Talent that spans the globe with industry-leading technical service, accomplished R&D, and operations in more than 30 countries.

Trust built through long-term partnerships over a 150-year history.

Technology leadership
- #1 in FCC catalysts
- #1 in resid hydroprocessing catalysts (ART)
- #1 in independent polyethylene catalysts
- #1 in independent polypropylene catalysts
- Leading supplier of hydrocracking catalysts and polypropylene technology licensing
For sure, the only constant is change. But, at times, the rate of change is more profound and rapid.

Our customers are adjusting to powerful forces carving change into the refining industry landscape: record low oil prices; fundamental shifts in feedstocks and the parts of the world where they’re produced; unprecedented global political and scientific attention on renewable energy; and unflagging increases in demand for fuel and petroleum-based products.

At Grace, the changes and challenges faced by our customers drive an imperative for us: step forward with new technologies, new processes, and new solutions to help each customer prosper. We do so in partnership, aligned on strategy, resources, and commitments.

Grace recently experienced an important change that will accelerate our support and improve that alignment. In the coming year, we have the unique opportunity to become more focused on our core—our catalysts and materials sciences businesses. In the first quarter of 2016, we completed the spin-off of our construction and packaging businesses. Each independent, publicly traded company retained its industry-leading position, exceptional brands and reputations, and talented employees and leaders. This makes Grace more agile, more responsive, and more committed to our catalysts customers and the investments we make to meet their future catalyst needs.

Meanwhile, the Grace leadership team has undergone a transition as well. I have been named President, Specialty Catalysts; and—effective after the end of Q1—I will assume the role of President, Materials Technologies following the retirement of Joanne Green. To that end, Tom Petti has returned from his service as president of our construction products business and is now President, Refining Technologies, which includes FCC and Advanced Refining Technologies (ART). Tom should be a familiar face to many of you, as he first joined Grace almost 25 years ago.

Grace has transformed many times since 1854, evolving from a shipping company, to banking, to passenger ship and airline services, to a massive conglomerate. Beginning in 2016, Grace will consist of the Catalysts Technologies segment—including Refining Technologies, Specialty Catalysts, and Advanced Refining Technologies (ART), our Chevron Joint Venture, as well as the Materials Technologies business which holds our global leadership in silica gel and other high-value technologies.

We have announced a major capacity addition in our ART hydroprocessing venture, and we will soon break ground on the first FCC catalyst plant in the Middle East.

**Partners in Change**

Growing more closely aligned with our customers’ needs means putting world-class R&D and manufacturing to work for you. It means delivering the best technologies and industry-leading technical support to help you capture the full value of catalytic innovations in your production facilities.

**Continued on Page 2**
In this issue of Catalagram®, we are focusing on our customer partners. Several featured papers demonstrate how refiners are driving profitability by maximizing jet fuel production, boosting gasoline octane, and achieving environmental compliance with cost-effective catalytic solutions.

We report on a number of 2015 customer training events held in locations around the world; events that spanned our entire catalyst portfolio, with more planned for next year. We also share highlights from various industry conferences in which we participated, including the AFPM Q&A session in New Orleans among others.

Charles Darwin said, “In the long history of humankind, those who learned to collaborate and improvise most effectively have prevailed.” The split at Grace will strengthen our technologies, our service, our manufacturing and logistics leadership, and our relationships with so many of the world’s leading companies, which are about to get stronger.

As always, I welcome your feedback and look forward to seeing many of you in the New Year. Thank you for your continued confidence in Grace as a solutions partner.

Al Beninati
President
Grace Specialty Catalysts
Grace and Chevron Joint Venture, ART, to Build World-Class Catalysts Plant at Grace’s Lake Charles, LA Site

Advanced Refining Technologies (ART), Grace’s joint venture with Chevron Products Company, will invest approximately $135 million to build a residue hydroprocessing catalyst plant and additional alumina capacity at the existing Grace manufacturing facility in Lake Charles, LA. Construction will be timed with market demand.

An ever-increasing global push for bottom-of-the-barrel upgrading is leading to a significant increase in investment by refiners for fixed bed resid hydrotreating and ebullating bed resid hydrocracking process technologies. The new ART plant will be designed to meet the increased catalyst requirements for these units, which are licensed and already under construction.

“This will be a world-class, world-scale catalysts plant that is responding to strong global demand for ART’s industry-leading products for residue upgrading, capitalizing on the success of our licensing partner, Chevron Lummus Global,” said Fred Festa, Grace Chairman and Chief Executive Officer.

“We are pleased that this investment with Grace will keep ART and Chevron at the forefront of hydroprocessing catalysis and technology,” said Mike Wirth, Chevron Executive Vice President, Downstream and Chemicals.

The Lake Charles facility is one of the largest refining catalysts plants in the world and represents a significant portion of Grace’s refining catalyst manufacturing capacity. Operating in Southwest Louisiana since 1953, the Lake Charles facility supplies major refiners around the globe. The 120-acre site consists of four major operations producing fluid cracking catalysts, hydroprocessing catalysts, and other intermediates.

Grace’s UNIPOL® polypropylene (PP) process technology and related services business announced two new contracts with large customers opening new facilities in the Asia Pacific region in 2018.

Grace has contracted with Yunnan Yuntianhua PetroChemical Co., Ltd. for its new PP production facility in Anning Yunnan, China, and Hyosung Corporation for its new facility in Ulsan, South Korea.

Yunnan Yuntianhua PetroChemical is a new subsidiary of Yuntianhua Group Co., Ltd., the largest chemical company in Kunming, Yunnan Province. It plans to purchase propylene for its new facility from the PetroChina Yuannan refinery and build a unit that will produce polypropylene at a rate of 150 kta, or kilotons per year.

Based in Seoul, Hyosung is a Korean industrial conglomerate operating in various industries, including machinery, IT, construction, and textiles. Its Ulsan facility is expected to produce polypropylene at a rate of 200 kta. This is the second UNIPOL® PP technology license for Hyosung.

Al Beninati, President of Grace Catalysts Technologies, said, “We’re delighted with the pace at which the UNIPOL® PP technology is being

Continued on Page 4
adopted in this growing market. Not only is the technology reliable, but it can be implemented with low investment and operating cost, is easy to operate, and will produce state-of-the-art PP products.”

Beninati continued, “Hyosung has experienced such success with its first license, that its leaders have decided to contract with us again for their new plant in Ulsan. But what truly helped us secure a new client with Yunnan and earn additional business from Hyosung was our commitment to customer service.”

Young-Gyo Choi, Hyosung’s Division President, said, “We are delighted to team up again with Grace, the world’s leading independent PP technology licensor and catalyst producer. Their UNIPOL® PP process technology offers us the most advanced PP product capability available. We are already producing market-leading PP products in our existing UNIPOL® PP technology line, and with this new line, we are planning to produce even more advanced PP products.”

Yuntianhua Deputy General Manager Jiang Ling, said, “We could not have found a better partner than Grace as we build a facility that will produce world-class products. We believe this agreement aligns with our goals for achieving optimum productivity and performance.”

Grace is a leading supplier of polyolefin catalyst technology and has the broadest portfolio of polyolefin catalyst technologies of any independent polyethylene/polypropylene catalyst producer. Grace’s industry-leading UNIPOL® PP technology licensing and related catalysts include the UNIPOL® UNIPAC®, process control software, SHAC®, catalysts systems, and sixth generation non-phthalate CONSISTA®, catalysts systems.

Grace recently was named Best International Supplier by oil refiner Orpic at its Fourth Annual Supplier Symposium in Sohar, Oman. Orpic is one of the largest companies and fastest-growing businesses in the Middle East oil industry. The company’s refineries at Sohar and Muscat, as well as aromatics and polypropylene production plants, provide fuels, chemicals, and feedstock domestically in Oman, as well as globally.

“It’s an absolute honor to receive this prestigious award from Orpic for the work we have been doing over the past several years,” said Nathan Ergonul, Director of Sales and Technical Services, FCC, Middle East. “We believe in the philosophy of building strong long-term partnerships, and we will continue to work tirelessly to demonstrate our commitment to Orpic and Sultanate of Oman.”

Ergonul said that many factors contributed to Grace receiving the award. He listed our products, technical service, logistics platform, Ecat management service, training and development efforts, and wider In-Country Value initiatives, such as the state-of-the-art analytical facilities Grace has installed at Sohar University.

Orpic hosts this annual supplier symposium to help enable engagement opportunities among its most valued suppliers. The event also helps strengthen ties by providing a platform for vendors to meet and interact with Orpic management.

photo:
Grace’s Nathan Ergonul (right) receives the Best International Supplier Award from Dr. Fahad bin Al Julanda, Assistant Secretary General of Innovation Development at the Research Council.
Shandong Shenda Achieves Successful Reactor Start-Ups With Support from Grace UNIPOL® PP Technology Licensing and Related Services

Shandong Shenda Chemicals (Shenda), a Grace UNIPOL® polypropylene technology and related services customer, has achieved success starting both of its reactors at its new UNIPOL® PP technology facility in Tengzhou, China.

Since starting the second reactor on July 31, Shenda has enabled production of a full product family, including homopolymer, as well as high-quality random and impact copolymers. Shenda is a subsidiary company of Levima, a member of Legend Holdings.

The Tengzhou facility has experienced outstanding results with its PP homopolymer reactor, which started nine months ago. This success led to the decision to start up the second reactor in July. After achieving the production of aim-grade impact products, Shenda smoothly transitioned to produce random products, and the quality has been better than expected.

“We worked closely with our partners at Grace to smoothly commission the two reactors, operating in series,” said Chen Deye, Vice President of Levima and General Manager of Shenda. “The implementation of the entire polypropylene process, from raw materials purification through the downstream facilities, has been a complete success.”

Tracy Cleckler, Grace Business Director, Licensing, said, “Shandong Shenda is focused on producing advanced PP products. Grace’s UNIPOL® PP Process Technology, along with our CONSISTA® and SHAC® catalyst systems, will enable them to produce market-leading PP products.”

Impact copolymers contain a rubber component that is produced in the second reactor, directly on the homopolymer matrix that is produced in the first reactor. In so doing, the polymer produced has a much better impact resistance, especially at lower temperatures due to the even distribution of the rubber component in the homopolymer matrix. These impact copolymers have great benefits in automotive and other high-value applications where a balance of impact resistance and stiffness are essential.

Shenda’s dedicated team worked closely with Grace experts to implement the plan and ensure the critical systems were functioning and ready for the impact copolymer production before transitioning. This led to stability throughout the entire run.

“All product mechanical properties met or exceeded the targets,” said Chen. “This success has extended the envelope of our product offerings, resulting in enhanced competitiveness and brand recognition.”

Grace Authors Published in Prestigious Encyclopaedia of Chemical Technology

Grace was invited to update an article on FCC catalyst technology for the Kirk-Othmer Encyclopaedia of Chemical Technology. The article titled “Fluid Catalytic Cracking (FCC) Catalysts and Additives” has recently been published online in the encyclopedia.

The authors of the article are Mike Berg, Stefan Brandt, Uday Singh, Ken Bryden, Rosann Schiller, and Wu-Cheng Cheng.

Written by prominent scholars from industry, academia, and research institutions, the Kirk-Othmer Encyclopaedia of Chemical Technology presents a wide scope of articles on chemical substances, including their properties, manufacturing, and uses. It also focuses on industrial processes and unit operations in chemical engineering, as well as covering fundamentals and scientific subjects related to the field. The Encyclopaedia is used worldwide by students and professionals in academia, research institutions, and industry. Chemical Engineering News describes the encyclopedia as, “The most indispensable reference in the English language on all aspects of chemical technology ... the best reference of its kind.”
UNIPOL® PP Team Customer Conference Features Advancements, Innovation, Exchange of Best Practices

Approximately 100 representatives from UNIPOL® PP Process technology licensees and Grace attended the 2015 Global Product and Process Technology Exchange Meeting (GP&P TEM), which was held June 8-12, 2015 in Orlando, FL. Delegates were present from UNIPOL® PP Process technology licensees including Braskem, GS Caltex, Hyosung, J. G. Summit, PIC/Equate, Esenttia, Slovnaft, Qinghai Damei, PetroChina Fushun, Shandong Shenda, and Reliance.

GP&P TEM is an annual conference designed for all licensees who are in the Improvements Program to learn about the latest advancements and innovation of UNIPOL® PP process technology, to exchange best practices and improvements within the UNIPOL® PP process and related PP product technology family, and to allow for networking among industry peers.

The format of the meeting included presentations to the whole group, Q&A, group discussions, one-on-one meetings with individual licensees, and, of course, very active networking. Attending on behalf of Grace were client team members from several functions, including product, process, engineering, manufacturing, commercial, and contractual, as well as subject matter experts and the UNIPOL® PP process technology Leadership Team.

A highlight of the meeting was the positive feedback received on Grace’s CONSISTA® polymerization catalysts and donors. Many licensees are in the process of converting from SHAC® catalysts and ADT Donors to CONSISTA® catalysts. PetroChina Fushun reported success with our non-phthalate, CONSISTA® C601 catalysts, having produced premium BOPP film product and superior impact products while achieving very high catalyst productivity.

Shandong Shenda, which started up in December 2014, presented information on a very fast project completion and quick start-up. The project performance set a record in China. The company’s representatives were very complimentary of the Grace team, which contributed to the project’s success.

Quotes from Shandong Shenda included: “The Grace Client Team for Shandong Shenda helped to identify the issues and worked with Shenda closely during project execution and post start-up. The trust built between Shenda and Grace makes the team work more efficiently.”

In addition to Tracy Cleckler, Global Business Director, UNIPOL® Licensing and Catalysts, other Grace leaders in attendance included GCT President Al Beninati and Vice President Matt Hellstern.

“The customer conference between the Grace Client Team and Shandong Shenda was mutually beneficial. Working closely with Shenda has built a sense of trust built between Shenda and Grace, which allows the project team to work more efficiently and effectively.”

Tracy Cleckler, Grace
ART® Technology Workshop in Italy Helps Promote New Catalysts to Global Customers

Advanced Refining Technologies (ART) held its Fourth Annual Ebullating Bed (EB) Resid Catalyst Technology Workshop in Milazzo, Italy in May 2015. The event was held after, and in conjunction with, a meeting for Chevron Lummus Global (CLG) customers at the site of ART’s long-term EB Resid customer Raffineria di Milazzo (RAM). The attendees all use LCFining technology, an EB process licensed by CLG that uses ART® catalysts.

The workshop was open to current and potential ART customers worldwide, and attended by 35 representatives from the U.S., Canada, Europe, Middle East, and Asia Pacific regions. The audience included customers from seven current operating EB resid hydrocracking (RHC) units, as well as four under design and/or construction.

Bruno Tombolesi, General Manager, ART, EMEA, said, “ART launched two of our newest EB RHC catalysts, developed over the last two years, which generated very good interest. In particular, the Q&A session went very well, as the open forum allowed an informal exchange of ideas.”

He said his team presented several technical papers and made joint presentations with customers on the commercial success of the Dual Catalyst System, which was launched three years ago.

ART Signs New Joint Development Agreement with Idemitsu Kosan Co., Ltd., Japan’s Second Largest Petroleum Refiner

Advanced Refining Technologies (ART) recently signed a new joint development agreement (JDA) with one of its most important customers, Idemitsu Kosan Co., Ltd. (IKC), Japan’s second largest petroleum refiner.

The contract signing came after several days of technical meetings in Columbia, MD between the two organizations and ART’s agent in Japan, Nomura Jimusho, Inc. (NJI).

Pictured here during the signing of the Joint Development Agreement between ART and IKC are: (seated, left to right) Shinji Araki, IKC’s Executive Officer and General Manager, Technology & Engineering Center; and André Lanning, ART’s Managing Director. (Standing, left to right) Yasunobu Kaneko (IKC), Osami Nakayama (IKC), Ryuchiro Iwamoto (IKC), Aira Ito (NJI), Darryl Klein (ART), Takehiro Matsuyama (NJI), Stan Plecha (ART), Keisuke Naka (NJI), Babu Patrose (ART), Ryo Fukuda (NJI), and Ryo Ebino (NJI).
FCC Technology Workshop Hosted in Worms, Germany

Grace Catalysts Technologies EMEA held the autumn edition of FCC Technology Workshop in Worms, Germany, September 21-25, 2015. This event, which occurs twice per year, is recognized by our customers for key training and updating on different aspects of FCC, including unit operation and optimization, process troubleshooting, and FCC catalyst/additive design fundamentals.

In total, 28 participants from 12 countries attended the workshop. Attendees included representatives from 18 refineries and two research institutes. A range of professionals attended the conference, from young FCC process engineers to senior technology managers across Europe, the Middle East, and Asia Pacific. The participants enjoyed technical presentation sessions spread over five days combined with social activities and the opportunity to network.

What the participants said about this Workshop:

“It is an excellent workshop to interact with various refiners and representatives from Grace. Having an overview of the Grace FCC catalyst manufacturing facility was very useful.”

-D.S. Orpic

“Very good chance to meet fantastic people working in the field of FCC.”

-C.H. Bayernoil

The autumn 2015 EMEA FCC Technology Workshop in Worms, Germany was well received by the 28 participants from 12 countries.
Early in 2013, Advanced Refining Technologies (ART) acquired exclusive rights to sell the highly respected ICR line of catalysts, which includes hydrocracking catalyst from Chevron Lummus Global (CLG). As a result, ART has become very active in hydrocracking catalyst sales, research and development, and product commercialization in the global market.

Around that time, one of ART’s newest customers was just starting up a load of hydrocracking catalyst in North America. The unit is a single-stage recycle design started operations in the early 1980s and previously had been operating with a competitor catalyst system. Operating objectives included:

- Maximizing unit operating cycle with higher endpoint feed
- Maximizing selectivity toward jet fuel
- Minimizing LPG and light gas yield

Feed planned for the upcoming cycle was a VGO/AGO blend with properties as follows:

<table>
<thead>
<tr>
<th>Stream Type</th>
<th>Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density – API</td>
<td>24.5</td>
</tr>
<tr>
<td>ASTM Method °F</td>
<td>D7169</td>
</tr>
<tr>
<td>IBP</td>
<td>233</td>
</tr>
<tr>
<td>5%</td>
<td>532</td>
</tr>
<tr>
<td>10%</td>
<td>583</td>
</tr>
<tr>
<td>30%</td>
<td>673</td>
</tr>
<tr>
<td>50%</td>
<td>728</td>
</tr>
<tr>
<td>70%</td>
<td>781</td>
</tr>
<tr>
<td>90%</td>
<td>845</td>
</tr>
<tr>
<td>95%</td>
<td>873</td>
</tr>
<tr>
<td>EP</td>
<td>939</td>
</tr>
<tr>
<td>Sulfur – Wt %</td>
<td>0.9</td>
</tr>
<tr>
<td>Nitrogen – wppm</td>
<td>800</td>
</tr>
<tr>
<td>Arsenic – wppb</td>
<td>50</td>
</tr>
<tr>
<td>Silicon – wppm</td>
<td>3</td>
</tr>
</tbody>
</table>

ICR 183 is a high-activity catalyst designed to maximize jet fuel yield at the expense of light gas production, resulting in maximum C5+ liquid yields. ICR 183 exhibits a very low deactivation rate, even while operating at high conversions. ICR 183 also has been designed to provide high nitrogen tolerance for those times when the nitrogen slip may increase from the hydrotreating section. ICR 183 utilizes an advanced method of metals deposition during manufacture to result in very uniform metals dispersion over the entire surface of the catalyst. This gives the catalyst excellent hydrogenation activity, resulting in optimal product properties. The superior metals distribution also contributes to the higher organic nitrogen tolerance and added stability for ICR 183.

For ART’s first operating cycle in this unit, the catalysts proposed were ICR 183 and ICR 214. These are two of ART’s newest catalysts, as you can see on the chart below:

**Figure 1:** ISOCRACKING® Catalyst Portfolio.

Continued on Page 10
ICR 214 was included as a component of this catalyst system, as it offers an activity advantage over ICR 183, while giving up a only modest yield of jet to light and heavy naphtha. Similar to ICR 183, ICR 214 yields very little light gas, thereby maximizing liquid products. The pilot plant testing directed by the customer confirms that the jet selectivity is only slightly less for ICR 214 as compared to ICR 183.

The proposed catalyst system was tested at a world class third-party laboratory selected by the customer. This testing was conducted by the customer for three competing catalyst vendors in addition to ART, and was designed to show side-by-side performance comparisons at conditions similar to the customer’s commercial operation. This also allowed the customer to compare the individual catalyst vendor proposals against the pilot plant results. The scope of the testing addressed activity, selectivity, and product quality across several operating conditions. Based on this testing, along with the technical support package and commercial offering, ART was selected.

As a result, the catalyst is currently well into its first cycle and is meeting all expectations. The cracking catalyst normalized average bed temperature (ABT) for the current cycle (red data points) is yielding a very low deactivation rate. The normalized ABT of the current cycle is shown in Figure 2.

The improved performance of the ART catalyst system over previous catalyst systems is presented in the following figures. As shown in Figure 3, the catalyst start of run activity and deactivation rate are much lower than the previous cycle, and similar to that of two cycles ago. However, it is evident from Figure 4 that the average feed rate of the current cycle is consistently higher than either of the prior two cycles.

More importantly, as a result of the excellent start-of-run activity and catalyst stability, the customer has been able to increase the feed endpoint much higher than previously planned at the outset of the current cycle. Figure 5 shows the feed distillation of the current cycle compared to the previous two cycles. We can see that 400 days into the current cycle, the customer has been able to increase the feed endpoint by 50°F higher than the previous two cycles.

Likewise, the feed API gravity is significantly lower, on average, than the previous two cycles, as shown in Figure 6.

Despite the higher feed endpoint, and lower feed API gravity, conversion has been maintained at 97 vol%, the same as much of the previous two cycles without compromise to the overall operation. The same conversion would appear to indicate the same severity in these three most recent cycles. On closer inspection, however, as a result of a higher average feed rate and fixed recycle oil rate, the conversion per pass in the current cycle is significantly higher than the previous two cycles as shown in Figure 7.
In fact, this increased severity is somewhat understated, since, with the higher endpoint and lower API gravity feed, the current cycle has less product range material in the feed than the previous two cycles, resulting in a higher net conversion as well.

*Continued on Page 12*
From these multi-cycle comparisons, it is evident that the customer has been able to utilize the improved performance of the ICR 214/ICR 183 catalyst system to its advantage in processing higher feed rates and heavier feed at increased operating severity. In spite of this, the jet yield at 400 days into the current cycle is the same as the previous two cycles and is much more stable than the previous cycle, as shown in Figure 8.

The improved performance is also evident in the total C5+ liquid yield, which, at 400 days into the current cycle, is stable and compares favorably with the previous two cycles in spite of the increased severity of the current operation, as shown in Figure 9.

Looking to the next operating cycle, the customer invited catalyst suppliers to bid for the next reload—this time with a higher endpoint and lower API gravity feed. Because the customer continues to demand the best possible catalyst system, the customer again went to third-party testing to see if anything better was available. ART proposed the same catalysts for this proposal with an optimized stacked loading containing a higher ratio of ICR 214 to ICR 183 compared to the current loading. This will further increase the activity of the cracking catalyst system and position the unit for a longer cycle length. Based on rigorous testing against several competing suppliers, and confidence in ART’s ongoing technical service, ART again has been chosen to supply the next load.

Selecting the right catalyst can be a very rewarding experience for both the customer and the supplier. It is very easy to become complacent with catalyst, as the risk of change is always a concern. However, a close working relationship between refiner and supplier can result in a stronger catalyst system that will meet and exceed all operating objectives. Risk of change can be minimized via third-party testing and proving stated yields and product properties. This particular customer has experienced a dramatic improvement in unit profitability by enabling the processing of more feed, and more difficult feed, without compromise. This strong relationship also includes a strong technical service component to assure that all objectives are met throughout the operating cycle.

Please contact your ART representative to see how you might improve your operation.
Global leader in hydroprocessing catalysts offering the complete range of catalysts and services

artcatalysts.com
The refinery octane pool is balanced and determined by the aggregate performance of multiple process units. The octane making units—naphtha catalytic reforming, light naphtha isomerization, etherification, and alkylation—provide the potential for octane improvement and optimized blending strategies that allow the refinery to comply with gasoline specifications, mainly octane, aromatic content, RVP, sulfur, and oxygen. However, the fluid catalytic cracking unit (FCCU), by far, provides the most flexibility. Over a wide range of feed stocks, the FCCU operation and catalyst formulation can be adjusted to increase octane and meet other yield objectives.

**Operating Conditions and Strategies to Maximize Octane**

FCC naphtha octane can be increased by adjusting operating conditions, such as riser outlet temperature (ROT). A general rule is that the gasoline research octane number (RON) increases by 1 number for every 18°F increase in ROT, whereas ROT has less impact on motor octane number (MON). Since further octane gains diminish as ROT is increased, the starting base octane must be considered.

Moreover, unit constraints like LPG handling capability, wet gas compressor limit, or regenerator temperature can limit FCC operating flexibility. From an operational standpoint, increasing mix zone temperature will increase octane, but also will increase conversion, potentially creating a challenging balancing act against an LPG handling constraint.

Depending upon available options, economics, and refinery constraints, it might be beneficial for the refinery to consider changes in feedstock composition to address the gasoline octane shortfall. For example, a more aromatic feedstock would tend to provide a higher octane gasoline component compared to a more paraffinic feedstock. Additional residual feedstock processing could also meet an enhanced octane objective. However, a change in the catalyst composition would likely also be required to enable the processing additional resid feed in the FCCU without exceeding some of the constraints of the operation like coke and gas make.

If the refinery is limited by wet gas compressor capacity, minimizing dry gas and hydrogen production will create room to make other operational changes to increase gasoline octane. Reductions in dry gas or hydrogen yield can be achieved catalytically or through optimization of operating variables. Operating changes that lower the mix zone temperature and modify heat balance can help reduce dry gas. Selection of feed stocks with reduced metal contaminants can impact the hydrogen and gas make by lowering the occurrence of dehydrogenation reactions promoted by Ni, and to a lesser extent V and Fe. Additionally, incremental FCC LPG olefinicity can provide more feedstock for the alkylation unit, which will ultimately increase the refinery octane pool. The option to boost LPG olefinicity may not prove as beneficial if the LPG constraint results from a hydraulic recovery capability, storage, alkylation capacity constraint, etc., downstream of the FCCU.

Operating conditions and strategies are of primary importance, but many refiners do not have the operating window to drive significant increases in octane with operational moves alone. A more dramatic shift can be achieved with catalyst optimization.

**Driving Octane through FCC Catalytic and Additive Strategies**

Catalysts provide several possibilities to drive octane (see Figure 1). Optimization of the FCC catalyst formulation can minimize hydrogen transfer reactions, which produce lower octane gasoline components in favor of isomerization or branching reactions; these, in turn, produce higher octane gasoline components.
Catalytically, hydrogen transfer reactions can be adjusted through control of zeolite unit cell size (UCS). Catalytic solutions also can help widen the range of unit operating conditions without hitting the FCC unit constraints. An example is a catalyst formulated to reduce hydrogen and dry gas, relieving a wet gas compressor capacity limitation, thereby providing an opportunity for increased operational severity.

In addition to traditional catalyst optimization for controlling hydrogen transfer activity and low value product selectivities, there are three main improvement routes for gasoline octane: new FCC catalysts, octane boosting FCC additives, and gasoline sulfur reduction additives.

**New FCC Catalysts to Maximize Octane**

Grace continuously drives innovation to address market changes. In 2014, Grace introduced ACHIEVE® 400 FCC catalyst, which is designed to provide a more olefinic yield slate. ACHIEVE® 400 catalyst is formulated with multiple zeolites and tailored acidity to deliver an optimum level of butylenes, to keep a downstream alkylate unit full and maintain refinery pool octane. Incorporation of isomerization activity into the catalyst particle itself results in a more desirable yield pattern than would be realized by use of a traditional octane boosting FCC additive. In addition, ACHIEVE® 400 catalyst has been shown to increase the octane of FCC naphtha. In multiple commercial trials, ACHIEVE® 400 catalyst is delivering incremental octane and butylene, worth on average $0.60/bbl.

Figure 2 shows field performance of ACHIEVE® 400 catalyst. LPG was shifted significantly, with a marked improvement toward light olefins, preferentially boosting butylene yield and selectivity, together with gasoline octane. Using ACHIEVE® 400 catalyst provides the advantage of a direct improvement in FCC gasoline octane, as well as operational flexibility to further increase FCC gasoline octanes, while increased butylene yield contributes to increased downstream high octane alkylation gasoline production.

**Traditional Octane Boosters**

ZSM-5 additives, such as Grace’s OlefinsUltra® additives, are proven solutions for boosting gasoline octane and petrochemical feedstocks. The use of FCC additives has recently surged in popularity due to their ability to increase LPG olefins. Propylene and butylene yields increase at the expense of FCC naphtha with ZSM-5 additive use, while resulting in FCC naphtha with a higher octane value, improving both RON and MON. As prevailing economics shift, the LPG olefin and octane benefit can be optimized by adjusting additive injection rates without changing the FCC catalyst system. Moreover, neat addition of ZSM-5 additives allows the refiner to increase LPG olefins and gasoline octane and adapt with additional flexibility to evolving market needs. Increasing FCC LPG olefinicity with ZSM-5 additives—and, as mentioned earlier, with more selective FCC catalysts—provides an efficient and flexible route to increase alkylate unit feedstock, improving gasoline pool octane and yields.

“Unconventional” Approaches to Maximize FCC Gasoline

Typical gasoline hydrotreating can significantly reduce the octane of the gasoline pool. Commercially proven gasoline sulfur reduction catalysts and additive solutions can reduce FCC gasoline sulfur, allowing the refiner to decrease gasoline hydrotreating severity, minimizing gasoline octane loss. Some refiners are already minimizing the octane loss in gasoline post-treatment units by lowering FCC naphtha sulfur with Grace’s GSR® FCC catalyst and additives. Gasoline sulfur reduction technologies with GSR® catalysts and additives can reduce FCC gasoline sulfur by 20-40%, preserving octane while meeting Tier 3 gasoline specifications. Since 2000, GSR® catalysts and additives have been used continuously around the globe to minimize sulfur in FCC gasoline. Yet, amid today’s regulatory environment, these products are frequently utilized for octane preservation.

**FCC Catalysts Solutions – Close Partnering with Refiners: A Key Response to the Octane Challenge**

Taking advantage of the flexibility that the FCC unit provides is at the heart of a strategy to drive higher gasoline octane. Several options exist to increase gasoline octane barrels and refinery profitability. These options include operating changes, feedstock management, catalytic optimization, and combinations thereof. Some key themes emerge from the octane challenge:

1. **Responses are highly refinery-dependent.** Challenges manifest differently at every refinery due to the unique combination of feedstocks, constraints, refinery configuration, and yield objectives. As such, the solutions are highly dependent on a solid understanding of these refinery-specific conditions.

2. **Most refiners are employing a multi-faceted approach to these challenges.** More than ever, these challenges require optimization of the entire refinery and not just individual units.

3. **Communication with industry partners is an integral part of successfully overcoming challenges.** While our customers are focused on octane maximization for the foreseeable future, the only dependable statement is that things are likely to change. The keys to success are establishing systems and promoting business practices that allow refiners to quickly capitalize on market changes.

*Continued on Page 16*
Selection of the optimal FCC catalysts and additives from Grace’s broad portfolio is the fastest route to higher octanes and maximum refinery profitability. Grace’s innovative catalytic and additive solutions provide ways of optimizing octane and refinery profitability. A close partnership and collaboration between Grace’s technical team and our refining customers accelerates FCC unit and catalyst optimization, translating into a faster route to profitability improvement in a demanding market environment.

**Figure 2.** ACHIEVE® 400 catalyst increased butylene yield and selectivity in a commercial FCCU.
In today’s refining environment, you need to be ready for anything.

The new ACHIEVE® series of FCC catalysts from Grace hands you the versatility and functionality you need for today’s dynamic refining environment. Select the ACHIEVE® catalyst advantage that’s right for your feeds, your process, and your business requirements.

**ACHIEVE® 100**  
High activity for light feedstocks

**ACHIEVE® 200**  
Coke-selective bottoms conversion

**ACHIEVE® 300**  
Propylene selectivity

**ACHIEVE® 400**  
Octane and butylene selectivity

**ACHIEVE® 800**  
Maximum metals tolerance and resid conversion

Get all the tools you need.  
Visit grace.com/achieve to learn more about how we can tailor a formulation to meet your most challenging requirements.
Catalyst Best Practices – Lessons from Resid FCC Units in the Middle East

Nathan Ergonoul
Director of Sales and Technical Services, Middle East

The Middle East expansion into the refined products market is driving large-scale, highly complex refinery projects. These projects include some of the world’s largest capacity FCC units, generally processing very challenging feedstocks.

Operating large FCC units on challenging feedstocks inevitably means that the choice of FCC catalyst will have a big impact on overall refinery profitability. In addition to performance considerations, logistics becomes critical to handling the large volume of fresh FCC catalysts and additives, which can be an order of magnitude larger than an average FCC unit. Along with that comes a considerable volume of spent catalyst that is generated.

The solution is a combination of performance; the right catalyst and experienced local technical service support; proven logistics capabilities, including supply logistics for the management and handling of a large volume of fresh catalysts and additives; and logistics for the environmentally friendly management of a large volume of spent catalyst (see Figure 1).

The Market in the Middle East

Originally commissioned in 1981, the Abu Dhabi Oil Refining Company (Takreer) in the United Arab Emirates (UAE), recently completed an expansion project with the aim of increasing production capacity by 417,000 bpd, taking the existing capacity from 400,000 bpd to 817,000 bpd. The core unit in the new configuration is an Axens IFP R2R™ RFCC. The new Takreer RFCC unit is one of the largest FCC units, and the largest RFCC unit in the world, processing heavy residual feedstocks with a design throughput of 127,000 bpd.

Grace is the global leader in resid catalyst and the preferred local catalyst supplier in the Middle East. Grace supplies catalyst to more than 60% of the resid catalyst market, and represents 80% of the Middle East catalyst demand. To support our local commitment in the region, Grace is building the first FCC catalyst manufacturing facility in the Middle East near Abu Dhabi, in a joint venture project with Al Dahra Agriculture. The first phase of construction on the $150 million facility was completed earlier this year with the commissioning of a catalyst logistics silo terminal.

Optimum Catalyst Performance

To enable maximum performance of Takreer’s RFCC unit, Grace proposed a finely tuned resid FCC catalyst that exhibits high zeolite stability due in part to a state-of-the-art vanadium trapping functionality. The catalyst also incorporates advanced nickel tolerance and a balanced mesoporosity to achieve the optimum level of coke-selective bottoms cracking. This will allow the refinery to achieve its FCC product objectives while helping to mitigate the contaminant metals present in their resid feedstock.

One of Takreer’s specific performance objectives is to increase LPG olefins production. Grace maximizes light olefins production with low hydrogen-transfer activity. In addition, propylene production will be enhanced further by Grace’s OlefinsUltra® HZ light olefins additive, a patented technology used in more than two-thirds of FCC units targeting maximum propylene.

Maximizing the performance of the catalyst-additive system also benefits from compatible physical properties of the catalyst and additives that Grace has engineered to complement each other. Both the FCC catalyst, Nektor™ ULCC, and the additive exhibit industry-leading attrition resistance, a hallmark of Grace technology. Grace’s superior attrition resistance minimizes losses from the FCC process.

Technical Support

Realizing the full value from the catalyst requires a highly experienced technical service team. Grace’s engineers bring experience from across the industry with design, operation, and troubleshooting expertise. Supported by comprehensive analytical service capabilities, Grace’s technical service team ensures that the value of the catalyst is optimized through regular performance reviews, benchmarking, and continuous optimization of the catalyst formulation and unit operation.

The Grace technical service team is highly experienced in refining, especially in the field of FCC design and operation. Based on this experience, Grace’s team is able...
to provide expert advice on a broad range of FCC and refining topics; for example, FCCU operational and mechanical troubleshooting. Grace technical service engineers regularly visit refineries to review unit operating data, evaluate catalyst management and unit performance, and provide specific recommendations to optimize unit operations.

Grace regularly assists with troubleshooting service around issues that impact FCC performance, including cyclone performance, stripper efficiency, catalyst circulation and aeration, slurry circuit fouling, and unit erosion.

In addition to regular follow-ups, Grace provides independent critical review services, which allows for a health check on FCC operations. Throughout the history of fluid catalytic cracking, these services have been relied upon by many oil companies for unit optimization, shutdown planning, and capital expenditure planning.

As the market leader in FCC catalysts, Grace has built up an extensive, unique pool of FCC experience and know-how. Grace shares this accumulated knowledge with customers in semiannual workshops specifically designed for FCC process engineers. These workshops cover such topics as catalyst

Continued on Page 20
fundamentals, feedstock characterization, heat balance, mass balance, unit optimization, and troubleshooting strategies. The workshops are offered at customer sites and regional locations, as well as our major manufacturing plants, research centers, and headquarters in the United States and Germany.

**Catalyst Handling**

To handle the large amount of FCC catalyst and provide security of supply for Takreer, and to maintain Grace’s position as the leading supplier in the region, Grace has invested significantly in local production. Phase 1 of a new grassroots FCC catalyst manufacturing plant was completed in 2015. Phase 1 provides Takreer with secure supply, with storage and handling facilities for a large volume of fresh catalyst and additives, as well as the expected volume of spent catalyst.

Another benefit of having logistics facilities close to the refinery is to allow FCC catalyst delivery by bulk truck rather than in smaller packaging; for example, super sacks. Delivery in bulk trucks helps limit the risk of environmental and operator exposure to the catalyst by eliminating dust emissions associated with the use of bags.

Working with Grace’s local FCC catalyst production plant enables Takreer and other Grace customers in the region to make rapid catalyst reformulations to meet changing operational or product objectives. Local facilities benefit refining companies in the region by reducing reformulation time from approximately two months to just a few days.

**Spent Catalyst Disposal**

The disposal of large amounts of spent catalyst (Ecat) in an environmentally friendly way is an important consideration for refineries. Grace has a permit to collect, store, handle, reprocess, and re-sell Ecat and fines generated from Grace manufactured FCC catalysts.

For Ecat containing high levels of contaminant metals, Grace has an agreement to rework such materials through various outlets, which are fully in compliance with REACH regulations. As an example, Grace has safely exported and reworked more than 30,000 MT of spent catalyst from the large resid FCC unit at Orpic in Oman.

**Conclusion**

Maximizing FCC profits requires selection of the right catalyst, supported by an extensive technical service team with a broad background in FCC and refinery operations. The trend toward large-scale refinery complexes, and FCC units with combined catalyst and additive usage rates several times that of typical, average-sized FCC units, as well as disposal requirements for the considerable volume of spent catalyst, requires extraordinary logistics capabilities. In some cases, the combination of high usage rates and a remote location requires local investment.

Drawing on extensive catalyst manufacturing capabilities, formulation expertise, technical service, and logistics capabilities, Grace is committed to the overall success of our customers. And, as demonstrated with the establishment of Grace facilities in the Middle East, Grace is uniquely positioned to rapidly meet the challenges of future FCC operators around the world.
Ask the Experts

This regular column will feature answers to frequently asked questions from Grace experts across the Catalysts Technologies Portfolio. In this issue, the experts tackle the FCC questions from the AFPM Q&A session held in New Orleans in October 2015.

If you have a question you would answered in a future issue, please submit it to Rick.Ostopowicz@grace.com.

Colin Baillie has been with Grace since 2006. He is currently the Environmental Additives Portfolio Manager within the Refining Technologies group. Colin obtained a Ph.D. in Chemistry from the University of Liverpool in 2004, and an MBA from the Open University in the UK in 2015.

Colin Baillie

Ken Bryden is Manager of Catalyst Evaluations Research and Services for Grace. He is also DCR Licensing manager. His team is responsible for developing and providing testing services to support customer technical service and development of new catalysts for the Refining Technologies product line. Ken holds a B.S. degree in Chemical Engineering from the University of California Davis and a Ph.D. in Chemical Engineering from the Massachusetts Institute of Technology. He is the co-inventor on one issued U.S. Patent and the co-author of 10 peer-reviewed journal articles and numerous trade press publications.

Kenneth Bryden

Ann Benoit is the FCC Technical Service Americas Leader. She holds a B.S. degree in Chemical Engineering from Tennessee Technological University. Ann joined Grace in 2008. Prior to joining Grace, she worked at CITGO Lake Charles refinery. During her tenure at CITGO, she held various positions such as FCCU process engineer, economic analyst, and logistics manager. Currently, Ann serves as the Grace technical representative on the American Fuel and Petrochemical Manufacturers (AFPM) screening committee. She also manages the North American Grace FCC Technical Workshops. She has 15 years of refinery and catalyst experience.

Ann Benoit

Shankhamala Kundu is working as R&D engineer in Grace RT Catalyst Synthesis Research group located at Columbia, Maryland. She is responsible for developing new catalysts for the Refining Technologies product line and providing research support to customer technical service. Shankha holds a M.S. degree in Solid State Physics from Indian institute of Technology, Delhi and a Ph.D. in Industrial Chemistry from Ruhr University Bochum, Germany, with Max Plank Research fellowship. Shankha worked at Brookhaven National Lab in New York, as Postdoctoral Research Associate before joining at Grace in 2013. She is the co-author of thirty peer-reviewed journal articles and numerous conference publications.

Shankhamala Kundu
Q: With environmental regulations becoming more stringent on FCC stack emissions what are your available options to achieve the required level of SOx and NOx emissions?

Grace has a portfolio of additives to help refiners reduce the amount of SOx and NOx produced in the FCC unit.

**SOx Reduction Additives:**

SOx reduction additives offered by Grace are Super DESOX® and Super DESOX® OCI additives, which have been used to control SOx emission levels to below 25 ppmv SOx. These SOx reduction additives are microspheroidal powders that have similar physical characteristics to those of FCC catalysts, and are typically used at dosing rates of 5 to 10 wt% of fresh catalyst additions. Figure 1 shows a back-to-back comparison of the two additives at comparable usage rates, excess oxygen and feed sulfur levels, in which flue gas SOx levels were maintained below 25 ppmv for both periods.

Super DESOX® and Super DESOX® OCI additives reduce flue gas SOx emissions through a three-part mechanism.

1. Sulfur bound in coke is oxidized to SO\(_2\) in the FCC unit regenerator. Grace’s SOx reduction additives subsequently promote the oxidation of SO\(_2\) to SO\(_3\), which is often the rate-limiting step.

2. The resulting SO\(_3\) is subsequently captured by the additive and converted into magnesium sulfate, which is facilitated through the incorporation of a patented magnesium spinel in the product.

3. The SOx additive is then transferred to the riser/stripper section where the magnesium sulfate is ultimately reduced back to its active state regenerating the additive and releasing the sulfur as H\(_2\)S.

Properly balancing the additive’s ability to promote each of the above three steps is necessary for achieving the best SOx reduction performance. Grace’s SOx reduction additives have been used in more than 100 commercial applications worldwide.

![Figure 1: Both Super DESOX® and Super DESOX® OCI additives controlled SOx to less than 25 ppmv.](image)

Another case study for Super DESOX® additives was published in a joint article with the BP Castellon refinery in Spain. Based on a commitment to reduce emissions as well as increasingly stringent emissions standards, the refinery trialed the Super DESOX® additive. Figure 2 shows the SOx emissions observed using the Super DESOX® additive compared to the correlated uncontrolled SOx levels that would have been obtained without additive. The refinery achieved their trial targets and observed SOx reductions of approximately 70%.

![Figure 2: SOx levels obtained using Super DESOX® additive compared to uncontrolled SOx emissions.](image)
NOx Controlling Additives

While SOx chemistry is well-understood, the chemistry of NOx formation within the FCCU regenerator is extremely complicated and typically unit specific. Early experiments by Grace showed that the source of NOx is the nitrogen bound to heavy molecules in the FCCU feed, which are ultimately burned as coke in the regenerator.

About 50% of the nitrogen in FCCU feed typically enters the regenerator; however, less than 10% of this nitrogen is usually emitted as NOx. Coke-bound nitrogen can take one of three paths: it can be reduced to N$_2$, oxidized to NO and NO$_2$, or it can remain in an intermediate stage, such as NH$_3$ or HCN. These intermediate stage nitrogen species have the potential to oxidize to N$_2$ or NOx, and there are several unit factors which can play a role in the direction they take. For example, high dosing rate of a CO promoter can cause these species to be oxidized to NO, increasing overall emissions. Use of CO promoters will also reduce the amounts of various reductants present in the regenerator; thereby further exacerbating NOx emissions in the flue gas. The simplified mechanism of NOx formation is shown in Figure 3.

Grace offers two types of catalytic additive technologies for reducing NOx levels in the FCC unit: Low NOx combustion promoters and standalone catalytic NOx reduction additives.

Low NOx Combustion Promoters:

CP® P combustion promoter is Grace’s 3rd generation non-platinum based, low-NOx combustion promoter. CP® P combustion promoter is designed to catalytically promote CO combustion with a similar efficiency of a traditional platinum-formulated CO promoter, yet with a reduced propensity to generate NOx emissions.

CP® P combustion promoter was recently used in a refinery trial as an alternative to a platinum-based promoter, with the objective of reducing NOx emissions while maintaining CO promotion activity. Factors affecting NOx formation are mainly feed nitrogen, Ecatal platinum content, regenerator air distribution, excess oxygen, dense bed temperature and dense bed level. Correlation models are important to determine catalytic additive performance in a dynamic environment, such as an FCC regenerator. Figure 4 shows the correlation made before the trial to calculate the predicted NOx emissions. From the data available, the best correlation found was related to excess oxygen. Figure 5 shows how the NOx emissions decreased when switching from the platinum-based promoter to CP® P.

Standalone Catalytic NOx Reduction Additives:

Grace’s portfolio includes DENOX® additive, which is a standalone NOx reduction additive without combustion promotion activity. Since its introduction in 1997, DENOX® has been successfully evaluated in a wide range of FCCUs. DENOX® is typically used at dosage rates of between 0.15 to 2.5 wt% of fresh catalyst additions and has provided a range of NOx reductions from 15 to 60% (Figure 6).

Continued on Page 24
DENOX® additive has been used to reach as low as 26 ppm NOx, as shown in Figure 7. In this FCC unit, DENOX® was used at 1 wt% of fresh catalyst additions and demonstrated 75% NOx reduction.

Several direct catalytic options exist for management of octane in the FCC. We will discuss the impact of ZSM-5 additives, and changes to base catalyst with respect to hydrogen transfer. Additionally, we will discuss the “indirect” use of Grace’s GSR® technologies to preserve refinery octane.

One way of increasing FCC gasoline octane is through the use of a ZSM-5 based additive. Figure 1 shows how RON can be boosted considerably by increasing the amount of additive in the inventory. The effect of ZSM-5 is more pronounced at lower initial conversion levels. Grace offers a variety of ZSM-5 based additives OlefinsMax®, OlefinsUltra® and OlefinsUltra® HZ FCC additives increase light olefins yield for petrochemical applications or alkylation feed while maximizing gasoline pool octane.

The FCC catalyst itself plays a significant role, with a lower unit cell size (UCS) typically providing higher gasoline octane though a reduction in hydrogen transfer reactions. As shown in Figure 2, RON and MON can be increased by 3 and 1 numbers, respectively, over a UCS range of 24.24 to 24.40 Å. The gain in gasoline octane comes at the expense of approximately 2 wt.% gasoline, which is cracked into LPG olefins.

Q: Octane may become an issue as refiners increase severity on the FCC gasoline post treatment units. What are your options available to address octane debits?

A: Colin Baillie

Several direct catalytic options exist for management of octane in the FCC. We will discuss the impact of ZSM-5 additives, and changes to base catalyst with respect to hydrogen transfer. Additionally, we will discuss the “indirect” use of Grace’s GSR® technologies to preserve refinery octane.

One way of increasing FCC gasoline octane is through the use of a ZSM-5 based additive. Figure 1 shows how RON can be boosted considerably by increasing the amount of additive in the inventory. The effect of ZSM-5 is more pronounced at lower initial conversion levels. Grace offers a variety of ZSM-5 based additives OlefinsMax®, OlefinsUltra® and OlefinsUltra® HZ FCC additives increase light olefins yield for petrochemical applications or alkylation feed while maximizing gasoline pool octane.

The FCC catalyst itself plays a significant role, with a lower unit cell size (UCS) typically providing higher gasoline octane though a reduction in hydrogen transfer reactions. As shown in Figure 2, RON and MON can be increased by 3 and 1 numbers, respectively, over a UCS range of 24.24 to 24.40 Å. The gain in gasoline octane comes at the expense of approximately 2 wt.% gasoline, which is cracked into LPG olefins.
The impact that the FCC catalyst can have on gasoline octane is demonstrated through a recent Grace publication.[1] The refinery switched from an alternate supplier to a Grace catalyst with an optimized UCS, which led to an increase in the FCC gasoline MON by 0.5 numbers enabling the refinery to produce 5% more premium grade gasoline.

In addition to increasing FCC unit octane, both the ZSM-5 additive option and the base catalyst UCS option have the added benefit of producing more olefinic yields – thus creating more alky feed for the refinery. This can provide a ‘double octane benefit’ to the refinery, presuming the refiner has the capability to alkylate the additionally produced light olefins.

The use of Grace’s GSR® technologies for gasoline sulfur reduction is also an option for maintaining or increasing gasoline octane. Decreasing the sulfur content of FCC gasoline in the cat cracker allows the severity of the post treatment to be reduced, which will preserve gasoline octane. This is highlighted by the following example from a North American refinery (originally published in AFPM AM-07-06).[2] A feed hydrotreater outage resulted in higher sulfur feeds being processed in the FCCU. The projected gasoline sulfur would have forced the refiner to hydrotreat approximately 5 MBPD of FCC gasoline to comply with emission specifications. The loss of octane from hydrotreating the FCC gasoline would have forced the refiner to hydrotreat the additional gasoline stream, which will reduce gasoline octane. This is highlighted by the following example from a North American refinery (originally published in AFPM AM-07-06).[2] A feed hydrotreater outage resulted in higher sulfur feeds being processed in the FCCU. The projected gasoline sulfur would have forced the refiner to hydrotreat approximately 5 MBPD of FCC gasoline to comply with emission specifications. The loss of octane from hydrotreating the FCC gasoline would have forced the refiner to hydrotreat the additional gasoline stream, which will reduce gasoline octane.

To summarize, there are several avenues in which gasoline octane can be increased, depending on the specific situation the refinery is facing. Refiners can consult their catalyst representative to find the current balance of products, as well as optimized UCS of the base catalyst to allow the refinery to meet the overall product performance goals.


While the question asks specifically about isopentane production, other C5 hydrocarbons also have significant vapor pressure. Isopentane has a Reid Vapor Pressure (RVP) of 20 psi, n-pentane has a RVP of 16 psi and the C5 olefins have RVPs between 14 and 26 psi.[1] For refineries desiring to minimize RVP, it is also important to minimize the quantity of C4’s in the gasoline pool since C4’s have even higher vapor pressures than C5’s.

Isopentane is mainly produced in the FCC unit via two pathways. The first pathway is cracking where isopentane is formed when a larger paraffin molecule cracks via β-scission to form isopentane and an olefin. The second main pathway for isopentane production involves hydrogen transfer reactions that transform C5 olefins into isopentane. Hydrogen transfer is a disproportionation reaction where hydrogen is moved between molecules. Isopentane production is influenced by operating conditions, feedstock properties, and the properties of the catalyst used. Factors that influence hydrogen transfer have the greatest impact on isopentane production.

As conversion is increased (by either increasing reactor temperature or by increasing catalyst-to-oil ratio), the quantity of isopentane (and gasoline) increases. At constant conversion, increasing reactor temperature will reduce the amount of isopentane produced, as hydrogen transfer tends to be favored at lower reactor temperatures. And since hydrogen transfer is a bi-molecular reaction, decreasing reactor pressure lowers hydrogen transfer and will lower the amount of isopentane produced.

As a feedstock becomes more naphthenic, the production of isopentane tends to increase. This is because naphthenes are good hydrogen donors and react with gasoline range olefins to make aromatics and gasoline range paraffins.[2]

FCC catalyst can affect the rate of isopentane production through hydrogen transfer activity. As hydrogen transfer increases, more paraffins are formed and isopentane production increases. Figure 1 presents isopentane yields on a fresh feed basis at 72% conversion for a series of catalysts with a range of unit cell sizes (UCS) between 24.22 and 24.44Å. In order to maintain similar activity, the higher UCS catalysts were formulated to a lower zeolite level. Figure 2 presents isopentane concentration in gasoline as a function of UCS for the same catalysts. As expected, isopentane yield and concentration in gasoline increase with UCS since the acid site density and the relative rate of hydrogen transfer to cracking is increasing.

The use of ZSM-5 based additives does not significantly change the yield of isopentane on a fresh feed basis, but will increase the relative concentration of isopentane in the gasoline. As the higher olefins in gasoline are cracked by the ZSM-5 to propylene and butylene, the gasoline becomes enriched in isopentane. Figure 3 presents isopentane yield on a fresh feed basis for a series of ZSM-5 additive levels. While there is a slight increase in isopentane yield with ZSM-5 additive level, the isopentane yields are all close together. Figure 4 presents isopentane concentration in gasoline for the same series of ZSM-5 additive levels. As seen in the figure, isopentane concentration in gasoline increases with increasing ZSM-5 additive level.

In summary, a number of factors influence isopentane production, including feedstock, unit operating conditions and the properties of the catalyst system used. Refiners desiring to reduce gasoline RVP should look at more than just isopentane since other C4’s and C5’s also contribute to vapor pressure. If catalyst changes are envisioned to minimize RVP, it is important to remember that multiple objectives must be met in FCC operation and careful consideration of operating objectives and unit constraints is needed when selecting a catalyst. Grace’s technical service team can help identify the best catalyst choice to meet refinery objectives.

Figure 1: Effect of base catalyst unit cell size on isopentane yields (fresh feed basis). DCR™ Pilot Plant results interpolated to 72 wt% conversion.

Figure 2: Effect of base catalyst unit cell size on isopentane concentration in gasoline. DCR™ Pilot Plant results interpolated to 72 wt% conversion.

Figure 3: Effect of ZSM-5 additive level on isopentane yield (fresh feed basis). DCR™ Pilot Plant results at 970°F reactor temperature.

Figure 4: Effect of ZSM-5 additive level on isopentane concentration in gasoline. DCR™ Pilot Plant results at 970°F reactor temperature.
Q: When relying primarily on FCC feed pretreating to meet FCC gasoline sulfur specifications (current or future Tier III), how do you manage feed pre-treater outages?

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

One such example of a refiner that used Grace’s GSR® 5 sulfur reduction additive during a feed hydrotreater outage is shown in Figure 1. The refiner was able to process higher than typical feed sulfur and maintain gasoline pool sulfur compliance. Use of GSR® 5 additive began two months prior to the 45-day feed hydrotreater outage. During that time, feed sulfur increased by as much as 35%. The three periods represented are typical operation (Base Period), GSR® 5 additive before and during the outage where gasoline sulfur reduction ranged from 20-25%, and finally GSR® 5 additive following the outage. The customer estimated that use of GSR® 5 additive netted $1.7 million of savings during the hydrotreater outage. The results were so encouraging that the customer elected to continue using GSR® additive technology, switching to a SuRCA® catalyst and operating with post-outage feed sulfur 10-15% higher than the typical operation. This change to their operation grew annual profits by approximately $8 million.\[1\]

Grace’s clean fuels technologies include D-PriSM® and GSR® 5 FCC additives, as well as SuRCA® FCC catalysts, which are the result of almost two decades of innovation. Grace’s clean fuels technologies have been used in more than 100 FCC applications worldwide delivering 20%-40% sulfur reduction in FCC naphtha in both full and partial burn operations. The D-PriSM® and GSR® additive technologies are used at a 10%-25% loading in inventory, whereas the catalytic solutions are a customized 100% drop-in replacement for your base catalyst. Grace’s clean fuels technologies allow for a truly customized solution for the management of feed pre-treater outages, or the compliance of environmental regulation.

Grace’s gasoline sulfur reduction technologies, GSR® FCC catalysts and additives, are the leading solutions to help meet fuels regulations. Refiners achieving 25%* FCC naphtha sulfur reduction can realize as much as $2-3 million per year in incremental margin with GSR® via octane preservation and naphtha endpoint optimization.

Get that last barrel into your gasoline pool.
Contact your Grace representative to determine how much more margin you can capture now with Grace’s Clean Fuels Technologies.

grace.com
catalysts@grace.com

*results may vary based on actual operating parameters
Grace’s GSR® additives are effective under a wide range of operating conditions in the FCC unit. There have been numerous case studies and references supporting the robust performance of GSR® technologies, in which 20-40% gasoline sulfur reduction has been observed for a wide range of:

- feed types
- feed sulfur levels
- gasoline sulfur levels

Grace’s GSR® additive technologies are particularly effective for removing mercaptans, sulfides, tetrahydrothiophenes, and thiophenes in the gasoline. Benzothiophenes are harder to remove, while dibenzothiophenes generally remain unaffected under FCC operating conditions. Therefore, a key factor in determining the actual level of gasoline sulfur reduction is the identification of the sulfur species present in the gasoline. Figure 1 shows gasoline sulfur species distributions for various non-hydrotreated feeds (U1-U3) and hydrotreated feedstocks (H1-H3). All of the gasoline streams contain the same types of sulfur species, although their distribution varies. Grace’s GSR® additive technologies would result in gasoline sulfur reduction for all of these streams, though higher reductions would be observed for those containing a lower proportion of benzothiophenes, highlighting the suitability of GSR® additive technology for various feed types.

Feed sulfur type plays a bigger role than feed sulfur content in the level of gasoline sulfur reduction observed. Multi-ring aromatic thiophenes in the feedstock will not contribute to sulfur species in the FCC gasoline, so have little impact on subsequent GSR® additive performance. In contrast, alkylbenzothiophenes in the feedstock undergo dealkylation resulting in benzothiophenes in the gasoline. These are harder to remove than the thiophenes, sulfides and mercaptans that result from the alkylthiophenes and cyclic sulfides in the feed. Therefore, although Grace’s GSR® additive technologies will provide gasoline sulfur reduction for all feedstocks, those with a higher proportion of alkylthiophenes compared to alkylbenzothiophenes will see a greater gasoline sulfur reduction.

Removing thiophenes is a key part of gasoline sulfur reduction, of which the reaction pathway is shown in Figure 2. The FCC catalyst component promotes the hydrogen-transfer (HT) reactions between thiophenes and tetrahydrothiophenes (THT). GSR® additive technology works by increasing the cracking of THT into hydrocarbons and hydrogen sulfide.
Any conditions that promote HT reactions are likely to be favorable for gasoline sulfur reduction. These include reduced riser temperature and increased pressure, as well as a catalyst with an optimized unit cell size (UCS), though these play less of a part than feed sulfur species. This is highlighted by the current users of Grace’s GSR® additive technologies that are achieving high levels of gasoline sulfur reduction operating under the following various conditions:

- Riser temperature: 965-995 °F
- Feed preheat temperature: 430-625 °F
- Cat-to-oil ratio: 6-10
- Ecat UCS: 24.27 to 24.32 Å

When considering the lowest gasoline sulfur levels for which GSR® additive products are effective, there are many interesting case studies from Japanese refiners, which are producing gasoline with less than 10 ppm sulfur. In addition many of these refiners operate their feed pre-treater unit very severely, resulting in low FCC feed and gasoline sulfur levels. One such refinery had average gasoline sulfur levels of 13 ppm prior to the use of GSR® additive technology. After switching to Grace’s SuRCA® catalyst technology, they managed to achieve upwards of 30% reduction to control gasoline sulfur levels to below 9 ppm. SuRCA® catalyst is a tailored catalytic solution for gasoline sulfur reduction, and is used as 100% drop-in replacement of the previous base catalyst, with no increase in catalyst addition rates required.
Q: What are your best practices to address increased levels of conventional and “new” metals (V, Ni, Fe, Ca, Cu etc.) in the FCC that come from Tight Oil processing in the refinery?

Ann Benoit

The first consideration should be removal or minimization of the contaminant metals upstream of the FCC. Since removing or limiting these contaminants may not be an option, other methods must be considered to address their negative impacts.

It is recommended to evaluate the FCC catalyst and ensure it is properly designed to handle the metals of concern in the unit. Catalysts can be formulated to incorporate Ni and V traps which reduce the negative impacts from the metals. Grace employs an integral rare earth oxide-based vanadium trap in the catalyst to reduce the deactivation caused by vanadium poisoning.[3] With regard to nickel, Grace utilizes a matrix alumina to trap the nickel to reduce the harmful effects. In this system, nickel that deposits on the catalyst undergoes a solid-state chemical reaction that diminishes nickel’s dehydrogenation activity.[4]

To address iron (Fe) and calcium (Ca), it is crucial to have an FCC catalyst that is designed to resist the negative impacts of the metals. High alumina catalyst, especially catalyst with alumina-based binders and matrices, such as Grace’s MIDAS® and ACHIEVE® catalyst families, are best suited to process iron- and calcium-containing feeds because they are more resistant to the formation of low melting-point phases that destroy the surface pore structure. It is recommended to monitor bottoms cracking, Ecat ABD, and catalyst diffusivity for evidence of iron and calcium poisoning. A loss of bottoms cracking, unusually high slurry API, loss of conversion, a drop in Ecat ABD, and poor catalyst diffusivity are all indicators that the unit may be experiencing iron and calcium poisoning. The loss of bottoms cracking is due to feed molecules being blocked from entering the particle and being cracked at an active site of the catalyst. The Ecat ABD drops due to the formation of nodules on the catalyst surface, which prevent the Ecat from packing as densely. SEM pictures of the catalyst can be taken to confirm the nodule formation on the surface of the catalyst. Fe and Ca poison will cause the catalyst to be diffusion limited due to pore closure, leading to a loss in bottoms conversion. Grace has developed a proprietary laboratory test method that can confirm adequate or inadequate diffusion into and out of the pore of a sample of FCC Ecat® for use in FCC troubleshooting activities. If the unit is indeed experiencing negative impacts due to Fe and Ca, flushing the metals with higher catalyst additions and switching to a more resistant catalyst will be necessary for the unit to return to normal operations.

Other contaminants such as alkali metals and alkaline earth metals may be present in unconventional feedstock. These contaminants can cause a loss of unit conversion. One example is magnesium (Mg). While not a concern at low levels (<0.5 wt%), at higher levels, Mg has a tendency to react with silica from the zeolite to form forsterite (Mg₃SiO₅), which will decrease zeolite stability and adversely affect unit conversion. Note that MgO present on Ecat can be due to the presence of SOx-reducing additives and not feed contaminations.[5] Ecat properties and unit yields need to be closely monitored for negative impacts from these contaminants. If these contaminants start to impact the catalyst activity and unit yields, flushing the unit with higher catalyst additions could be required to return to normal operations.

In summary, the first strategy should be to evaluate removing or limiting the amount of contaminant metals that are in the FCC feed. This can be done by putting guidelines in place which set a maximum limit on the amount of contaminants being processed at the FCC. Also, when the economic analyses on these different feedstocks are being conducted, ensure they are being properly evaluated for the impact they will have on the FCC. It is suggested to close the loop on predicted yields and operating expense with actual yields and operating expense. Next, it is recommended to evaluate the catalyst and make certain that it is designed properly to handle the contaminant metals. Depending on the amount of contaminant metals levels and if the unit starts to experience negative impacts due to high contaminants, a flushing strategy may be required to get the unit back to normal operations. If purchased Ecat is being considered in the flushing strategy, it is important to evaluate and choose the right purchased Ecat that meets unit objectives. If needed, the refiner should discuss the different catalyst options with the technical service catalyst representative.

[4] Zehender, M., 2009 AFPM QA Question #44
Capture the Full Value of Your FCC Catalysts and Additives With the Most Advanced Addition Systems from Grace

Since 1986, Grace has supplied more than 260 catalyst and additive injection systems. From the first basic shot-pot designs for small-scale manual additive injection, Grace’s equipment has evolved into today’s large capacity automated systems capable of handling a refinery’s complete catalyst and additive addition requirements with a single system.

Grace’s latest systems utilize the most advanced control systems and an intuitive touch screen operator interface. These systems are capable of injecting multiple products directly from virtually any delivery or storage system, while limiting the risk of environmental and operator exposure.

For more information, visit us at grace.com

Supplying precision FCC catalyst and additive addition systems to the refining industry for 30 years.
Iron (Fe) is present in FCC catalyst as an element in the clay used in manufacture. Hence the iron content of the fresh catalyst is dependent on the clay source and the clay content of the catalyst and will vary from supplier to supplier and catalyst to catalyst. Additional iron comes into the FCC unit from contaminants in the feed and this additional iron can have adverse effects on catalyst performance when it results in an iron-rich glassy shell on the surface of catalyst. The shell inhibits diffusion thereby lowering conversion and increasing slurry yield.\[1\]

One of the first descriptive scientific publications on the subject of iron mobility was the Grace paper “Mechanism of Cracking Catalysts Deactivation by Fe,” that was published in 2004 in volume 149 of *Studies in Surface Science and Catalysis*.\[2\] In this paper, sink/float density separation was used to separate equilibrium catalyst into different age fractions. For a unit with a low to moderate amount of deposited iron, the iron showed a sharp, non-uniform distribution with catalyst age, suggesting that the iron had much lower mobility than V and Na in the unit and that iron mobility was similar to Ni (Figure 1). However, for a unit with a very high level of deposited iron, the iron distribution was relatively uniform between the different age fractions, suggesting that the interparticle mobility of iron was the same or higher than the vanadium mobility (Figure 2). In sink/float analysis of Ecat from additional units, Grace has found that iron can be mobile in some units and for those units the iron mobility is typically of the same magnitude as vanadium mobility.

In laboratory experiments where iron rich Ecat is steamed with fresh catalyst without deposited iron, we have found that some iron migration can occur to the fresh catalyst. The level of iron transfer increased with increasing steaming temperature and increasing contaminant iron level. In these experiments, we did not observe any reduction in the iron nodules present on the iron-enriched Ecat, and no nodule formation was observed on the fresh catalyst.

What is not fully understood is how iron moves from particle to particle within a unit and if this movement has any effect on catalyst performance. Detailed SEM and EPMA analysis of Ecat particles has found that deposited iron is always on the exterior surface of the particle and is not present in the interior of the catalyst particle. This suggests that iron does not migrate within an individual particle. If the iron transfer was via a gas-phase diffusion process, it would be expected to also move within an individual particle, which is not observed. The most likely means of iron mobility is physical transfer upon particle/particle contact. In the 2004 *Studies in Surface Science and Catalysis* paper, Grace noted that deposited iron in a unit comes from different sources (organic iron, finely dispersed sub-micron colloidal iron, and iron particulates), and that iron migration may be due to loosely attached iron rich dust migrating from particle to particle. It may be that the iron species that can move from particle to particle in a unit are not the same iron species that are responsible for the nodule formation on the surface of Ecat. Iron migration appears to be dependent on unit conditions and the types of iron present in the feed. The mechanism of iron migration in the FCC unit is an area of ongoing study.

To manage iron poisoning, refiners should reformulate to more iron-resistant catalysts and consider higher fresh catalyst additions. Catalyst design can be optimized to resist the effect of contaminant iron and calcium. High alumina catalyst, especially catalyst with alumina-based binders and matrices, such as Grace’s MIDAS® and ACHIEVE® catalyst families, are best suited to process iron- and calcium-containing feeds because they are more resistant to the formation of low-melting-point phases that permanently destroy the surface pore structure. Optimum distribution of mesoporosity (pores in the 100-600 Å size range) also plays a role in maintaining performance because diffusion to active sites remains unhindered, even with high levels of contaminant metals. The resistance of MIDAS® and ACHIEVE® FCC catalysts to iron and calcium poisoning has been demonstrated in numerous commercial applications.\[3\] \[4\] \[5\]

Continued on Page 36
When you can’t predict what’s in the pipeline

THINK MIDAS® FCC CATALYST
TO CAPTURE THE VALUE OF OPPORTUNITY CRUDES

grace.com
Some refiners also consider the use of flushing Ecat to temper Fe poisoning. This strategy can help to limit the effect of Fe on fresh catalyst, but comes with several caveats. One must make sure the Ecat in use is not contaminated with Fe (Fe poisoning can occur at levels as low as 0.2 wt% added Fe); additionally, the quality of the Ecat may require a change to the fresh catalyst strategy (either formulation or addition rates) to maintain desired unit performance.

In summary, iron can be mobile in an FCC unit, but it is unclear how iron mobility affects catalyst performance. Not all the factors influencing iron mobility are understood, but it appears to depend on iron concentration, temperature and the types of iron contaminants present in the FCC feed.


Simplicity is a key characteristic of UNIPOL® Polypropylene Process Technology:

- Fewer moving parts and less equipment overall compared to competing systems
- Smallest Inside Battery Limits (ISBL) footprint in the industry
- Easy access to key plant equipment for simplified maintenance

The result of our simple, common sense design approach is that the licensee will enjoy low capital costs and the low operating costs compared to competing systems.