrogen values are significantly higher. Figure 5 compares the conversion of sulfur and nitrogen through the reactor for the CoMo catalyst, and similar to the NiMo catalyst significant sulfur conversion occurs in the top 40% of the reactor. The nitrogen removal, however, occurs at a much slower rate over the CoMo catalyst and requires almost 90% of the reactor to achieve product nitrogen levels that the NiMo system accomplished in less than 50 percent of the reactor.

The reaction rates achieved by these two catalyst systems are similar for sulfur removal, and quite different for nitrogen removal. This has implications for aromatic saturation activity since nitrogen is known to poison saturation sites on catalysts. Interestingly, a comparison of the product sulfur to product nitrogen for the NiMo system through the reactor shows that regardless of residence time in the reactor, it is possible to predict one directly from the other, indicating that the kinetic activity of both mechanisms are similar as shown in Figure 6.

Figure 7 shows that this is not the case for the CoMo catalyst. The product sulfur levels do not directly predict the nitrogen values, thus require some understanding of residence time as well.

Since organic nitrogen in the feed is known to impact the HDS and HDA activity of downstream catalyst, it is imperative to know what the corresponding levels are throughout the reactor in order to optimize the next layer of catalyst. In this example, although the CoMo catalyst is adequate for sulfur removal through the hydrotreater, it is inadequate for nitrogen removal. If the primary goal is to utilize additional available hydrogen and boost distillate yield, then nitrogen removal must be maximized in order to significantly improve aromatics saturation reactions.
The differences between the NiMo and CoMo systems can be used to understand the effect of nitrogen on ICR™ 1000. The product sulfur levels in this study are nearly identical for the NiMo and the CoMo, (Figure 8), while there is a significant difference in product nitrogen levels as the feed moves through the reactor (Figure 9).

**Figure 8:** Comparison of sulfur through the reactor

**Figure 9:** Comparison of nitrogen through the reactor

It is expected that the impact of the ICR™ 1000 series on volume swell will be different when included in a catalyst system with NiMo or CoMo because of the differences in the feed nitrogen going into the ICR™ 1000 bed. Using API upgrade as the indication of product volume gain, the NiMo catalyst easily produces a 0.5 API higher product compared to the all CoMo system. This corresponds to roughly 50-60 SCFB higher hydrogen consumption for the NiMo catalyst. Adding a layer of ICR™ 1000 to the system shows the NiMo/ICR™ 1000 system results in an additional 1 number API improvement compared to a 0.6 API improvement for the CoMo/ICR™ 1000 system. Figure 10 compares the four systems for API improvement.

The increased product API for the NiMo/ICR™ 1000 system corresponds to about 100-115 SCFB of additional hydrogen into the product for increased product volume gain.

**Figure 10:** API improvement

This work led to additional pilot plant testing for an ART customer to validate the location of ICR™ 1000 and improvements in activity and volume gain. This work was completed on the customer’s feed, and the work was conducted to show the improvements between using a 100% CoMo catalyst system, a 100% NiMo system, and a NiMo system with ICR™ 1000. As expected, the all-CoMo system is the base for sulfur and volume gain. As expected, the all NiMo system in this work was significantly better than the all-CoMo system in terms of sulfur activity and volume gain. Adding ICR™ 1001 to the catalyst loading showed an additional 0.5 to 0.7 API upgrade, which provides nearly a 0.8 vol% increase in distillate yields at shown in Figure 11. ICR™ 1001 was located near the bottom of the catalyst bed to ensure lower concentrations of organic nitrogen and improved volume swell.

**Figure 11:** API and activity gains with ICR™ 1000 series catalyst

Continued on Page 36
If the refiner’s objective is to maximize the distillate pool, it is important to understand the key relationships between sulfur and nitrogen and their impact when designing a catalyst system to optimize unit performance. All of the combinations presented show the need for refiners to follow an integrated approach to managing the catalyst and the operation in order to have a continuously optimized hydrotreater cycle, and to significantly increase refiner revenue.

Both the hydrotreating catalyst system and the operating strategy are critical to providing the highest quality products. Driving the hydrotreater to remove nitrogen and PNA’s improves product value as well as product volume gain. Use of tailored SmART CATALYST SYSTEM® technology will optimize the ULSD hydrotreater. This creates a stable operating system that is flexible and allows the refiner to increase throughput and produce higher quality diesel.

The complex relationship between catalysts in a hydrotreater underscores the importance of working with a catalyst technology supplier that has the capabilities to understand the interaction between the hydrotreating performance, yield structure, and sulfur and nitrogen distributions through the unit. ART offers such capabilities and delivers them through tailored SmART CATALYST SYSTEM® technology and ApART™ catalyst systems to meet the refiner’s specific needs and operation constraints. ©
Delivering value in the refining business means more than polishing a few facets of your operation. It means taking a close-up look at the financial performance of your business.

Grace custom catalyst solutions, co-developed with you, are about more than chemistry. They’ve been shown to improve refinery margins and profits.

In some cases, the difference between our refinery customers’ financial return on Grace technologies versus the alternative has reached into eight figures.

If you’re ready to refine the financial return on your FCC operation, we’d like to show you how we can help.

At Grace, value is all about our customers’ financial success.

Learn more at grace.com/value.
Improving FCC Unit Profitability

Stelios Kyriakou  
HELPE S.A. Refineries Technical Services  
Director, Hellenic Petroleum S.A.

Costas Plellis-Tsaltakis  
Process Section Head of HELPE S.A.  
Aspropyrgos Refinery, Hellenic Petroleum S.A.

Dimitris Gkanis  
Process Engineer, Hellenic Petroleum S.A.

Emmanuel Smaragdis  
Technical Sales and Service Manager, FCC,  
W. R. Grace & Co.

Matthias Scherer  
Regional Marketing Director, FCC, EMEA,  
W. R. Grace & Co.

Daniel McQueen  
General Sales Manager, FCC, Europe,  
W. R. Grace & Co.

Close collaboration was key to helping Hellenic Petroleum S.A.’s (HELPE) Aspropyrgos refinery enhance FCC unit profitability.

Aspropyrgos refinery’s FCC unit is an Exxon FlexiCrackeR® design, aiming primarily at propylene production at minimum bottoms yield. The FCC team is focused on continuous improvement in their operation supported by Grace since 2004. To enhance profitability, HELPE made a series of improvements to debottleneck certain downstream units which resulted in higher capacity for propylene and LPG processing. Grace worked closely with the HELPE FCC team ahead of the revamp in order to prepare a catalyst formulation that would fit the increased challenges.

Thanks to an extensive screening program and close cooperation with the HELPE FCC team, Grace provided an enhanced catalyst system using MIDAS® catalyst and OlefinesUltra® MZ additive technologies. Clear target setting from the HELPE FCC team, as well as the reliability of the data provided aided in the reformulation, while Grace worked with the FCC team to ensure a smooth transition to the new catalyst system.

Following the successful introduction of MIDAS® catalyst, Grace continues to work with HELPE to further enhance the FCC unit’s profitability by tailoring its latest catalyst and additives technology according to operating targets. The estimated improvement in the unit’s profitability via the new technology amounts to at least 0.6 $/bbl, excluding any gasoline octane premium.
This article presents the results of the common efforts between Grace and the FCC team of Hellenic Petroleum S.A.’s (HELPE) Aspropyrgos refinery to further enhance FCC unit profitability. In this context, Grace proposed adding MIDAS® catalyst to the base Grace catalyst which had been used until then in combination with OlefinsUltra® MZ additive, the latest ZSM-5 based technology launched in the EMEA. The clear improvement in profitability was based on lower bottoms to coke and higher product olefinicity at no higher dry gas, while at the same time reducing catalyst addition.

The reformulation and subsequent evaluation was based on clear target setting from the HELPE FCC team as well as the reliability of the data provided. Grace worked with the FCC team to manage the change and ensure a smooth transition to the new catalyst system. This was achieved by performing a series of lab studies to predict the new catalyst system’s performance and by discussing with the FCC team ways to optimise the process to achieve maximum benefit. The estimated further improvement in the HELPE FCC unit’s profitability via the new technology amounts to at least 0.6 $/bbl.

Following the successful introduction of MIDAS® as an efficient matrix component to further improve bottoms upgrading, Grace continues to work with HELPE to further enhance the FCC unit’s profitability by tailoring its latest catalyst and additives technology according to operating targets.

Aspropyrgos refinery’s FCC unit is an Exxon FlexiCrackeR® design, aiming primarily at propylene production at minimum bottoms yield. The FCC team is focused on continuous improvement in operations, supported by Grace since 2004. To further enhance profitability, HELPE made a series of improvements to debottleneck certain downstream units. This resulted in higher capacity for propylene and LPG processing.

**Grace’s Catalyst and Propylene Additive Technology**

The benefits of Grace’s base catalyst were enhanced by the addition of MIDAS® catalyst as a blending component.

MIDAS® is a high matrix input, high porosity FCC catalyst, maximising conversion of bottoms. MIDAS® catalyst has been successfully applied in over 130 applications worldwide and its success is driven by the fact that it effectively cracks all feed types: heavy resids, severely hydrotreated light feeds, and shale oil derived feed streams. The catalyst design minimises the thermal and catalytic factors that result in coke formation. Optimal porosity is required for effective kinetic conversion of bottoms. The result is deep bottoms conversion, regardless of the starting feedstock.

It should be stressed that the introduction of the matrix component in the case of the HELPE FCC unit was very carefully tailored to the targets of the unit, by exploiting the ‘best of both worlds’: the highly selective base catalyst component on the one hand, and the highly active matrix of the MIDAS® catalyst on the other. This ensured further improved activity and stability, while achieving higher product olefinicity and lower bottoms to coke, without compromising dry gas make or attrition resistance.

As a leading supplier in the LPG olefins maximisation segment, Grace is serving the majority of the high propylene FCC units worldwide. To support the demands of this market segment, the company continuously invests in R&D innovation. The latest development in LPG olefins maximisation technology is OlefinsUltra® MZ additive, launched in 2015. This was supplied for the HELPE FCC unit to be added to the catalyst system on an as-need basis to boost LPG make further.

**Performance of the Catalyst Blend and Additive**

The addition of MIDAS® catalyst as a blend component and the upgrade to the OlefinsUltra® MZ additive were decided after a screening study which took place in Grace’s laboratory facilities in Worms, Germany. The selected formulation showed:

- Lower bottoms to coke
- Substantially higher propylene and isobutylene selectivity
- No debits in dry gas make
- Excellent attrition resistance
- Higher activity retention and metals tolerance, resulting in lower delta coke and catalyst additions.

An extract of the performance benefits is depicted in the following graphs, based exclusively on the raw data provided by the HELPE FCC unit team. More specifically, Figure 1 shows the clear improvement in bottoms to coke, which is particularly important when planning to process worse feedstocks under coke limitations.

**Figure 1: Bottoms (>343°C) to coke**

---

**Continued on Page 40**
This feature is based on the lower delta coke make of new formulation, as can be seen in Figure 2. This graph shows the difference between the temperatures of the regenerator dense bed and reactor outlet temperature (a direct measure of delta coke) against the Concarbon processed in the unit (a measure of the delta coke contribution from the feed). For the same coke make tendency level, the base catalyst/MIDAS® catalyst blend results in lower delta coke and therefore lower regenerator temperatures.

![Figure 2: Delta coke as a function of Concarbon processed](image)

It is important to stress that this could not have been achieved without a well tuned and balanced zeolite to matrix ratio. Excess matrix would have had the opposite effect.

The significant operational flexibility gained is complemented by increased LPG olefins selectivity (see Figures 3 and 4). Propylene and isobutylene selectivities are plotted against the P$_2$O$_5$ content of the inventory in order to account for the other two major factors contributing to LPG olefins selectivity: conversion and ZSM-5 additive content.

The increase in propylene selectivity is to be attributed mainly to the OlefinsUltra® MZ additive which brings higher activity for the same content in the inventory. The C$_4$ olefinicity is the combined effect of the MIDAS® catalyst component as well as OlefinsUltra® MZ which were implemented simultaneously.

![Figure 3: Propylene ex-reactor versus the P$_2$O$_5$ content in the circulating inventory](image)

![Figure 4: Isobutylene ex-reactor versus the P$_2$O$_5$ content in the circulating inventory](image)
As mentioned previously, these performance benefits came at no increase in dry gas make (see Figure 5).

In addition to the performance benefits, Figure 6 shows the specific catalyst additions needed to maintain activity versus the vanadium equivalent in the feed. The average difference was at 0.3 kg per ton of feed processed and, apart from the offset, the trend lines have a different slope, indicating less deactivation of the base catalyst/MIDAS® catalyst blend under the effect of metals. Although the improvements in unit operations and performance prevail by far in unit economics, a reduction in catalyst additions also assists in catalyst handling and opex minimisation.

With the aid of commercial simulation software, the unit performance under the two catalyst systems was compared by normalising data for the same operating conditions and feed quality. The simulation confirmed that: slurry is reduced by 1.1 wt% at the same coke, increasing the useful fraction between C₃ and standard LCO (343°C cut point) at significantly higher LPG olefinicity. Furthermore, by using standard product prices for Mediterranean refineries, the calculated profit increase was at least 0.6 $/bbl, excluding any premiums from the higher gasoline octanes.

**Conclusion**

Based on an extensive screening programme and close cooperation with the HELPE FCC team, Grace provided an enhanced catalyst system using MIDAS® catalyst and OlefinesUltra® MZ additive technologies. This upgrade resulted in:

- Significantly improved bottoms to coke
- Substantially higher propylene and isobutylene selectivity
- No debits in dry gas make
- Higher activity retention and metals tolerance, resulting in lower delta coke and lower catalyst additions
- Excellent attrition resistance and retention.

The clarity of the evaluation was largely based on the reliability of the raw unit data provided by the HELPE FCC unit team. The further performance improvement is estimated to be adding at least 0.6 $/bbl to unit profitability, excluding any gasoline octane premium.

This cooperation between Grace and HELPE also extends to operational optimisation recommendations, and is an ongoing process driven by the need for flexibility and continuous improvement in unit profitability within an ever changing and challenging business environment.

**References**

1. Hellenic Petroleum; www.helpe.gr

It is important to repeat that this higher activity retention comes at no penalty on delta coke. No higher catalyst losses were observed, and attrition was kept to a minimum.