Worried about the cost of rare earth? Grace has the solution:

REpLaCeR®

Rare-earth price inflation is a serious issue facing the global refining industry. Grace, with our long history of innovation and strong R&D, leads the industry with the first line of commercially successful zero/low rare-earth FCC catalysts: the REpLaCeR® family.

Launched in the first quarter of 2011, the REpLaCeR® family includes five new catalysts for both hydrotreated and resid feed processing with zero and low rare-earth content. The REpLaCeR® family of catalysts utilizes proprietary zeolites and state-of-the-art stabilization methods to deliver performance similar to current rare-earth-based FCC technologies.

We’re also investing in our plants to bring these products to the refining industry quickly and globally.

So if you’re concerned about rare-earth pricing and availability, but need optimal FCC performance, call the technical experts at Grace. We’ll customize a solution using one of our new zero/low rare-earth catalysts that delivers the yields you expect.

Grace Catalysts Technologies
7500 Grace Drive
Columbia, MD USA 21044
+1.410.531.4000

www.grace.com
www.e-catalysts.com

Enriching Lives, Everywhere.®
Editorial

A new year is upon us and the refining industry is again faced with significant challenges in 2012. Last year all of us were consumed by the rapid inflation in rare-earth price and the impact on our businesses. This year, capacity rationalization is occurring at a similar rapid pace. Growth in transportation fuels demand is shifting the base to the emerging regions, where new mega-refining projects have recently started up or are under construction. Refiners in mature markets, particularly those around the Atlantic basin will be at an economic disadvantage relative to the new players; already we have seen several large facilities along the East Coast shutdown due to poor margins. And for the first time, the US became a net exporter of gasoline in 2011 due to declining demand domestically.

So what does it mean? It means that we are operating in a truly global marketplace, where to compete and maintain profit margin, you need the right catalyst at the right time to make the right products. This issue of the Catalagram® highlights various ways that we can help you stay competitive by either reducing your exposure to rare-earth price, using our products to reduce your commodity chemical spend or maximizing the yield of diesel in your refinery.

This isn’t our first challenge and it won’t be the last but the team at Grace is dedicated to helping you achieve success with innovative catalytic solutions from our broad catalyst portfolio. Our new organization, which is described in the “People on the Move” article in this issue, is as focused as ever at working towards a total Grace solution for your refinery, leveraging our expertise in FCC and HPC to drive your profitability in the right direction.

Sincerely,

Rosann K. Schiller
Senior Marketing Manager
Grace Catalysts Technologies

Alternatives to Rare Earth - Commercial Evaluation of REpLaCeR® FCC Catalysts at Montana Refining Company

Maximize Distillate Yield to Meet Growing Market Demand

People on the Move

Improve Wet Gas Scrubber Economics with Super DESOX® Additives

Improve Contaminant Metals Fluxing with TITAN™

Grace Upgrades Ecat Test Laboratory in North America

Maximize Yields of High Quality Diesel
Abstract

After the sweeping reduction of Chinese export quotas, rare-earth metals experienced price hyperinflation in the range of 2700% between August 2010 and July 2011. FCC catalyst has experienced unprecedented inflation as a result. Rare earth is used to stabilize FCC catalyst zeolite in order to provide high FCC catalyst activity, liquid selectivities and superior coke selectivity. Removing rare earth from FCC catalyst will provide relief in catalyst expenses; however, it is not an economical solution in most FCC operations due to a lower activity and product value.

Alternate materials and processing must be used to stabilize the FCC zeolite to ensure a profitable yield slate without rare earth. Grace has recently developed and commercialized its new REpLaCeR® family of catalysts, a portfolio of low and zero rare-earth catalysts applicable to a broad range of FCC applications. Presently, over 50 units worldwide use REpLaCeR® FCC technology.

Montana Refining Company (MRC) partnered with Grace to commercialize a rare-earth-free REMEDY™ catalyst from Grace’s new REpLaCeR® family of catalysts. MRC has successfully applied a zero rare-earth REMEDY™ over a moderate rare earth GENESIS® FCC catalyst. Commercial results demonstrate similar unit conversion at similar catalyst additions. Coke selectivity and slurry cracking were maintained with REMEDY™ while gasoline selectivity increased.

MRC is an independent refiner located in Great Falls, MT. Sour heavy crudes are processed in their complex refinery producing low sulfur gasoline, ultra-low sulfur diesel, jet and a full slate of asphalt products. W.R. Grace & Co. is the world’s leading supplier of FCC catalysts and additives with headquarters in Columbia, MD.
REpLaCeR® Technology

Grace’s zero and low rare-earth REpLaCeR® catalyst portfolio quickly gained momentum in 2011. The explosive growth of the technology was sparked by rare-earth hyperinflation stemming from Chinese export quota restrictions in 2010.¹

Grace’s REpLaCeR® technologies include zero and low rare-earth catalysts for all FCC applications.² Today there are over 50 applications of REpLaCeR® technologies ranging from low to moderate metal vacuum gas oil (VGO) applications to operations with high metals residual feedstocks. Those REpLaCeR® applications are described in Table 1. In over 20 current REpLaCeR® applications, all of the rare earth has been removed from the FCC catalyst. These applications range from low metals to as high as 4700 ppm Ni plus V. For higher metals operations, 20 to 80% of the rare earth can be eliminated with REpLaCeR® catalyst. Some current resid applications are operating with Ecatal Ni plus V levels greater than 10,000 ppm and V plus Na levels higher than 9,000 ppm.

The purpose of zeolite stabilization is to preserve acid site density and control catalyst activity and product selectivities. Rare earth has been traditionally used to stabilize the zeolite by controlling de-alumination, which increases hydrogen transfer and activity.³

Unit cell size (UCS), as measured by x-ray diffraction, is a common benchmark to judge zeolite stabilization and acid site density. Until recently, rare earth was the most cost effective material to stabilize the zeolite. Now Grace is using alternative materials and processing to stabilize the zeolite to achieve desired catalyst activity, stability and selectivity without rare earth.

Grace’s current catalyst portfolio is described in Figure 1. The REpLaCeR® catalysts are the grades listed in blue. Catalysts listed on the far left are high zeolite to matrix catalysts while the low zeolite to matrix catalysts are shown on the right. Catalysts listed in the middle, such as GENESIS®, incorporate a combination of technologies and provide excellent coke selectivity and slurry cracking.

### Table 1: REpLaCeR® Catalyst Commercial Successes

<table>
<thead>
<tr>
<th>Application No.</th>
<th>% Reduction</th>
<th>Ni + V, ppm</th>
<th>V + Na, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>56</td>
<td>2,700</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>250</td>
<td>3,500</td>
</tr>
<tr>
<td>22</td>
<td>100</td>
<td>2373</td>
<td>5,276</td>
</tr>
<tr>
<td>23</td>
<td>100</td>
<td>4743</td>
<td>5,466</td>
</tr>
<tr>
<td>24</td>
<td>80</td>
<td>1798</td>
<td>4,714</td>
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<tr>
<td>25</td>
<td>80</td>
<td>8263</td>
<td>9,478</td>
</tr>
<tr>
<td>47</td>
<td>30</td>
<td>8229</td>
<td>7,759</td>
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<tr>
<td>52</td>
<td>20</td>
<td>11195</td>
<td>5,810</td>
</tr>
</tbody>
</table>

![Figure 1: Grace Has the Broadest Catalyst Portfolio in the Industry – [REpLaCeR® Technologies Shown in Blue]](image-url)
REMEDY™ technology is zero or low rare-earth catalyst designed for VGO applications. REDUCER® catalysts incorporate low levels of rare earth for FCC units that process high metals residual FCC feedstocks.

Two principal zero rare-earth catalysts that can be used in Grace’s REMEDY™ technology are REACTOR® and REBEL™ catalysts.

REACTOR® is a zero rare-earth catalyst which incorporates Grace’s Z-22 zeolite. Relative to rare earth ultra stable Y zeolite (RE USY), Z-22 provides equivalent activity, higher LPG olefins and gasoline octane as a moderately exchanged rare earth zeolite. A proprietary stabilization process is used to provide zeolite acidity and preserve activity similar to what has traditionally been accomplished by rare earth.²

REACTOR® catalyst is high zeolite to matrix catalyst from Grace’s Alumina-Sol catalyst platform. As a Grace Alumina-Sol catalyst, REACTOR® will provide excellent yield selectivities, low attrition index and flue gas stack particulates similar to other Grace Alumina-Sol catalysts such as AURORA® and IMPACT®.⁴

REBEL™ is a zero rare-earth, low zeolite to matrix catalyst formulated with Z-21 zeolite. REBEL™ is an extension of Grace’s industry leading bottoms cracking MIDAS® catalysts. Z-21 also uses a distinctive proprietary zeolite stabilization process to provide necessary activity and yield selectivities without rare earth.²

Isobutylene, iC₄⁺, selectivity is a common benchmark to judge hydrogen transfer activity. Figure 2 shows the relative iC₄⁺ selectivity of two catalysts with RE USY zeolites together with rare-earth free catalysts, one using Z-21 and the other Z-22 zeolite. This data was generated in an Advanced Cracking Evaluation Unit (ACE) using metals free deactivated catalysts.⁴

The catalyst with an 8% rare earth on zeolite RE USY (8% RE/Z corresponding to a UCS of ~24.31Å) produces the lowest iC₄⁺ selectivity and hence the highest hydrogen transfer activity. Isobutylene selectivity was the highest from the 3% rare earth on zeolite catalyst (3% RE/Z corresponding to a ~UCS of ~24.27Å).

The catalyst using Z-21 provided similar iC₄⁺ selectivity as the catalyst with 8% RE/Z. The high hydrogen transfer activity exhibited by the Z-21 zeolite suggests similar acid site density and zeolite stabilization as the 8% RE/Z base catalyst. Z-22 zeolite, which is used in the REACTOR® catalyst, provided slightly less iC₄⁺ selectivity than the 3% rare earth on zeolite catalyst, confirming slightly higher acid site density for the Z-22 system.

Figure 3 shows total acidity for catalysts with a 3% RE/Z USY zeolite, Z-21 and Z-22 zeolites. Total acidity was measured by a NH3-STPD technique. STPD method (Stepwise Temperature Programmed Desorption) can be used to differentiate acid site density in aluminas, clay, zeolites, fresh catalysts, and deactivated catalysts. Zeolites, especially, possess heterogeneous acid sites of discrete strengths which can be identified by measuring ammonia desorption.

Z-21 provides higher total acidity than the RE USY zeolite catalyst. Z-22 zeolite has less total acidity than Z-21, but similar acidity as the RE USY with 3% RE/Z. The relative acidity of the catalyst shown in Figure 3 is consistent with the iC₄⁺ selectivity ranking shown in Figure 2.

Figures 2 and 3 suggest that the proprietary materials and processing used for Z-21 and Z-22 zeolite provide similar hydrogen transfer activity as a traditional rare-earth system.

Rare earth has also been used to control zeolite surface area stability especially in high metals applications. Zeolite stability is commonly judged by zeolite surface area retention, the ratio of de-
activated zeolite surface area to fresh zeolite surface area, as a function of deactivation temperature and contaminant metals. Figure 4 shows zeolite surface area retention for REBEL™ with Z-21 compared with a MiDAS® catalyst with 8% RE/Z as a function of contaminant metals. Rare-earth free REBEL™ with Z-21 zeolite provides similar zeolite surface area retention as MiDAS® with a RE USY zeolite.

In Figure 5, a similar comparison of zeolite surface area retention is made between rare-earth free REACTOR® with Z-22 zeolite vs. an AURORA® catalyst with approximately 4% RE/Z. In this Figure, Z-22 provides a slight improvement in zeolite stability compared to a RE USY AURORA® catalyst.

Figures 4 and 5 confirm the proprietary stabilization compounds used for Z-21 and Z-22 can maintain zeolite surface area like a traditional RE USY catalyst.

**Montana Refining Company**

MRC is an independent energy company engaged in crude oil refining and the wholesale marketing of refined petroleum products. They operate one of the last small, independent full production refineries in the USA, producing approximately 10,000 barrels per day of various petroleum products.

The refinery is a complex refinery (Nelson Complexity Factor of 9.3) able to process heavy sour crude oil that is received via pipeline and railcar. A basic process flow for the MRC facility is shown in Figure 6. MRC produces a wide range of high quality products ranging from multiple grades of low sulfur gasoline (including ethanol blended gasoline) to ultra-low sulfur diesel, jet fuels, LPG’s and asphalt products. The finished gasoline and distillate products are distributed through MRC’s terminal in Great Falls and the asphalt products are marketed over racks at the refinery.

MRC, with nearly ninety years in the Great Falls community as a petroleum refiner with stringent quality control standards, has earned a reputation as a dependable supplier of high-quality fuel and road paving products. MRC is a wholly owned subsidiary of Connacher Oil and Gas Limited, a Calgary-based Canadian crude oil and natural gas company.

The FCC at MRC processes a hydrotreated VGO at a nominal rate of ~3,000 barrels per day. During the summer months the unit is constrained by the air blower and main column overhead condensers hydraulics. Reactor temperature is controlled to a relatively low value of ~940°F as the unit generally operates in a maximum Light Cycle Oil mode.
Grace’s Super DESOX® OCI is used to control SOx to less than 25 ppm. NOx is controlled by minimizing excess O₂ levels and the use of Grace’s low NOx CP® P combustion promoter.

FCC gasoline is not hydrotreated at the facility. As a result gasoline sulfur specifications are met by controlling the end point and FCC feedstock sulfur. Grace’s SuRCA® gasoline sulfur reduction technology is used to extend the VGO hydrotreater run length by providing ~30% gasoline sulfur reduction, allowing lower FCC feed hydrotreater temperature for a target FCC gasoline sulfur.

MRC meets its FCC flue gas particulate limits without any external particulate recovery device such as tertiary separator or electrostatic precipitator (ESP). As a result, FCC catalyst attrition and retention qualities are critical.

Grace is a long-term supplier of FCC catalysts and additives to MRC. During that time several Grace products have been commercialized at MRC including:

1. D-PrisM® and SATURN® Gasoline Sulfur Reduction technologies
2. XP® and LIBRA® FCC catalysts
3. Super DESOX® OCI – reduced rare-earth SOx reduction additive
4. CP® P – Non Platinum Low NOx Combustion Promoter

Reformulations Ahead of the Surcharge

In 2011, Grace offered MRC FCC catalyst technology from its new REpLaCeR® portfolio to avoid pending rare-earth surcharges.

MRC reformulated their fresh FCC catalyst in two steps. REMEDY™ 1 GSR® reduced rare earth by a third, while REMEDY™ 2 GSR® completely removed rare earth from the catalyst. Fresh catalyst properties are shown in Table 2. The objective of each reformulation was to maintain the current yields, gasoline sulfur and gasoline octane as the base rare-earth containing GENESIS® grade.

REMEDY™ 1 GSR® incorporates Grace’s REACTOR® technology together with MIDAS®. MIDAS® is low zeolite to matrix, industry-leading bottom cracking catalyst. REMEDY™ 2 GSR® uses both REACTOR® and REBEL™ technologies and is a rare-earth free catalyst. The original GENESIS® GSR® incorporated Aurora® and MIDAS® technology. All FCC catalyst technologies incorporate Grace’s gasoline sulfur reduction SuRCA® technology which provides ~30% gasoline sulfur reduction.

MRC reformulated to REMEDY™ 1 GSR® in January 2011 minimizing the first quarter 2011 rare-earth surcharge by one third. When REBEL technology was available in August 2011, MRC reformulated to REMEDY™ 2 GSR® and avoided the large third and fourth quarter rare-earth surcharges entirely, as shown in Figure 8.
TABLE 2: Montana Refining Company Fresh Catalyst Properties

<table>
<thead>
<tr>
<th>Activity, wt.%</th>
<th>GENESIS® GSR®</th>
<th>REMEDY™ 1 GSR®</th>
<th>REMEDY™ 2 GSR®</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE₂O₃, wt.%</td>
<td>1.5</td>
<td>1.0</td>
<td>Trace</td>
</tr>
<tr>
<td>Al₂O₃, wt.%</td>
<td>51</td>
<td>51</td>
<td>47</td>
</tr>
<tr>
<td>Zeolite Surface Area, m²/gm</td>
<td>200</td>
<td>200</td>
<td>220</td>
</tr>
<tr>
<td>Matrix Surface Area, m²/gm</td>
<td>90</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>0 to 40μ, %</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

Results

The following REMEDY™ 2 GSR® data reflects operating data after over 50% of the La₂O₃ had been purged from the inventory. GENESIS® GSR® data represents weekly test run data from March 2010 to July 2010, while REMEDY™ 2 GSR® data is from November through December 2011 operations. During the GENESIS® GSR® operation ~7.5% OlefinsMax® (ZSM-5) was used, while the REMEDY™ 2 GSR® operation employed just 2.5% OlefinsMax®.

FIGURE 7: REMEDY™ 2 GSR® and GENESIS® GSR® Technology

FIGURE 8: Each Reformulation Occurred Prior to an Increase in Rare-Earth Price
Much of the MRC operating data is represented in box plots. An example of a box plot is shown in Figure 9. A box plot is a graphical summary of the distribution of a data set that shows its shape, central tendency, and variability.

Figure 9 shows the key parts of the box plot. Box plots can be used to quickly understand a data distribution and are particularly useful for comparing different data sets. The following box plots compare the data distribution between GENESIS® GSR® and REMEDY™ 2 GSR® at MRC.

Figure 10 shows that mean catalyst additions on a pound of catalyst per barrel of feed basis were maintained at ~0.14 lb/b for both GENESIS® GSR® and REMEDY™ 2 GSR® operations. Conversion corrected for 430°F for the REMEDY™ 2 GSR® operation was within the conversion range with GENESIS® GSR®. The median value conversion was 77.5 vol.% during the REMEDY™ 2 GSR® operation compared to 76 vol.% for the GENESIS® GSR® period.

General operating conditions and feed properties are shown in Figure 11. Feedstock API was lower with REMEDY™ 2 GSR® with a median value of ~26.5°API compared to 27.3°API with GENESIS®. Reactor temperature increased to 940°F while using REMEDY™ 2 GSR® and feed rates were ~150 bpd lower. Differences in key independent operating...
variables including reactor temperature, feedstock properties and feedstock temperature were modeled and the conversion differences between both periods were <0.25 vol.%. As a result, the conversion shifts shown in Figure 10 are not influenced by differences in operating temperatures and feedstock properties.

Coke selectivity was maintained with REMEDY™ 2 GSR® as Figure 12 shows similar coke yield versus corrected conversion between the two catalysts. Slurry cracking is a critical attribute for all catalyst systems and Figure 12 confirms that the operation with REMEDY™ 2 GSR® provided similar or lower slurry as a function of conversion.

Gasoline selectivities increased during the operation with REMEDY™ 2 GSR® as shown in Figure 12. Gasoline and LPG yields are corrected for ZSM-5 in Figure 12. Higher gasoline selectivity from rare-earth free REMEDY™ 2 GSR® confirms that the zeolite is stabilized similarly to a traditional rare-earth catalyst. Gasoline octane was maintained with REMEDY™ 2 GSR®.

Zero rare-earth catalyst often produces higher dry gas rates. However, similar dry gas rates as a function of reactor temperature were observed between REMEDY™ 2 GSR® and GENESIS® GSR® as noted in Figure 13. Dry Gas rates are very low at MRC, consistent with the low reactor temper-
Corrected conversion values for a given catalyst-to-oil ratio are similar for both operations, suggesting similar in-unit activity from both catalysts.

Equilibrium catalyst (Ecat) activity was maintained with REMEDY™ 2 GSR®. Figure 14 shows the median Ecat activity value of both REMEDY™ 2 GSR® and GENESIS® GSR® is identical at 71 wt.%. Zeolite surface area increased to a median value of 115 m²/gm with REMEDY™ 2 GSR® consistent with higher fresh catalyst zeolite surface area. Zeolite surface retention, the ratio of Ecat ZSA to fresh ZSA, is 54% for both catalyst systems, despite the lack of rare-earth stabilization in REMEDY™ 2 GSR®. Unit cell size median values dropped from 24.29Å to 24.27Å. A 24.27Å UCS confirms that the proprietary material in REMEDY™ 2 GSR® has successfully stabilized the zeolite. The traditional zero RE catalysts typically equilibrate to a zeolite UCS in the range of 24.21 to 24.24Å, depending on the severity of the unit. Constant activity and zeolite surface area retention were observed, despite a ~750 ppm increase of median values of vanadium plus sodium levels on Ecat.

**FIGURE 13: MRC Achieved Similar In-Unit Activity and Conversion with RE Free REMEDY™ without an Increase in Dry Gas Yield**
**Conclusions**

Commercial data at MRC confirms that rare-earth free REMEDY™ performance is comparable to the base rare-earth GENESIS® catalyst providing a significant economic benefit. Specifically REMEDY™ showed the following at similar catalyst additions at MRC compared to GENESIS®:

- Similar unit conversion
- Similar coke and slurry selectivities
- Higher gasoline selectivity
- Similar Ecat activity

Grace offers a family of REpLaCeR® catalysts with zero to low rare-earth that has comparable hydrothermal stability and acidity as a traditional rare-earth catalyst.

The REpLaCeR® family of catalysts is currently used in 52 refineries globally processing both VGO and resid. REpLaCeR® technology is a great alternative to rare-earth containing catalysts, mitigating the risk associated with the uncertainty in price and supply of rare earth.

**Acknowledgements**

The authors thank MRC management for permission to publish this data and Rosann Schiller of Grace for her valuable assistance.

**References**


6. www.montanarefining.com

Maximize Distillate Yield to Meet Growing Market Demand

Rosann Schiller  
Senior Marketing Manager  
Grace  
Columbia, MD, USA

Despite a mild winter thus far, industry analysts forecast ULSD demand growth in the second half of 2012. This is in part due to global demand growth for middle distillates\(^1\) and in part due to new sulfur regulations set to take effect later this year. In 2012, the State of New York will become the first state to require that all oil used for heating meet ULSD standards, which means that No. 2 heating oil sulfur levels will have to be reduced to 15 ppm. Other Northeast states have announced dates to phase-in ULSD for heating oil.\(^2\) The pending regulations could raise regional ULSD demand by 20%. Over the last 6 months, over 50% North-east refining capacity has been idled as well as the HOVENSA refinery in the Virgin Islands, which was a major importer of transportation fuels into the Northeast. The loss of refining volume serving the Northeast coupled with bottlenecks in the transportation network from the Gulf Coast could potentially result in high prices and potential shortages of ULSD in New York, Pennsylvania, and New England.

FCC and ART Synergy

Refiners with additional sulfur removal capacity can increase profitability by maximizing the refinery yield of ULSD. If you have room to process additional FCC LCO in your diesel hydrotreaters, Grace\(^\text{®}\) and Advanced Refining Technologies\(^\text{®}\) technical service can work with you to help maximize your refinery profitability by enhancing both the yield and quality of your diesel and heating oil blending streams. We’ve published numerous articles on the topic, which illustrate that the greatest challenge in a max LCO operation is managing the incremental bottoms yield that accompanies a reduction in unit operating severity. Positive yield impact can be achieved via an optimization of key operating variables discussed below.

<table>
<thead>
<tr>
<th></th>
<th>Competitive Catalyst</th>
<th>GENESIS(^\text{®}) 1 (Max Gasoline) relative to base</th>
<th>GENESIS(^\text{®}) 2 (Max LCO) relative to base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline, lv.%</td>
<td>Base</td>
<td>+3.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>LCO, lv.%</td>
<td>Base</td>
<td>+1.5</td>
<td>+5.0</td>
</tr>
<tr>
<td>Bottoms, lv.%</td>
<td>Base</td>
<td>-1.5</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

**TABLE 1: GENESIS\(^\text{®}\) Catalyst Delivers Flexibility to Shift Between Gasoline and LCO Operating Modes**
Maximizing LCO from the FCCU

In general the following process changes should be made as a refinery moves from a maximum gasoline/conversion operation to a maximum LCO operation:

- Remove diesel range material from the FCC feedstock
- Reduce gasoline endpoint
- Reduce FCC conversion by:
  - Reducing riser outlet temperature;
  - Raising feed temperature and;
  - Lowering Ecatal activity
- Initiate HCO or slurry recycle
- Optimize catalyst formulation

Grace has several low Z/M catalyst options to help you increase LCO yield. The workhorse high MSA catalyst in our portfolio is MIDAS®, which is well suited for any refiner seeking deep bottoms conversion. MIDAS® has been applied in over 100 refineries (Figure 1), alone or as part of a GENESIS® catalyst system. MIDAS® can increase FCC LCO yield and profitability by as much as $1.50/bbl.

Any refiner can take advantage of short term economic opportunities with a GENESIS® catalyst system. By simply adjusting the blend ratio of two complete FCC catalysts, we can shift the Z/M ratio of the total blend and deliver a significant selectivity shift in a short period of time. The refinery in Table 1 was able to improve profitability by shifting the catalyst formulation as well as operating conditions to match current market demand.

New Additions to the Portfolio

We are also pleased to offer two new choices for maximizing LCO and bottoms conversion the FCC. REBEL™ is the only 100% rare-earth-free high matrix FCC catalyst solution available in the marketplace. Introduced in the wake of the rare-earth crisis of 2011, REBEL™ utilizes Z-21 zeolite technology and is in nine commercial applications at press time. In testing, REBEL™ has been shown to have equivalent activity relative to MIDAS® in low to moderate metal environments. These yield shifts have been confirmed by several third party laboratories. Figure 2 demonstrates how without rare earth, REBEL™ achieves the similar activity (cat-to-oil ratio) as the rare-earth exchanged MIDAS® catalyst. In commercial testing, REBEL™ retained bottoms conversion and helped to maintain catalyst addition levels at baseline.

Another challenge of a max LCO operation is maintaining total liquid volume. LPG and gasoline may still be important products from the FCC even when diesel pricing is at a premium. In order to maximize total yield (and dollars) it is important to appropriately balance zeolite, matrix and activity. For those units that want to drive to maxi-
mum total fuels (gasoline + distillate) yield, but still require activity to stay within unit constraints, we recommend ALCYON® M technology. ALCYON® M combines the high activity zeolite of ALCYON® with the proprietary matrix architecture of MIDAS® in a single FCC catalyst that is primed to deliver deep selective bottoms conversion while maintaining total liquid yield. High hydrogen transfer activity in ALCYON® M facilitates conversion of the bottom of the barrel of aromatic feedstocks, such as those derived from coker gasoils and Canadian heavy crudes. If you still require more LPG, Grace’s light olefins additives such as OlefinsUltra® and OlefinsUltra® HZ can be pre-blended with your fresh catalyst to maintain LPG olefinicity despite reduced FCC severity.

In summary, Grace has multiple catalyst solutions in order to maximize LCO yield in your FCC. MIDAS® is our benchmark bottoms conversion catalyst, with commercial success well documented in over 100 refineries around the world. The same conversion capability can now be achieved without rare earth, which is available in the new Grace REBEL™ catalyst technology. Now in nine applications and growing, REBEL™ delivers similar activity and bottoms cracking conversion as MIDAS®. Lastly, for those units desiring deep bottoms conversion, but without sacrificing in-unit activity to get there, we can offer ALCYON® M catalyst. Designed for short contact time units desiring deep bottoms conversion, ALCYON® M will crack the bottom of the barrel without giving up activity or violating unit constraints such as circulation rate.

Contact your ART and Grace technical service reps to understand just how much more LCO you can produce and treat to maximize ULSD yield and profitability in 2012.

References
People on the Move

Grace has announced a realignment of its business into three operating segments: Grace Catalysts Technologies, Grace Materials Technologies and Grace Construction Products. “This new business segment structure allows us to align our segments more closely with our markets and to pursue operational efficiencies and reduce overhead costs,” said Chairman and Chief Executive Officer Fred Festa. “We are excited about the opportunities that lie ahead, and are as committed as ever to supporting and anticipating the needs of our customers.”

Reporting to Grace’s President and Chief Operating Officer Gregory Poling will be Shawn Abrams, President of Grace Catalysts Technologies. Abrams most recently served as Vice President, Refining Technologies within the former Grace Davison operating segment. The new Grace Catalysts Technologies segment includes catalysts and related technologies used in refining, petrochemical and other chemical manufacturing applications. 2011 revenues for this segment were approximately $1.4 billion. Grace’s Advanced Refining Technologies joint venture is managed in this segment.

Andre Lanning has been named General Manager- EMEA, Refining Technologies (RT). In his new role, Andre will have overall responsibility for all EMEA (Europe, Middle East, Africa) commercial and research business activities in support of the global RT strategy. He will be a member of the RT global leadership team, reporting directly to Shawn Abrams.

Li Yong has accepted the position of Managing Director, Refining Technologies (RT) China. In this newly created role demonstrating our long term commitment to the China market, Li will develop and lead commercial growth opportunities throughout China. Li has the unique set of experience, knowledge and relationships with government officials, customers and vendors, needed to accelerate our significant investments and growth in China. He will report to Jim Nee for all commercial activities and to Shawn Abrams for business development activities. His office will remain in Shanghai.

Dan McQueen has accepted the position of Director, Marketing & Business Development, Refining Technologies EMEA, reporting directly to Andre Lanning. In his new role, Dan will focus on improving our strategic position and portfolio within the EMEA region by bringing together the market requirements and trends, the R&D focus for technology development as well as ensuring our asset base meets current and future requirements.

Bob Riley has rejoined the North American Refining Technologies organization as a Technical Sales Representative. For the past two years as Commercial Development Manager, Bob has been successful in leading global sales and strategic partnership activities in the emerging biofuels market, enhancing the growth of the Renewable Technologies/Incubator business. In his new role, Bob will continue to support several of these start-up initiatives, while resuming responsibility for providing sales and technical service expertise to our Refining Technologies customers. Bob will assume account management responsibilities for several customers on the West and Gulf Coasts, reporting to Shahab Parva.
Grace’s Super DESOX® product line of SOx reduction additives provides an effective way to reduce wet gas scrubber caustic consumption, and improves the overall economics of SOx removal.

Sodium hydroxide, or caustic soda, is one of the most widely used commodity chemicals. Refiners utilize it in FCCU wet gas scrubbers (WGS) to remove SO₂ from regenerator flue gas stack emissions. Caustic pricing tends to be cyclical, depending not only on the demand for caustic, but also on the demand for the co-produced chlorine. The continued slow-down in the housing market has reduced the demand for chlorine derivatives, thus limiting caustic production, and has been a contributing cause in caustic soda price increases. Currently, caustic soda price is forecasted to exceed $600 per dry short ton through the third quarter of 2012—a price threshold where use of SOx reduction additives can be cost effective. This situation has prompted some refiners to consider use of Super DESOX® additives to reduce the SO₂ loading on their WGS.

The high efficiency of Super DESOX® additives, at modest SOx reduction levels, makes them an economically attractive option to reduce WGS caustic consumption. Using Super DESOX® MCD, Grace’s most cost-effective additive to reduce the amount of SOx going to the WGS, provides refiners an opportunity to lower caustic consumption. To illustrate the potential savings, consider an FCCU with uncontrolled SOx emissions of 700 ppmv upstream of the WGS. A moderate pick-up factor (PUF) of 30 at 40% SOx reduction is assumed for Super DESOX® MCD efficiency. Also assumed is that for every one mole of SOx removed, 2.2 moles of caustic could be eliminated. Optimal savings occur near 40% SOx reduction, potentially exceeding $220,000 annually in caustic consumption alone, while also taking into account the cost of the additive. Additional savings may result from reduced water, utilities, and waste disposal.

For more information on reducing WGS caustic consumption, please contact your Grace technical sales representative.

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**Eric Griesinger**  
Marketing Manager  
Grace  
Columbia, MD, USA
The escalating price of rare earth in fluid cracking catalyst sparked increased demand from refiners for equilibrium catalyst (Ecat) as a means to control expenses. During this same period, the available supply of high quality, low metals Ecat had decreased. In response to the shrinking supply of Ecat, Grace introduces TITAN™, a unique catalyst solution for removing contaminant metals from refining operations.

Unlike traditional equilibrium catalysts, TITAN™ is completely free of nickel, vanadium and additives. These contaminants can lead to elevated NOx, H₂, dry gas or coke, making TITAN™ a preferred option to avoid additional operating constraints. As shown in Figure 1, TITAN™ yields 2.5# lower cat-to-oil when compared with a standard 75 MAT equilibrium catalyst, providing even more value.

As with all Grace products, TITAN™ can be offered in blends with any combination of fresh catalysts, equilibrium catalysts and additives. Although TITAN™ is manufactured as a fresh catalyst product, Grace’s continuous improvement initiatives along with investments in new processing equipment allows for TITAN™ to be offered without a rare-earth surcharge. TITAN™’s performance is backed by the support of our Grace world-class Technical Service team.

For additional information on TITAN™, please contact your Grace representative.

Figure 1: TITAN™ Delivers Lower Cat-to-Oil Ratio vs. a Standard Ecat.
Grace Upgrades Ecat Test Laboratory in North America

In an effort to improve our level of customer service, Grace has completed a major upgrade to our routine equilibrium catalyst (Ecat) evaluation program. This past September, we renovated the Ecat testing laboratory in Curtis Bay, MD and commissioned Advanced Cracking Evaluation (ACE®) units for routine sample analysis. The new ACE units replaced the Micro Activity Test (MAT) which was historically used to evaluate Ecat performance.

Transition from MAT to ACE is a significant step forward and enhances the quality of our Ecat testing. The new ACE testing will improve the precision of the Ecat activity measurement.

Did you know?

The feed rate in a MAT or ACE unit is 1/1,000,000 of the size of a commercial FCCU, hence the conversion measured is the $10^{-6}$ activity or microactivity.

In addition to the instrument upgrade, we have also changed our standard feedstock to reflect the observed increase in industry resid processing. The new feedstock is heavier, containing more ConCarbon and 1050°F+ material than the previous benchmark.

Grace remains committed to providing our customers with superior technical support and in 2012, we will be completing a similar ACE upgrade in our Ecat testing laboratory in Worms, Germany.
Global growth in distillate demand has driven refiners to investigate ways to increase middle distillate yields. Figure 1 shows the diesel-gasoline spot price differential for the Gulf Coast. As the figure demonstrates, diesel prices have remained strong relative to gasoline prices which are incentivizing refiners to look for more opportunities to increase diesel yield. Options for refiners include increasing diesel yield from FCC Pretreat units by operating in a mild hydrocracking (MHC) mode or extending the endpoint of the feed to a diesel unit and converting the heavy fraction into distillate range material.

There are many challenges associated with both approaches utilizing the mild hydrocracking (MHC) approach, with a significant one being the need to minimize production of excess light ends and naphtha to avoid overloading the existing downstream fractionation system. These issues become even more important as end of run approaches and the reactor temperatures are higher which increases the conversion of the MHC catalyst. Another potential obstacle is dealing with the possible negative impacts on other diesel from product properties such as diesel product color and cold flow properties.

Many of these concerns can be alleviated through the proper design and selection of a catalyst system for the hydrotreater. Advanced Refining Technologies® (ART) has conducted extensive pilot plant work in an effort to better understand these potential options for refiners wishing to increase diesel yields. This work has shown that a catalyst system design approach incorporating a mild hydrocracking component is a viable option for the production of higher yields of middle distillate.

The use of an MHC catalyst component in the FCC pretreater allows for an opportunity to achieve incremental conversion above that typically experienced with a hydrotreating catalyst system. In addition, the operating mode of the FCC pretreater can be used to adjust overall yields of gasoline and middle distillate giving the refiner more flexibility to change the product mix to meet market demands. In order to assess the effectiveness of the MHC catalyst it is important to understand the level of boiling range shift that can be achieved simply thought hydrotreating. 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 through saturation of aromatic rings. The table demonstrates that a fair amount of boiling point shift occurs through hydrotreating.
Understanding the different catalyst attributes and their impact on unit performance is important to designing the best catalyst system. Most hydroprocessing catalysts have an acidic and an active metals component. For typical hydrotreating catalysts these metals are either cobalt-molybdenum or nickel-molybdenum on an alumina or silica-alumina support. In a hydrocracking catalyst a significant amount of the support is made with amorphous silica-alumina or zeolite. This substantially increases the acidity of the catalyst and is what gives hydrocracking catalyst cracking activity. In a typical hydrocracker NiMo hydrotreating catalyst is used to convert organic nitrogen to ammonia since hydrocracking catalysts are poisoned by organic nitrogen. This allows the hydrocracking catalyst to effectively perform its cracking function.

In mild hydrocracking (MHC) the goal is to achieve a lower amount of cracking conversion compared to a full conversion hydrocracker, so organic nitrogen levels can be relaxed. It does, however, require properly balancing the amount of hydrocracking catalyst with hydrotreating catalyst in order to achieve the optimum in terms of yields and product qualities.

One recent study completed by ART investigated the tradeoffs observed by adding MHC catalyst to the catalyst system in an FCC pretreater. The feedstock used in this work is shown in Table 2. The feed is full range vacuum gas oil (VGO) with just over 1600 wppm nitrogen and 2.75 wt.% sulfur. The breakdown of the aromatic compounds present in the feed is also given. The feed is relatively aro-

<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>Benzothiophene</td>
<td>430</td>
<td>ethyl Benzene</td>
<td>277</td>
</tr>
<tr>
<td>Decylmercaptan</td>
<td>455</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>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>β-Naphthoquinoline</td>
<td>662</td>
<td>α-propyl Naphthalene</td>
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<tr>
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<td>Tetralin</td>
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<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**
matic and has a significant quantity of poly aromatic compounds. One of the goals of this work was to investigate the tradeoff in HDS/HDN activity with cracking activity as more MHC component was incorporated in the catalyst system. The hydrotreating catalysts selected were current generation Type II catalysts from ART’s DX® catalyst series. The MHC components were selected based on cracking activity and selectivity to diesel products.

Figure 2 shows how the HDS activity of the catalyst system changes as the fraction of the MHC component increases. Not surprisingly, the base case hydrotreating catalyst system, which contains no MHC catalyst, shows the highest activity for HDS. Adding in 10% MHC catalyst results in essentially the same HDS activity as the base case system. Increasing the MHC component to 20% results in a slight decrease in HDS activity at low temperatures, but the same HDS activity at higher temperatures. Finally, at the highest fraction of MHC catalyst (35%) the HDS activity is consistently lower than the base case activity suggesting that the system contains too much MHC catalyst relative to hydrotreating catalyst.

A comparison of the HDN activity of the different catalyst systems is shown in Figure 3. Again the base case system shows the highest activity, but only for lower HDN conversion (higher product nitrogen). Interestingly, the data shows that adding in MHC catalyst results in a system which has higher HDN activity relative to the base case for higher nitrogen conversions. This suggests that the stronger acidic function of the MHC catalyst improves nitrogen removal of the catalyst activity. Note that increasing the fraction of MHC catalyst too far does result in a decrease in HDN activity except for very high nitrogen conversions.
In terms of HDS and HDN activity there is an interesting interaction between the hydrotreating and MHC catalyst components. HDS activity is not significantly affected by the addition of MHC catalyst until higher percentages are reached. For HDN activity there is an optimum level of MHC catalyst where HDN activity is improved over the base case performance. Figure 4 summarizes how the cracking conversion is impacted by the addition of MHC catalyst to the system. The conversion is defined as the difference between the amount of 680°F+ material in the feed and product. The figure shows that at lower temperatures all the catalyst systems behave similarly and show the same level of boiling range shift as achieved with hydrotreating alone. As the temperature is increased there is a point at which the conversions for the MHC catalyst systems start to differentiate themselves from the base case.

The conversion observed for the base case increases only gradually as temperature is increased. Adding only 10% MHC catalyst results in a slightly faster increase in conversion with increasing temperature, and adding 20% MHC catalyst results in an even faster increase in conversion. The 20% system provides 10 numbers higher conversion relative to the base case with only about a 10-15˚F increase in temperature.

Figure 4 also shows that there can be too much MHC catalyst in the system. Adding as much as 35% MHC catalyst actually results in a decrease in conversion relative to the 20% system. This is primarily due to the fact that the 35% MHC system no longer has enough hydrotreating activity, so the MHC catalyst is severely poisoned by organic nitrogen slipping though the hydrotreating catalyst bed.

Figure 5 summarizes the middle distillate yield (360-680°F) achieved from each catalyst system. The distillate yield is essentially the same for all catalyst systems at low temperature similar to what was observed in Figure 4. At higher temperatures the systems again begin to differentiate themselves. The distillate yield increases with increasing amounts of MHC catalyst, but again there is an optimum amount of MHC catalyst which maximizes the diesel yield beyond which the diesel yield decreases.

The mild hydrocracking approach to increase distillate yields will result in an increase in hydrogen consumption over a hydrotreating base case. Product API increase is often used as a rough indication of hydrogen consumption, and is shown in Figure 6 for the different catalyst systems in this study. Not surprisingly, the data exhibits similar behavior as described for conversion and distillate yield where there is a point where too much MHC catalyst has a negative impact on unit performance. The systems all provide about the same increase in API gravity at lower temperatures, and, similar to what was observed with cracking conversion, the various systems provide different degrees of API uplift at higher temperatures. Note again that the system containing 20% MHC catalyst stands out in terms of the whole liquid product API increase.
In addition to increased diesel yields and an increase in hydrogen consumption, it is important to consider the impact of MHC on the diesel product properties. In most cases the diesel resulting from an MHC operation will have to be further hydrotreated in order to be used in the ULSD pool. Operating in areas of lower conversion, the sulfur in the diesel fraction is similar with the lower levels of MHC catalyst, and decreases as the system approaches 35% MHC catalyst as shown in Figure 7. When changing the operation to higher conversion targets in order to produce more distillate products, the product sulfur can drop to what appears to be quite low until the quantity of MHC catalyst goes beyond the point where the hydrotreater can actually remove the sulfur efficiently. In this case, it makes a higher sulfur product.

The diesel product nitrogen shows a slightly different response. As one might expect, as the MHC catalyst concentration is increased, the system is more efficient in nitrogen removal. Figure 8 compares the diesel product nitrogen with the percent MHC catalyst at both lower conversion and high conversion points. The data show that at high conversion there is an optimum quantity of MHC catalyst in order to achieve the lowest product nitrogen. Lower product nitrogen can also be associated to some degree with lower aromatic content due to the need to saturate or open ring molecules to remove the bound nitrogen.

There are also other improvements in the diesel quality that can be affected with MHC. Figure 9 compares the improvement in cetane index at three MHC conditions. At lower operating temperatures and conversion, the addition of excess MHC catalyst can have a negative impact on cetane index relative to simple hydrotreating. This does not make the cetane index poor, simply that it is lower than conventional hydrotreating. Increasing conversion shows that there is an improvement in cetane index, which when coupled with the product sulfur and nitrogen data, indicate that there is an optimum in order to achieve the greatest yield of distillate products with the greatest value to the refinery.

Choosing the correct MHC catalyst system is critical to avoid too much conversion throughout the cycle as well as being able to tailor the HDS and HDN activity. Excess or undesirable cracking or poor hydrotreating performance can cause a refiner to be limited on available hydrogen or short on cycle life, thus hurting the performance of the hydrotreater. Balancing the differences between selectivity for cracking and the HDS/HDN activity is critical to a stable system as well as the yield slate.

Figure 10 shows the differences in conversion between two different MHC catalysts. MHC 1 exhibits a higher hydrocracking activity as compared to hydrogenation activity, whereas the reverse is the case for MHC 2. It is apparent from the figure that a more active MHC catalyst can achieve higher conversions even when a lower volume is used in the system. This adds another degree of flexibility when designing a system to meet specific objectives, as less MHC catalyst allows for improvements in HDS, HDN and HDA.
There is an optimum in terms of the relative amounts of MHC and hydrotreating catalysts which delivers the best combination of HDS, HDN and conversion activity. Clearly there is a need to maximize the HDS and HDN activity as well as saturation when trying to determine the optimum system. As the data just discussed indicates the catalyst selection has a significant impact as does the quantity of MHC catalyst in the hydrotreater. High activity MHC catalysts are better at boiling point conversion and can be utilized in a system that is limited in HDS and HDN in order to minimize the impact on the downstream FCC. The use of even a small amount of MHC catalyst will prove to be beneficial in order to alter the boiling range of the product and to minimize any impact on the removal of the difficult sulfur and nitrogen.

Advanced Refining Technologies can work closely with refining technical staff to help in selecting the appropriate MHC system to take advantage of this opportunity. One of the keys is being aware of the potential impacts MHC operation will have on unit performance. This process presents unique challenges and ART is well positioned with its experience at providing customized catalyst systems for FCC and MHC FCC applications. Opportunities exist for the refiner to consider when choosing the appropriate catalyst system to maximize unit yields and performance.
SAVE THE DATE

Join Grace and Advanced Refining Technologies for our Biennial Seminar

Thursday, August 23, 2012
Location TBA
Houston, Texas

Save the date to hear the latest on FCC and hydroprocessing catalysts technologies. Industry experts will also be on hand to discuss trends on catalysts and processes.

For more information or to be put on the mailing list, contact betsy.mettee@grace.com.