Let’s do the math.

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

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

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


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

Learn more at grace.com/value.

grace.com
Recently, I was asked if I could sum up in a few words why our customers buy from us. My answer was simply: “Value.” I truly believe that our customers make more money because they do business with us.

Of course, the word “value” has different meanings. “Value buys” at your local retailer usually mean low quality and low price. That’s not what we’re talking about here.

Our standards are much higher, and so are our goals. We never want to be viewed as the “value buy” catalyst provider, with a one-size-fits-all approach. Our products and services are highly technical and are tailored to the specific needs of each customer.

So, let me explain what value means when it comes to partnering with us.

At Grace, value is all about our customers’ financial success. Our world-class technical service and catalyst solutions, developed collaboratively with our customers, provide more than just technology and performance. They are designed to increase each customer’s bottom line—by improving yields, increasing throughput or reliability, or solving a problem within the FCC, hydropochemistry or polylefin unit. Our goal is not just to sell good catalysts; our goal is to strengthen our customers’ businesses by providing exceptional financial return on their investment (and faith) in Grace’s talent and technology. And then, to prove it!

Our value to our customers takes many forms throughout the life of our relationship. It begins with the catalyst selection. Our team takes particular care in selecting the right catalyst formulation for the right reason for each of our customers. While an “off the shelf” solution may help them get by, we can go further to tailor our solutions to meet—or exceed—our customers’ expectations. And we continually review our technology to better our products through reformulations and new product development.

Another dimension of value comes from our collaboration with our customers. Catalagram and countless presentations at conferences like the AFPM Annual Meeting feature success stories that demonstrate our value. Last year at AFPM, we presented a case study on fighting the detrimental effects of a high-iron feedstock at a customer refinery—a collaboration that improved yields and increased customer profitability. At this year’s meeting, we are presenting case studies on Tier 3 gasoline and how Grace employs different strategies to help refiners maximize octane in an ultra-low sulfur gasoline market—and ultimately to improve their business.

Finally, our value comes from our efforts beyond delivering product solutions. Our Global Customer Technology team has extensive operational expertise and is dedicated to providing a full range of advanced FCC technical services, including site visits for troubleshooting of complex problems and unit-specific FCC consultation. We host workshops at our facilities in Worms, Germany and Columbia, Maryland that focus on helping our customers get the most from their FCC operations. And we continue to invest in research and development to adapt to new challenges and ever-higher performance standards.

At Grace, we take pride in the ability to deliver the talent, technology, and trust to make a significant positive impact for our customers. Those aren’t just a tagline—they are the tenets by which we operate, and the standard by which we measure our efforts.

Thank you for taking time to read this issue of Catalagram and to explore the value Grace has provided to a few of the customers named in these success stories. I welcome your feedback, and I invite you to explore new areas where we can work together to refine the financial performance of your operations.

This is what we mean by Value Delivered.
IN THIS ISSUE of the Catalagram® W. R. Grace & Co. experts demonstrate the value of doing business with Grace. From improved product performance to increased profitability, Grace’s FCC catalysts and additives and ART’s hydroprocessing catalysts and catalysts systems deliver significant value in today’s challenging refining environment.

What’s Inside

EDITORIAL
1 VALUE DEFINED, REFINED, AND DELIVERED

GRACE IN THE NEWS
4 STATOIL Chooses Grace As A Key Catalyst Technology Partner

5 Grace Makes Fast Progress Toward Sustainable Fuels

6 ECAT Lab in Oman Is First of Its Kind

SUCCESS STORIES
8 CEPSA Boosts Profitability Through FCC Catalyst Selection

16 ART FCC Pretreat Catalysts Provide Superior Technology, Performance

20 Additives Reduce Sulfur Content in FCC Naphtha

ASK THE EXPERTS
29 Q&A From The 2016 AFPM Cat Cracker Seminar
Statoil Chooses Grace as a Key Catalyst Technology Partner

**FCC Catalyst Supply Contract Extended Four Years**

Grace and Statoil, a multinational Norwegian energy company, announce the signing of a Framework Agreement for the continued supply of fluid catalytic cracking (FCC) catalysts to the Statoil Mongstad refinery in Norway as part of a four-year contract extension.

“Four years ago Statoil chose Grace to be a key FCC catalyst technology partner for the coming years,” said Tom Petti, President of Grace’s Refining Technologies business.

The wholly owned Statoil refinery at Mongstad is a modern, highly upgraded plant with an FCC resid processing unit. Grace is the leading supplier of FCC catalysts globally and has developed state-of-the-art technology designed to uplift the resid feed into lighter, more valuable products. As part of the four-year agreement, Grace will continue to provide Statoil with its resid catalysts, including Grace’s NEKTOR™ 4G technology.

“We are delighted that Statoil has chosen Grace to be a key FCC catalyst technology partner for the coming years,” said Tom Petti, President of Grace’s Refining Technologies business.

Get more information about Grace’s FCC catalysts at grace.com/catalysts-and-fuels.

**Innovative Catalyst Solution Unlocks Value in the FCCU**

**Grace and Rive Collaborate with Motiva on Successful Trial**

Maximizing diffusion of feed into and products out of an FCC catalyst is critical to unlocking the full value potential of an FCC unit in which the riser residence time is only a few seconds. Through a collaborative effort between Motiva, Grace, and Rive Technology, an innovative catalyst solution incorporating Rive’s mesoporous zeolite was designed and trialed at a Motiva U.S. Gulf Coast (USGC) refinery. This technology engineers a precise series of mesopores into Y zeolite, the primary active component of all FCC catalysts, which greatly enhances diffusion of molecules into and out of the catalyst.

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

During the 2017 AFPM Annual Meeting in San Antonio, Rive will present a technical paper that further investigates Rive’s Molecular Highway™ technology and how it was successfully used to improve performance at a Motiva USGC refinery.
Grace Makes FAST Progress Toward Sustainable Fuels

Grace Hosts FASTCARD Project Review Meeting and Exposition

On Jan. 10-11, 2017, Grace hosted a review seminar in Worms, Germany for researchers involved in the FASTCARD project (FAST Industrialization by CAtalyist R&D), an EU-funded initiative to facilitate the use of biomass in the production of transportation fuels.

The project focuses on the gasification of biomass with subsequent Fischer-Tropsch synthesis and partial hydrodeoxygenation of pyrolysis liquids followed by FCC co-processing of bio-oil and fossil fuel-based feed. Grace’s German subsidiary Grace GmbH & Co. KG is leading the development of dedicated FCC co-processing catalysts as part of a project consortium consisting of 14 members, including European refiners ENI and REPSOL along with leading universities, R&D institutes, and innovative subject matter experts.

Silke Loening, a Principal Engineer at Grace, organized the seminar, which analyzed the practical results arising from the science, including potential IP and licensing activities, public dissemination, and knowledge transfer.

The review portion of the meeting included presentations and progress reports. Two of the eight project presentations were led by Grace’s Stephan Wellach, Manager, Catalyst Development, and Edgar Jordan, Principal Scientist, Refining Technologies. The meeting garnered positive feedback from the EU’s project monitor, Professor Silvia Schintke, who is head of the Laboratory of Applied NanoSciences at the University of Applied Sciences Western Switzerland.

During the upcoming and final year of the project, Grace will focus on pilot scale testing, as well as the economic and environmental evaluation of the optimized value chains.

Grace Marks 30-Year Partnership With BP’s Castellón Refinery

Grace’s FCC team in Europe, the Middle East, and Africa (EMEA) joined BP for a ceremony to celebrate more than 30 years of continuous FCC catalyst supply and service by Grace to BP’s Castellón refinery in Spain.

Located north of Valencia, Spain, the BP Castellón refinery is wholly owned by BP and has a capacity of 110,000 barrels per day.

During the event, refinery manager Jose Luis Garcia Galera and his team reflected on the long history of partnership and cooperation between Grace and BP and praised the Grace team for the technology, technical service, and support provided over the years.

Some recent examples of Grace’s value-added services were quantified and showcased by Rafael González Sánchez, Technical Sales Manager, Spain and Portugal.

At the conclusion of the ceremony, Enrico Caccone, Vice President Sales, FCC EMEA, presented a plaque to the refinery manager and his team as Daniel McQueen, General Sales Manager for Grace’s FCC business in Europe, expressed his appreciation.
Ecat Lab in Oman Is First of Its Kind

Grace Develops Unique Partnership to Serve the Middle East

Starting in mid-2017, Grace will provide local support for Middle East refineries through new Ecat laboratories located in Oman at Sohar University. Up-to-date Equilibrium Catalyst (Ecat) information is a key component to boosting profitable FCC unit operations, and the new labs will eliminate the need to send samples abroad for testing.

The Oman Oil Refineries and Petroleum Industries Company (ORPIC) identified the need for these professional labs in Oman and played an instrumental role in moving the agreement forward. Currently, all of ORPIC’s periodic, daily, and weekly material characterization tests are conducted at labs in Germany.

The first-of-a-kind labs are expected to serve not only the petrochemical industry in Oman, but similar industries throughout the Cooperation Council for the Arab States of the Gulf (GCC), which includes Oman as well as Saudi Arabia, Bahrain, Kuwait, Qatar, and the United Arab Emirates.

Omani staff will manage and operate the labs and will be highly trained by Grace’s technical experts. The collaboration provides an excellent opportunity for Sohar University to enhance the scientific, academic, and research activity of students and professors, including conducting joint materials development research with Grace. Also, the lab will contribute to developing a skilled local workforce while reducing the cost involved in testing samples. This industrial-academic collaboration model is unusual in the region. It will pave the way to bring models like this to levels of higher sophistication and produce more benefits as Sohar University and Grace professionals transfer knowledge and build capacity.

The laboratories will provide analysis of:
- ACE Catalytic Testing
- Surface Area
- Elemental Analysis
- Water Pore Volume
- Carbon on Catalyst (CRC)
- Attrition Resistance DI
- Particle Size Distribution (PSD)
- Apparent Bulk Density (ABD)
- Combustion Promotion CO Index

Meet Grace’s New Global Customer Technology Team

In 2016, Grace announced the formation of a Global Customer Technology Team to serve FCC customers. This team will meet critical high-level service needs around the world, develop best practices and tools for regional technical support teams, develop models to quantify financial value of our catalyst and service offerings, and provide insight into customer’s product needs.

The new team is led by Dennis Kowalczyk, Vice President of FCC Global Customer Technology for Grace.

Michael Federspiel
Michael joined Grace in 2007 as a Technical Sales Manager supporting customers in the U.S. East Coast region, Canada, and the Caribbean. Michael was Technical Sales Manager for Southeast Asia from 2010 to 2013, when he returned to North America as a National Technical Sales Leader responsible for managing FCC sales and service. Michael brings a wealth of hands-on FCC field experience to the Global Customer Technology team. Prior to joining Grace, Michael worked on the commissioning and start-up of FCC units globally with UOP and then held FCC engineering and operations roles with the Hovensa refinery (USVI). He holds a Bachelor of Science in Chemical Engineering from the University of Wisconsin.

Stéphane Montmasson
Stéphane joined Grace in 2011 as a Regional Technical Service Manager for Refining Technologies responsible for providing technical service to current and prospective customers in Europe, the Middle East, and Africa. Stéphane has more than 25 years of oil refinery experience and knowledge that he brings to the Global Customer Technology Team. Prior to joining Grace, he held roles with SAIPEM Engineering, Tamoil refinery, and Foster Wheeler. Stéphane earned an engineering degree from the Ecole superieure des mines – Saint Etienne.
SUCCESS STORIES
Cepsa Boosts Profitability through FCC Catalyst Selection

Rafael González  
W. R. Grace & Co.

Christophe Chau  
W. R. Grace & Co.

Javier Llano  
Compañía Española de Petróleos SAU (Cepsa), Gibraltar-San Roque Refinery

Berta Aramburu  
Cepsa Research Centre

Rafael Larraz  
Cepsa Research Centre

With an acute supply shortage in propylene, several producers in the U.S., China, and the Middle East have announced capacity expansions, increasing the propylene imbalance in Europe. Compañía Española de Petróleos SAU’s San Roque Refinery in Gibraltar, the largest refinery in the Iberian Peninsula, with a crude oil processing capacity of 240,000 barrels per day, took steps to address this pressure. They conducted rigorous back-to-back trials of Grace’s customized FCC catalyst and the product of another supplier to explore increased propylene yield.

Grace’s customized FCC catalyst, combined with a dedicated and proactive technical support team, enabled Cepsa’s refinery to maximize propylene and isobutylene yields, enhance total LPG production, maintain gasoline yield, improve bottoms upgrading, and expand the FCC unit operating window to allow the refinery to process heavier feed.

Cepsa can now take advantage of the wider FCC unit operating window and Grace confirmed its ability to reformulate and optimize FCC catalyst to match the refinery’s objectives. With leading technology and a history of customer-focused innovation, Grace demonstrated once again the added value provided to its refinery partners.
Cepsa’s (Compañía Española de Petróleos SAU) Gibraltar-San Roque Refinery operates as a fully integrated refining and petrochemical site. The refinery, originally started up in 1967, is designed to produce a large range of transportation fuels and petrochemical feedstock and is strategically located next to the Straits of Gibraltar, supplying the local and export markets with a wide range of products. The Gibraltar-San Roque Refinery is the largest refinery in the Iberian Peninsula, with a crude oil processing capacity of 240,000 barrels per day.

The fluid catalytic cracking (FCC) unit is the primary hydrocarbon conversion unit in the modern petroleum refinery. It uses heat and catalyst to convert a variety of high molecular weight feeds (e.g., gas oils, cracked gas oils, deasphalted gas oils, and atmospheric/vacuum residens) into lighter, more valuable products such as gasoline, light fuel oil, and petrochemical feedstocks such as propylene and butylenes [1]. The rapid demand growth for propylene in China and the shift to shale gas based ethane cracking in North America have created an acute supply shortage in propylene [2]. Several propylene producers have announced capacity expansions utilizing new on-purpose technologies such as PDH, propane dehydrogenation. The majority of the capacity expansion will be in the U.S., China, and Middle East, increasing the propylene imbalance in Europe. Refiners, particularly those integrated with petrochemical complexes, have the opportunity to increase propylene yield on the FCC, help reduce the supply gap, and realize higher FCC product margins.

The FCC unit at Cepsa’s Gibraltar-San Roque Refinery is a UOP High Efficiency design with a throughput of approximately 5,200-5,500 MT/day. The FCC unit is a key process unit of the refining complex upgrading low value feedstock, primarily gas oils-SRVGO (Straight Run Vacuum Gas Oils) and HTVGO (Hydrotreated Vacuum Gas Oils) blends—with FCC slurry recycle, but also atmospheric residue, furfural extracts, and visbreaker naphtha, to deliver higher value alkylate, gasoline, and diesel for blending in the refinery fuels pool and to provide aromatic rich feedstock and propylene to the petrochemical site.

After almost 20 years of partnership between Grace and the Gibraltar-San Roque Refinery, during which time numerous new catalyst technologies were introduced that delivered successive improvements in FCC unit operating profitability, Cepsa challenged the status quo and implemented back-to-back FCC catalyst trials with Grace and an alternative FCC catalyst supplier. The performance of Grace’s customized FCC catalyst compared to the previous Grace catalyst yielded a considerable improvement of FCC unit and refinery operating profitability. Grace provides proactive access to state-of-the-art catalysts that enable our refinery partners to adapt to challenging and changing operating targets and constraints while maximizing refinery margins.

**Trial Objectives and Operating Constraints**

The refinery defined three primary FCC unit objectives to increase unit and refinery operating profitability as part of Cepsa’s selection of the catalyst technology through in unit back-to-back trials:

1. Maximize propylene production
2. Maximize LPG at constant gasoline production
3. Minimize bottoms

Gibraltar-San Roque Refinery’s main FCC unit operating constraints are typically:

1. Wet gas compressor (WGC) capacity
2. Regenerator temperature
3. Regenerator air blower capacity

**Grace’s Customized FCC Catalyst Technology**

The customized FCC catalyst used for Cepsa belongs to Grace’s family of propylene maximization technology for both hydrotreated and non-hydrotreated feed applications. It was initially developed during the period of rare earth hyperinflation, and is a member of our low or no rare earth FCC portfolio, RepLaCeR® catalysts. The RepLaCeR® family of catalysts delivers optimum performance at lower rare earth concentrations minimizing refinery exposure to the hyperinflation. The customized FCC catalysts used for Cepsa are an extension of the ProtAgon™ catalyst family and are manufactured using Grace EnhanceR™ technology, the leading manufacturing platform in Europe, the Middle East, and Africa. Grace has an extensive catalyst and additive portfolio for increasing...
propylene yields, as demonstrated by Grace’s global market leadership position for LPG maximization applications (Figure 1).

The customized FCC catalyst for Cepsa was designed with an optimized zeolite to matrix ratio and finely-tuned rare earth content, providing:

- Low hydrogen transfer activity for enhanced olefins production
- High ZSM-5 activity to selectively crack gasoline range olefins into LPG olefins
- Best-in-class delta coke and dry gas, allowing the expansion of the FCC unit operating window within the unit operating constraints
- Premium bottoms upgrading with best bottoms-to-coke selectivity
- Targeted catalytic activity without any increase in catalyst additions.

To maximize propylene in an FCC unit, high ZSM-5 activity and stability are required in the circulating catalyst inventory. The activity of the ZSM-5 must be balanced with sufficient zeolite-Y based FCC technology, to boost LPG olefins production. The ProtAgon™ catalyst family of technologies delivers both of these attributes in a single particle system.

Catalyst retention is critical to the FCC unit operation and Grace’s customized catalyst technology provided considerably better attrition resistance compared to the alternative technology trialed. With improved physical properties, Grace helped Gibraltar-San Roque Refinery to further minimize catalyst losses (i.e., reduce particulate emissions) and improve the reliability of the expander operation.

Laboratory Testing

Prior to the FCC catalyst trials, pilot plant testing in Cepsa’s R&D laboratory was conducted to compare FCC catalyst performance for each supplier. The FCC catalysts were steam deactivated to mimic the Ecatal properties in the commercial unit, and tested in the DCR™ Circulating Riser pilot plant. The testing highlighted the improved performance of Grace’s customized FCC catalyst compared to the alternative catalyst technology trialed in terms of LPG olefins make, the primary objective of the unit for max FCC profitability (Figure 2). The catalyst’s improvement on bottoms upgrading capability is described in Figure 7 with commercial unit data.

<table>
<thead>
<tr>
<th>C/O</th>
<th>Coke</th>
<th>Fuel Gas</th>
<th>LPG</th>
<th>Gasoline - C5&lt;210°C</th>
<th>LCO - 210-350°C</th>
<th>HCO - 350°C+</th>
</tr>
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**Figure 2.** Improved performance with Grace’s customized FCC catalyst demonstrated by Cepsa’s pilot plant test results.

FCC Catalyst Trial Results

As shown in Figures 3 and 4, when comparing Grace’s Customized FCC catalyst and the incumbent base Grace technology, propylene and butylenes yields were boosted significantly at both constant conversion and constant coke yield.

The improvement in LPG olefins make was exhibited over a broad range of operating severity and feedstock quality as demonstrated in Figure 5. Significant gains in LPG olefins yields, both with propylene and butylenes—were obtained with Grace’s customized FCC catalyst with increasing riser outlet temperature (ROT). This is explained by the optimized, lower hydrogen transfer of the catalyst that results in enhanced selectivity and yields of gasoline range olefins, the precursors to LPG olefins.
Figure 3. Grace’s customized catalyst improves FCC Unit propylene yields at (left chart) constant conversion and (right chart) constant coke.

Figure 4. Grace’s customized catalyst improves FCC Unit butylenes yields at (left chart) constant conversion and (right chart) constant coke.

Figure 5. Grace’s customized catalyst maximizes FCC Unit LPG olefins yields over a range of reactor severities (riser outlet temperature).
Continued from Page 11

An important objective for Cepsa’s FCC unit was to maintain gasoline yields. In general, an increase in the ZSM-5 content in a catalyst formulation results in a noteworthy decline in gasoline yield, due to the cracking of gasoline range olefins. However, the customized FCC catalyst demonstrated superior activity to crack the heaviest feedstock fractions into gasoline, therefore offsetting the enhanced cracking of gasoline into LPG range products, and hence minimizing gasoline loss (Figure 6). The gasoline octane remained similar (RON) or slightly better (MON) with the reformulated catalyst as compared to the base catalyst. The improved bottoms cracking demonstrated by the customized catalyst in the commercial unit is shown in Figure 7.

Figure 6. FCC naphtha yield was maintained.

**Figure 7. Superior bottoms upgrading was observed.**

### Gas Make

One of the major constraints of the Gibraltrar-San Roque Refinery is the volumetric flow rate of its wet gas compressor. As shown in Figure 8, Grace’s customized FCC catalyst demonstrated very low gas make and the lowest hydrogen yield. The gas selectivity is due to the inclusion of premium metals trapping functionality and its tailored hydrogen transfer activity. Lower gas make allowed the refinery operation team to widen the operating window compared to the alternative technologies and alternative catalyst supplier. Improved selectivity also minimizes the risk of profitability losses arising from constrained operation during the warmer summer months, due to excessive dry gas make constraining the WGC wet gas compressor. Industry benchmarking of Ecatal hydrogen yields reveals that the customized FCC catalyst has the lowest hydrogen yield at a given metals level (Figure 12).

### Table 1

<table>
<thead>
<tr>
<th>Performance</th>
<th>Base Catalyst</th>
<th>Customized Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, wt%</td>
<td>Base</td>
<td>+1.0</td>
</tr>
<tr>
<td>C3=, wt%</td>
<td>Base</td>
<td>+0.6</td>
</tr>
<tr>
<td>C4=, wt%</td>
<td>Base</td>
<td>+0.9</td>
</tr>
<tr>
<td>LPG, wt%</td>
<td>Base</td>
<td>+2.1</td>
</tr>
<tr>
<td>LPG olefins, vol%</td>
<td>Base</td>
<td>+2.2</td>
</tr>
<tr>
<td>Total Naphtha, wt%</td>
<td>Base</td>
<td>-0.4</td>
</tr>
<tr>
<td>LCO, wt%</td>
<td>Base</td>
<td>+0.4</td>
</tr>
<tr>
<td>Slurry, wt%</td>
<td>Base</td>
<td>-1.5</td>
</tr>
<tr>
<td>Coke, wt%</td>
<td>Base</td>
<td>-0.1</td>
</tr>
<tr>
<td>Unit profitability, M€/yr</td>
<td>Base</td>
<td>+ 4.0</td>
</tr>
</tbody>
</table>

Table 1. Grace’s customized catalyst delivered improved performance in the commercial FCC unit.
**Catalyst Delta Coke**

The Grace customized FCC catalyst has tailored and enhanced metals trapping technology to yield very low delta coke. Improving delta coke enabled the FCC operations team at Gibraltar-San Roque refinery to expand the FCC unit operating window and maximize LPG without breaching regenerator temperature constraints. The alternative technology trialed exhibited higher delta coke and poorer bottoms to coke selectivity (Figure 9). As a result, regenerator temperature increased by as much as 25°C dense phase at similar propylene levels (Figure 10). When compared to global benchmarks, the coke selectivity of the customized catalysts as measured in Ecat ACE testing is considered “best in class” as demonstrated in (Figure 13).

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**Figure 8.** Grace’s customized FCC catalyst reduced hydrogen in dry gas, here as a function of (left chart) Ecat Ni and (right chart) propylene yield (ACE testing).

**Figure 9.** Grace’s customized FCC catalyst lowered slurry make and improved delta coke relative to the alternate supplier.

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Continued on Page 14


**Benchmarking**

A benchmarking study performed on a global basis (Figure 11) allowed for a comparison of Grace’s customized catalyst at Cepsa’s Gibraltar-San Roque Refinery, including the FCC units worldwide that target maximum propylene production. Based on Grace’s global Ecet benchmarking by ACE testing, the customized catalyst used at Gibraltar-San Roque Refinery demonstrates amongst the highest yields of best in class propylene and LPG olefins in the industry.

The outstanding LPG olefins performance was achieved whilst maintaining industry leading coke and gas selectivity, as exhibited by Ecet ACE benchmarking (Figures 12 and 13, respectively). The hydrogen yield and coke selectivity obtained with Grace’s customized FCC catalyst is among the best on a worldwide basis.

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**Figure 10.** The coke selectivity advantage of the customized catalyst lowered regenerator dense phase temperature.

**Figure 11.** Grace’s customized FCC catalyst exhibits leading propylene and LPG selectivity (Ecet ACE global benchmark).
Conclusion

Cepsa conducted a rigorous FCC catalyst selection process that comprised lab testing at the Cepsa R&D facility and back-to-back in-unit trials at Gibraltar-San Roque Refinery. The goals of the selection process were to evaluate catalyst performance and increase overall FCC unit profitability. Maximizing LPG olefins and improving bottoms upgrading at the lowest bottoms-to-coke were the main objectives of the catalyst selection. Grace’s customized FCC catalyst, combined with a dedicated and proactive technical support team, enabled the Cepsa’s Gibraltar-San Roque Refinery to maximize propylene and isobutylene yields, enhance total LPG production, maintain gasoline yield, improve bottoms upgrading and expand the FCC unit operating window to allow the refinery to process heavier feed.

The increased propylene yield supports Cepsa’s activities in the petrochemicals area, while the increased C₄ olefins yield minimizes the need to import feed for the ethyl tertiary butyl ether (ETBE) unit. The improved upgrading of low-value components, otherwise destined for fuel oil production, improved the efficiency and profitability of the overall refinery operation. In addition, the reliability and sustainability of the FCC unit operation were improved with the best attrition resistance of Grace’s customized FCC catalyst. Lower catalyst losses meant that the refinery environmental emissions legislative constraints were not exceeded (stack emissions). The economic and reliability benefits of moving to Grace’s customized FCC catalyst have been confirmed by the Cepsa’s Gibraltar-San Roque Refinery.

With Grace’s customized FCC catalyst, Cepsa’s Gibraltar-San Roque Refinery can choose to take advantage of the wider FCC unit operating window by increasing reaction severity and/or introducing lower cost feedstock such as atmospheric residue. Grace confirmed its proven capability and flexibility to reformulate and optimize FCC catalyst to match the refinery’s objectives. With leading technology and a history of customer-focused innovation, Grace demonstrated once again the added value provided to its refinery partners.

References

Advanced Refining Technologies (ART), Grace’s joint venture with Chevron, steps up to meet the challenges of clean fuels regulations with its newest ApART® Catalyst System ultra high activity FCC pretreat catalysts: 586 DX® and 486 DX®.

The original ApART® Catalyst System technology, introduced in 2002, was designed to provide maximum HDS activity while also providing significant upgrading of FCC feeds.

The addition of 586 DX® and 486 DX® catalyst to the ApART® catalysts system portfolio enhances the flexibility and performance of these systems for FCC pretreat. They expand the capability to significantly reduce required SOR temperatures for both HDS and HDN. The optimized system of 586 DX®/486 DX® catalyst offers refiners enhanced ability to generate lower sulfur FCC products as well as still delivering the benefits of nitrogen removal and poly aromatic saturation.

Extensive pilot testing and expertise enable ART to provide the right catalyst system tailored for maximum refinery profit. The new technology available through 586 DX® and 486 DX® catalyst will enable refiners to enhance their operation with either increased cycle length or additional feedstock processing in order to maximize margin. The ability of these catalysts to perform in different configurations provides a high level of versatility and makes it a top tier catalyst capable of exceeding refiners’ needs in demanding FCC pretreat applications.
Advanced Refining Technologies (ART), Grace’s joint venture with Chevron, first introduced the ApART® catalysts system for superior FCC feed pretreating in 2002. This technology was designed to provide maximum HDS activity while also providing significant upgrading of FCC feeds. This technology has been widely accepted with over 70 units in commercial service since its inception. As challenges in meeting clean fuels regulations continue to become more daunting, ART continues to improve its line of ultra high activity FCC pretreat catalysts, and strives to provide refiners with superior technology and first-class performance.

There is a lot that goes into the process of optimizing a catalyst. A few of the keys are designing the proper pore size distribution into the catalyst, optimizing the metals composition, and maximizing the metals utilization. ART has completed extensive work defining the optimum pore architecture of catalysts for processing heavy feeds. Figure 1 summarizes some of the results of that work. The figure compares the relative activity of different catalyst preparations as a function of increasing catalyst pore size. Pore size and surface area of a catalyst are dependent variables meaning that as the pore size increases, the surface area decreases, and thus the number of active sites decreases. On the left side of Figure 1, the catalysts have a high surface area, but the pores are too small to allow the large VGO molecules access to the active sites. On the right side of the figure, the pores are very large and allow easy access, but the surface area is (and number of active sites) is quite low. In both cases the activity is low. The optimum support has a pore size distribution which minimizes diffusion constraints and maximizes the number of accessible active sites.

Another important parameter for catalyst performance is the active metals composition. Figure 2 shows the relationship between the relative activity of a catalyst and the active metals loading. As expected, activity increases with increasing metals level, but there is a limit. The figure indicates there is an optimum metals loading beyond which adding more metals actually hurts catalyst performance. Catalyst activity decreases when excess metals are added because they begin to block the pores.

Figure 1. Optimized pore structure is key to performance.

Continued on Page 18
Yet another critical aspect is the metals utilization or maximizing the number of active sites. Current generation catalysts typically rely on the formation of Type II active sites during catalyst activation. Type II sites are known to provide significantly higher activity at the same metals loading as catalysts containing Type I active sites. An effective way to maximize the concentration of Type II active sites is through the use of chelate technology during the metals impregnation step. ART has been steadily improving the application of chelates with their DX® catalyst technology, and ART’s current catalyst portfolio benefits from these improvements.

The latest catalysts developed via this optimization process are 586 DX® and 486 DX® which are new catalysts designed for maximum performance in FCC pretreat applications. The NiMo catalyst 586 DX® comes with significantly improved HDS and HDN activity. In FCC pretreat applications this catalyst can provide superior nitrogen removal as well as Aromatic and PNA saturation in order to provide significant FCC feed upgrading for increased FCC yields. Figure 3 compares the activity of 586 DX® and AT775. The figure shows that 586 DX® catalyst has nearly 20% higher HDN activity and 15% higher HDS activity compared to AT75. ART’s 586 DX® catalyst has a large pore size distribution similar to AT75 which gives the catalyst exceptional stability on heavy feeds.

It benefits from the latest advancement in the DX® catalyst technology. It has lower LOI than conventional chelated catalysts and requires no special handling or start up procedures. In just a short time since commercialization 586 DX® catalyst has been installed in four FCC pretreat units. The performance has been excellent with as much as 10°F improvement in HDS activity over the previous catalyst. ART’s 586 DX® catalyst has already been selected for another cycle in a couple of these units which speaks to its superior performance.

Another recent advancement to ART’s FCC pretreat catalyst technology is 486 DX® catalyst, which is a CoMo catalyst that has outstanding HDS activity coupled with high HDN activity. Figure 4 shows a comparison of the activity of several generations of ART HDS catalysts for FCC pretreat along with 486 DX®. The results from side-by-side testing clearly show that 486 DX® catalyst is a significantly improvement in performance over the prior generation. It is apparent that there has been continuous improvement in activity with each generation since the introduction of the ApART® catalysts system in 2004. Most recently, 486 DX® catalyst shows both a 20% HDS advantage as well as a 10% improvement for HDN over AT795.

It benefits from the latest advancement in the DX® catalyst technology. It has lower LOI than conventional chelated catalysts and requires no special handling or start up procedures. In just a short time since commercialization 486 DX® catalyst has been installed in four FCC pretreat units. The performance has been excellent with as much as 10°F improvement in HDS activity over the previous catalyst. ART’s 586 DX® catalyst has already been selected for another cycle in a couple of these units which speaks to its superior performance.
In lower pressure applications, 486 DX® catalyst continues to maintain its advantage over previous generations including AT795 as shown in Figure 5. Figures 4 and 5 demonstrate the robustness of 486 DX® catalyst performance and indicate that it is an effective catalyst over a wide range of conditions.

Both the hydrotreating catalyst system and the operating strategy for the pretreater are critical to providing the highest quality feed for the FCC. Driving the hydrotreater to remove nitrogen and PNA’s improves FCC product value when targeting gasoline production, but this needs to be balanced against the increased costs of higher hydrogen consumption and shorter cycle length that result from this mode of operation. To address this need, ART utilizes the ApART® catalysts system for FCC pretreatment. This technology is designed to provide significant increases in HDS conversion while at the same time providing significant upgrading of FCC feedstock quality and increasing yields. In essence, an ApART® catalysts system is a staged bed of high activity NiMo and CoMo catalysts where the relative quantities of each catalyst can be optimized to meet individual refiner’s goals and constraints. ART has continued to develop a better understanding of the reactions and kinetics involved in FCC pretreating, and through its relationship with Grace Refining Technologies, a detailed understanding of the effects of hydrotreating on FCC unit performance.

The proper choice of an FCC pretreat catalyst system must, in addition to other potentially important considerations such as feed metals removal, represent an optimization of sulfur removal capability as well as HDN and saturation activity. The flexibility of the ApART® system offers the potential to provide maximum HDS activity, and thus lowest FCC gasoline sulfur content, while also providing a maximum in FCC unit conversion at constant coke operation.

The addition of 586 DX® and 486 DX® catalyst to the ApART® system portfolio enhances the flexibility and performance of these systems for FCC pretreat. They expand the capability to significantly reduce required SOR temperatures for both HDS and HDN. The optimized system of 586 DX®/486 DX® catalyst offers refiners enhanced ability to generate lower sulfur FCC products as well as still delivering the benefits of nitrogen removal and poly aromatic saturation. Figure 6 shows a comparison of an AT575/AT795 system with the new 586 DX®/486 DX® catalyst system. There is a clear and significant improvement in both HDS and HDN activity with the new ApART® system.

The additional HDS activity combined with maximum nitrogen removal and aromatic saturation allows refiners to utilize 586 DX® catalyst as a stand-alone catalyst for maximum upgrade in refinery markets demanding increased yields. Refiners can also choose to utilize 486 DX® as a stand-alone catalyst in order to minimize hydrogen consumption while still achieving excellent sulfur removal for meeting Tier 3 sulfur regulations. Coupling these two catalysts in a ApART® catalysts system, is ideal for hydrotreaters that need to operate with controlled or minimized hydrogen consumption yet still require the lowest sulfur and maintaining the yield gains in their FCC. These units are able to benefit from a lower start of run temperature as well as being able to gain some additional improvements that are not often achieved in a system of 100% NiMo or CoMo.

Extensive pilot testing and expertise enable ART to provide the right catalyst system tailored for maximum refinery profit. The 586 DX® and 486 DX® catalysts will enable refiners to enhance their operation with either increased cycle length or additional feedstock processing in order to maximize margin. The ability of these catalysts to perform in different configurations provides a high level of versatility and makes it a top tier catalyst capable of exceeding refiners’ needs in demanding FCC pretreat applications.

Figure 5. 486 DX® catalyst shows excellent performance in low pressure FCC pretreat.

Figure 6. Comparison of AT575 / AT795 and 586 DX® / 486 DX® ApART® catalysts systems.
Global governments have intensified regulations to reduce sulfur concentration in gasoline while the automotive industry continues to refine engine design to improve performance and minimize environmental impact. This is driving innovation as refiners seek options for achieving the highest production standards.

Considering that the naphtha produced in the FCC unit of a refinery is the major and limiting component in sulfur content in the gasoline pool, the catalytic additives with sulfur reduction functions are a possible short-term alternative along with the planning, development and execution of long-term capital projects.

The Axion Energy refinery in Argentina conducted a commercial trial in its FCC unit, using Grace’s GSR®-5 catalytic sulfur reduction technology and discovered that they could optimize the use of molecules with lower sulfur content and minimize imported products in the finished gasoline pool. The benefits of sulfur reduction also are extended to the quality and production of catalytic diesel (LCO) in that the heavy fraction of the naphtha is sent to middle distillates.

This fascinating case study demonstrates that the use of catalytic additives to reduce sulfur in gasoline is a viable alternative for the refining industry, whose permanent challenge is to produce a greater volume of fuel at the highest quality standards.
Preface

Gasoline sulfur specification is currently a hot topic in the US due to the Tier 3 legislation for 10 ppm gasoline sulfur coming into affect this year. However, this is not just an issue faced by North American refiners; many other countries have already switched to tighter gasoline sulfur levels, or are in the process of doing so. The move to lower gasoline sulfur, and the drive to minimize octane loss as a result, is a need that increasingly crosses national and regional boundaries.

Japan was the first country to adopt a national limit of 10 ppm gasoline sulfur, with the industry moving on a voluntary basis to lower sulfur at the beginning of 2005, even though it was only made compulsory from January 2008. This was particularly challenging for Japanese refiners considering that a maximum limit of 10 ppm gasoline sulfur was imposed, rather than the weighted average approach being adopted in Tier 3. In India, the move to lower gasoline sulfur has been somewhat fragmented. Legislation in 2010 required 13 major cities to move from 150 to 50 ppm gasoline sulfur, while the rest of the country transitioned from 500 ppm to 150 ppm. By 2017, it is expected that 50 ppm sulfur will be a requirement throughout India entirely, followed by a 10 ppm sulfur requirement by 2020. In China, gasoline sulfur specification was decreased nationwide from 150 to 50 ppm in 2014, with a move to 10 ppm expected in 2018. However, the 10 ppm specification is already in place in some of the major cities. The majority of other countries in Asia Pacific are currently at either the 50 or 150 ppm sulfur limits, though South Korea is one exception having implemented a 10 ppm gasoline sulfur limit in 2009.

In 2005, a maximum limit of 50 ppm sulfur in Europe was imposed on all gasoline supplied in EU member states, which was tightened to 10 ppm sulfur by 2010. In Russia, the government set out a plan to meet 10 ppm gasoline sulfur specifications by 2015. Although many refineries in Russia are producing exclusively 10 ppm gasoline sulfur, there have been delays in achieving these standards across the board due to problems with supplying enough gasoline to meet domestic demand. There remains a variety of gasoline specifications in the countries in and around the FSU, ranging from 10-500 ppm sulfur. In the Middle East, many refineries are producing 10 ppm gasoline sulfur for export markets. However, despite a rapid increase in vehicle numbers in the Middle East countries, use of high sulfur gasoline continues to be the norm. An exception to this is Israel, where as from 2009 the maximum sulfur content in gasoline has been set to 10 ppm.

The move to lower sulfur gasoline is also being played out in some Latin American countries. Chile is one of the most advanced countries in the region with regards to reducing the sulfur content in its gasoline, with a nationwide limit of 15 ppm being in effect since 2012. Argentina has taken a stepwise approach, moving from a limit of 300 ppm sulfur in 2012 to a targeted 30 ppm in 2017, and ultimately 10 ppm in the coming years. In Mexico two grades of gasoline are available, Premium and Regular. Premium gasoline has adhered to an average target of 30 ppm sulfur since 2006, a reduction from the previous range of 250-300 ppm. Mexico had targeted 2009 to reach the same sulfur levels in Regular gasoline, but has not yet achieved this nationwide. Other countries have made less progress moving to tighter sulfur specifications. For example in Brazil, gasoline with up to 1000 ppm sulfur was sold in some areas until the end of 2013. This level has been reduced to 500 ppm, though some metropolitan areas have a maximum gasoline sulfur content of 30 ppm.

Significant investment in global refinery operations has been required to reduce gasoline sulfur content, primarily in increased hydrotreating and hydrocracking capacity. To complement these investments and minimize octane loss in the hydrotreaters, Grace’s GSR® catalytic sulfur reduction technology has played an important role in the overall strategy of many refineries to comply with tighter gasoline sulfur specifications. Grace’s GSR® technology has been used by more than 70 refineries worldwide, representing more than 15 countries. For example, over 50% of Japanese refiners are using Grace’s GSR® technology. A recent example where Grace’s GSR® technology has played an important role in reducing fuel sulfur levels is described in the subsequent case study from Axion Energy.

Note: Wood Mackenzie is the data source for gasoline sulfur specifications.

The Need to Reduce Sulfur

The maximum content of sulfur in finished gasoline continues to decline steadily around the world due to environmental issues and the improvement in the quality of fuels, which has been forcefully demanded by the automotive industry.

In Latin America, the current range in finished premium naphtha varies between 10 to 50 ppm of sulfur, where the gasoline produced in fluid catalytic cracking (FCC) units is the major component of the gasoline pool. Approximately 5% of the sulfur present in the FCC feedstock ends in the catalytic naphtha, later impacting 90% of the total sulfur of the gasoline pool in each refinery.

The Axion Energy refinery in Argentina conducted a commercial trial in its FCC unit, using Grace’s GSR®-5 catalytic sulfur reduction technology to anticipate the new challenges of quality in fuels and achieve a specification limit of 50 ppm of sulfur in its premium naphtha. During the trial, a reduction between 25-30%wt in sulfur was observed in the catalytic naphtha, with specific events of 40-45%wt at maximum severity of the FCC unit.

Reductions of 30%wt of the sulfur content were also recorded as an additional benefit in the production of catalytic butane and propane. This

Continued on Page 22
Continued from Page 21

meant an improvement in the margin due to the lower consumption of the caustic soda used to remove mercaptans in the unit for the caustic treatment of liquefied petroleum gas (LPG).

Since the late 20th century there has been increased awareness of the environment. For that reason, guidelines for the production of fossil fuels has changed to produce clean energy that is free of contaminants.

Global governments have intensified the use of processes to reduce sulfur concentration in the gasoline by regulating composition and establishing new limits annually, which translate into best practices and new production technologies in refineries. The main objective is to reduce emissions associated with sulfur. This improvement is also driven by the automotive industry, which continues to refine the design of its engines to improve performance and minimize environmental impact.

This trend of industrialized countries such as Canada, the United States, and members of the European Union has been transferred to Latin America by globalization. In the specific case of Argentina, the sulfur reduction process launched in 2006 by the Secretariat of Energy, which contemplates successive stages for the production of liquid fuels with increasingly lower levels of contaminants, in order for the industry to have enough time to be able to plan and adapt its facilities for this purpose.

In this global scenario, technological alternatives have appeared, and there is a combination of capital investments, optimization of processes, and new quality objectives where production is the key to meeting the needs of a more demanding market. One option with zero impact in terms of required investment in construction and facilities is the new catalysts and additives for catalytic cracking units that have shown good results in desulfurization processes.

Finished gasoline in a refinery is made up of a blend of several streams from different refining process. The catalytic naphtha produced in FCC unit is the largest single contributor of the sulfur content of the finished gasoline pool, which is why the focus should be on the various aspects affecting the production and the sulfur content of this particular gasoline.

Processing of low sulfur content crudes is an option for refineries, but it is not necessarily sustainable as fossil fuels are a limited resource. Another possibility is to install a hydrotreatment process either for the FCC feed or naphtha produced by this unit. The capital investment for these alternatives is approximately 3 to 1. It is convenient to hydrotreat finished naphtha due to the smaller volume of product to be processed.

The last option, which carries a high capital investment, is to have a naphtha splitter unit downstream from the typical fractionating tower of an FCC unit. This facility allows you to have two or three cuts, whose sulfur contents differ in complexity from the species, thus allowing the application of different removal treatments. The light fraction contains mainly sulphides and mercaptans that can be easily removed through caustic treatment or Merox process. The intermediate and heavy fractions contain complex species (thiophenes, alkylthiophenes, thiol, benzo thiophenes and others) so segregating these naphtha’s optimizes sulfur content and maximizes the respective volumes in the respective pool of finished gasoline.

One option that does not require the installation of equipment and facilities is to reduce the end point of catalytic naphtha, considering that the largest proportion of sulfur is contained in the heavy fraction of the cut. The direct cost of performing this action is a significant loss of gasoline production volume.

The challenge is to find a break-even point between a substantial capital investment in facilities that require long-term projects and the sustained loss of gasoline volume due to the partial removal of naphtha volume to comply with pollutant specifications. This is where the investment in catalytic technology comes into play as a situation of commitment, allowing the sustainable achievement of the new quality objectives in the products, and minimizing the implementation time.

In advance of the implementation of the legal specification of 50 ppm in the naphtha, Axion Energy has worked with Grace to test of one of these additives. A prior base case was established where all the operational information was obtained along with data on the quality of products needed to calculate sulfur removal efficiency. The quality of
the catalytic naphtha was analyzed, and based on the type of sulfur compounds and the distribution thereof on the basis of boiling range, the appropriate technology was chosen. The expectation of sulfur removal efficiency was set in the range of 30-35% since no complex sulfur species were detected hence favoring the performance of the additive.

**Development of the Work Plan**

In August 2012, Axion Energy planned a back-to-back catalyst inventory replacement in the FCC unit, by incorporating a sulfur reduction additive, Grace’s GSR®-5 technology. It maintains the basis of the formulation of Axion’s FCC catalyst, because the matrix and zeolite content remains constant, in order to minimize the impact on the unit’s typical volumetric yields. The desulfurization range in which the additive typically operates varies between 20 and 30% depending upon the complexity of the sulfur species to be removed.

The primary objective was to reach 50 ppm of sulfur in the finished naphtha pool, maximizing the catalytic naphtha content and minimizing alkylate imports, which is not available in the country in the volumes required to achieve the above specification.

**Establishing the base-case and the commercial trial**

Prior to the new additive commercial trial in the FCC unit, a base case study was conducted. This process, which took approximately two months, allowed the consolidation of a database to be used by the Grace technical team to predict the efficiency of sulfur removal. The information used mainly consisted of the analyses of the different naphtha cuts carried out by Axion’s laboratory. Physicochemical analyses were performed systematically on the typical feed sent to the FCC reactor and the main products, naphtha and diesel, such as distillation curves according to ASTM, density, sulfur content by different analytical methods, and others. The distillation curves of the finished products were used to calculate the cut-point or cut-off points of the fractionating tower downstream from the unit reactor. This information led to the segregation of the different sulfur removal efficiencies based on the naphtha cut-off point. The higher the naphtha’s final boiling point (FBP), the more difficult it is to remove the heavy sulfur species, such as benzothiophenes and dibenzothiophenes. When the naphtha’s FBP decreases, there will be greater sulfur removal and an improvement in the quality of the catalytic diesel due to the incremental volume of desulfurized naphtha cut included in the middle distillate product.

During the study, the operational variables of the FCC unit were also monitored to understand and confirm how the severity of the cracking reactions, the reactor conversion level, reaction temperatures and pre-heating of the feed, as well as the catalyst-oil (C/O) ratio would affect the gasoline desulfurization process.

In the initial planning of the test, it was established that a tracer compound should be chosen in the equilibrium catalyst (Ecat) to monitor the amount of additive in the Ecat inventory. Since the formulation of GSR®-5 technology contains a vanadium component that differs by at least one order of magnitude with respect to the feed quality of Axion Energy’s FCC unit, it was decided that this element would allow the monitoring of the evolution of the inventory replacement. The variation in vanadium content observed during the test is illustrated in Figure 1. The analyses of the equilibrium catalyst were conducted on a weekly basis in Grace’s Process Innovation Center.

![Figure 1. Vanadium concentration of the equilibrium catalyst of the FCC unit.](image-url)
Since the metal content in the feed for the catalytic cracking is not constant, and given that operational instability in a unit upstream from the FCC reactor can generate the undesired contamination of the catalyst, it was necessary to take this point into account. A typical “base” vanadium content in the initial inventory was established based on historical analysis, and it was agreed that the nickel content in the catalyst would be monitored, which has a behavior similar to that of vanadium. If there were no changes in the nickel pattern, it would be assumed that the only change in the vanadium pattern would be due to the entry of the additive.

Grace developed a correlation for the site to estimate the content of GSR®-5 technology in the total inventory based on the vanadium content measured in the Ecalt catalyst (Figure 2).

When a decrease in nickel content was detected on the Ecalt catalyst, which indicates that the Ni+V concentration in the feed to the FCC had declined, adjustments were made in the base value of vanadium, thus modifying the correlation accordingly.

Figure 3 shows the evolution of GSR®-5 technology in the total inventory of Ecalt based on the vanadium concentrations submitted in Figure 1. The behavior of both curves is identical.

Once the tools to monitor the addition of the GSR®-5 technology were defined, the catalyst replacement rate was established, according to the back-to-back modality. This methodology consists of the controlled and sustained dosing of a new product at typical addition rates, allowing the observation of the gradual evolution of the different target properties.

According to Grace’s recommendation, the addition of additive in the unit was configured in two stages. The first, called the “accelerated addition phase,” contained 37%wt of GSR®-5 technology regarding the typical addition, which is 37% additive and 63% of the base catalyst. Once 25%wt of additive was achieved in the Ecalt inventory, the proportion would be reduced to 25%wt of unit’s addition rate, according to the requirements of the GSR®-5 technology. The accelerated phase would allow quick replacement in order begin to see the benefit of sulfur reduction.

For the purposes of calculating removal efficiency, Grace developed an equation for the site (Equation 1), to estimate the sulfur content in the catalytic naphtha based on the density and distillation of the product and the sulfur content in the feed to the cracking unit.

**Equation 1**

\[
S_{NC} (\text{ppm}) = 3238.92 + 2.9523 \text{FBP}_{NC} - 5336.83 \text{SG}_{NC} + 2.6805 \text{MeABP}_{NC} + 486.43 S_{\text{feed}} \%\text{wt} \\
R^2 = 1
\]

Where \( S_{NC} \) is the sulfur content of the FCC naphtha, \( \text{FBP}_{NC} \) is the final boiling point of the crude, \( \text{SG}_{NC} \) is the specific gravity of the naphtha, \( \text{MeABP}_{NC} \) is the middle aromatic boiling point, and \( S_{\text{feed}} \%\text{wt} \) is the sulfur content in the feed.

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Once the catalyst replacement process had begun and coinciding with the increase in additive content in the equilibrium catalyst, the progressive effects of desulfurization were observed.

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point of the naphtha and $S_{\text{feed}}$ is the feed sulfur concentration. The range of application of Eq.1 is $S_{\text{NC}} = 230$ to 285 ppm and FBP$_{\text{NC}}$ between 160-195°C.

This correlation was obtained based on experimental production data collected in the base case, which allowed the estimation of theoretical sulfur content, as if the additive had not entered the unit. The adjustment obtained between the prediction and the experimental sulfur data obtained prior to the test is shown in Figure 4.

The efficiency of the additive is calculated as detailed in Equation 2, based upon the theoretical prediction indicated in Equation 1, and the actual measurement of sulfur content in the laboratory.

**Equation 2**

$$Ef = \frac{S_{\text{NC}} (\text{Ec.1}) - S_{\text{NC}} (\text{laboratorio})}{S_{\text{NC}} (\text{Ec. 1})}$$

**Results**

Figures 5 and 6 present the results for the evolution of the sulfur content in naphtha and the calculation of GSR®-5 technology efficiency.

A sustainable 25 to 30%wt decrease of total sulfur was observed in catalytic naphtha, with specific events of 40-45% at maximum severity of the FCC unit. 53% of the samples taken showed a sulfur reduction higher than 20% during the test and only 4% of the samples presented an additive efficiency below 5%.

Figure 7 shows the distribution of sulfur compounds for different samples taken during the GSR®-5 technology test.

The sample analyses dated 2/23/2012 and 9/12/2012 corresponds to the results of the naphtha’s before the addition of the GSR®-5 technology, while the sample dated 11/8/2012 shows the result with 25% of the GSR®-5 technology in inventory. These sulfur distribution curves indicate a 34% sulfur reduction with respect to the base case, comparing the base case (9/12/2012) results and after reaching 25% of additive in the catalyst inventory (11/8/12). The sulfur reduction in the catalytic naphtha was very significant, and this allowed the development of a project to shut down a treatment unit for

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the removal of mercaptans on the naphtha product downstream from the FCC unit. Incorporating the GSR®-5 technology allowed the removal of all the light sulphides and mercaptans compounds in the reactor of the FCC unit, making subsequent treatments unnecessary for the FCC naphtha product.

The use of additives to decrease the sulfur content of the naphtha involves replacing up to 25%wt of the catalyst inventory. This must not affect the yields of the FCC unit significantly, provided the additive has the same catalytic base. This means that, in composition, the amount of active components (zeolite, matrix and ReO3) content be similar to the unit’s base catalyst. With regard to the trial conducted at Axion Energy, a slight decrease in the ACE Ecact activity was observed, which did not significantly affect the volumetric yields of the unit.

Other effects observed

Using GSR®-5 technology to reduce sulfur in FCC naphtha had additional benefits on other products of interest. In the case of Axion Refinery, the benefits of incorporating the GSR®-5 technology were reflected in the quality of the diesel (LCO, light cycle oil), and in the quality of the total propane and butane streams.

When running the FCC unit at maximum diesel production, a minimal volume of naphtha was extracted at the minimum final boiling point (FBP). This minimizes sulfur, not only in the naphtha, but also in the LCO fraction, due to delivery of the heavy fraction of naphtha in the fraction of middle distillates. This effect is shown in Figure 8, where the distillation of diesel is analogous to that presented in Figure 7 for naphtha.

Decreasing total sulfur content in the diesel allows the increase in the volume of this cut in the gasoil pool, thus upgrading molecules in the refinery.

There were also reductions in sulfur content in the LPG (liquefied petroleum gas), which had not been considered at the beginning of the commercial trial. The total butane (C₄) and propane (C₃) streams before entering the caustic treatment unit for mercaptan removal showed an average decrease of 30%wt, which meant a margin improvement and reduction of the caustic soda consumption.

It is important to note that the 30% sulfur reduction does not consider the changes in FCC feed quality. The estimate of the sulfur reduction is conservative because, at the time of the additive trial, the total sulfur content in the FCC feed was slightly increasing. This should have increased the sulfur content in the two main components of LPG (propane and butane). However, Figures 9 and 10 show the trends observed in the sulfur content in the total C₃ and C₄ in the FCC feed demonstrating that although the sulfur content of the feed increased during the trial, the concentration of sulfur compounds in these two streams decreased significantly, with the greatest decrease in the total C₄.

![Figure 7. Sulfur distributions compounds in catalytic naphtha samples.](image1)

![Figure 8. Distribution curves of sulfur compounds in catalytic diesel (LCO) samples.](image2)
Conclusions

To satisfy the increasingly demanding market in vehicle design and environmental restrictions, it is important to have alternatives for achieving the highest production standards. Considering that the naphtha produced in the FCC unit of a refinery is the major and limiting component in sulfur content in the gasoline pool, catalytic additives with sulfur reduction functions are presented as a short-term alternative along with the planning, development, and execution of capital projects in the longer term.

There are currently FCC catalysts and additives that integrate the sulfur reduction function. Both technologies allow the reduction of sulfur levels in naphthas from 20 to 35%wt according to the product’s range of distillation, characteristics of crude oil processed in the refinery and the feed of the FCC unit.

To ensure the proper evaluation of the technologies of additives to reduce sulfur in the naphthas produced in the FCC commercial units, it is essential to create a good base case to correlate the main process variables with naphtha sulfur content.

Since the GSR® technology has the same formulation of the base catalyst, it does not affect the yields significantly. Therefore, there was no detriment in the volume of liquid products after incorporating the additive in the catalyst inventory.

The direct incentives arising from the use of this technology include optimizing the use of molecules with lower sulfur content and minimizing imported products in the finished gasoline pool.

In addition, the benefits of sulfur reduction are extended to the quality and production of catalytic diesel (LCO) in the case that the heavy fraction of the naphtha is sent to middle distillates.

An additional benefit was observed in the sulfur reduction (mercaptans and sulfides) in the total C₃ and C₄ streams, allowing the refinery to reduce consumption in the treatment unit of gasoline with caustic soda thus reducing cost and facilitating the logistics of this chemical.

The use of catalytic additives to reduce sulfur in gasoline is a technological advantage and a viable alternative for the refining industry, whose permanent challenge is to produce a greater volume of fuel at the highest quality standards. ❇️
Global leader in hydroprocessing catalysts offering the complete range of catalysts and services

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Q&A from The 2016 AFPM Cat Cracker Seminar

This regular column features answers from Grace experts in response to frequently asked questions or common scenarios. In this issue, Grace Technical Service Leader Ann Benoit provides insight into improving FCC unit operations.

Ann Benoit is the FCC Technical Service Leader for Grace in the Americas. She holds a B.S. degree in Chemical Engineering from Tennessee Technological University and has 15 years of refinery and catalyst experience. Prior to joining Grace in 2008, 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 Grace’s technical representative on the American Fuel and Petrochemical Manufacturers (AFPM) screening committee. She also manages the North American Grace FCC Technical Workshops.
The following questions and answers are based upon a Process Q&A session that took place at the American Fuel & Petrochemical Manufacturers (AFPM) Cat Cracker Seminar in August 2016. Answers were provided by Ann Benoit, North America Technical Service Leader for FCC at Grace. The answers appearing here may vary from the event transcript in order to provide context and/or clarity.

**How does arsenic in the FCC feed impact operation and catalyst performance? What testing do you apply to monitor arsenic?**

At the low levels of arsenic seen on Ecat, we have not seen any negative effect on FCC cracking catalyst. I would, however, like to address the second part of the question regarding testing, and talk about the importance of the analytical methods used to test arsenic on Ecat. We would caution anyone using the ICP-AES (inductively coupled plasma atomic emissions spectrometry) method, since lanthanum in Ecat can interfere with the arsenic line and cause incorrect high levels of arsenic to be reported.

You can see the interference with lanthanum in this graph. That light blue line at the very top is the signal for a sample containing 400 ppm lanthanum. The bottom dark purple line is a sample with 10 ppm arsenic only, and the red line is a lanthanum containing Ecat sample spiked with 2 ppm arsenic. As you can see, it would be very easy for someone to report an inaccurate high level of arsenic. Some of the methods you can consider using for arsenic analysis instead of ICP-AES are ICP-MS (inductively coupled plasma mass spectrometry) or NAA (neutron activation analysis). These methods can potentially experience interference with arsenic, but they can be corrected for it.

**What are the best practices to minimize risk when choosing to process an opportunity FCC feedstock?**

The key to minimizing risk during the selection of an opportunity feedstock is to first determine the characteristics of the material and understand the variability in those properties over time. It is important to have a process in place to monitor incoming opportunity feedstocks for metals and other key properties. Best practice would be to sample and test each shipment coming into the refinery. When processing any type of opportunity feedstock, refiners will often experience some type of metals excursion on the circulating FCC Ecat. Monitoring allows one to be prepared for these potential metals excursions. It is important to identify, in advance, catalyst management options such as increasing fresh catalyst addition rates, lowering the catalyst activity that allows you to increase fresh catalyst addition rates, and potentially purchasing Ecat for metals flushing. It is also important to assess the capability of your catalyst transfer and loading system to ensure that it will be able to handle the increased solids loading. After the fact, it is important to compare the model yields versus the actual yields and make adjustments to any purchasing feedstock guidelines, if needed.
What catalyst properties/characteristics impact FCC catalyst losses?

It is important to note that operation and mechanical factors can greatly influence catalyst losses, but this question specifically asks about fresh catalyst properties. The first fresh catalyst factor that influences catalyst losses is the fines coming in with the fresh catalyst; the second factor is the propensity of the catalyst to generate fines in the circulating inventory; and, the third factor is how well the catalyst can be retained by the cyclones.

Figure 1. Function of Catalyst Losses

In the top left corner of Figure 2, you will see the theoretical depiction of a cyclone’s ability to retain particles. The DPh is the smallest particle size that can be retained by the cyclone. The red zone is the particle sizes that are predominantly lost via the cyclone. For example, this would be your 0-to-20-micron range. We looked at Grace’s Ecatalyst database. No North American units can retain 0-to-20 microns. We also looked at the Ecatalyst 0-to-40-micron content. Across the industry, the average FCC holds approximately 3.5% 0-to-40. For fresh catalyst, the goal is to minimize the particle sizes in this red zone area, keeping in mind that manufacturing and circulation limitations can limit your options.

The next factor is particle density. Particle density can influence the smallest particle size a cyclone can retain. An increase in the particle density will decrease the smallest particle size a cyclone can handle due to the centrifugal force acting on the heavier particle. However, particle density is not the same as ABD (apparent bulk density). Industry typically measures and reports ABD as part of the routine Ecatalyst analysis, but this should not be mistaken for particle density.

The next factor is the propensity of the catalyst to generate fines in the circulating inventory. Inherent attrition resistance and morphology are the factors that can influence fines generation. Attrition resistance can be influenced by the catalyst manufacturing binding process. Industry measures attrition resistance via a variety of different tests. Grace uses the DI (Davison Index) test. A lower DI will indicate that the catalyst has a lower propensity to generate fines. Note that when comparing attrition testing with different labs, you should make sure that they are using the same procedure and that their results are comparable.

Figure 2. Theoretical Depiction of a Cyclone’s Ability to Retain Particles

Continued on Page 32
Additionally, it is important to note with attrition testing that the energy applied on attrition testing is much more severe than a circulating unit.

The last factor is catalyst morphology. The graphic in Figure 3 shows an example of bad morphology and good morphology. The bad morphology has jagged edges which tend to break off in the unit and get lost via the cyclone. The good morphology has a smoother surface, and this catalyst tends to generate less fines in the circulating inventory. Fresh catalyst attrition, morphology, particle density, and the fines entering the system via the fresh catalyst can all directionally impact catalyst losses. In Figure 3, the bad morphology is a fresh catalyst SEM.

**Figure 3.**

Bad Catalyst Morphology  
Good Catalyst Morphology

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**What operational and catalytic changes can be implemented to optimize C₄ olefin yield for the alkylation unit while producing lower sulfur FCC gasoline?**

To maximize C₄ olefins, we first need to understand the mechanism of formation. In Figure 4, the green lines are favorable pathways to maximize butylene. The red lines are undesired pathways. The first stage is to crack the feed into naphtha olefins. The naphtha olefins can then undergo hydrogen transfer to form naphtha paraffins or naphtha olefins can crack into propylene and butylene.

Keep in mind that ZSM-5 is going to crack gasoline olefins to butylene and propylene much faster than a traditional Y zeolite. The butylene and propylene can undergo hydrogen transfer that will form propane, isobutane, and normal butane, which is an undesired pathway for maximizing butylenes.

Looking at Figure 4, you can see that one of the ways to increase butylene is to reduce hydrogen transfer. This process can be done by reducing the rare-earth on zeolite or by adjusting the Z/M ratio. You can increase the matrix to reduce hydrogen transfer since the matrix has lower hydrogen transfer activity compared to zeolite.

Next you can consider using ZSM-5. As you know, ZSM-5 cracks gasoline olefins into propylene and butylene. Keep in mind that this might not be the best option if you do not have an outlet for propylene because ZSM-5 typically cracks more propylene over butylene.

**Figure 4. Butylene Maximization Fundamentals**

<table>
<thead>
<tr>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO/Resid Cracking</td>
<td>Hydrogen Transfer</td>
<td>Olefin Cracking (ZSM-5 &gt;&gt; Y-Zeolite)</td>
<td>Hydrogen Transfer Zeolite &gt;&gt; Matrix</td>
</tr>
<tr>
<td>(Zeolite or Matrix)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td>Naphtha Olefins</td>
<td>Naphtha Paraffins</td>
<td></td>
</tr>
</tbody>
</table>

**Butylen Drivers**

- **Catalyst/Additive Drivers**
  - Reduce hydrogen transfer
  - ZSM5
  - C₄ selective catalyst/additive

- **Operational Drivers**
  - FCCU conversion
  - Feedstock
There are \( C_4 \) selective catalysts and additives on the market. These technologies are specifically targeted to favor butylene selectivity. Figure 5 is an example where a refinery went from a base catalyst to a \( C_4 \) selective catalyst. And as you can see, it achieved more butylenes per propylene.

You can also change operational conditions to maximize butylene. Figure 6 shows a DCR (Davison circulating riser) pilot plant study that Grace did to show the relationship between total \( C_4 \)s and conversion. Total \( C_4 \) production depends on conversion, regardless of whether the conversion is achieved by reactor temperature or catalyst-to-oil ratio. Keep in mind that as you increase conversion, you increase total \( C_4 \)s and can increase butylenes.

Next, of course, is the fact that feed quality always impacts the products being produced in the FCC. More naphthenic feed will produce lower LPG olefins because the naphthenes, or good hydrogen donors, react with the gasoline olefins to produce gasoline aromatics and gasoline paraffins. Since gasoline range olefins are the precursors to LPG olefins, you are depleting the pool of material available to make LPG olefins.

We went through the \( C_4 \) drivers. Now I am going to address the part of the question about the gasoline sulfur. One way to increase butylenes and achieve a lower gasoline sulfur is to look at combining multiple technologies, such as a ZSM-5 or a \( C_4 \) selective catalyst, with gasoline sulfur reduction technologies. In Figure 7 is an example of a refinery that used gasoline sulfur technologies with and without ZSM-5. As you can see, the yellow triangles represent when the refinery was using ZSM-5, and the red diamonds show the results when no ZSM-5 was used. We saw similar gasoline sulfur reduction on gasoline sulfur technologies with and without ZSM-5.

Butylenes are influenced by a number of factors in the FCC. Proper choice of operating conditions, catalyst, and additives is critical to maximize butylene. Gasoline sulfur technologies can be used in combination with catalyst and additives to achieve higher butylenes and lower gasoline sulfur.

Continued on Page 33
What FCC operating and catalytic changes can impact gasoline sulfur while retaining octane? How would feed hydrotreatment impact these options? How would the FCC operating and catalytic changes impact gasoline post-hydrotreating?

Gasoline sulfur can be reduced 20 to 40% using gasoline sulfur reduction technology, which catalyze the hydrogen transfer reactions between thiophenes and tetrahydrothiophenes. The tetrahydrothiophenes then crack into hydrocarbons and H2S (hydrogen sulfide). Grace has seen gasoline sulfur reduction using these technologies in units both with and without hydrotreated feeds, as shown in Figure 8. In these two examples, one unit is processing a hydrotreated feed and the other unit is processing a non-hydrotreated feed. Both units saw approximately 20% gasoline sulfur reduction.

Why is this? The reason gasoline sulfur reduction technologies work for all types of feeds is due to the fact that the FCC naphtha contains the same species under typical gasoline boiling range, regardless of the feed, catalyst, and/or unit operations. This is evident in Figure 9 depicting our analysis of several different gasoline samples from units with and without hydrotreated feeds. The sulfur concentration of each of these naphtha samples varied based on different operations, feed qualities, and cutpoints. The important part is that the amount and type of gasoline species will determine the amount of sulfur reduction that can be attained using these technologies.

Another way to lower gasoline sulfur is by lowering gasoline endpoint. Lowering gasoline endpoint can have varying effects on octane. We have seen that reducing the gasoline endpoint can have a minimum effect on octane. We have also seen that reducing the gasoline endpoint can make octane worse. And then, there are some units in which reducing gasoline endpoint can potentially increase octane. The reasons for the variability are the gasoline composition and the starting gasoline endpoint. Because of the variability, we recommend doing a test run to understand the impact of adjusting your gasoline endpoint and its effect on octane.

One part of question asked about the impact on the post-treater. Reducing the gasoline sulfur to a post-treater unit can reduce the post-treater severity, which also could potentially reduce the octane debit across the unit, reduce hydrogen consumption, and extend the life of the post-treater catalyst. As we discussed in the previous example, you can use a combination of technologies to increase octane and lower gasoline sulfur. ☺️
Figure 8. Gasoline Sulfur Technologies

Figure 9. Gasoline Sulfur Technologies
Compete at a higher level.

In an industry where success is about profits as well as performance, you want to trust a partner who can lift you to the next level.

Grace custom catalyst solutions, co-developed with you, are about more than chemistry. They're designed to lift your financial performance.

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

If you’re ready to finish on top, call us to show you how we can help.


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

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