Dear Friends,

After 24 years in the chemical industry and many commercial and business leadership roles, it’s truly a pleasure to settle at Grace and assume leadership of an organization built on the greatness of its members. And it’s an honor to lead a global business that develops and manufactures catalysts and related technologies for energy and refining, polyolefins and plastics, as well as petrochemical and other chemical manufacturing applications.

Grace Catalysts Technologies develops and manufactures catalysts and related products/technologies used in energy and refining, polyolefins and plastics, as well as petrochemical and other chemical manufacturing applications.

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In fact, longtime Catalagram® readers will notice that, for the first time in a decade we have incorporated news from across our catalysts portfolio, including an article introducing our UNIPOL® Polypropylene Process Technology.

As I meet new people now, it’s tempting to introduce Grace in terms of its amazing history of catalysts technology breakthroughs and decades-long relationships with some of the best companies in the world. But it’s even more intriguing to look ahead to the opportunities to help customers succeed in the new landscape driven by non-traditional crudes, rising demand for plastics, environmental imperatives, true global markets, and so much more.

What strikes me as so promising is that Grace’s model of close customer partnership, technology leadership, and flexible worldwide manufacturing is so well suited to the uncertainty and change driving our industry.

Of course, we’re very proud of our top positions in FCC catalysts, resid hydroprocessing catalysts, independent polyethylene and independent polypropylene catalysts. Yet, I’m especially excited about what these leadership positions mean for our customers. Working with a leader means you’re not left wondering if there is a better team to solve the complex riddles of catalysts chemistry and refinery operations, or to reach across the portfolio to address a variety of catalysts challenges. Working with the leader means you don’t have to worry that you’re not delivering the most reliable catalyst to your process. Working with the leader means partnering with an organization whose commitments you can count on and who is focused on excellence. If there’s anything I’ve learned in this life, it’s that excellence is fun.

This fall the Grace Catalysts Technologies teams are pleased to be participating in the 2014 AFPM Q&A and Technology Forum in Denver and the ERTC 19th Annual Meeting in Lisbon. Through customer visits and other industry events, I look forward to meeting the fascinating people who form the global community of Grace customers and partners.

Al Beninati
President, Grace Catalysts Technologies

On June 30, 2014, Grace announced the appointment of Albert F. Beninati Jr., as President of its market-leading $1.1 billion Grace Catalysts Technologies segment.

“I’m excited to challenge Grace’s global catalysts teams to continue to put customer value at the center of the world’s broadest, fully-integrated portfolio of complementary catalysts technologies.”

A Global Leader in Catalysts, Materials and Construction Technologies

Catalysts Technologies
- #1 in FCC catalysts
- #1 in resid hydroprocessing catalysts
- #1 in independent polyethylene catalysts
- #2 in hydrocracking catalysts
- #2 in polypropylene catalysts

Leading polypropylene process licensor

Materials Technologies
- #1 in specialty silica gel
- #1 in can sealants

Construction Products
- #1 in cement additives
- #2 in concrete admixtures

Built on talent, technology, and trust, Grace® high-performance specialty chemicals and materials improve the products and processes of our customer partners around the world. A Fortune 1000 company, Grace (NYSE: GRA) is a leading global supplier of catalysts, engineered and packaging materials, specialty construction chemicals, and building materials.

Grace Catalysts Technologies develops and manufactures catalysts and related products/technologies used in energy and refining, polyolefins and plastics, as well as petrochemical and other chemical manufacturing applications.
Building on Orpic ICV Achievements
Orpic, Grace, and Sohar University to Create State-of-the-Art Laboratory in Oman

Sohar, Sultanate of Oman—On September 3, at the Crowne Plaza Hotel Sohar, officials from Orpic, W. R. Grace & Co. (NYSE: GRA), and Sohar University signed a Memorandum of Understanding (MoU) marking the first phase in a three-party collaboration designed to create and sustain a state-of-the-art R&D facility at Sohar University at an estimated cost of over USD 3 million.

The R&D facility will be equipped with the latest catalyst testing technology, and will employ highly skilled Omani scientists. The advanced catalyst testing techniques utilized in the laboratory will result in a high-quality service with rapid response times for many of the technical requirements of the nearby Orpic refinery. Grace will provide technical support in the training of personnel and, as the world’s leading supplier of FCC catalysts, will assist in knowledge transfer to support Sohar University’s research programs.

The agreement is a result of discussions early in 2014 between Orpic and Grace regarding ways of creating In-Country Value, a key policy in Oman and one which Orpic wholeheartedly supports. Having access to such a modern laboratory will be of paramount significance to Omani students, and it will be just 20 km away from Orpic’s Sohar Refinery, reinforcing the support our refinery teams need to safely and profitably develop and operate their business. The initiative underscores Grace’s commitment to the petroleum refining industry in Oman and the Middle East and represents the first step toward long-term cooperation intended to spur more joint activities, technology development, training, and knowledge transfer to Oman.

Commenting at the ceremony, Abdullah Al-Farsi, Orpic’s Head of ICV, said, “This is a fine example of creating In-Country Value, a key policy in Oman and one which Orpic wholeheartedly supports. Having access to such a modern laboratory will be of paramount significance to Omani students, and it will be just 20 km away from Orpic’s Sohar Refinery, reinforcing the support our refinery teams need to safely and profitably operate our business. The initiative represents excellent technology and knowledge transfer opportunities to Omani scientists as well.”

“This cooperation will enhance Sohar University’s research and development capability by providing access to world-class expertise in the field of catalysis, as well as bringing skilled jobs to the country,” said Professor Ray Volker from Sohar University.

André Lanning, the General Manager for Grace in the region, said “We’re excited by this collaboration, which will serve the interests of all three partners. Grace will be able to improve service with a faster response to its customers in the region thanks to the close proximity of the laboratory to key customers including Orpic. We’re also pleased to further our cooperation with Oman’s oil refining industry as well as ties to the local community in Oman.”

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“Building on Orpic ICV Achievements Orpic, Grace, and Sohar University to Create State-of-the-Art Laboratory in Oman” - André Lanning, Grace

“Building on Orpic ICV Achievements Orpic, Grace, and Sohar University to Create State-of-the-Art Laboratory in Oman” - André Lanning, General Manager for Grace in the region.
Advances in Propylene Maximization from the FCC Unit

Udayshankar Singh, Senior R&D Engineer
Mike Ziebarth, Director Catalyst Research
Terry Roberie, Director Corporate Analytical
Wu-Cheng Cheng, Director Research & Development
Jürgen Knöll, Senior Analytical Chemist
Christoph Fougre, Manager Catalyst Evaluations
Stefan Brandt, Director Evaluations and Technical Support
Jeff Nicolich, Senior Analytical Chemist

Abstract: Using UCV to Understand ZSM-5 Deactivation and Stabilization
ZSM-5 containing additives are widely used to increase propylene and butylene yields, as well as gasoline octane, in fluid catalytic cracking (FCC) units. The stability of the ZSM-5 additives, both with respect to surface area retention and resistance to deactivation, under FCC operating conditions is key to maximizing their effectiveness and selectivity. This paper discusses the use of unit cell volume (UCV) to understand the fundamentals of ZSM-5 deactivation and stabilization. The fundamental understanding of ZSM-5 deactivation, obtained in these studies, has led to the development of improved stabilization technologies, which have been incorporated into new ZSM-5 additives with step-out activity and selectivity. Pilot plant results for the performance of the new additives are presented, along with case studies of how refiners can benefit from applying this technology to increase propylene yield from the FCC.

Introduction
Since its invention by Mobil Technologies in 1972, ZSM-5 has been used commercially in a wide variety of catalytic applications. The regular three dimension structure and the acidity of ZSM-5 can be utilized in various shape-selective reactions and acid-catalyzed reactions. ZSM-5 has been used for decades as a catalyst and catalyst support in chemical reactions including petrochemicals (for the isomerization of meta-xylene to para-xylene), synthetic rubbers, and many other products. FCC supplies production of gasoline, polymers, antifreezes, solvents, synthetic rubbers, and many other products. FCC supplies 30% of the propylene consumed by the petrochemical industry and the flexibility of the FCC mitigates the risk of large swings in propylene demand and price.

The demand for propylene is primarily driven by the rapid increase in polypropylene usage. In recent years, the global demand for propylene has expanded in line with the economic growth of developing countries such as China and India and in the Middle East. The demand for propylene is projected to increase by 5% per year. To keep up with the demand, a significant increase in propylene production from FCC units will be required. The use of ZSM-5 based additives in FCC is expected to increase.

The ZSM-5 based additive, OlefinsUltra® HZ, is Grace’s patented technology and is the market leading additive to maximize propylene production in the FCC unit. The composition provides a unique combination of stability, selectivity, and outstanding attrition resistance. Grace is committed to continue to provide step-out FCC technology to the market. This paper describes our understanding of factors which influence the hydrothermal stability of olefins additives. The concept of using unit cell volume (UCV), is introduced for the first time, in the characterization of fresh, laboratory deactivated, and commercially deactivated ZSM-5 based olefins additives. The paper also describes Grace’s methodology for separating commercially deactivated olefins additive from Ecat. Using the fundamental understanding gained from these studies, Grace introduces our new olefins additive, OlefinsUltra® MZ, which provides a step-out improvement in activity and stability over the current industry-leading OlefinsUltra® HZ.

ZSM-5 based catalysts are referred to as additives in FCC. During the cracking process, the catalyst is deactivated due to the hydrothermal conditions in the regenerator leading to deamination of the zeolites, in which the aluminum sites are removed from the framework. For Y-zeolite, which has a cubic structure, the reduction in Si/Al ratio has been correlated with its unit cell size (UCS). The UCS of Y-zeolite is measured by powder x-ray diffraction where the peak position of a certain reflection is measured accurately, from which the UCS can be calculated with a precision of 0.01 Å. To correct for any displacement errors silicon powder with known reflection positions is added to the sample as an internal standard. However for ZSM-5, which crystallizes in an orthorhombic system, where the three dimensions of a unit cell a, b, and c are not equal, the length of all three edges are necessary to describe the unit cell (Figure 1). Alternatively, the product of all three can be used to calculate the unit cell volume. As the orthorhombic lattice system produces a much more complex diffraction pattern, the UCV cannot be measured accurately enough by just measuring the peak positions for some reflections. In this case, the use of Rietveld refinement which evaluates the whole diffraction pattern, is required. This method uses a least squares minimization technique to refine a theoretical powder pattern until a best match with the observed one is achieved. The theoretical pattern contains all the information about the sample from which the UCV of the ZSM-5 can be calculated.

In this paper, we have made use of UCV to characterize the fresh, laboratory deactivated, and commercially deactivated ZSM-5 in the samples of olefins additives. The effect of phosphorous on the UCV of fresh and deactivated ZSM-5 was compared. The fundamental understanding learned on the stabilization of ZSM-5 in these studies was used to

Table 1: Correlation of silico-to-alumina ratio (SAR) in the ZSM-5 framework with UCV and the Brønsted acidity.

<table>
<thead>
<tr>
<th>ZSM-5 Samples</th>
<th>Bransted Acid Site ( \text{[micromoles / g]} )</th>
<th>UCV, ( \text{Å}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAR 27</td>
<td>1832</td>
<td>5393</td>
</tr>
<tr>
<td>SAR 55</td>
<td>922</td>
<td>5382</td>
</tr>
<tr>
<td>SAR 80</td>
<td>592</td>
<td>5372</td>
</tr>
<tr>
<td>SAR 250</td>
<td>168</td>
<td>5354</td>
</tr>
<tr>
<td>SAR 400</td>
<td>133</td>
<td>5349</td>
</tr>
<tr>
<td>SAR 1000</td>
<td>3</td>
<td>5343</td>
</tr>
</tbody>
</table>

ZSM-5 Cubic System
Ortorthobic System

Figure 1: Unit cell size versus unit cell volume.
design and develop Grace’s new highly active and stable olefins additive, OlefinsUltra® MZ.

Table 1 shows the aluminum content in the ZSM-5 framework, as reported by the silica-to-alumina ratio (SAR) and the UCV for the as-synthesized ZSM-5 samples. The Brønsted acidity, as measured by isopropyl amine titration, is superimposed. The data shows a nice correlation between the SAR, acidity, and the UCV. The UCV and the acidity decrease with the increase in the SAR ratio providing a nice calibration curve for the analysis of deactivated samples.

To understand the correlation better, a fresh sample of OlefinsUltra® was deactivated in the laboratory at 1500 °F for 24 h at atmospheric pressure and varying steam concentration of 0 to 100%. The relationship between total acid sites, as determined by ammonia temperature programmed desorption (TPD), and the UCV is shown in Figure 2. The data show that as the steam concentration increases the desalumination from the framework increases, which leads to a decrease in the UCV of the ZSM-5 crystal. The data also show that UCV correlates very well with the total acidity. The sample steamed at 1500 °F for 24 h in 100% steam shows UCV of 5363 Å², which is comparable to the UCV of 5362 Å², of a standard ZSM-5 produced with a SAR of ~80, shown in Table 1. This shows there is a significant loss in framework alumina, which causes the loss of acidity of ZSM-5 crystal.

The UCV measurements were used to compare OlefinsUltra® HZ, with Grace’s proprietary stabilization process, versus an unstabilized ZSM-5 additive. Both additives contained equal amounts of ZSM-5. The additives were deactivated using a standard steaming protocol of 1500 °F in 100% steam for various times between 0 h and 24 h. The deactivated samples were characterized by BET surface area, unit cell volume, and by propylene activity as determined by NH₃ TPD. The OlefinsUltra® sample was deactivated at 1500 °F for 24 h at various concentration of steam.

Use of UCV to Characterize Commercially Deactivated Olefins Additives

The concept of UCV was extended to characterize the commercially deactivated ZSM-5 based olefins additives towards stability and propylene activity. Samples of Ecat with two different ZSM-5 additives, from the same refinery, were collected. The ZSM-5 additives were isolated from the FCC base catalyst by a sink-float density separation technique as described by Boock et al.⁴ The density separation is performed by adding the catalyst sample to a mixture of tetrabromoethane (TBE) and tetrachloroethane (TCE), which have density values of 2.96 g/cm³ and 1.58 g/cm³, respectively. The skeletal density of the olefins additive is lower than that of the FCC base catalyst. The density of solvent is adjusted by controlling the ratio of TBE to TCE. Separation of the catalyst components occurs, as shown in Figure 4, when the density of the TBE/TCE mixture is in between the skeletal density values of the olefins additive and the base catalyst.

The sinks and float fractions isolated after density separation were characterized by XRD for sample purity and UCV, by N₂ sorption measurement for BET surface area, and by ICP for chemical analysis. The XRD pattern of Ecat, Figure 4, shows that it is a blend of FCC catalyst and olefins additive. The diffraction peaks due to Y-zeolite and ZSM-5 are apparent for Ecat. The float fraction, which is comprised mainly of olefins additive, shows the diffraction pattern of ZSM-5. The peaks due to Y-zeolite are negligible, indicating a clean separation of the additive from the Ecat. The sink fraction shows peaks only due to the Y-zeolite. The physical and chemical properties of OlefinsUltra® HZ versus competitor olefins additives, separated from the Ecat by density separation method, are shown in Table 2. The chemical analysis shows that the contamination of metals such as nickel, and iron, in both additives is similar. These metals accelerate the deactivation of catalysts under hydrothermal conditions in the FCC unit. The similar contaminant metals indicate that both additives were subjected to comparable deactivation conditions in the commercial unit. The data show the surface areas for these samples are identical but the measured
UVO of 5361 Å³ and 5353 Å³ for OlefinsUltra® HZ and the competitor additive, respectively, are considerably different. The OlefinsUltra® HZ maintains higher UVO under the commercial hydrothermal conditions of the FCC unit. This demonstrates that the OlefinsUltra® HZ, which is formulated by our proprietary stabilization technology, is more stable towards deactivation under commercial deactivation conditions.

The activity of olefins additives for propylene yield was determined by testing in an ACE unit. For ACE testing, the commercially deactivated olefins additives, which were isolated from the Ecat, were blended back into a steamed deactivated FCC base catalyst at 5wt% level. Performance for propylene activity in ACE was compared at constant conditions. The ACE data, at a constant conversion of 75wt%, are shown in Table 3. The high activity of OlefinsUltra® HZ is revealed by higher propylene yield when compared to the competitor’s olefins additive, shown in Figure 5. The increase in propylene yield is accompanied by a decrease in gasoline yield which is due to cracking of gasoline range olefins (Table 3). The data show that the OlefinsUltra® HZ deactivates 40% more incremental propylene compared against the competitor’s high ZSM-5 olefins additive. The higher activity of OlefinsUltra® HZ is a result of its superior hydrothermal stability and resistance to deactivation, as indicated by the UVO measurement. These results are consistent with the higher activity and stability observed in the field and support the market-leadership position of OlefinsUltra® HZ.

Grace’s Newest High-Performance Additive OlefinsUltra® MZ

To keep up with growing propylene demand refineries around the world use significant amounts of olefins additive to boost propylene production from the FCC units. The high usage of olefins additives in the FCC unit may lead to a loss in conversion, due to the dilution of the base catalyst. To minimize dilution effects max-propylene units require a highly active and propylene selective additive. The activity of olefins additive can be enhanced either by adding more ZSM-5 to the formulation or by improving the stability of the ZSM-5.

Exploiting our understanding of ZSM-5 stabilization, Grace has designed a new olefins additive, OlefinsUltra® MZ, which provides a step-up improvement in stability and propylene activity over the industry leading OlefinsUltra® HZ. OlefinsUltra® MZ combines the features of high ZSM-5 input with our proprietary stabilization technology without any compromise on attrition resistance. Table 4 shows OlefinsUltra® MZ has higher surface area, but has similar bulk density and attrition properties to that of OlefinsUltra® HZ.

Most laboratory deactivation protocols are designed to simulate the field deactivation of base FCC catalysts, and may not properly simulate the field deactivation of olefins additives. It is important that we compare the properties and performance of olefins additives using a deactivation protocol which will mimic the deactivation of commercial units. To identify the appropriate deactivation conditions, a sample of OlefinsUltra® was steamed at 1500°F in 100% steam for 5 h, 10 h, and 25 h. The properties and propylene activity of the steamed samples were compared against a commercially deactivated sample of OlefinsUltra®, which was separated from Ecat by density separation.

The data reveals that the propylene activity of laboratory deactivated sample overlaps with the commercially deactivated sample after 20 h of hydrothermal steaming, shown in Figure 6. Therefore, to match the performance of a commercially deactivated sample the olefins additive in the laboratory has to be steamed for a minimum of 20 h in 100% steam at 1500°F. These conditions are severe, but necessary for the development of additives in the laboratory to simulate the conditions the additives will face in commercial units.

The properties and performance of OlefinsUltra® MZ were compared against OlefinsUltra® HZ after 4 h, 6 h, and 24 h of hydrothermal deactivation in 100% steam at 1500°F. The data are summarized in Table 4, which shows the OlefinsUltra® MZ maintains its high surface area and UVO after deactivation. Both samples show an initial increase in surface area after deactivation, likely due to the unblocking of pores of the ZSM-5 crystals and the matrix during steaming. The additives were evaluated for propylene activity in ACE at standard FCC conditions, after blending with an Ecat at 5wt% and 25wt%. The high blending rate was used to evaluate its application for the max-propylene units. The ACE data for 5wt% olefins additive, at constant conversion, is shown in Table 5. The data reveal that the OlefinsUltra® MZ, after severe deactivation, makes higher propylene compared to the OlefinsUltra® HZ. A corresponding decrease in gasoline is observed, which is due to the cracking of gasoline range olefins to light olefins. The OlefinsUltra® MZ shows a 20% increase in delta propylene yield over the current best technology in the market, OlefinsUltra® HZ, as shown in Figure 7. The ACE data for the higher blend level, shows a similar propylene yield advantage for OlefinsUltra® MZ (Figure 7). The data demonstrate that the OlefinsUltra® MZ, with its high activity and stability, can be used in any FCC unit for a wide range of blending levels.

Table 3: ACE interpolated yields at constant conversion of 75wt%. Olefins additives were blended at 5wt% with the base FCC catalyst and were tested in ACE at constant conditions.

<table>
<thead>
<tr>
<th>ACE Yields</th>
<th>Base</th>
<th>5wt% Competitor</th>
<th>5wt% OlefinsUltra® HZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal-to-Oil Ratio</td>
<td>5.8</td>
<td>6.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Hydrogen, wt%</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethylene, wt%</td>
<td>0.6</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Total Dry Gas, wt%</td>
<td>1.7</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Total C3’s, wt%</td>
<td>6.3</td>
<td>9.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Propylene, wt%</td>
<td>5.5</td>
<td>8.2</td>
<td>9.5</td>
</tr>
<tr>
<td>Delta Propylene</td>
<td>2.7</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Total C4’s, wt%</td>
<td>12.5</td>
<td>14.8</td>
<td>15.4</td>
</tr>
<tr>
<td>Total C5+ Gasoline, wt%</td>
<td>51.4</td>
<td>46.5</td>
<td>44.2</td>
</tr>
<tr>
<td>LCO, wt%</td>
<td>19.4</td>
<td>19.2</td>
<td>19.2</td>
</tr>
<tr>
<td>Cokes, wt%</td>
<td>5.6</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>3.0</td>
<td>2.8</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 4: Physical and chemical properties of OlefinsUltra® MZ compared to that of OlefinsUltra® HZ

<table>
<thead>
<tr>
<th>Sample</th>
<th>OlefinsUltra® HZ</th>
<th>OlefinsUltra® MZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABD, gm/cm³</td>
<td>0.72</td>
<td>0.75</td>
</tr>
<tr>
<td>DI, &lt;</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>APS, microns</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>Surface Area, m²/g</td>
<td>156</td>
<td>184</td>
</tr>
<tr>
<td>UCV, Å³</td>
<td>5363</td>
<td>5360</td>
</tr>
<tr>
<td>Deactivation: 4 h at 1500°F in 100% Steam</td>
<td>Surface Area, m²/g</td>
<td>181</td>
</tr>
<tr>
<td>UCV, Å³</td>
<td>5360</td>
<td>5360</td>
</tr>
<tr>
<td>Deactivation: 8 h at 1500°F in 100% Steam</td>
<td>Surface Area, m²/g</td>
<td>172</td>
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<tr>
<td>UCV, Å³</td>
<td>5360</td>
<td>5360</td>
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<tr>
<td>Deactivation: 24 h at 1500°F in 100% Steam</td>
<td>Surface Area, m²/g</td>
<td>161</td>
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<tr>
<td>UCV, Å³</td>
<td>5360</td>
<td>5360</td>
</tr>
</tbody>
</table>

Figure 5: Propylene yield for commercially deactivated olefins additives isolated by density separation method. The separated additives were blended back at 5wt% with base catalyst for ACE testing.

Figure 6: Propylene activity of laboratory deactivated OlefinsUltra® compared against commercially deactivated OlefinsUltra® isolated by density separation method. The laboratory sample was deactivated at 1500°F in 100% steam for various times. Additives were blended at 2.5 wt% level and tested in ACE at constant conditions.
Grace proprietary stabilization technology delivers improved propylene yields and is the clear choice for max-propylene units.

Conclusion: A Valid Technique
In this paper we have shown the significance of unit cell volume for the characterization of ZSM-5 in the additive formulation. We have shown that the technique is valid for fresh, laboratory deactivated, and commercially deactivated ZSM-5 additives, where other catalyst properties such as surface area can be misleading. The fundamental understanding of the deactivation of ZSM-5 gained in these studies has lead to the development of improved stabilization technologies, which have been incorporated into our new ZSM-5 additive. The introduction of OlefinsUltra® MZ raises the bar on olefins additive performance, providing step-out catalyst stability and propylene activity, for the next generation max-propylene catalytic solution.

Reference:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>OlefinsUltra® HZ</th>
<th>OlefinsUltra® MZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-Oil Ratio</td>
<td>6.8</td>
<td>7.0</td>
</tr>
<tr>
<td>Hydrogen, w%</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Total C1's &amp; C2's, w%</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Ethylene, w%</td>
<td>0.81</td>
<td>1.0</td>
</tr>
<tr>
<td>Total C3's, w%</td>
<td>10.2</td>
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</tr>
<tr>
<td>Propylene, w%</td>
<td>9.1</td>
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<tr>
<td>Total C4's, w%</td>
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<td>Isobutane, w%</td>
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<td>Isobutene, w%</td>
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<td>MON</td>
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<td>LCO, wt%</td>
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<td>Bottoms, wt%</td>
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<td>6.7</td>
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<tr>
<td>Coke, w%</td>
<td>3.0</td>
<td>3.0</td>
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Table 5: ACE interpolated yields at constant conversion of 76wt%.

Olefins additives were blended at 5wt% with the base FCC catalyst and were tested in ACE at constant conditions.

Addressing Polypropylene Demand with Efficient Solutions

Ella Chen (Grace)

Polypropylene is a colorfast, heat- and corrosion-resistant plastic, has experienced steady growth in use since its discovery in 1954. From food packaging to medical equipment to automotive parts and more, it has become a preferred material for a variety of applications due to its high versatility. Its low density, recyclability, and higher heat distortion temperatures compared to other plastics, along with processing ease in conventional systems, have made polypropylene the plastic of choice among manufacturers and consumers.

“The UNIPOL® brand and the capabilities it represents are highly respected in the marketplace. Grace is committed to strengthening that position with its capabilities and full portfolio of products and services to our customers and the broader global marketplace.”

Polypropylene Market Growth

The steady growth the polypropylene market has seen is expected to continue with Chemical Market Resources reporting global capacity growth of 6% annually through 2017. Ninety percent of announced polypropylene capacity will be concentrated in Asia, Middle East, and Eastern Europe, with China encompassing nearly 40% of new supply. China, which is becoming less reliant on imported raw materials, is experiencing a growth rate closer to 11% per year, making it a high-growth market for such material. For China the increase in locally manufactured polypropylene will cut down on import costs and provide easy access to polypropylene resins.

Grace is helping to address the growth in demand through expansion of its capabilities and catalyst portfolio. Last year Grace completed the acquisition of the polypropylene licensing and catalysts business of The Dow Chemical Company (DOW). The acquisition includes UNIPOL® polypropylene process technology and makes Grace the second largest polypropylene licensor in the world based on installed capacity, advancing Grace’s leadership in the broader polyolefin sector.

coil-based propylene as the feedstock. That success has proven UNIPOL® PP process technology as the natural fit for the emerging coal-to-polyolefin industry, particularly for the coal-rich Chinese market.

The UNIPOL® PP process technology is simple to build, operate and maintain. It offers manufacturers a one-stop shop for polypropylene with the ability to streamlin the process. UNIPOL® PP process technology is an all gas-phase technology based on a fluidized bed reactor system. With single line capacities up to 650 KTA it is the largest amongst all the polypropylene manufacturing technologies. UNIPOL® PP process technology provides the highest operating on-stream time in the industry while also providing the ability to produce high-quality polypropylene. Many licensees have achieved the benefits of operating significantly above their nameplate capacities with UNIPOL® technology. The core UNIPOL® PP process facility (purification, reaction, purging, vent recovery, additive addition, and pelleting) has the smallest footprint in the industry. Additionally, it is the least complex of all polypropylene process technologies requiring the fewest number of reactors and major pieces of rotating equipment.

A State-of-the-Art Process

The UNIPOL® PP process technology, which includes the UNIPOL UNIPAC® process control software, is a recognized leader in the industry. Globally there are 51 UNIPOL® PP process licensees with 16 plants in the design and construction phase. In China there are seven plants successfully making polypropylene with eight startups over the next three years, four scheduled for 2015, one for 2016, and three for 2017. The successful UNIPOL® start-ups include the first ever Chinese polypropylene plant using UNIPOL® technology in the marketplace. Grace is committed to strengthening that position with its capabilities and full portfolio of products and services to our customers and the broader global marketplace.”
Catalyst Technology Innovation
Grace is the only polypropylene licensor to make and sell both proprietary catalysts and donors that are designed specifically for gas phase processes. UNIPOL® PP process licensees benefit from Grace’s sustained investment in R&D resulting in access to a continuous innovation pipeline that puts them ahead of the competition. With growing market demand in China, along with growing demand for higher performance grade polypropylene, Chinese customers have the necessary tools to address current consumer demand without the use of expansive imported resins. UNIPOL® PP process technology, combined with CONSISTA® or SHAC® catalyst systems, can produce differentiated, high-quality, market-leading products and has the flexibility to produce high quality basic resins.

The CONSISTA® and SHAC® catalysts and donor systems allow one production of a wide variety of high value products in a simple, easy to operate process. Particularly, CONSISTA® polypropylene catalyst is a 6th generation, non-phthalate based technology that offers the ability to produce higher performance resins with broader applicability at a competitive cost position. This catalyst technology offers excellent product performance via resins that are cleaner. It allows the fabricators to produce lighter and clearer articles at a faster speed allowing for potential light weighting without loss of stiffness, increased cycle time efficiencies, enhanced environmental advantages, and preferred optics.

CONSISTA® catalyst with CONSISTA® donors provides the benefits of excellent reactor operability and on-stream time. This is a “drop-in” technology with advanced product benefits that can be used broadly in commodity grade production. The UNIPOL® PP process technology tailored SHAC® catalysts systems, 6th generation non-phthalate CONSISTA® catalysts and advanced donor systems all enhance Grace’s polyolefin catalysts portfolio. These products complement Grace’s polypropylene catalyst families of POLYTRAK®, and HYAMPP® and its polyethylene catalyst systems such as Cr-based catalysts (MAGNAPORE®), Ziegler-Natta catalysts, and Single Site Catalysts.

Grace’s investment in R&D offers UNIPOL® PP process technology customers access to continuous innovations in catalyst and donor technology and, as a result, access to product improvements without requiring any change to the basic process. This drop-in technology development allows producers to keep their process and product technology up to date without requiring any changes to the process. UNIPOL® PP process technology customers receive best-in-class technology transfer for smooth design, construction, and startup and the fastest time from startup to production of prime grade polypropylene products.
Question: What FCC gasoline sulfur reduction technologies are being used to control sulfur during cat feed hydrotreater or gasoline product hydrotreater outages? Will these products be a viable option for Tier 3 gasoline sulfur specs?

Stuart Kipnis (Grace)

Refiners have created operating flexibility during hydrotreater outages by utilizing Grace’s clean fuels GSR® additive technology, proper management of FCC feed hydrotreater outages becomes increasingly important as more and more refiners rely on hydrotreating to meet their per gallon gasoline sulfur limits. Running at higher severity increases the frequency of turnaround. Conventional methods of ensuring that the gasoline pool stays below the sulfur limit during the hydrotreater turnaround are purchasing low sulfur feed or reducing FCC throughput. Either approach can significantly reduce refinery profitability. An alternative is to use one of Grace’s gasoline sulfur reducing technologies during the outage to provide operational flexibility while maintaining sulfur compliance and profitability.

One such example of a refiner that used Grace GSR® technologies is to use one of Grace’s gasoline sulfur reducing technologies during the outage to provide operational flexibility while maintaining sulfur compliance. Savings during the hydrotreater outage. The results were so encouraging that the customer elected to continue using Grace GSR® technology, switching to a SuRCA® catalyst and operating with post-outage feed sulfur 10-15% higher than the typical operation. This change to their operation grew annual profits by approximately $8 million.

Continued operation during a hydrotreater outage is just one way that refiners can benefit from application of Grace’s patented GSR® technologies. In-unit reduction of FCC gasoline sulfur creates a variety of opportunities and options for refiners to drive profitability while meeting new Tier 3 gasoline requirements.

Grace’s GSR® clean fuels solutions create economic advantages around:
- Feedstock blending
- Asset optimization to:
  - Preserve octane
  - Maximize throughput
  - Extend pre-treatment and/or post-treatment hydrotreater life
- Gasoline stream blending options
- Generation of gasoline sulfur ABT credits to defer capital investment

Tier 3 regulations require the reduction of average gasoline pool sulfur level to ≤10 ppm with an 80 ppm cap by January 2017, compared to the current limit of ≤30 ppm with an 80 ppm cap. Grace has substantial experience in similarly demanding environments like Japan. In the mid 2000’s, Japan committed to lower gasoline sulfur levels. As early adopters of more stringent gasoline quality regulations, Japanese refiners faced similar challenges that US refiners face today in meeting Tier 3. Since 2006, these refiners have successfully utilized Grace GSR® products to maintain compliance, observing 35%-40% reduction in the gasoline sulfur / feed sulfur ratios allowing them to meet the 10 ppm gasoline specifications.2

An example of a Japanese refiner meeting 10 ppm gasoline sulfur spec without increasing gasoline post-treater severity can be seen in Figure 2. In this case, as much as 35% gasoline sulfur reduction was achieved with SuRCA® catalyst.

Another example [Figure 3] shows a Japanese refiner that was able to maintain compliance with the 10 ppm gasoline sulfur spec while maintaining flexibility to either blend high sulfur coker gasoline into the gasoline pool or extend the VGO hydrotreater catalyst life. Again, SuRCA® catalyst technology was used and the refiner observed approximately 40% reduction in gasoline sulfur.

Grace GSR® technologies: D-PnSM® and GSR® 5 FCC additives and SuRCA® FCC catalysts, are the result of almost two decades of innovation. Grace GSR® technologies have been used in more than 100 FCC applications worldwide delivering 20%-40% sulfur reduction in FCC naphtha in both full and partial burn operations. The GSR® additive technologies are used at a 10%-25% loading in inventory, whereas the catalytic solutions are a customized 100% drop-in replacement for your base catalyst. GSR® products can be used for short or long term applications; the longest continuous application is now 12 years.

Grace’s multiple product offerings allow for a truly custom GSR® clean fuels solution for your refinery’s Tier 3 compliance plan. Ask your Grace representative which product is best for your operation.

Reference:
1. L. Blanchard, C. Borchert, M. Pu, NPRA Annual Meeting, AM-07-06, 2007
The increase in light tight oil as a percentage of North American crude slate has resulted in lower FCC feed production, and consequently a reduced FCC feed rate at several refineries. To address these issues, what strategies have been implemented operationally and catalytically? Are refiners looking at sending new streams to the FCC or increasing the proportion of existing streams such as resid? If so, what steps do refiners take to evaluate these potential new feedstocks and what steps do refineries take to minimize uncertainty and reduce risk?

Kenneth Bryden (Grace)

The increase in the quantity of tight oil as a percentage of the North American crude slate has resulted in numerous changes at refineries. Tight oils, like other light sweet crudes, have a much higher ratio of 650°F- to 650°F+ material when compared to conventional crudes. Bakken tight oil has a nearly 2:1 ratio, while typical crudes such as Arabian Light, have ratios near 1:1. A refinery running high percentages of tight oil could become overloaded with light cuts, including reformer feed and isomerization feed, while at the same time short on feed for the fluid catalytic cracking unit (FCCU) and the coker. Some refiners have balanced the use of larger amounts of tight oil with increased use of heavier crudes such as Canadian syncrude. Other refiners have charged a portion of whole tight oil to the FCC to keep the FCC full.

As refineries consider new feedstocks, testing is a valuable tool to reduce risk. Testing provides understanding of feed properties and potential yield changes. Below are examples of potential tests to use when evaluating a new feedstock.

- Testing of feed metals levels is especially important since tight oil derived feeds often contain varying levels of conventional contaminants such as sodium, nickel and vanadium and unconventional contaminants such as iron and calcium. Understanding the expected metals levels of a new feed allows refiners to work with their catalyst vendor to choose catalyst options that mitigate the challenges of these metals.
- Feed properties such as API, concarbon and hydrocarbon types can provide insight into the expected crackability of a feed, but may not tell the whole story. A fuller understanding of how a feed will crack in a unit can be obtained through testing. Either bench-scale testing (ACE or MAT) or pilot-scale testing (such as Grace’s DCR™ circulating pilot plant) can be done. MAT and ACE testing have the advantages that they are easy to set up and require small amounts of material. However, these units cannot provide the detailed product analysis or feedback on extended operation that pilot scale units can. Larger scale test equipment such as a pilot unit can provide sufficient liquid product for distillation and detailed analysis (such as API gravity and aniline point of LCO produced, viscosity of bottoms, octane engine testing of gasoline, etc.) and can provide information on continuous operation. Additionally, compared to bench scale units, the DCR™
(Tight Oil continued)

pilot plant has the advantage that it mimics all the processes present in commercial operation and it can operate at the same hydrocarbon partial pressure as a full-scale commercial unit.

Grace’s technical service and R&D teams help refiners assess potential challenges from feedstock shifts before they occur via feed characterization, feed component modeling, and pilot plant studies. Understanding feed impacts earlier provides an opportunity to optimize the operating parameters and catalyst management strategies, enabling a more stable and profitable operation.

**Question:** What are the best practices in the industry for profitable LCO maximization? Please elaborate on (a) FCC catalyst/additive technologies, (b) cetane maximization, (c) process design and operations strategies and (d) any impact on naphtha octane and how to mitigate it.

- Ann Benoit (Grace)

Maximizing light cycle oil (LCO) is largely a slurry management process. To increase LCO, refiners can simply change operating conditions and lower catalyst activity to shift operations into a lower conversion regime. The negative impact of shifting to a lower conversion regime is that this shift will typically decrease volume swell and also increase bottoms, unfavorably impacting profitability. The true challenge is to maximize LCO without producing incremental bottoms while maintaining volume expansion.

In general, refiners tend to focus on the following strategies to maximize LCO yield:

1. Distillation changes (reduce gasoline end point and increase LCO end point)
2. Feedstock
   - Removal of diesel range material from the FCC feedstock
3. Recycle Streams
   - Heavy cycle oil (HCO) or bottoms
4. Operating Conditions
   - Lower reactor temperature
   - Higher feed temperature
   - Lower equilibrium catalyst activity
5. Catalyst Optimization
   - Increased bottoms conversion
   - Lower zeolite-to-matrix surface area
   - Maintenance of C3+ liquid yield and gasoline octane

A quick, simple and effective way to increase LCO is to make distillation adjustments such as lower gasoline endpoint and/or increased LCO endpoint. Flash point specification and main fractionators salting often will determine how low a refiner can reduce the LCO initial boiling point (reduce gasoline end point). Maximum main fractionator bottoms temperature, slurry exchanger fouling and diesel hydrotreating constraints will often determine how much the LCO endpoint can be increased.

Regarding feedstock, it is recommended that diesel range material be removed from the FCC feedstock. This material is typically higher quality diesel for the overall refinery diesel pool. Recycle streams can be employed to fully maximize LCO at reduced conversion. The quality of the recycle stream can make a difference in the products being produced. The effects of different recycle streams are discussed in detail in the AFPM paper “Strategies for Maximizing FCC Light Cycle Oil” (Hunt, et al, AM-09-71). The 650°F – 750°F recycle stream produced the most LCO and gasoline at the lowest coke for a given conversion. However, this stream is not produced in sufficient quantities to fully maximize LCO. The 650°F and 750°F streams have high Conradson carbon levels (consistent with higher quantities of teta-aromatics and heavier compounds) which limit the yield of LCO when these streams are recycled to the FCC. The 650°F to 800°F or 650°F to 850°F recycle streams produced the highest LCO when recycled against a coke burn and bottoms constraint.

Adjustments to operating conditions such as reactor temperature, preheat, and/or catalyst activity to lower conversion and increase LCO can be made, but this may come with a price. By reducing conversion through operating conditions, LCO yield and potentially cetane will increase, but so will slurry. The primary challenge in the FCC unit is to increase LCO, while minimizing incremental slurry yield and maintaining volume swell. Gasoline octane may also be a concern due to lower reactor temperature and lower conversion. This is why a catalyst reformulation strategy is needed to address the incremental slurry, lower volume swell, and lower gasoline octane when operating conditions are adjusted to maximize LCO.

Application of the correct catalyst technology is critical for high LCO yield and minimal bottoms and coke yield. Keep in mind that a balanced approach is required to achieve maximum bottoms upgrading to LCO and other valuable products. An LCO maximization catalyst is typically an improved bottoms cracking catalyst with a low zeolite-to-matrix ratio. Grace typically considers our MIDAS® technology in LCO maximization applications due to premium high matrix bottoms cracking ability. Due to the economic penalty with lower volume swell, ZSM-5 additives such as OlefinsMax® or OlefinsUltra® should be considered to maintain or improve volume swell and/or gasoline octane while operating at a lower conversion. If butylene has a greater value than propylene, a reformulation to the Grace’s AGHIEVE® 400 FCC catalyst could be optimal. AGHIEVE® 400 catalyst features a moderate Z/M ratio and dual-zeolite functionality, delivering increased gasoline octane and butylene yield at minimum bottoms.

There are several avenues that can be taken to increase LCO yield on the FCC, but overall refinery economics will dictate which move or combination of moves proves the most beneficial to the refiner. Catalyst reformulation strategy should always be considered in LCO maximization cases since this can address the incremental slurry and lower volume swell in a lower conversion regime.

Question: What are the characteristics of FCC catalyst to minimize particulate emissions at the stack?

John Aikman (Grace)

While there are several operational and mechanical factors that can influence a unit’s particulate emissions, the question asks specifically about the FCC catalyst; as such, the following discussion will address characteristics of fresh catalyst only.

There are four basic characteristics of FCC catalyst that can have direct effects on particulate emissions. These same characteristics will also affect particulate losses to the fractionator and slurry product.

The first characteristic is simply the amount of fines content coming into the unit with the fresh catalyst due to the manufacturing process. Figure 1 is an example of a typical fresh catalyst particle size distribution, with a theoretical depiction of a cyclone’s ability to retain fresh catalyst particles. $D_{p_{10}}$ is the smallest particle diameter which can reliably be collected by a cyclone and is used to model cyclone performance. Particles below this size will be lost by the cyclone.

A review of the Grace Ecat database showed that none of the FCCU’s in North America can retain any 0-20 μ range particles. In addition, they only retain an average of approximately 4.0 wt.% in the 0-40 μ range. Fresh catalyst typically ranges anywhere from 9% to 16% of 0-40 μ depending on the supplier and manufacturing process. Some units require higher amounts of 0-40 μ range particles to help with circulation.

The next characteristic of fresh catalyst that must be considered is the inherent attrition resistance of the fresh catalyst. Industry measures the attrition resistance via a variety of tests, with the primary goal of providing a relative indication of catalyst attrition resistance. Grace utilizes similar tests, but with a primary goal of providing a relative indication of catalyst attrition resistance.
the DI test or Davison Index. On the DI scale, a lower number is less likely to cause attrition and generate microfines. It is usually not valid to compare attrition resistance results obtained from different laboratories. Additionally, it is important to note that the energy applied to a catalyst sample during attrition testing is much more severe than commercial conditions.

As discussed above, the majority of the microfines created in the FCCU will leave the unit through either the reactor or regenerator cyclones, with the latter potentially contributing to increased particulate emissions at the stack.

The attrition resistance of the catalyst is a function of the manufacturing process and the binder material utilized during the manufacturing process. In order to demonstrate this visually, Figure 3 presents SEM’s (scanning electron microscopy) of “bad” and “good” fresh catalyst morphology for a side by side comparison.

In conclusion, there are several characteristics of fresh catalyst that can be controlled to reduce particle losses and thereby reduce flue gas emissions. Specifically, to lower emissions the fresh FCC catalyst should possess the following characteristics: a particle size distribution with an optimal range of 0-40 µ particles, higher catalyst particle density, lower DI, and superior morphology. Grace’s alumina-sol technology provides superior binding to the catalyst particle leading to best-in-industry attrition resistance. The versatility and performance of alumina-sol catalysts coupled with Grace’s manufacturing capability, have resulted in wide-market acceptance and as a result, Grace is the preferred FCC technology for loss sensitive units around the world.

Question: What factors influence butylene selectivity in the FCC LPG?

What is the relative role of feedstocks, catalysts, additives, and operating conditions?

- Kenneth Bryden (Grace)

Fundamentals:

A number of factors influence butylene selectivity in the FCC LPG stream. Figure 1 summarizes the fundamentals of butylene selectivity and maximization. The cracking pathways involved can be thought of as four stages. In Figure 1, the desired pathways for maximizing butylenes are in green and the undesired pathways are in red. The first stage is cracking of the feed to naphtha range olefins. These cracking reactions can occur on zeolite or matrix. In the second stage, these naphtha olefins can react to naphtha paraffins by hydrogen transfer (an undesired pathway), or crack to C3 and C4 olefins. The cracking of gas range olefins to C3 and C4 olefins is much faster on ZSM-5 zeolite than Y-zeolite. Catalyst factors that influence the selectivity of butylene versus propylene will be discussed later in this answer. The C3 and C4 olefins that are produced in Stage 3 can further react by hydrogen transfer to form propane, iso-butane and butane, which are undesired when maximizing butylene. These reactions occur much faster on zeolite than on matrix. Based on this fundamental reaction scheme, butylenes can be maximized by decreasing the hydrogen transfer activity and by minimizing the cracking of naphtha olefins to propylene. The effects of individual factors on butylene selectivity are discussed in detail below.

Feedstock Effects:

The chemical nature of the starting feedstock will affect the products that can be produced from it. As a feed becomes more paraffinic, butylene production increases. As a feed becomes more aromatic, olefinic, the olefinicity of the FCC stream will drop. \(^1\) As a feedstock becomes more naphthenic, LPG olefin production drops. This is because naphthenes are good hydrogen donors and react with gasoline range olefins to make aromatics and gasoline range paraffins. \(^2\) Since gasoline range olefins are the precursors to LPG olefins, this depletes the pool of available material to make LPG olefins and reduces LPG olefinicity.

Operating Condition Effects:

Typically total C4 production depends on conversion, regardless if the conversion is achieved by reactor temperature or catalyst-to-oil ratio. \(^3\) However, the ratio of isobutane to butylene...
is strongly influenced by reactor temperature. Since hydrogen transfer has higher activation energy than cracking, the rate of cracking increases faster with temperature than the rate of hydrogen transfer. Thus, as reactor temperature increases, the ratio of iC4/C4 is lowered. As a rule of thumb, the ratio of iC4/C4 drops by 0.025 per 10°F increase in reactor temperature.

Changing reactor pressure will also affect the olefinicity of the C4 stream. Since hydrogen transfer is a bi-molecular reaction, decreasing reactor pressure decreases hydrogen transfer and lowers olefinicity of the LPG stream. Data quantifying the effect of reactor pressure on butylene selectivity can be found in Reference 5.

Increased carbon on regenerated catalyst (CRC) reduces the rate of hydrogen transfer reactions and results in a more olefinic LPG stream. Also, increased CRC will usually lower overall conversion.

**Catalyst Effects**

Base catalyst affects butylene selectivity through both the rate of hydrogen transfer and through the amount of naphtha range olefins produced. Since increased hydrogen transfer reduces LPG olefinicity, butylene olefinicity drops as the amount of rare earth on zeolite increases, as measured by unit cell size (UCS). Higher matrix activity increases C4 olefinicity. Lowering the zeolite/matrix ratio of the base catalyst increases gasoline range olefins and thus the amount of butylene produced from these precursors.

ZSM-5 based additives have a significant effect on the olefinicity of the LPG stream. ZSM-5 cracks the C6+ gasoline range olefins to propylene and butylene. Adding more ZSM-5 additive will deplete the gasoline range olefins and produce both more propylene and butylene. The increased propylene yield with ZSM-5 additives is not always desirable. A better solution is to boost zeolite isomerization activity within the catalyst to selectively increase the yield of FCC butylene.

Grace’s ACHIEVE® 400 catalyst is formulated with multiple zeolites with tailored acidity, to deliver an optimum level of butylene to keep the alkylation unit full and maintain refinery pool octane. With traditional ZSM-5 technology, cracking of gasoline olefins continues past C7 into the C6+ gasoline range olefins and generates a disproportionate amount of propylene relative to butylenes as shown in Figure 2. The newly developed dual-zeolite technology in ACHIEVE® 400 catalyst works synergistically with Grace’s high diffusivity matrix, to selectively enhance olefinicity, preferentially cracking gasoline olefins at C7 and above into butylene. The result is a higher ratio of C4 to C3 olefin yield than separate light olefins additives.

Figure 3 illustrates the butylene selectivity improvement of ACHIEVE® 400 catalyst compared to a system using conventional ZSM-5 based additive.

**Figure 2:** Selectivity from cracking gasoline range olefins over ZSM-5 additive and ACHIEVE® 400 Catalyst

**Figure 3:** Butylene selectivity improvement of ACHIEVE® 400 catalyst compared to a system using conventional ZSM-5 based additive.

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**Reference:**
**Question:** What is a minimum cloud point improvement that makes economical sense to apply catalytic dewaxing vs. traditional (i.e. additives and kero blending) Cold Flow improvement methods?

The target market for these products requires much more than several degrees decrease in cloud point below the value of the feed, which is generally beyond that observed by hydrotreating alone. The utility of catalytic dewaxing needs to be weighed against the costs/benefits of other cold flow improvement methods. The ability to improve the cold flow properties of the diesel in the hydrotreater using a dewaxing technology can have significant economic advantages that other options do not provide especially if a high degree of cold flow improvement is desired. Understanding the cold flow requirements is necessary to create an individually tailored process and avoid the pitfalls associated with inappropriate quantities of hydrodewaxing(HDW) catalyst, such as yield losses and not having the flexibility to meet market demands.

Understanding the Trade-offs as Dewax Catalyst is Changed

The typical process of dewaxing utilizes a ZSM-5 type catalyst. The structure of ZSM-5 is such that only straight chained hydrocarbon molecules (normal paraffins or n-paraffins) fit inside the cage structure and are cracked into smaller, lighter molecules. These molecules have significantly lower cloud and pour point characteristics. One of the keys to successfully combining a dewaxing catalyst with an hydrodesulfurization(HDS) catalyst system is an understanding of the tradeoffs between dewaxing activity and HDS activity as the amount of dewax catalyst is changed. Similar to a hydrocracking reactor, as the temperatures are increased over the bed of HDW catalyst, the ability to convert the n-paraffins increases. The extent of cloud point reduction at a given temperature depends on the LHSV over the dewax bed as well as the hydrogen partial pressure of the unit. Once the temperature is high enough to begin dewaxing, the kinetic response for converting the n-paraffins is linear against the costs/benefits of other cold flow improvement methods. The HDW function is to break the n-paraffins into smaller molecules in order create less waxy molecules in the finished diesel product. This chain breaking reaction has the potential disadvantage that it can convert diesel boiling range material into naphtha and lighter materials. These materials, if the
Question: How are refiners planning to meet Tier 3 gasoline specifications? Please share strategies for post-treat and pre-treat options, feedstock selection and catalyst technologies.

Tier 3 gasoline regulations require that all gasoline contain ≤10 wppm sulfur. This is a decrease from the current Tier 2 regulations of ≤30 wppm sulfur. This change in product sulfur can have a dramatic impact on refiners that have a significant portion of their gasoline pool generated from the FCC. In order to meet this regulation, there are only two methodologies to reduce the gasoline sulfur pool. Both involve some level of hydrotreating, either before or after the FCC unit. The process of hydrotreating after the FCC unit can have a dramatic effect on gasoline octane levels due to the additional diesel saturation that occurs when reducing the product sulfur sulfur.

Hydrotreating Before or After the FCC Unit

For those refiners that utilize a hydrotreater in front of their FCC unit, changes to that operation need to be considered in order to meet the desired product targets. To address these needs, ART utilizes the ApART® catalyst system for FCC pretreatment. This technology is designed to provide significant increases in HDS conversion while significantly upgrading FCC feedstock quality and increasing yields. In essence, an ApART® catalyst system is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each catalyst can be optimized to meet individual refiner’s goals and constraints. ART continues to develop a better understanding of the reactions and kinetics involved in FCC pretreating, and through its relationship with Grace, a detailed understanding of the effects of hydrotreating on FCC unit performance.

It is clear that FCC pretreating plays an important role in reducing the sulfur content of FCC products. ART has completed many studies analyzing the effects of hydrotreating on FCC performance and the quality of the FCC products. The data demonstrate that reducing the sulfur in FCC gasoline and LCO simply requires a reduction in the sulfur of the FCC feed by increasing the severity of the pretreater. Figure 1 shows the relationship between FCC feed sulfur and the resulting sulfur of the FCC gasoline.

This data is generated using a variety of FCC feeds that had been hydrotreated over several types of catalysts and catalyst systems. There is a positive correlation between FCC feed sulfur and the corresponding FCC gasoline sulfur. In this case, the sulfur content in the FCC gasoline is roughly 100 times less than the sulfur in the feed to the FCC. Increasing the severity of the pretreater operation to reduce product sulfur will tend to move the catalyst towards more of a PNA mode of operation. This mode, while beneficial to the FCC in many ways, can impact the cycle length due to increased temperatures.

Both the hydrotreating catalyst system and the operating strategy for the pretreater are critical to providing the highest quality feed for the FCC. Optimizing the hydrotreater to remove nitrogen and PNAs improves FCC product value when targeting gasoline production. But this needs to be balanced against the costs of higher hydrogen consumption and shorter cycle length that result from this mode of operation. Use of tailored ApART® catalyst systems with 486DX® and 586DX® can optimize the FCC in order to produce high quality feeds to the FCC as well as lower sulfur products resulting in less impact on downstream hydrotreating. A result is less impact on downstream hydrotreating. This tailoring can also be beneficial if the lower sulfur and higher gravity FCC products can be blended directly without hydrotreating, minimizing potential octane loss.
Question: Silicon uptake on hydrotreating catalysts is an increasing problem. What operating conditions favor maximum silicon pickup by the catalyst? Are there differences between silicon from coker antifoams and other sources? Does the presence of other contaminants such as nickel and vanadium affect the silicon pick-up by the catalyst? What best practices are used for monitoring silicon pick-up by the catalyst?

Silicon is probably the most widespread catalyst poison encountered in hydrotreater feeds. The main source of silicon is from delayed coker operations that use a poly(dimethyl)siloxane-based anti-foam agent to suppress foaming in the coker drums. The siloxane polymer breaks down in the coking process to primarily methylsiloxane trimers. These species are volatile at coker temperatures with boiling points ranging from 270–475°F (132-246°C). As a result, these compounds tend to concentrate on the overhead products, and as a general rule of thumb, 70-80% of the silicon injected to the coker ends up in the naphtha fraction, the balance is in the distillate fraction. More recently, refineries have experienced silicon poisoning of hydrotreating catalysts. These refineries have begun processing synthetic or other opportunity crudes and the process of making synthetic crude often involves a coking step. In addition, it is becoming more common to use silicon additives in the drilling process, and for pipeline companies to use them for both flow enhancing performance and foaming issues. Silicon additives also are sometimes used in barge unloading.

In the hydrotreater, the silica fragments from the antifoam agent undergo a condensation reaction with the alumina surface of the catalyst forming a strong chemical bond. Once the silicon is bound to the alumina surface, it cannot be removed by regeneration or other means. It is a more moderate poison compared to contaminants like sodium or arsenic, but it nonetheless results in activity loss on the order of 5-10°F (3-6°C) for each 1.0 wt% Si deposited on the hydrotreating catalyst. A variety of analytical techniques have been applied to silicon poisoned catalysts, and this confirms that the silicon is associated with the alumina support as opposed to the active metal sulfides of the catalyst. Furthermore, the silicon in the coker naphtha depends on the type and amount of antifoam chemical at the delayed coker unit. Delayed cokers have cycles ranging anywhere between 8 – 24 hours. The coker unit is continually producing a coker naphtha stream during these cycles, which is typically being sent from the fractionator straight into the naphtha hydrotreater feed drum. The antifoam chemical is not usually added for the entire coker cycle. This means that the silicon in the naphtha stream will vary with the timing of the coker cycle. In order to get a representative amount of silicon in the coker naphtha stream, a composite should be made of hourly samples mixed together for the time of the cycle. For example, an eight-hour cycle, eight samples would be mixed and the composite sample analyzed for silicon. To measure the silicon, an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrument can be used. This instrument/method can measure very low (ppb) metal concentrations.

Alternatively, the refinery could measure the amount of anti-foam used by the coker over the course of a month. Assuming that 70-80% of the silicon ends up in the naphtha fraction, the refiner then could estimate the amount of silicon going into the naphtha hydrotreater. While this would be less accurate than the preceding method, it would also be less costly. ✤

Fuels that are produced when vegetable oils or animal fats are processed in traditional refining processes are considered co-processed renewable diesel. Some common sources of renewable feeds are those produced for food-grade oils such as soybean, rapeseed, and other vegetable oils. The traditional process for introducing these sources into the diesel pool is to use the transesterification reaction for breaking the glycerol from the fatty acid chains. Diesel produced via transesterification is called biodiesel and earns the Biomass-Based Diesel Renewable Identification Number (RIN) under the EPA’s RFS2 program. Co-processed renewable diesel qualifies for the Advanced Biofuel RIN.

ART has completed extensive pilot plant studies demonstrating that these types of feeds can be co-processed with traditional diesels in an existing ULSD unit. To ensure the finished blend quality, refiners who use the co-processing method have precise knowledge of the bio-based fuels that are incorporated into the diesel pool.
the oxygen will react with the hydrogen to form water. This water, if generated in a significant enough quantity, may cause problems such as weakening the catalyst support or redistribution of the active metals and loss of surface area. At the expected blending ratios of 10%, the oxygen content is around 1 to 1.5 wt%, and even if all of the oxygen is converted, this is unlikely to generate enough water to be a significant problem.

An increase in hydrogen consumption to saturate C=C bonds is expected due to the addition of unsaturated chains from the bio component. The co-processing of renewable components may yield improvements in the diesel cetane due to the increase in n-paraffin content in the diesel product. These n-paraffins, however, raise concerns about the biofeed-based diesel cloud point. Normal paraffins have a significantly higher cloud point than other hydrocarbons of similar carbon number. Since hydrotreating converts the fatty acid chains into long chain n-paraffins, it is expected that the cloud point of the hydrotreated product will significantly increase compared to the product when processing just an SR-base feed.

Reducing SOx Emissions at BP Castellon Using FCC Additives

- Ana Piera, Marta Calvo, Angel Llanes (BP Castellon)
- Colin Baillie, Rafael Gonzalez (Grace)

Explore the technical factors behind BP’s decision to use additives, rather than more costly alternatives.
Additives Offer an Attractive Alternative to Reduce SOx Emissions

Refiners often choose specialized additives to achieve SOx reduction because it is an extremely effective and flexible way to reduce SOx emissions from the FCCU.

The other, more costly options for reducing SOx emissions include flue gas scrubbing (FGS), the use of lower sulfur-containing feedstocks, and hydrodesulfurization (HDS). FGS requires a significant capital investment and the operating costs are high. In addition, discarding the spent treating compounds such as lime, caustic soda, or other compounds can be problematic. Choosing to process lower sulfur feeds can be expensive and may not even be a viable option. HDS provides improved yields as well as lower SOx emissions, the conditions leading to increased sulfur content in the FCCU typically processes in full burn with a capacity of 30,000 bpd. The FCCU typically processes an Exxon Flexicracker model operating in full burn with a capacity of 30,000 bpd. The FCCU typically processes a VGO feedstock with slurry recycle, and sometimes processes additional Atmospheric Residue feedstock. As emissions standards tighten, the refinery seeks to reduce environmental emissions from the FCC unit and from the refinery as a whole.

Operating Variables that Affect SOx Emissions

Feedstock sulfur is the source of SOx in the FCC unit. To a certain extent SOx emissions correlate to feed sulfur levels with typically two to 10 percent of the feedstock sulfur ending up in the coke, which when burned off in the regenerator creates SOx. The actual amount of sulfur going to coke is largely affected by the sulfur feedstock molecules. For example, hydrodesulfurization severely plays a large role. Although hydrotreated feedstocks typically have lower sulfur content, a higher amount of the sulfur can end up in coke, with as much as 30 percent observed for severely hydrodesulfurated feeds. In addition, aromatic or thiophenic feed sulfur is more likely to go to coke compared to mercaptans. As a result, there is often a stronger correlation between SOx emissions with aromatic or thiophenic feed sulfur than overall feed sulfur content. There is also often a better correlation of SOx emissions with slurry sulfur content than feed sulfur content. Although sulfur content in the slurry itself is not a cause of SOx emissions, the conditions leading to increased sulfur content in the slurry are similar to those leading to increased sulfur content in coke, and thus SOx emissions.

Stripper operation also plays a significant role in SOx formation with lower efficiency resulting in higher SOx emissions. For example, higher entrained hydrocarbons tend to be high in sulfur content, and if not effectively removed from the catalyst in the stripper, will result in higher levels of sulfur entering the regenerator.

There are additional variables that affect the performance of SOx additives. Units with a high catalyst circulation rate generally observe higher pick-up factors when using SOx reduction additives. This is attributed to more available catalytic sites for SOx capture. The performance of SOx additives are negatively affected by higher regenerator temperatures. The oxidation of SO2 to SO3 is a critical reaction pathway in the SOx reduction mechanism since the emissions control additive reacts with SO3 not SO2. Although a higher temperature increases the oxidation of SO2 to SO3, the resulting sulfates are less stable in the regenerator. In contrast, high reactor temperatures favor the required reduction of sulfates to H2S in the reactor, thus decreasing SOx levels.

One of the key variables is the influence of oxygen concentration and distribution in the regenerator. Because the oxidation of SO2 to SO3 is a key step for SOx removal, an increase in excess oxygen or improved distribution enhances additive performance. Not only does improved stripper efficiency result in a decreased amount of sulfur-containing hydrocarbons entering the regenerator, but it also helps to fully hydrolyze the sulfide intermediate to H2S, thus increasing additive performance. Finally, the presence of combustion promoters can assist the performance of SOx additives by helping to catalyze the reaction of SO2 to SO3.

With the various factors that influence SOx emissions, evidence shows that before beginning a SOx reduction additive trial it is necessary to establish a baseline for uncontrolled SOx emissions. This will allow the subsequent comparison of SOx levels obtained with and without SOx reduction additives at constant conditions.

Grace Super DESOX® Trail at BP Castellon for SOx Reduction

The BP Castellon refinery in Spain has a nameplate crude capacity of 110,000 bpd. The FCC unit is an Exxon Flexicracker model operating in full burn with a capacity of 30,000 bpd. The FCCU typically processes a VGO feedstock with slurry recycle, and sometimes processes additional Atmospheric Residue feedstock. As emissions standards tighten, the refinery seeks to reduce environmental emissions from the FCC unit and from the refinery as a whole.

Accordingly, in the fourth quarter of 2013, the refinery began a trial of Super DESOX®, a SOx reduction additive from Grace. Prior to the trial, FCC feed sulfur levels at BP Castellon were typically between 0.6-1.7 wt %, regenerator temperatures were typically around 720 °C, with flue gas excess oxygen content about 0.9 to 1.1%

The primary objective of the trial was to decrease typical flue gas SOx levels by approximately 40% with a further secondary target of just over 50% reduction (Figure 1). The introduction of Super DESOX® at ca. 6% of the catalyst addition rate decreased SOx levels to below the secondary target, achieving SOx reduction levels of close to 70% (Figure 2).

All Grace’s additives including Super DESOX® can be pre-blended with the FCC catalyst, or added separately through the use of a Grace additive system. Grace offers a variety of catalyst and additive addition system models to enable accurate control of the circulating inventory activity. Optimum performance is achieved by providing smaller, more frequent catalyst or additive doses, thus avoiding large slug additions.

BP Castellon Reduced SOx Emissions with Grace Environmental Additives

Based on the company’s commitment to reduce emissions as well as increasingly stringent emissions standards, the BP Castellon refinery is reducing SOx emissions using FCC environmental additives from Grace. In a recent trial, Super DESOX® achieved SOx reductions of approximately 70%.

These results affirm the performance of Super DESOX®, with its patented magnesium-alumina spinel structure, as the leading SOx reduction additive, successfully used by over 100 refiners worldwide.
Improving Safety, Reliability and Profitability at the Orpic Sohar Refinery

Maadh Al Badri and Dilip Singh (Orpic)
Nathan Ergonul, Talal Al-Rawahi, Colin Baillie (Grace)

The FCC catalyst is one of the key factors in the profitability of Orpic’s resid FCC unit at Sohar, which places a high level of responsibility on the supplier for both the product technology and technical service. This article describes the many steps Grace has taken to help improve safety, reliability, and profitability at the Orpic Sohar refinery.

Orpic Background
The first oil was discovered in Oman in 1963 at the Naith Field. Oman’s first refinery was commissioned nearly 20 years later in 1982 at Mina Al Fahal with a capacity of 50,000 barrels per day. A series of investments in the early 2000s yielded the first production of unleaded gasoline followed by ultra low sulfur diesel. In 2006, Orpic opened a new refinery in Sohar with a capacity of 116,000 barrels per day, and commissioned a new polypropylene plant. Oman’s first aromatics plant went into operation in Sohar in 2010.

The resid FCC unit is a core process of the refining complex at Orpic Sohar. It is a 75 KBD UOP design, which processes untreated atmospheric residue from Oman crude as feedstock. The Mina Al Fahal and Sohar refineries are integrated to optimize “molecule management.”

Improving Profitability
As shown in Table 1, there have been four distinct periods of catalyst technology that have been applied at the Orpic Sohar resid FCC unit.

Orpic started up the RFCC unit at Sohar using an FCC catalyst from Competitor B. The RFCC unit at Sohar processes an extremely challenging feedstock. After a period of underperformance, a Grace resid catalyst was introduced in 2009, based on independent third-party laboratory testing. Table 2 shows average feedstock properties, operating conditions, Ecat properties and product yields for periods using catalysts from Competitor B and Grace. This illustrates that feedstock properties deteriorated, with specific gravity, sulfur, ConCarbon, nickel, and vanadium increasing considerably under comparable operating conditions. The table also shows that, despite the poorer feed quality, unit performance significantly improved after switching from Competitor B to Grace. Additionally, conversion increased by more than 1 wt.%, translating to a significant increase in propylene yield, which is a key unit objective. Bottoms yield was reduced by nearly 1 wt.%.

In 2011, Chinese export quotas hit the FCC industry with skyrocketing prices of rare-earth metals, a critical component of FCC catalysts. The key index for FCC catalysts is the cost of 99% lanthanum oxide FOB from China, which increased dramatically from $2,300/MT in January 2007 to more than $100,000/MT in August 2011, according to the Asian Metals Index. In response, Grace led the development of alternative technologies and was the only supplier to commercialize low and zero rare-earth FCC catalysts. In the case of Orpic, Grace developed a low rare-earth version of the previous catalyst being used at the resid FCC unit at Sohar.

Feedstock properties deteriorated during this trial. As shown in Table 3, feed API, feed nickel, feed vanadium and feed ConCarbon all increased. Despite the decline in feedstock quality, the low rare-earth technology maintained the excellent performance seen in the unit. Table 3 shows how the key FCC unit yields improved with the low rare-earth FCC catalyst from Grace. Conversion was maintained (even slightly increased) without a coke penalty and without increasing the catalyst addition rate.

In 2013, Orpic carried out a rigorous catalyst selection process using pilot plant testing in an independent third-party laboratory to evaluate the impact of using catalysts from the main suppliers on FCCU profitability. Results from these tests were used by a second independent company that completed advanced process modeling simulating the commercial unit performance of the screened catalysts. The outcome clearly demonstrated that the optimized Grace catalyst was the most suitable catalyst for the challenging operation at the Sohar RFCC unit. As a result, Grace’s supply contract was extended.

Table 1: RFCC History at the Orpic Sohar Refinery

<table>
<thead>
<tr>
<th>Period</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2006-2009</td>
<td>RFCCU startup using competitor catalyst</td>
</tr>
<tr>
<td>2 2009-2011</td>
<td>Switch to Grace catalyst</td>
</tr>
<tr>
<td>3 2011-2013</td>
<td>Move to low rare-earth Grace catalyst</td>
</tr>
<tr>
<td>4 2013-</td>
<td>Application of optimized Grace catalyst</td>
</tr>
</tbody>
</table>

Table 2: FCC Unit Data Comparing Competitor B and Grace Technology

<table>
<thead>
<tr>
<th>Feed Properties</th>
<th>Competitor B</th>
<th>Grace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td></td>
<td>+0.003</td>
</tr>
<tr>
<td>Sulfur Content</td>
<td>wt. % base</td>
<td>+22%</td>
</tr>
<tr>
<td>ConCarbon</td>
<td>wt. % base</td>
<td>+9%</td>
</tr>
<tr>
<td>Nickel Content</td>
<td>ppm base</td>
<td>+23%</td>
</tr>
<tr>
<td>Vanadium Content</td>
<td>ppm base</td>
<td>+23%</td>
</tr>
</tbody>
</table>

Operating Conditions
- Feed Temperature: °C base +14 °C
- ROT: °C base -3 °C
- Cat-to-Oil Ratio: g/l 9.6 8.5
- SCAR: kg/s/F base +4%

Ecat Properties
- Nickel: ppm base +17%
- Vanadium ppm base +13%

Product Yields
- Conversion: wt. % base +1.1 wt. %
- Dry Gas: wt. % base -0.1 wt. %
- Propylene: wt. % base +1.0 wt. %
- LPG: wt. % base +0.3 wt. %
- Total Naphtha wt. % base -0.3 wt. %
- LCO: wt. % base -0.3 wt. %
- Slurry: wt. % base -0.8 wt. %
- Coke: wt. % base -0.8 wt. %

Table 3: FCC Unit Data Comparing Competitor B and Grace

<table>
<thead>
<tr>
<th>Feed Properties</th>
<th>Competitor B</th>
<th>Grace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur Content</td>
<td>wt. % base</td>
<td></td>
</tr>
<tr>
<td>ConCarbon</td>
<td>wt. % base</td>
<td></td>
</tr>
<tr>
<td>Nickel Content</td>
<td>ppm base</td>
<td></td>
</tr>
<tr>
<td>Vanadium Content</td>
<td>ppm base</td>
<td></td>
</tr>
</tbody>
</table>

Reliability and Profitability
Grace additives.

In 2010, an additional system from Grace was installed to allow multiple components to be dosed, enabling the refinery to operate at maximum flexibility and reliability (Figure 1). This customized device now allows the refinery to handle up to four components, including fresh FCC catalyst, Ecat and ZSM-5 additive. In 2011, a critical component of FCC catalysts is the cost of 99% lanthanum oxide FOB from China, which increased dramatically from $2,300/MT in January 2007 to more than $100,000/MT in August 2011, according to the Asian Metals Index. In response, Grace led the development of alternative technologies and was the only supplier to commercialize low and zero rare-earth FCC catalysts. In the case of Orpic, Grace developed a low rare-earth version of the previous catalyst being used at the resid FCC unit at Sohar.

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Table 4 shows the FCC unit yields obtained from the optimized Grace catalyst compared to the previous catalyst. Bottoms conversion was increased by over 1.5 wt.%, resulting in a substantial increase in conversion by nearly 2 wt.% due to a lower quantity of ZSM-5 in the Ecat, as well as the improved gasoline selectivity, naphtha yield was increased by nearly 2 wt.% at the expense of LPG yield. The optimized Grace catalyst led to a drop in delta coke, which enabled greater operational flexibility to process heavier feeds. As shown in Table 4, the optimized catalyst allowed feed rate to be increased by 10%.

Improving Reliability and Safety
In the original system design at the Sohar refinery, four hoppers were used for the storage of fresh FCC catalyst, Ecat and ZSM-5 additive. In 2010, an additional system from Grace was installed to allow multiple components to be dosed, enabling the refinery to operate at maximum flexibility and reliability (Figure 1). This customized device now allows the refinery to handle up to four components from different hoppers and/or flowbins, and achieve total dosage rates of up to 30 MT/day. In total, two of these devices were installed and operated on a stand-by basis, which allows operators to maintain an uninterrupted dosage of fresh catalyst to the FCC unit. An extra flow bin also was included to allow separate injections of Grace additives.

The catalyst and additive injection system was supplied by Grace’s partner, Pneumix, which has installed over 130 loaders worldwide. Grace’s partner for 25 years, Pneumix provides innovative, state-of-the-art solutions for catalyst and additive bulk handling to FCC units globally.
In the conventional operation at Sohar, approximately 20-30 super sacks (1000 kg each) of fresh catalyst were unloaded every day into the storage hopper. The handling of such a large volume of material previously had been costly, intensively time consuming, and environmentally unfriendly. There also were safety concerns associated with the forklift truck movements in the area. In addition, during the unloading operation, dust generation created catalyst loss, as well as safety issues that constrained maintenance activities.

One effective way to avoid the handling of super sacks is to deliver larger volumes of catalyst and additives overseas in more suitable containers. A trailer tipper was supplied to allow the refinery to move to a safer and logistically cleaner container system (Figure 2). This solution was successfully installed on site without requiring engineering and construction. The frame is adjustable to variable trailer heights, accommodating maximum 40 ft-trailers without the front car. During the unloading operation, the trailer is locked with chains and a safety bar is placed over the container. The catalyst is then transported into the storage hopper by the Power Pipe system (Figure 2). This easy-to-use device is operated by vacuum, noticeably reducing unloading times.

In addition, Grace has built a dedicated silo storage and logistics management facility at Orpic’s Sohar refinery to guarantee the timely and secure delivery of product (Figure 3). This facility was opened in 2013, and is operated by local Omani employees. The silo hub plant was designed to accommodate a large volume of catalyst, enabling security of supply. Storing this material at the plant avoids overloading the Orpic warehouse, which saves considerable costs.

Grace also provides Orpic with valuable Ecat reworking solutions. The Sohar resid FCC unit processes feedstock high in Conradson carbon and contaminant metals, which initially posed the refinery with Ecat disposal challenges. Grace subsequently explored various options, and found a solution that complied with local environmental regulations, and granted Orpic a governmental export license for spent catalyst. A Grace partner recycles the Ecat from Orpic at their facilities in

### Table 3: FCC Unit Data Comparing Competitor B and Grace Technology

<table>
<thead>
<tr>
<th>Feed Properties</th>
<th>Prior Grace</th>
<th>Grace Low Rare-Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>base</td>
<td>+0.11</td>
</tr>
<tr>
<td>Nickel Content</td>
<td>ppm</td>
<td>base +5%</td>
</tr>
<tr>
<td>Vanadium Content</td>
<td>ppm</td>
<td>base +6%</td>
</tr>
<tr>
<td>ConCarbon</td>
<td>wt.%</td>
<td>base +0.12</td>
</tr>
<tr>
<td>Ecat Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rare Earth</td>
<td>wt.%</td>
<td>3.0</td>
</tr>
<tr>
<td>Operating Conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst Addition Rate</td>
<td>MT/day</td>
<td>base</td>
</tr>
<tr>
<td>Product Yields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>wt.%</td>
<td>base +0.8 wt.%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>wt.%</td>
<td>base -0.1 wt.%</td>
</tr>
<tr>
<td>C1-C2's</td>
<td>wt.%</td>
<td>base +1.0 wt.%</td>
</tr>
<tr>
<td>LPG</td>
<td>wt.%</td>
<td>base +0.3 wt.%</td>
</tr>
<tr>
<td>Total Naphtha</td>
<td>wt.%</td>
<td>base -0.3 wt.%</td>
</tr>
<tr>
<td>LCO</td>
<td>wt.%</td>
<td>base -0.3 wt.%</td>
</tr>
<tr>
<td>Slurry</td>
<td>wt.%</td>
<td>base -0.8 wt.%</td>
</tr>
<tr>
<td>Coke</td>
<td>wt.%</td>
<td>base -0.8 wt.%</td>
</tr>
</tbody>
</table>

### Table 4: FCC Unit Data Highlighting the Effect of Moving to the Optimized Grace Technology

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Prior Grace</th>
<th>Optimized Grace Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate</td>
<td>BPD</td>
<td>base +10%</td>
</tr>
<tr>
<td>ROT</td>
<td>°C</td>
<td>base</td>
</tr>
<tr>
<td>Feed Temperature</td>
<td>°C</td>
<td>base</td>
</tr>
<tr>
<td>Cat-to-Oil Ratio</td>
<td></td>
<td>base +0.44</td>
</tr>
<tr>
<td>Regen Bed Temp</td>
<td>°C</td>
<td>base -15 °C</td>
</tr>
<tr>
<td>Product Yields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>wt.%</td>
<td>base +1.8 wt.%</td>
</tr>
<tr>
<td>LPG Olefins</td>
<td>wt.%</td>
<td>base -1.0 wt.%</td>
</tr>
<tr>
<td>Total Naphtha</td>
<td>wt.%</td>
<td>base +1.8 wt.%</td>
</tr>
<tr>
<td>LCO</td>
<td>wt.%</td>
<td>base -0.4 wt.%</td>
</tr>
<tr>
<td>Slurry</td>
<td>wt.%</td>
<td>base -1.6 wt.%</td>
</tr>
<tr>
<td>Coke</td>
<td>wt.%</td>
<td>base</td>
</tr>
</tbody>
</table>

(continued on page 42)
Germany, while operating under Grace’s REACH registration umbrella. This rework utilizes two different patented processes within the steel production and building industries.

**A Partnership to Maximize Profitability**

Throughout its partnership with Orpic, Grace has worked constantly to enable the Sohar RFCC unit to maximize profitability through the introduction of state-of-the-art catalyst technologies. This has allowed the refinery to reach its targets despite processing an extremely challenging feedstock. Grace has also provided Orpic with unique catalyst management solutions that have resulted in an improvement of unit safety and reliability.