70th Anniversary of FCC
Only Grace Catalysts Technologies offers refiners a full portfolio of high technology, state-of-the-art FCC catalysts and additives. Driven by our world-class research and development in the U.S. and Europe, only Grace Catalysts Technologies can customize products designed specifically to optimize your operation.

Our industry-leading technical service provides support, including unit monitoring and troubleshooting, backed by our high level of analytical services including Ecat, spent catalysts and fines analysis.

We have been the leader in FCC catalysts since inventing the first FCC catalyst over 70 years ago and we are committed to the future of the refining industry.

Have Grace Catalysts Technologies design your optimal catalyst. Contact us.

We don’t just make FCC catalysts, we make FCC catalysts for you.
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In August 2012, Grace hosted the 3rd Biennial Houston FCC seminar where we celebrated the 70th anniversary of the FCC process. At the seminar, industry analysts from Wood Mackenzie and Hart discussed the challenges and opportunities North American refiners face as product demand shifts to emerging regions and unconventional feedstocks become the norm. We hosted an expert panel comprised of refiners and industry consultants that focused on operating flexibility. Our customers, along with Grace engineers, presented updates on our newest products.

One of the most interactive talks of the day was given by Phil Niccum of KBR. He presented a thorough review of the history of the FCC process titled: “FCC: Driven by Competition, Fueled by Trial.” Initiated as part of the war effort, a 1,000 member consortium was formed to invent a process to increase supply of high octane aviation gasoline. The consortium was comprised of scientists and engineers, who enjoyed an unprecedented level of cooperation as they worked towards a common goal. That team needed only a few short years to take the FCC process from concept to commercial scale, and the first FCCU was started up in Baton Rouge LA on Davison, now Grace, synthetic silica-alumina catalyst in 1942. Rapid growth in the industry immediately followed. Three FCC’s built by Kellogg in the 1940’s at the Citgo refinery in Lake Charles, later prompted the construction of the largest FCC catalyst manufacturing facility, our Lake Charles plant. Interestingly, Niccum said, “The design life for FCC was originally 5 years, because that was how long they believed the war would last; [FCCU’s] were not built to last.” Yet here we are celebrating the 70 years of FCC; many of those same units are still running, and most incredibly, the FCC process itself remains largely unchanged. And, from the reaction to Niccum’s paper, there is no lack of interest in its history or the future potential of FCC as a key process unit in the refinery.

In this issue we are featuring several of the seminar papers that highlight how FCC catalyst technology can expand the FCC operating window to maximize profitability, and how pilot testing can be used as a predictor of performance. We also have provided updates on our organization and global technical service activities. We at Grace remain committed to providing world-class technical service and product innovation to enable you, our customers, to remain successful now and in the years to come.

Sincerely,

Rosann K. Schiller
Senior Marketing Manager
Grace Catalysts Technologies
Enhanced Bottoms Cracking and Process Flexibility with MIDAS® FCC Catalyst

This premium bottoms cracking FCC catalyst family is formulated with advanced zeolite stabilization technology plus matrix metals passivation technology and has been successfully applied to a wide range of feed and feed contaminants.

Middle distillates, including on-road and off-road diesel, marine fuels and No. 2 heating oil, represent the largest and a growing market share of refined petroleum products. However, the renaissance of North America crude production will have a profound effect on refinery yield slate. Many of the new crudes are lighter and will increase refinery light ends yield. Growing volumes of domestic crude are being processed outside of PADD's II and III despite pipeline congestion. Several refiners have announced projects to source light oil via rail, barge or truck to plants along the US East and West coasts. Longer term, surpluses are expected in the lighter products (LPG and naphtha) and deficits forecasted for gasoil and diesel.

Overall, the trade balance for distillate streams is tight globally. The closures of large refining complexes in the Atlantic basin, changing fuel specifications, and growing demand for gasoil and distillate in the emerging regions and Europe add to the expected supply imbalance. Amid declining gasoline demand in North America, refiners require an FCC catalyst that enhances distillate production yet selectively minimizes light product yield. In a world where fuel demand is satisfied through a careful balance of free trade, a single storm or refinery upset often triggers price volatility in product markets. The ability to respond quickly to capture short-term market opportunities is critical. Grace's premium bottoms cracking family, the MIDAS® catalyst series, can be used to enhance your FCC process flexibility and capture incremental profit as opportunity arises. MIDAS® cracks deep into the bottom of the barrel, enhancing total distillate and liquid yield, and has been proven in over 100 refineries that vary broadly in feed composition and operating modes. The flexibility that MIDAS® brings to your refinery, used neat or as a component in a GENESIS® catalyst system, can enhance the yield value by $0.40-1.00/bbl of FCC feed.

MIDAS® is a moderate zeolite to matrix ratio FCC catalyst that has been successfully applied in half of all the North America FCCU capacity. Its success is driven by the fact that MIDAS® effectively cracks all feed types: heavy resids, severely hydrotreated light feeds, and shale oil-derived feed streams, via the three-step
bottoms cracking mechanism discovered by Zhao. The catalyst design minimizes the thermal and catalytic factors that result in coke formation. The result is deep bottoms conversion, regardless of the starting feedstock.

Resid streams present the greatest challenge in terms of deep bottoms conversion. The dynamic molecular dimensions of paraffins and aromatic species vary based on carbon number and molecular configuration. Paraffins species present in the 700-1000°F boiling point fraction of FCC feed are typically in the nC14 to nC34 range for normal paraffins. The dynamic molecular size of these compounds is 12-20 angstroms (Å). The heavy resid fraction also contains an abundance of aromatic molecules (C14 to C60) in the 700-1000°F boiling range. The range of molecular size for aromatics is 12-25Å. Even aromatic carbon molecules up to 60 carbon number are still less than 30Å in molecular size.

Porphyrins are organic, cyclic macromolecules that consist of a ring of nine or more atoms. Porphyrins are aromatic species often present in resid fractions and characterized by a central gap that can bond to a metal atom, such as nickel, vanadium, or iron. If a porphyrin is complexed with vanadium, it is termed a vanadyl porphyrin. The size of these metallic complexes also varies with carbon number, but is in the same dimensional range as typical resid hydrocarbons: 10-30Å.

The relatively large molecules at the bottom of the barrel that need to be converted must first be cracked by the catalysts’ matrix acidity. With molecular sizes of 10-30Å, the hydrocarbons are too large to fit into the zeolite pores, which are typically below 7.5 Å. It is important that the catalyst have the proper pore size distribution to enable large feed molecules to enter, crack into lighter products, and diffuse out before being over-cracked to coke and gas. For free diffusion of resid molecules (>1000°F) to occur, the catalyst pore diameter needs to be 10-20x the size of the molecule, or 100-600 Å. The desired pore volume should be in the large mesopore region 100-600 Å. The benefit of mesoporosity for bottoms cracking is well understood. However, not all the measured pore volume is created equal. Catalysts with similar total pore volume measurements can vary widely in pore size distribution. MIDAS® is designed to have high mesoporosity in the 100-600 Å range, typically twice as high as competitive offerings (Table 1). Optimal porosity is required for effective kinetic conversion of bottoms. Midas catalysts crack deeper into the bottoms than competitive technologies in the market today.

Commercial examples of high MIDAS® mesoporosity, as measured by Hg porosimetry of Ecats, are shown in Figure 1. Note that Hg intrusion measures the porosity greater than 36 Å, therefore the result specifies the porosity associated with the catalyst matrix only; N2 adsorption or desorption must be used to capture zeolite porosity. Grace’s in-house manufacturing and quality monitoring of the specialty alumina used in MIDAS® provides control over the resulting porosity. It is generally accepted that micropores (<100 Å diameter), though effective for cracking, lead to poor coke and gas selectivity as a result of poor diffusivity and over-cracking. Some competitive benchmarks with high surface area and activity are also high in matrix microporosity, resulting in wet gas compressor limitations that suppress feed rate and ultimately profitability. In contrast, MIDAS® catalyst has the lowest amount of small pores and the highest amount of large mesopores. Optimal porosity guarantees best-in-industry gas selectivity and coke-selective bottoms conversion. High pore volume also serves to enhance the fluidization characteristics.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Micropores</th>
<th>Mesopores</th>
<th>Macropores</th>
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<tr>
<td>Total</td>
<td>36-100Å</td>
<td>100-600Å</td>
<td>600+Å</td>
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<td>MIDAS®</td>
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<td>0.092</td>
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<td>MIDAS®</td>
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<tr>
<td>Cat 2</td>
<td>0.413</td>
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**Table 1: Mesoporosity Comparison with Competitors**

**FIGURE 1: Pore Volume Comparison of Commercial Ecats**
Several units have observed substantial improvement in the Ecatal fluidization factor following a reformulation to MIDAS® or GENESIS®. Later in this paper, the selectivity advantages of MIDAS® will be highlighted with commercial examples of catalytic performance.

The proprietary matrix in MIDAS® can withstand the most severe applications, particularly those challenged by high levels of contaminant iron and calcium. High alumina content in FCC catalyst is known to reduce the degradation of the catalyst surface due to Fe and/or Ca poisoning. Optimum distribution of mesoporosity also plays a role in maintaining performance, because diffusion to the active sites remains unhindered despite the high contaminant metals. MIDAS® has been successful in maintaining bottoms conversion in units with some of the highest levels of contaminant Fe on Ecatal in the industry.

A good bottoms cracking catalyst requires high matrix surface area (MSA). However the activity of a high matrix catalyst needs to be balanced with an appropriate level of zeolite without compromising attrition characteristics. Additionally, an appropriate rare-earth exchange level on the zeolite is critical to ensure optimal coke selectivity. An optimum exists in the relationship between zeolite unit cell size (UCS) and coke selectivity. Too often, high matrix catalysts also have a high UCS, meaning they are over-exchanged with rare earth. Low zeolite input formulations with high rare-earth exchange (albeit low total rare earth on catalyst) will retain a higher percentage of the fresh zeolite surface area in a severe regenerator, but the penalty for this over-exchanged zeolite is poor coke selectivity. The rare-earth exchange in MIDAS® catalysts is optimized to result in a formulation that lays in the so-called ‘sweet’ spot for best coke selectivity. Table 2 shows the average Ecatal properties of MIDAS® relative to competitive high MSA catalysts. The right distribution of mesoporosity coupled with optimal activity and UCS gives MIDAS® the coke selectivity edge in commercial cracking.

**Commercial Experience**

MIDAS® design features have led to superior performance in many commercial examples. The first example comes from Refinery A that has an FCCU processing a mix of VGO and light resid. The feed is moderately high in metals with good cracking characteristics. The base catalyst was a competitive high MSA catalyst with high rare-earth exchange. The unit suffered from a dry gas constraint, especially in the summer. When the refiner switched to MIDAS®, a 5-10% drop in total dry gas yield at equivalent riser temperature and metals loadings was observed (Figure 2A); this allowed the refiner to maintain maximum feed rate throughout summer. The better coke selectivity of MIDAS® also manifested itself in better coke to bottoms. The charts shown in Figures 2A-C contain actual unit operating data, normalized and presented on a relative basis, demonstrating the superior selectivity of MIDAS®.

**TABLE 2: MIDAS® has an Optimal UCS to Minimize Coke**

<table>
<thead>
<tr>
<th>Z/M</th>
<th>MIDAS®</th>
<th>Competitor A</th>
<th>Competitor B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.9</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**FIGURE 2A: MIDAS® Delivers Improved Gas Selectivity at Refinery A**

**FIGURE 2B: MIDAS® Reduced Bottoms Yield Despite Higher Rates of Resid at Refinery A**

**FIGURE 2C: MIDAS® Improved Bottoms Cracking and Coke Selectivity at Refinery A**
At Refinery B, the FCCU was also processing light resid using a high matrix, high UCS competitive catalyst. While rare-earth levels on the zeolite were high, the catalyst itself had low total rare earth because zeolite input was very low. In spite of the high rare-earth exchange and resulting UCS, the unit was constrained on total wet gas and bottoms yield. There wasn’t enough zeolite present to complete the second stage of the bottoms cracking mechanism. Zeolite is critical to reduce the size of the hydrocarbon via dealkylation. Insufficient zeolites cause coke precursors to condense on the catalyst surface and become coke before they can be converted into transportation fuels. Poor coke selectivity translates into subpar bottoms conversion.

Introduction of MIDAS® provided a reduction in bottoms make on the order of 8% for Refinery B. Higher zeolite and optimal UCS improved coke selectivity, and the refinery increased not only the fresh feed rate but also the amount of resid in the feedstock by almost 10%. Higher zeolite also increased the circulating activity, enabling a reduction in catalyst additions on a lb/bbl basis. Incremental resid at lower cat additions caused Ecat metals to increase by 1,000 ppm, which drove a corresponding increase in dry gas. However, the balanced zeolite and matrix surface areas of MIDAS® meant that more feed was converted into valuable gasoline and distillate, rather than LPG and coke (Figure 3).

At Refinery C, the FCCU was processing resid feedstock high in iron (Fe) and calcium (Ca). Over time, the unit suffered from classic symptoms of iron poisoning. As iron nodules built on the surface, Ecat activity, unit conversion and bottoms cracking all began to suffer. A switch to MIDAS® provided higher activity and improved coke selectivity (Figure 4). The coke selectivity advantage drove deeper bottoms conversion. Eventually the feed became heavier and more contaminated. Midas never lost its selectivity edge over the competitive high MSA formulation, despite subsequent increases in Fe + Ca. The high mesoporosity is particularly effective in preventing a loss in cracking activity often seen during periods of high metals loadings. Fe + Ca can form eutectics that serve to essentially melt over the catalyst surface, blocking pores and suppressing conversion. The high mesoporosity of MIDAS® ensures that high diffusivity is maintained. MIDAS® is the preferred FCC catalyst technology for FCCUs processing high Fe feedstocks.

Refinery D routinely processes heavy resid in the FCCU. Similar to the other examples, the objectives were to reduce dry gas and improve the yields of liquid fuels (Gasoline + Distillate), without compromising feedrate. A switch to MIDAS® catalyst met the objectives despite deteriorating feed quality coming to the FCC. Over time, the feedstock became heavier, contained more Concarbon, and had higher metals loadings. Lower dense bed temperatures minimize thermal cracking, reducing dry gas yield. Slurry yield was held constant (Figure 5).
The primary operating objective of the FCCU at refinery E is to maximize LCO yield. Reformulating to a high matrix catalyst from the starting low matrix catalyst presented a challenge for this refinery. A wholesale change in the catalyst formulation was deemed to be risky. Grace introduced MIDAS® to the FCCU in a step-wise fashion. Initially, MIDAS® was blended with their base high zeolite catalyst (also a Grace catalyst) in a 50/50 ratio. The FCCU realized a reduction in slurry yield of 12% (Figure 6). Refinery E later increased the amount of MIDAS® to 100% of the fresh catalyst requirement. Again, a step-change improvement in slurry was observed, and the incremental conversion was maintained as distillate as desired. Higher distillate yield (+15%) was observed over a wide range of conversion levels with MIDAS® over the original base catalyst.

FIGURE 4: Despite Higher Contaminant Metals, MIDAS® Improved Bottoms Cracking and Coke Selectivity at Refiner C

FIGURE 5: At Refinery D, MIDAS® Increased G+D Yield and Reduced Dry Gas at Similar Feed Rate
**Performance Summary**

MIDAS® is Grace’s premium high matrix bottoms cracking catalyst family. MIDAS® is designed to possess the key characteristics necessary for selective conversion of heavy FCC feed molecules. These characteristics are controlled during proprietary manufacturing processes of Grace specialty aluminas, zeolites and ultimately the whole catalyst itself. The net result is a product with:

- Maximum matrix mesoporosity to minimize coke and gas formation and maximize bottoms upgrading
- Ideal pore size diameters to preserve free diffusion in and out of the catalyst, even in the face of metals contamination
- Optimized rare-earth exchange to deliver best-in-industry coke selectivity
- Balanced zeolite-to-matrix activity to maximize product value from the FCC

MIDAS® contains the highest mesoporosity in the desired range of 100-600 Å and the most optimal UCS in the market, providing a clear selectivity advantage over competitive catalysts. Several distinct grades are available, suitable for a wide range of feed and operating objectives. The catalyst’s excellent in-unit fluidization properties are an ideal solution for FCCs with fluidization or circulation difficulties. Applied neat or in a GENESIS® catalyst system, MIDAS® provides refiners the option of running difficult or opportunity feedstocks to the FCC without suffering from poor coke and gas selectivity. Finally, MIDAS® provides the flexibility to fine-tune the yield of the individual product streams to exploit short or long term economic opportunities.

In summary, MIDAS® FCC catalyst should be considered by any refiner who desires:

- Deeper bottoms cracking
- Enhanced bottoms conversion against an air blower constraint
- Ability to process high Fe and Ca feedstocks, such as Bakken or Eagle Ford
- Incremental fuels yield, i.e., LCO or G+D maximization
- Relief against a wet gas compressor constraint when cracking resid
- Capability to process opportunity crudes
- Improved catalyst fluidization characteristics
- Flexibility to capture the value of opportunity crudes
- Ability to shift between gasoline and distillate modes of operation
- Rapid catalytic response to capture short-term economic opportunities

**FIGURE 6:** Refiner E Observed Higher Distillate Yield Over a Range of Conversion Levels with MIDAS®
In our continuing effort to support the growth and productivity activities in Grace Catalysts Technologies, the following changes have been made in the Refining Technologies organization:

**Hongbo Ma** recently transferred to FCC Technical Sales Representative, reporting to Jeff Koebel. Since joining Grace in 2007, Hongbo was a Senior R&D Engineer for Technical Support in RT. He holds a Ph.D. in Chemical Engineering from the University of Wisconsin.

**Jeff Koebel** has been promoted to the position of National Technical Sales Leader, reporting directly to Bob Gatte. Jeff joined Grace in 2004 and has been serving as Technical Sales Representative within the RT North America business. Before joining Grace, Jeff spent 14 years at UOP, serving as a Design Engineer, before being promoted to a Senior FCC Technology Specialist. Jeff has a B.S.in Mechanical Engineering from the University of Illinois.

**Kristen Wagner** recently transferred to FCC Technical Sales Representative reporting to Jeff Koebel. Kristen, who was previously Clean Fuels Product Manager in RT Marketing, joined Grace in 1997 as a Process Supervisor at our Curtis Bay Works. She has held various positions in Manufacturing, Quality Assurance and Marketing at Grace. Kristen received her B.S.Ch.E from the University of Maryland.

**Steve Gremillion** recently joined Grace as an FCC Technical Sales Representative reporting to Shahab Parva. Prior to joining Grace, he held process engineering positions at CITGO Petroleum, JAB Energy Solutions and Polaris Solutions. A registered Professional Engineer, Steve holds a B.S.Ch.E from McNeese State University.
Grace Catalysts Technologies successfully commercialized the REpLaCeR® family of catalysts that include low and no rare-earth (RE) catalysts such as REACTOR®, REBEL®, RESolution®, ResidUltra™, REMEDY® and REDUCER® for both hydrotreated and resid feed applications. The zero RE formulations utilize Z-21 and Z-22 zeolites that are stabilized with proprietary elements to match the performance of corresponding RE-USY zeolites. A number of articles\(^1\)-\(^4\) have been published to demonstrate their similar surface area stability and unit cell size (UCS) as compared to traditional RE catalysts, and their commercial success.

REACTOR\(^®\) is a RE-free catalyst built upon Grace’s alumina-sol technology platform and incorporates the new rare earth-free zeolite, Z-22. The alumina sol platform provides superior binding properties, minimizing catalyst attrition and maximizing unit retention. The breakthrough Z-21 zeolite technology in REBEL\(^®\) offers similar performance as compared to base RE containing MIDAS®, providing a significant economic savings. Despite the absence of rare earth, REBEL\(^®\) has metals tolerance similar to the benchmark MIDAS® formulation.

REMEDY® and REDUCER® catalyst systems contain a mix of RE-free and RE-containing catalyst technologies that are optimized to match the specific unit feedstock for the best economic value. The formulation flexibility provides optimal performance via excellent coke selectivity, enhanced bottoms cracking and high metals tolerance.

**Acidity of Z-21 and Z-22 Zeolites**

The acidity measurement with ammonia STPD method (Stepwise Temperature Programmed Desorption) allows a differentiation of acid sites\(^1\). Zeolites possess heterogeneous acid sites of discrete strengths which can be identified by measuring the ammonia desorption at different temperatures. In a typical experimental setup about 2 g of sample is placed in a quartz reactor and calcined in inert gas flow; then NH\(_3\) is adsorbed at 150°C. The system is flushed with inert gas, and temperature is raised stepwise to 540°C to desorb the ammonia. Ammonia desorbs at different temperatures depending on the strength of acid sites; while the area of the peak corresponds to the number of acid sites. The higher temperature peak is the result of the strongest acid sites. Grace’s ultrastable Y zeolite (USY) was tested by STPD with and without any stabilizing elements (Figure 1). Grace’s Z-21 and Z-22 zeolites are comparable to RE-USY with low rare-earth exchange and superior to USY without any stabilizing agent.
Commercial Experience with REpLaCeR® Catalysts

The REpLaCeR® family of catalysts achieved deep market penetration while providing significant economic value to our customers in 69 refinery applications to date. As RE prices eased, the demand for these catalysts softened but they are still in over 50 FCC units globally. In addition to economic incentives, REpLaCeR® catalysts offer tangible yield benefits, beyond the cost of rare earth, and are expected to remain in the Grace RT FCC catalyst portfolio.

The REpLaCeR® family of catalysts offers both RE-free and low RE options. As shown in Figure 2, 40% of reformulations to a REpLaCeR® catalyst do not contain any RE; the remaining contain a mix of RE-free and RE-containing catalyst technologies that customize the catalyst recipe for specific refinery needs. The figure highlights that RE-free technologies are used to reduce the RE content between 20 and 100%. Typically, units that require high activity or units with very high metals content utilize a blend of Z-21 and/or Z-22 based catalysts along with traditional RE based catalysts. This catalyst-system approach lowers RE content while maintaining the performance advantages of rare earth, namely stable activity, and excellent coke and gas selectivity.

Commercial Success of REMEDY®

This article highlights one of such commercial successes at a refinery in the US with REMEDY® catalyst. The refiner using VGO feedstock started the commercial trial of REMEDY® replacing a competitive catalyst with the following objectives:

- eliminate rare earth market pricing risk,
- improve coke selectivity,
- increase LPG olefin yield without ZSM5,
- improve physical properties, and
- improve slurry conversion.

REMEDY® catalyst used in this particular refinery is a blend of 80% REBEL® and 20% Alcyon®. REBEL® is similar to the state-of-the-art MIDAS® bottoms cracking catalyst formulated with Z-21 zeolite instead of RE-USY and Alcyon® is an ultra-high activity Al-sol catalyst.
FIGURE 3: Properties of Competitor and REMEDY® Equilibrium Catalysts

FIGURE 4: Performance of Competitor and REMEDY® Equilibrium Catalysts by ACE Testing
The selected Ecatalyst properties of REMEDY® and competitor’s incumbent catalysts are plotted in Figure 3. The RE content of REMEDY® is about 50% lower resulting in a lower UCS. The ABD of REMEDY® is lower as a result of higher pore volume (PV). Ecatalyst zeolite surface area (ZSA) of REMEDY® is higher than the base by about 20 m²/g while the mesoporous surface area (MSA) is slightly lower (~5 m²/g).

The REMEDY® trial was evaluated at 80% turnover by conducting an ACE study where Ecatalyst samples of the incumbent competitor’s catalyst and REMEDY® were tested on the refinery’s own feedstock. Ni and V contents on REMEDY® were higher than the incumbent catalyst. Even so, activity is higher, while gas and coke factors are lower on REMEDY® catalyst, demonstrating its excellent stability.

The change in operating conditions and yields after moving to REMEDY® are summarized in Table 1. The feed temperature dropped by 10 °F and regen dense temperature dropped by 7 °F while the coke remained the same.

REMEDY® is slightly more active and yields higher gasoline, lower LCO and lower bottoms. It also maintained excellent gas and coke factors despite increased nickel and vanadium contents. The higher pore volume in REMEDY® helped the strippability of hydrocarbon and reduced regeneration temperature. Lower carbon on catalyst indicates improved regenerator efficiency and higher effective “in unit” activity. The lower ABD coupled with better catalyst retention and physical properties enhanced the fluidization characteristics of the inventory.

### Summary

REMEDY® demonstrated excellent in-unit performance, achieving all the performance benefits expected by the refinery. The use of REBEL®, a RE-free catalyst, allowed reduction of RE by about 50%. Although RE prices have stabilized since last year, the yield benefits provided by REMEDY® continue to provide economic incentives for the refinery beyond the risk related to RE supply and price. At constant reactor temperature and feed rate, REMEDY® demonstrated the following against a competitor’s catalyst:

- Increased Conversion (+0.5 vol.%)
- Reduced Dry Gas (-20 scf/bbl)
- Increased \(C_3^+ + C_4^+\) Liquid Yield (+ 1.0 vol.%)
- Increased \(C_3^+ + C_4^+\) (+ 0.7 vol.%)
- Reduced Slurry (-0.2 vol.%)
- Lower Dilute Temperature (-33°F)

When rare-earth inflation spiraled out of control, Grace Catalysts Technologies responded quickly with the RepLaCeR® family of low RE or RE free catalysts, relieving the budgetary pressure without incurring performance yield penalties. Grace’s technical service team is committed to work with each refiner to customize the catalyst formulation to suit their needs.

### References


2. O. Topete, C. Baillie, R. Schiller, Optimizing FCC Operations in a High Rare-Earth Cost World: Commercial Update on Grace Davidson’s Low and Zero Rare-Earth FCC Catalysts, Catalagram® 110, 2011.


FLOWMOTION® is a rescue additive specifically designed to help recover normal operating conditions during times of reduced or unstable FCC catalyst circulation. Common causes of circulation problems in standpipes are:

1. Low slide or plug valve differential pressure
2. Inability to circulate additional catalyst despite changes in slide valve position
3. Erratic slide valve differential pressure
4. Physical bouncing or hopping of catalyst standpipes

Why FLOWMOTION®?

Redesigning the fresh FCC catalyst particle size distribution can provide some relief from circulation problems. However, the time to feel the relief will vary, depending upon the current inventory of fresh catalyst. Injection of a fluidization aid, such as FLOWMOTION®, can accelerate the recovery to normal standpipe operations.

The success of FLOWMOTION® is attributable to its optimum particle size distribution (PSD) which quickly improves the critical particle size range of the entire FCC catalyst inventory. The effect of injecting a high 0-40μ additive into the circulating inventory can be measured by the fluidization factor or Umb/Umf:

\[
\text{Umb} = \frac{2300 \rho_g^{0.126} \mu_{0.52} \rho_{0.716}^{0.716} F^b}{d_{50}^{0.8} g^{0.54} (\rho_p - \rho_g)}
\]

\[
\text{Umb} = \text{Minimum Bubbling Velocity; } F = 0-45\mu \text{ fines (weight fraction)}
\]

Increasing the amount of fines in the circulating inventory (which is directly proportional to F) will improve the fluidization factor and increase the stability of your standpipe operation.
FLOWMOTION® also contains a lower 0-20µ fraction than other fluidization aids, which limits losses at the time of injection. The typical properties of FLOWMOTION® are:

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0-20µ, wt.%</td>
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<td>APS, µ</td>
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</table>

Commercial Experience

A refiner experienced a steady increase in APS on their Ecat over a 1-year period and, over the same time frame, a chronically low 0-40µ fraction in the circulating inventory. At the point which catalyst circulation became too constrained to operate normally, FLOWMOTION® was injected and the refiner observed a rapid response both in Ecat PSD and circulation stability, enabling the FCCU to continue operating until their scheduled turnaround.

References

Introduction

Why do we do testing? We do testing because we want to predict in the lab what is going to happen in the field. Leo Baekeland, an entrepreneur and pioneer in the plastics industry, famously spoke to the importance of lab and pilot plant testing when he stated in his 1916 Perkin Medal acceptance speech: “The principle: ‘Commit your blunders on a small scale and make your profits on a large scale,’ should guide everybody who enters into a new chemical enterprise.” Conducting testing before commercial implementation reduces risk for a refiner. Examples of questions that pilot testing can answer include:

- What will be the effect of a potential feedstock change on yields?
- How will a new catalyst technology perform?
- Which catalyst technology is best for my operating goals?
- What effect will an additive have on my yield structure?

Figure 1 outlines what pilot testing intends to accomplish. On a lab scale, the goal is to match the complex processes occurring in a commercial FCC unit. In the unit, catalyst deactivates over a period of many weeks due to temperature, steam, and contaminant metals. Commercial deactivation conditions are too slow to be practically copied in the lab, so an accelerated lab deactivation is done to generate a simulated Ecat to match the chemical and physical properties of the commercial Ecat. Bench scale (ACE or MAT) or pilot-scale (DCR) test equipment is then used to simulate the reaction conditions in the FCC unit and react catalyst and feed to produce products.
**Laboratory Deactivation Approaches**

When studies are being done for feedstock selection or process development, commercial Ecat is usually used and no lab deactivation is needed. However, catalyst selection studies and catalyst R&D start with fresh catalyst. Fresh FCC catalysts need to be deactivated before testing because fresh catalysts are too active and the selectivities seen in fresh catalysts do not represent Ecats in the FCC unit. Temperature, metals and steam are therefore used to turn fresh catalyst into simulated Ecat. Commercial Ecat properties that we want to match with simulated Ecat include: surface area, unit cell size (UCS), metals concentration, metals oxidation state, and metals distribution.

Accelerated conditions to simulate hydrothermal deactivation of zeolite typically involve times of 2 to 50 hours, temperatures between 1400°F and 1525°F, and steam concentrations between 50 and 100%¹. At temperatures below 1400°F, it may be impossible to match the equilibrium unit cell size, and at temperatures above 1525°F unrealistic zeolite sintering can be encountered.

Contaminant metals such as nickel and vanadium accelerate catalyst deactivation and have dehydrogenation activity that increases coke and hydrogen. It is important to test catalysts with contaminant metals in order to realistically assess the performance of catalysts with metals trapping and passivation technologies. The best way to simulate the contaminant metals is to apply the same metals level to the fresh catalyst that is present on the Ecat, and then deactivate all the fresh catalyst samples in a study under the same conditions.

Deactivation methods that simulate poisoning by contaminant metals include the Mitchell method (MM), cyclic metals impregnation (CMI) and cyclic propylene steaming (CPS)². The Mitchell method involves impregnation of fresh catalyst with organic Ni and V naphthenates followed by steam deactivation for 4 to 20 hours. The CMI method involves multiple cycles of cracking with metals spiked feedstock and regeneration, resulting in a deactivation time of more than 50 hours. The CPS method involves impregnation of fresh catalyst with organic Ni and V compounds, followed by aging in a cyclic redox environment for ~20 hours. The reducing atmosphere (which simulates the riser) is a blend of steam, nitrogen and propylene, and the oxidizing atmosphere (which simulates the regenerator) is a blend of steam, air and SO₂. Grace developed the CPS deactivation method, and additional details can be found in references 3 through 6. The CPS method provides a good match to Ecat properties and yields as seen in Tables 1 and 2 where the properties and pilot plant yields of fresh catalyst deactivated via CPS are compared to commercial ECAT. The CPS method has been adopted by many labs around the world and can be easily fine-tuned to match the severity and specific deactivation conditions of different commercial units by adjusting the temperature, the number of redox cycles, and the amount of oxygen in the regeneration atmosphere.
Table 3 provides a comparison of the different lab deactivation methods to the conditions in a commercial unit. In deactivating catalyst with contaminant metals, it is important to include the effect of sulfur competition by using SO₂ as part of the simulated regenerator conditions. Under commercial regenerator conditions, calcium oxide and barium-based metal traps are rapidly poisoned by sulfur and lose their vanadium trapping ability. This sulfur poisoning does not happen with rare earth-based vanadium traps. Testing of vanadium traps in the laboratory without simulating the SO₂ present in a commercial regenerator can give a false prediction of catalyst metals trapping ability.

Commercial FCC units differ in their catalyst turnover rates. When it is desired to very closely match lab simulated Ecat to Ecat from a specific refinery, age distribution deactivation can be used. Commercial Ecat consists of catalyst particles with varying age, surface area, unit cell size (UCS), metals level, activity, and selectivity. Sink/Float experiments that separated refinery Ecat into age fractions have determined that activity and selectivity are dominated by the youngest fraction of the catalyst. Typically, the youngest 20% of the inventory contains less than 10% of the contaminant metals and contributes about 50% of the overall activity. For a specific unit, the metals and activity distribution will depend on catalyst addition rate, deactivation rate and catalyst activity. Figure 2 presents the contaminant nickel and activity distribution for Ecat from a refiner on the United States East Coast and how this age distribution can be simulated by deactivating three separate catalyst fractions—one representing the youngest 20%, one representing the middle 20% and one representing the oldest 60%. A greater number of fractions could be used in the simulation, but Grace has found that three age fractions results in the least complexity while still giving a good match to commercial yields. Table 4 gives the chemical and physical properties of the three fractions that were deactivated. Table 5 shows how the properties of a blend of the three fractions match those of commercial Ecat.

**Table 1:** CPS Provides a Good Match to Ecat Properties

<table>
<thead>
<tr>
<th>Conversion = 74</th>
<th>Ecat</th>
<th>CPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat to Oil</td>
<td>8.2</td>
<td>7.7</td>
</tr>
<tr>
<td>H₂ Yield, wt.%</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>C₁ + C₂, wt.%</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Total C₅, wt.%</td>
<td>5.3</td>
<td>4.9</td>
</tr>
<tr>
<td>C₅ⁿ, wt.%</td>
<td>4.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Total C₆, wt.%</td>
<td>9.5</td>
<td>9.3</td>
</tr>
<tr>
<td>C₆ⁿ, wt.%</td>
<td>6.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>51.6</td>
<td>52.5</td>
</tr>
<tr>
<td>G-Con RON EST</td>
<td>92.9</td>
<td>93.2</td>
</tr>
<tr>
<td>G-Con MON EST</td>
<td>80.7</td>
<td>80.7</td>
</tr>
<tr>
<td>LCO, wt.%</td>
<td>17.8</td>
<td>17.9</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>8.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>5.5</td>
<td>5.4</td>
</tr>
</tbody>
</table>

**Table 2:** CPS Matches Yield Selectivities in DCR Evaluation

<table>
<thead>
<tr>
<th>Method</th>
<th>Mitchell Method</th>
<th>CMI</th>
<th>CPS</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deactivation Environment</td>
<td>Inert/oxidizing</td>
<td>Cyclic redox</td>
<td>Cyclic redox</td>
<td>Cyclic redox</td>
</tr>
<tr>
<td>Effect on Vanadium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanadium valence</td>
<td>+5</td>
<td>+3 to +5</td>
<td>+3 to +5</td>
<td>+3 to +5</td>
</tr>
<tr>
<td>Vanadium mobility</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Zeolite Destruction</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Effect on Nickel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel valence</td>
<td>+2</td>
<td>+2 to 0</td>
<td>+2 to 0</td>
<td>+2 to 0</td>
</tr>
<tr>
<td>Reaction with Sb</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Sulfur effects</td>
<td>Minimal</td>
<td>S/V competition</td>
<td>S/V competition</td>
<td>S/V competition</td>
</tr>
<tr>
<td>Metals Distribution</td>
<td>Uniform</td>
<td>Shell Concentrated</td>
<td>Uniform/Shell*</td>
<td>Shell Concentrated</td>
</tr>
<tr>
<td>Metals age distribution</td>
<td>Uniform</td>
<td>Non-uniform</td>
<td>Uniform</td>
<td>Non-uniform</td>
</tr>
<tr>
<td>Implementation</td>
<td>Easy</td>
<td>Tedious</td>
<td>Easy</td>
<td>-</td>
</tr>
</tbody>
</table>

*Grace is developing a shell impregnation method.
FIGURE 2: Lab Deactivation to Simulate Age Distribution (AD-1)

Simulate the age distribution of Ecat with three fractions:

- **20% No Metals** (Mild Steam)
- **20% Low Metals** (10% of Total Metals) (Standard Steam)
- **60% High Metals** (90% of Total Metals) (Severe Steam)

Youngest 20% has ~2% of the Ni but contributes ~50% of the activity.

Middle 20% has ~8% of the Ni and contributes 30% of the activity.

Oldest 60% has ~90% of the Ni but contributes only ~20% of the activity.

Deactivation Procedure

<table>
<thead>
<tr>
<th></th>
<th>5 hrs at 1500°F, 50 wt% steam</th>
<th>5 hrs at 1500°F, 50 wt% steam</th>
<th>5 hrs at 1500°F, 50 wt% steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presteamming</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals Deactivation</td>
<td>None</td>
<td>2150 ppm Ni, 2500 ppm V</td>
<td>4300 ppm Ni, 5000 ppm V</td>
</tr>
<tr>
<td>Analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite SA, m²/g</td>
<td>183</td>
<td>141</td>
<td>83</td>
</tr>
<tr>
<td>Matrix SA, m²/g</td>
<td>52</td>
<td>44</td>
<td>34</td>
</tr>
<tr>
<td>Unit Cell Size, Å</td>
<td>24.32</td>
<td>24.29</td>
<td>24.27</td>
</tr>
<tr>
<td>Ni, ppm</td>
<td>31</td>
<td>2130</td>
<td>4370</td>
</tr>
<tr>
<td>V, ppm</td>
<td>40</td>
<td>2770</td>
<td>5430</td>
</tr>
<tr>
<td>MAT</td>
<td>78</td>
<td>68</td>
<td>49</td>
</tr>
<tr>
<td>Kinetic Conversion</td>
<td>3.56</td>
<td>2.15</td>
<td>0.97</td>
</tr>
<tr>
<td>Activity Contribution</td>
<td>41%</td>
<td>25%</td>
<td>34%</td>
</tr>
<tr>
<td>Metals Contribution</td>
<td>0.2%</td>
<td>14.0%</td>
<td>85.8%</td>
</tr>
<tr>
<td>Fraction in Blend</td>
<td>20%</td>
<td>20%</td>
<td>60%</td>
</tr>
</tbody>
</table>

Three fractions with varying metals levels and activity.

TABLE 4: CPS with Age Distribution
and Table 6 provides yields from DCR evaluation of commercial Ecat and the simulated Ecat produced by the AD-1 protocol. As seen in the DCR results, there is excellent agreement between the yields of the Ecat and the AD-1 deactivated catalyst. The discrepancy in hydrogen yield is likely due to the presence of passivating antimony on the Ecat, but not on the AD-1 deactivated catalyst.

In summary, fresh FCC catalysts need to be deactivated before testing. Cyclic propylene steaming (CPS) is a rapid method to match Ecat properties and yields. To better match a specific refinery’s Ecat, CPS with age distribution can be used, but it is more time consuming.

### FCC Catalyst Testing

Performance testing of FCC catalysts can be done by either bench scale testing or pilot plant scale testing. Examples of bench scale testing equipment include fixed bed microactivity testing (MAT) and fixed fluidized bed testing, one example of which is the ACE® (Advanced Cracking Evaluation) instrument marketed by Kayser Technology. Several pilot plant designs are in operation throughout the world and include both once through and circulating designs. The most common is the Grace developed Davison Circulating Riser (DCR®). Table 7 provides a comparison of the conditions in these test units to commercial operation.

MAT and ACE testing have the advantages that they are easy to set up and require small amounts of material. The DCR pilot plant has

<table>
<thead>
<tr>
<th>Conversion = 77</th>
<th>Ecat</th>
<th>AD-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat to Oil</td>
<td>11.8</td>
<td>10.9</td>
</tr>
<tr>
<td>( \text{H}_2 ) Yield, wt.%</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>( \text{C}_1 + \text{C}_2 ), wt.%</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>( \text{C}_3= ), wt.%</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Total ( \text{C}_3 ), wt.%</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>( \text{C}_3= ), wt.%</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Total ( \text{C}_4 ), wt.%</td>
<td>11.3</td>
<td>11.4</td>
</tr>
<tr>
<td>( \text{C}_4= ), wt.%</td>
<td>8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>50.1</td>
<td>50.4</td>
</tr>
<tr>
<td>G-Con P, wt.%</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>G-Con I, wt.%</td>
<td>19.8</td>
<td>19.4</td>
</tr>
<tr>
<td>G-Con A, wt.%</td>
<td>34.7</td>
<td>34.7</td>
</tr>
<tr>
<td>G-Con N, wt.%</td>
<td>10.4</td>
<td>10.2</td>
</tr>
<tr>
<td>G-Con O, wt.%</td>
<td>32.2</td>
<td>32.8</td>
</tr>
<tr>
<td>G-Con RON EST</td>
<td>93.9</td>
<td>94.0</td>
</tr>
<tr>
<td>G-Con MON EST</td>
<td>80.3</td>
<td>80.5</td>
</tr>
<tr>
<td>( \text{LCO} ), wt.%</td>
<td>16.8</td>
<td>18.9</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>5.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>

### Table 6: Good Agreement Between Ecat and AD-1 in DCR Evaluation

|  | Ecat | AD-1 |
|  | Al, wt.% | 39.2 | 40.2 |
|  | Re, wt.% | 2.8  | 2.6  |
|  | \( \text{Na}_2 \)O, wt.% | 0.4  | 0.3  |
|  | Fe, wt.% | 0.8  | 0.5  |
|  | \( \text{P}_2 \)O_5, wt.% | 0.2  | 0.1  |
|  | CaO, wt.% | 0.3  | 0.1  |
|  | Ni, wt.% | 3330 | 3050 |
|  | V, wt.% | 3090 | 3870 |
|  | Sb, wt.% | 689  | <50  |

### Table 5: Age Distribution Deactivation Provides a Good Match to Commercial Ecat
the advantage that it mimics all the processes present in commercial operation and it can operate at the same hydrocarbon partial pressure as a commercial unit. Figure 3 is a schematic drawing of the DCR. The system consists of three main units—a riser, a stripper, and a regenerator. Both the regenerator and the stripper are equipped with slide values for control of catalyst circulation rate. The DCR is typically operated in an adiabatic mode, where changing feed preheat or regenerator temperature will result in a change in catalyst circulation to maintain reactor outlet temperature, the same process control strategy used in many commercial FCC units. Due to the similarity between the DCR riser and the commercial FCCU riser, yields obtained from the DCR simulate commercial FCCU yields closely. Table 8 compares DCR yields to commercial yields when the DCR was run at the same conditions as a commercial FCCU with Ecat and feed from the unit.

The DCR is a highly flexible pilot plant and has been used to successfully evaluate many different feedstocks including resid, naphthas, gases, and feeds from non-petroleum sources such as vegetable oils and pyrolysis oils. Due to its simplicity of operation and ability to match commercial yields, the DCR has become the leading commercially available technology for small scale FCC pilot units. There are currently 26 DCR technology licenses worldwide.

<table>
<thead>
<tr>
<th>Nature of Operation</th>
<th>MAT/ACE</th>
<th>Circulating Riser</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Contact Time</td>
<td>Unsteady State</td>
<td>Steady State</td>
<td>Steady State</td>
</tr>
<tr>
<td>Temp. Range</td>
<td>930 to 1100°F</td>
<td>930 to -1100°F</td>
<td>980 to 1030°F</td>
</tr>
<tr>
<td>Hydrocarbon Partial Pressure</td>
<td>-12 psia</td>
<td>20 – 45 psia</td>
<td>20-50 psia</td>
</tr>
<tr>
<td>Catalyst Inventory</td>
<td>5 to 10 grams</td>
<td>2 to 3 kg</td>
<td>100 tons</td>
</tr>
<tr>
<td>Advantage</td>
<td>Easy to set up</td>
<td>Mimics commercial operation</td>
<td></td>
</tr>
</tbody>
</table>

| TABLE 7: Comparison of Test Unit Conditions to Commercial FCCU Conditions |

FIGURE 3: DCR Pilot Plant Schematic
In order to minimize risk, proper catalyst deactivation and testing are important in predicting commercial unit performance. Table 9 describes the typical strategies for different testing objectives. Grace Catalysts Technologies has extensive catalyst deactivation and testing capabilities in our labs. We use these capabilities to support the development of new products, the customization of existing products, and to provide customer technical support. Our goal in testing is to reduce risk and uncertainty by identifying the optimum catalysts on the lab scale so that refiners can “make their profits on a large scale.”

**Summary**

**References**


6. What catalyst and metallurgy design considerations are important when evaluating the co-processing of highly acidic renewable distillates? What can be done to mitigate carbon monoxide formation?

Bob Riley, Technical Sales Representative

There are two main types of acidic renewable “distillates” available: triglyceride based (animal fats or vegetable oils), or pyrolysis oils to be considered when co-processing is an option at the refinery. Grace is leading development of technologies to be utilized for the process of either of these types of oils in a petroleum refining environment.

Triglyceride based oils derive their acidity mainly from free fatty acids in the oils. The level of impact of corrosion on processing equipment will depend on the type of feedstocks (animal fats or vegetable oils) and their level in the overall blend going to the refinery processes. To evaluate co-processing of these oils in a hydrotreater, several other factors must be understood as well:

- Triglyceride based oils have a new suite of metals contaminants. They are typically lean in nickel and vanadium, but very rich in calcium, magnesium, phosphorous, and other transition metals. Left unchecked, these metals can have a strong detrimental effect on the catalyst bed. Grace Davison has studied the treating of these oils extensively, and recommends a pretreatment system to remove metals. Guard beds have been suggested, but the suitability of a guard bed depends on its size and the amount of oil to be processed; it is likely to require bed replacement much sooner than a typical VGO hydrotreating guard bed. The combination of a separate pretreatment system and an in-situ guard bed is typically the approach preferred for commercial operation.
- Triglyceride oils also contain between 10 and 15 wt.% oxygen typically. The removal of this oxygen creates a high level of water, carbon dioxide, and carbon monoxide, and due to the higher oxygen concentration, releases heat at a much higher rate than desulfurization of VGO. Care must be taken to ensure that the hydrotreating unit can handle additional heat release.
- Triglyceride oils release higher than typical amounts of water, carbon dioxide, carbon monoxide and propane when hydrotreated. One must review the downstream gas system to ensure that higher volumes of these products will be appropriately handled by the existing equipment.
- In this type of system, production of carbon monoxide happens via the de-carbonylation route. To minimize the production of carbon monoxide, some process conditions can be changed, including increasing the available hydrogen, and selecting a catalyst system that is designed for deoxygenation. However, if co-processing renewable stocks, these moves are likely to have an impact on the non-biobased portion of the feedstock, and must be evaluated against the reduction in carbon monoxide.

Pyrolysis oils are a wide class of oils that are produced via cooking biomass in an oxygen free environment. The level of acidity and other properties ultimately depends on the production process with a typical pH range from 2.0 to 4.0. These oils are newer to commercial markets, and experience is limited in being processed in existing refining equipment. It is safe to say that the points below do not apply to all commercially available oils, however the following points should be considered:

- These oils are typically very hydrogen deficient, and the average molecular weight can be quite large. They easily lay down on the surface of an extruded catalyst to condense (form coke), and thus coking and pressure drop increases in a hydrotreater is an important concern. Catalyst activity could be manipulated to a degree to compensate, but the range of compensation may not be wide enough, depending on the quality of the pyrolysis oil.
- There are often miscibility concerns when co-processing with standard VGO material. Phase separation could also ultimately lead to unintended coking in the unit, including the plugging of feeding equipment.
- These oils often have extremely high metals levels, and may need to be pretreated in some fashion to remove those metals.
- Another option is to consider processing these oils in other units in the refinery (FCC or coker). Though not without issues, these units may be more suitable to handle the metals levels and the coking tendency of pyrolysis oils.

In all cases, one should closely examine the blending percentage of the renewable oil to be co-processed as a key variable. Minimizing this percentage will minimize disruption to an existing unit. In addi-
tion, one should also closely examine the regulatory environment to
determine if there are benefits to co-processing or if standalone pro-
cessing (100% renewable) adds additional benefits in the form of tax
credits.

79. What tools are being used to monitor the FCC performance? What are the key performance indicators (KPIs) and expectations?

Bob Riley, Technical Sales Representative

There are many tools that are available to monitor FCC unit perfor-
manence. Most FCC operators monitor in process, or “as produced”
yields and operating conditions, and additionally they complete unit
mass balances at routine intervals (often weekly or more frequently).

Of primary importance is the net product value produced by running
the FCC. This is most often examined using mass balanced data
from the unit, in conjunction with refinery specific product and feed
values (pricing). In many refineries, FCC profitability is driven by
overall volume gain, so this is an important KPI.

Unit reliability is also a very important profitability parameter, and
(along with a strong routine maintenance program), many refiners
monitor in process operating parameters to ensure that limits are not
being exceeded. Some of these parameters are directly measured
in the unit, and some are calculated using in-process or mass bal-
danced data.

Measured parameters include unit temperatures (at various points in
the unit, including reactor outlet, regenerator bed, reactor and regen-
erator dilute phases, and others), unit pressures (reactor & regen-
erator), wet gas compressor suction and power, regenerator
emissions, and slide valve / standpipe differential pressures.

Calculated parameters, which are important to monitor, include yield
selectivities (yields / conversion), coke make, superficial velocities
(especially in cyclones), and catalyst circulation (or cat-to-oil ratio).

The recommended ranges for all of these parameters are specific to
the FCC unit’s configuration, feed and catalyst type, and operating
strategy.

As a service to its customers, Grace provides routine technical serv-
ice reports, including equilibrium catalyst analysis. These reports
can be a critical tool to monitor FCC unit performance, and to trou-
bleshoot the various problems that can arise in typical FCC unit op-
eration. They are most effectively used when they are incorporated
into routine operating reviews with the catalyst supplier. During the
reviews, recommendations are often made to adjust operating
strategies or fresh catalyst formulation to address future operations
or issues that are expected/anticipated for the refinery. These rou-
tine reviews are a critical component of the successful operation of
the FCC.

The catalyst KPI’s include cracking data (ACE or MAT), physical
properties of the catalyst, and chemical analysis of the catalyst. As
with yield and operating KPI’s the expectation for these KPI’s varies
greatly depending on the feed processed, unit design, catalyst type,
and operating strategy of the refinery.

In addition, equilibrium catalyst data can be used to benchmark unit
performance against similar units, feed types, catalyst types, or a
number of other variables. Advanced analytical tools and methods
have been developed by catalyst suppliers to understand how age
distribution, cyclone performance, contaminant metals, and other
variables may impact the performance of the FCC catalyst. These
analyses are typically performed “on request” as problems arise.

80. We are considering severe hydrotreating of our FCC Feed. What yield shifts or unusual operating problems might we ex-
pect? What can be done to address these issues?

Bob Riley, Technical Sales Representative

Severe hydrotreating of the FCC feed offers a mix of benefits and
challenges for the typical FCC operator. Benefits can include dra-
matically lower sulfur content in products, lower flue gas SOx or
NOx, and improved yields; however the price for these benefits is
often a dramatically lower coking tendency of the feedstock. Many
units which operate with severely hydrotreated feed struggle to
make enough coke to maintain heat balance within unit circulation
constraints. In addition, one may see slurry yield decrease to mini-
num acceptable levels, increased bottoms circuit fouling due to the
lower volumes, heat removal limits in the gas concentration units
due to higher volumes of light and wet gases, and lower overall
product olefinicities.

To counteract that challenge, several operating changes are possi-
ble. These include:

• Use of higher activity FCC catalyst – For units which will run
severely hydrotreated feed for long periods of time,
reformulation to a higher activity FCC catalyst is often the
most cost effective means of increasing the ECAT activity, and
bringing the unit into heat balance.

• HCO recycle – HCO can be recycled to the reactor to aid in
additional coking and to increase the heat requirement on the
reactor side. This strategy causes an economic penalty when
the unit is operating at maximum fresh feed rates, as fresh
feed will need to be backed out.

• Use of regenerator torch oil – Torch oil is often used in the
regenerator to add additional heat. However, the severe
hydrothermal environment, coupled with the high velocities
near the injection point(s), creates a very challenging environment for FCC catalyst particle integrity. In addition, many refineries use LCO material as torch oil, which is a substantial hidden cost.

- Use of the fired air heater – Some units will activate the fired air heater to reduce the heat requirement in the regenerator. In some cases, this air heater does not offer a great deal of flexibility in its duty, so its use can “swing” the unit from very low regenerator temperatures to much higher regenerator temperatures.

- Reduction in stripping steam – Some refiners elect to reduce stripping steam, sending some unstripped hydrocarbon with the catalyst into the regenerator. While this is a viable source of heat on the regenerator side, it results in a net loss of total liquid volume, and unit profitability can suffer. Additionally, the hydrogen-rich unstripped hydrocarbons burn rapidly creating local hot spots which can deactivate the catalyst.

- Higher FCC catalyst addition rates – For units that process severely hydrotreated feeds intermittently, catalyst reformulation may not be practical. However, a short term increase to the FCC catalyst addition rate can increase the equilibrium activity and bring regenerator temperatures up, which will allow the unit to maintain heat balance.

Each of these methods should be evaluated for both its feasibility in a given refinery and for its economic impact to the plant. It is often the case that higher catalyst addition rates, or a high activity catalyst reformulation, is the most economically favorable option.

81. Is there experience with continuous torch oil and/or air preheater firing and for what reasons? What are the demonstrated effects from doing either of these?

Bob Riley, Technical Sales Representative

The use of “dry circulation” is a common event in many refineries. Often upstream or downstream problems in a refinery can cause the FCC to pull feed, and during these times, many units elect to continue “hot” catalyst circulation to avoid a complete thermal cycle on the FCC. Typically, these events are short-lived (up to about one week). During this time, refiners may add fresh, or more typically, equilibrium catalyst to the unit to maintain catalyst bed levels.

Using torch oil creates a severe hydrothermal environment, with temperatures at the nozzle tips often eclipsing metallurgical recommendations, and velocities well over 100 ft/s. These nozzle tips are often buried in the dense bed of the regenerator, causing areas of severe stress on the catalyst particles. Attrition and catalyst deactivation are the outcomes of this activity.

The use of torch oil or fired air heating while feeding oil is less common. In units that process severely hydrotreated feedstocks, opera-
tors often use torch oil to create additional heat in the regenerator to maintain the heat balance. This operating strategy often comes at a high cost, as many refineries use LCO material for torch oil. A more economically attractive option is to add higher amounts of FCC catalyst and to pursue a reformulation to higher fresh FCC catalyst activity.

We have noted one refinery that, after a turnaround, started up on a substantially lighter feed. This unit started up using the fired air heater and did not turn it off, as the new lighter feed resulted in an unacceptable drop in regenerator temperature. Catalyst addition rates were increased, and eventually, the unit reformulated to a higher activity catalyst. This reformulation, along with other moves in the operation, allowed them to discontinue the use of the fired air heater.

Another refinery with a similar short-term “lightening” of the feedstock elected to fire torch oil to maintain heat in the regenerator. This unit continued this practice until they shut down for a planned turnaround. They observed increased fines generation, and complete destruction of the torch oil nozzle tip. After their turnaround, the refiner reformulated to a more active catalyst to remove their dependence on torch oil to keep the regenerator hot.

89: With the increase in rare earth costs, many units have decreased the rare earth oxide (REO) content or used rare earth substitutes in their FCC catalyst. What is your experience with these in terms of activity maintenance, delta coke, conversion, attrition, and yield selectivities? How have operating conditions changed?

Ann Benoit, Technical Service Representative

Rare earth plays a key role in FCC catalyst and has been traditionally used in stabilizing zeolite which preserves catalyst activity and modifies selectivity. Rare earth has also been successfully utilized

![FIGURE 1: As Rare Earth on Catalyst Decreases, LPG Yield Will Increase](image)
as a contaminant metals trap, reducing deactivation caused by vanadium. There are several different avenues one could take to lower rare earth on catalyst with wide ranging impacts on FCCU yields and selectivities.

The following avenues will be discussed:

1. Lowering rare earth on zeolite
2. Lowering rare earth and using a rare earth substitute
3. Lowering rare earth used for metals traps

Simply lowering rare earth on zeolite with no other changes made to the catalyst system will typically reduce catalyst activity at similar catalyst additions. Conversely, higher catalyst additions will be required to maintain similar catalyst activity. If activity/conversion is maintained, catalysts with lower rare earth will typically be more LPG selective than gasoline selective. The graph below showing this relationship was presented at the 2012 Cat Cracking seminar. The data are pilot plant yields from merely reducing rare earth on an FCC catalyst with constant zeolite and matrix input.

For further information on the function rare earth plays in FCC catalyst and yield selectivities please refer to the Grace paper “Role of the Rare-Earth Elements in Fluid Catalytic Cracking”. One thing to note is that removing rare earth from FCC catalyst typically provides relief in catalyst expenses, but is not necessarily an economical solution as most FCC operations cannot accommodate lower activity and/or product value.

One alternative to lower rare earth while maximizing FCCU profitability is to use alternate materials and processing to stabilize the zeolite. Grace has recently added the REpLaCeR® family to its catalyst portfolio. REpLaCeR® is a collection of low and zero rare-earth catalysts which have been applied in a wide range of FCC applications. REMEDY® catalyst, one of the REpLaCeR® family of catalysts with low rare-earth content, has been proven to have similar unit conversion at similar catalyst additions, similar slurry/coke selectivity, similar Ecatal activity, and higher gasoline selectivity when compared to a moderate rare-earth containing catalyst. In one refinery example, the catalyst was reformulated from a traditional 1.5 wt.% rare earth catalyst, GENESIS® GSR®, to REMEDY®2 GSR®. As shown in Figures 2 and 3, the catalyst additions on a lb/bbl of feed basis were maintained with REMEDY®2 GSR® while maintaining similar conversion. Figure 4 shows both catalysts have similar coke selectivity. Also, REMEDY®2 GSR® proved to be more gasoline selective when compared to GENESIS® GSR® which is shown in Figure 5. It is also worth noting that the lower rare-earth catalyst reformulation in this example did not negatively impact catalyst retention.

With regard to rare earth being utilized as a metals trap, Grace has been successful in reducing rare earth by 40% without sacrificing activity or selectivity with the re-optimization of our IMPACT® technol-
ogy, ResidUltra™. Commercial experience proves that unit performance is nearly interchangeable. In lab testing, ResidUltra™ and IMPACT® samples were deactivated with metals levels of 3000 ppm V and 2000 ppm Ni and tested side by side in the ACE unit over a residual feedstock. The constant conversion data is summarized in Table 1. In this scenario, relative to IMPACT®, ResidUltra™ has similar catalytic activity, the same hydrogen selectivity, slightly better coke selectivity, similar gasoline, similar LCO, and similar bottoms yield. ResidUltra™ yields slightly higher octane number and LPG olefins.

In summary, the means by which a catalyst supplier might lower rare earth may have no impact or a substantial impact on catalyst activity and FCCU yields and selectivities. Your unit objectives and constraints will dictate which catalyst reformulation best fits your FCCU.

References
2. 2012 Cat Cracking Seminar Q&A

TABLE 1: Constant Conversion ACE Yields

<table>
<thead>
<tr>
<th>CAT/OIL RATIO</th>
<th>IMPACT® Catalyst</th>
<th>ResidUltra™ Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>HYDROGEN, wt.%</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>DRY GAS, wt.% FF</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>PROPYLENE, wt.% FF</td>
<td>4.5</td>
<td>4.4</td>
</tr>
<tr>
<td>TOTAL C3, wt.%</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>TOTAL C4s, wt.%</td>
<td>5.5</td>
<td>5.8</td>
</tr>
<tr>
<td>GASOLINE, wt.%</td>
<td>50.2</td>
<td>50.8</td>
</tr>
<tr>
<td>LCO, wt.%</td>
<td>18</td>
<td>18.1</td>
</tr>
<tr>
<td>BOTTOMS, wt.%</td>
<td>6.0</td>
<td>5.9</td>
</tr>
<tr>
<td>COKE, wt.%</td>
<td>7.7</td>
<td>7.8</td>
</tr>
<tr>
<td>RON</td>
<td>90.9</td>
<td>91.2</td>
</tr>
</tbody>
</table>

90. Can ZSM-5 be used to make propylene from high metal resid feeds? What is the effect of Ni and V on this kind of operation?

Bob Riley, Technical Sales Representative

Yes, ZSM-5 additives are being used successfully, for example, in Asia and the Middle East, where the predominant FCC feedstock for maximum propylene FCC units is heavy, high metals resid. We have developed our AP-PMC and PROTAGON catalyst platforms to address the demands of these units. In addition, there are numerous resid applications around the world that target moderate propylene increases in which ZSM-5 additives are used. Regardless of the product to be maximized, the foundation for a superior resid cracking catalyst is coke-selectivity and bottoms cracking activity, and these are primary considerations in the design of these catalyst families. Grace’s ZSM-5 additives such as OlefinsMax® and OlefinsUltra® HZ are being used successfully in many resid units together with AP-PMC, Protagon, IMPACT®, Nektor™ ULCC and ResidUltra™ in blends together with AP-PMC and PROTAGON max propylene FCC Catalysts as well as in blends with resid catalysts such as IMPACT®, Nektor™ ULCC and ResidUltra™.

Industry experience indicates that high levels of Ni + V do not affect the performance of Grace’s ZSM-5 additives. Our customers have operated successfully with a combined Ni + V of up to 13,500 ppm. On the other hand, feed properties have a significant influence on product yields, including propylene selectivity.

Fundamental research has shown that ZSM-5 additives do not accumulate metals at the same rate as base cracking catalysts. This, in part, helps to explain why metals effects on ZSM-5 are not easily observed in commercial operation.
Grace Catalysts Technologies has made a significant upgrade to its routine equilibrium catalyst (Ecat) evaluation program. On September 3, 2012, we commissioned the new state-of-the-art Advanced Cracking Evaluation (ACE®) units in our Ecat testing laboratory in Worms, Germany. The ACE test is based on a fixed fluidized bed and will lead to improved precision by more than 20% over the formerly used Microactivity Test (MAT). The switch to ACE Ecat testing has already been successfully implemented in our US laboratories in 2011 and is the final step of a global Grace initiative to deliver the latest analytical technology to our customers.

In addition, a new standard feedstock has been chosen to better reflect the average industry feed quality. The new feed will be used globally for Ecat testing. The shifts in feedstock properties is summarized in the below table. The investment Grace has made in the Ecat evaluation program reflects our continued commitment to delivering the highest quality FCC technical support to our customers around the globe.

<table>
<thead>
<tr>
<th>Feed Name</th>
<th>MAT</th>
<th>New ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>0.919</td>
<td>0.915</td>
</tr>
<tr>
<td>K Factor</td>
<td>11.46</td>
<td>11.85</td>
</tr>
<tr>
<td>Conradson Concarbon, wt.%</td>
<td>0.25</td>
<td>1.5</td>
</tr>
<tr>
<td>Distillation 95% (°C)</td>
<td>517</td>
<td>648</td>
</tr>
</tbody>
</table>

**TABLE 1: Summary of Feedstock Property Changes**
Learn about new developments and trends in FCC, hydroprocessing, chemical catalysts, and related operational innovations and improvements, refined product quality, and environmental solutions tailored to the challenges of Asia Pacific refiners.

For more information, including a detailed agenda and registration details, contact your Grace or ART representative or you may contact john.haley@grace.com
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