Are You Ready for IMO 2020?

Whether your goals are handling difficult feeds or producing more diesel, Advanced Refining Technologies (ART) offers you a better perspective on hydroprocessing.

Partner with us to meet IMO 2020 regulations head on and come out ahead. ART is the proven leader in providing excellent solutions for today’s refining industry challenges.

- High Si Capacity Solutions for Coker Naphtha
- High Metals Capacity Solutions for FCC Pretreat
- Distillate Selective Catalysts for Increasing Diesel Demand
- High Metals Capacity Hydrocracking Solutions
- High Metals Capacity Catalysts for Opportunity RDS and EBR Feeds
- Specialized Catalyst(s) for DAO Containing EBR Feeds

Visit arthydroprocessing.com
Global Connections Help Solve Global Challenges

Scott Purnell, Vice President, Research and Development, Refining Technologies, W. R. Grace & Co.

As we near the end of the second decade of the 21st century, the world in which we live continues to be more and more globally connected. This is obvious for technology and communications. We all now carry phones in our pockets with more computing power than the spacecraft that carried men to the moon. These devices allow us to send messages instantly around the world and even hold video conferences from the palm of our hand. And these same phones allow us rapid access to information via the entirety of the world wide web.

Markets are also more global than ever. Commodities are priced and traded globally. Economic results in one country or region ripple across the world, affecting global equity and currency markets. Politics and trade tensions only serve to reemphasize these effects.

Our refining industry is no different. Refineries are located across the globe and are impacted by global ebbs and flows of the crude oil, transportation fuels, and petrochemicals markets. Regions which were once remote and undeveloped have become vibrant centers of growth and investment.

At Grace and ART, we have witnessed these trends and adapted our businesses accordingly. Our manufacturing plants are located around the world and able to efficiently supply our global customer base. Our sales and technical service teams are deployed across the globe to better serve our customers. In most cases this includes being in the same time zone and speaking the same language as our customer. Our research and development resources are centrally organized and are innovating to solve global challenges. In addition, these same R&D resources are also very focused on customer-centric projects which can be leveraged to the broader market.

"As we progress on this path to one connected world, we continue to be focused on you, our customers."

Scott Purnell  
Vice President, Research and Development, Refining Technologies

In this issue of Catalagram, you will see repeated evidence of the global reach and focus of the Grace and ART organizations. Since our last issue, we led an FCC Technology Conference in Rotterdam with more than 140 delegates from 55 companies. At this same conference we convened a panel of industry executives to discuss present and future FCC challenges. We met with senior executives from our key clients in the Arabian Gulf during the Gulf Downstream Association (GDA) Conference in the Kingdom of Bahrain. We celebrated 35 years of serving the KMG Pavlodar refinery in Kazakhstan, and we sponsored and were a key presenter at the 5th Latin American and Caribbean Refining Congress held in Buenos Aires, Argentina. Further in this issue you can read answers from our experts to industry questions from the 2018 AFPM OPT Summit and will also note that the ART and Grace teams are ready to be part of your solution to IMO 2020 compliance.

As we progress on this path to one connected world, we continue to be focused on you, our customers. We want to solve your problems and add value to your bottom line. We can do this best when we are working closely together. Include us as part of your team and I think you’ll see the benefits.

As always, we welcome your feedback and look forward to more ways in which we can work together to deliver value now and into the future. ☺
IN THIS ISSUE of Catalagram®, our 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 catalyst systems deliver significant value in today’s challenging refining environment.

What’s Inside

GRACE IN THE NEWS

4 Hudson La Force succeeds Fred Festa as Grace CEO
4 ART recognized at leading middle east conference
5 Grace celebrates more than three decades with KMG Pavlodar refinery
5 ART rolls out new look, website
6 Grace talks sulfur reduction at technical and commercial conference for latin american refiners
6 Teaching the fundamentals of value
6 ART presents advances in EBR technology at RPTM 2019

SUCCESS STORIES

11 Industry leaders weigh in on the future of refining
16 Generating value in the FCC through innovative catalyst technologies and technical services

ASK THE EXPERTS

22 Q&A from the 2018 AFPM operations and process technology summit

Remembering Betsy Mettee
More profit from your FCC? Rive May be your solution
GRACE IN THE NEWS
Hudson La Force Succeeds Fred Festa as Grace CEO

W. R. Grace & Co.’s Board of Directors designated Hudson La Force as President and Chief Executive Officer upon the retirement of Fred Festa on Nov. 1, 2018. Festa will remain as non-executive Chairman on the Grace board.

La Force has been Grace’s President and Chief Operating Officer since February 2016 with responsibility for Grace’s Catalysts Technologies and Materials Technologies business segments and global manufacturing and supply chain operations. He joined the company as Senior Vice President and Chief Financial Officer in 2008. Prior to joining Grace, he served as Chief Operating Officer and Senior Counselor to the Secretary at the U.S. Department of Education. Before entering public service in 2005, he held general management and financial leadership positions with Dell, Inc., AlliedSignal, Inc. (now Honeywell), Emerson Electric Co., and Arthur Andersen & Co.

Christopher J. Steffen, Lead Director and Chair of the Board’s Nominating and Governance Committee, pointed to La Force’s deep understanding of Grace’s customers and operations, strategic vision, proven leadership, and track record as key reasons for the selection. “Grace is well positioned with market leading businesses and excellent prospects for solid growth,” said Steffen. “Hudson is a talented leader with command of the strategic levers needed to grow our company, and is a strong successor to Fred Festa.”

ART Recognized at Leading Middle East Conference

In October of 2018, Grace and Advanced Refining Technologies (ART) sponsored and exhibited at the Gulf Downstream Association (GDA) Conference in the Kingdom of Bahrain, which is a leading conference for regional and international stakeholders in the downstream segments of the refining industry.

ART, along with Chevron Lummus Global (CLG), was formally recognized at the event by GDA Conference Chairman Suleman Al Bargan, who is also Vice President of Saudi Aramco’s Downstream and NGL Fraction. ART Managing Director, André Lanning, is a member of the GDA steering committee.

GDA is a non-profit organization aimed at bringing downstream players from business and academia together to further develop the industry and draw benefits from knowledge sharing and best practices.

Grace’s Refining Technologies President, Tom Petti, joined André and members of Grace and ART’s global commercial teams to meet with representatives from key Middle East refineries, oil ministries, and national oil companies such as Saudi Aramco, the Bahrain Petroleum Company (BAPCO), Kuwait National Petroleum Company (KNPC), and Abu Dhabi National Oil Company (ADNOC), along with CEOs from several private companies.

Grace and ART both hosted exhibits, with ART collaborating with Chevron Lummus Global (CLG).

From left: Audah Al-Ahmadi, GDA Secretary General; Suleman Al Bargan, GDA Conference Chairman; André Lanning, Managing Director, ART; and Leon de Bruyn, Co-Managing Director, CLG; Dr. Dhafer Al Jalahma, National Oil & Gas Holding Company, Kingdom of Bahrain.
Grace Celebrates More Than Three Decades with KMG Pavlodar Refinery

In 2018, Kazakhstan’s state-owned JSC National Co. KazMunayGas (KMG) celebrated the 40th anniversary of its Pavlodar Refinery in Pavlodar, Kazakhstan. Grace was invited to participate in the two-day celebration which included presentations by vendors, suppliers and partners, as well as a refinery tour, roundtable discussion, and gala dinner with fireworks.

Grace was recognized as a key partner during the gala and awarded a commemorative 40th anniversary medal. In return, Grace presented Pavlodar Refinery management with a crystal gift signifying the teamwork between the companies. During our 35-year cooperation with Pavlodar, Grace has delivered FCC catalysts, optimization, unit inspections and troubleshooting, and exceptional technical service to the refinery.

Grace was a close partner during the refinery’s recent major modernization and FCC unit expansion. The improvements allow the refinery to cut deeper into the barrel and significantly improved their financial position. They now can produce Euro-4 fuels and will transition to Euro-5 standard fuels as needed. Grace worked with the refinery, licensor, and the project team to advise on post-restart optimization, including recommendations for catalysts and additives to further improve FCC performance.

This relationship is a testament to Grace values and industry leadership. It represents hard work and dedication by many generations of Grace employees across all functions. Thank you to everyone for making this celebration possible.

ART Rolls Out New Look, Website

On Oct. 1, 2018, Advanced Refining Technologies (ART), the joint venture of Chevron and Grace, debuted a new look and launched a new website to communicate more clearly and consistently the value ART delivers to customers.

ART, a Chevron and Grace joint venture, is a leading supplier of hydrotreating catalysts that produce cleaner fuels. ART offers a complete portfolio of resid hydrotreating, resid hydrocracking, hydrocracking, lube hydrotreating, and distillate hydrotreating catalyst technologies through a global manufacturing network. ART combines Chevron's extensive expertise in refining operations, catalyst technology and development, process design leadership, and licensing with Grace's materials science, specialty chemical manufacturing, and global sales and technical service strengths, to improve refiners' profitability through catalytic solutions that improve the quality and yields of fuels refined from a wide variety of feedstocks. Along with Chevron Lummus Global (CLG), ART provides complete hydrotreating solutions for refiners.

Therefore, our roll out includes a new go-to-market brand – ART Hydroprocessing™ – to highlight the markets that ART serves. While the legal name of the business remains unchanged, our new promotional materials and our new logomark will reflect the ART Hydroprocessing™ brand.

Visit ART's new website at arthydroprocessing.com to preview the new look and get more information about hydrotreating solutions.
Grace Talks Sulfur Reduction at Technical and Commercial Conference for Latin American Refiners

In the fall of 2018, Grace's FCC team gathered with refiners in Latin America at the 5th Latin American and Caribbean Refining Congress, sponsored by the Argentinean Institute of Petroleum and Gas (IAPG). The Congress, held every two years, is the premier technical and commercial conference for Latin American refiners outside of Mexico and Brazil.

During the conference, Leonardo Betancourt, Technical Sales Manager, FCC, presented on a commercial application of Grace's GSR™ technology for gasoline sulfur reduction in the FCC unit at Axion Energy. Additionally, Bob Riley, Regional Marketing Manager Americas, FCC, presented on a comparison of experience with processing tight oils in North America and Argentina.

Eduardo Estrada, Senior Technical Sales Manager, FCC, managed several high-level business discussions with key refinery business partners during the meeting. The conference afforded Grace the opportunity to reinforce the key values of talent, technology, and trust, and to emphasize Grace's commitment to refiners in the region.

Teaching the Fundamentals of Value

Grace's global sales and technical service teams deliver value by sharing their FCC expertise and knowledge with our customers during technical workshops at Grace locations as well as on site at refineries around the world.

While Grace hosts regional technical workshops several times a year in Europe and North America, we also develop workshops for individual customers that are presented on site at their refineries. On Nov. 7-8, 2018, 50 engineers and refinery operators learned more about catalyst technology fundamentals at a workshop customized for unique challenges and needs of Repsol Petróleo S.A (Repsol Group) in Puertollano, Spain.

Rafael González at Grace partnered with Repsol Group to customize content and conduct a FCC Fundamentals and Troubleshooting Workshop in Spanish for the benefit of Repsol’s employees in Puertollano.

ART Presents Advances in EBR Technology at RPTM 2019

ART and Chevron Lummus Global (CLG) had a strong presence in the prestigious Refining and Petrochemical Meet (RPTM) industry event. ART and CLG were cosponsors of the 23rd RPTM, Jan. 12-14. The meeting was attended by more than 1,000 downstream industry experts and leaders representing technology licensors, catalyst manufacturers, and equipment suppliers from all over the world.

Members of our India team were joined by Balbir Lakhanpal, ART’s Ebullating Bed Resid Hydrocracking (EBR) expert, who presented a technical paper about the advances in EBR technology. Balbir’s presentation generated great interest among attendees, an indication of the excitement about planned upgrading projects, including LC Fining projects, planned in India. The presentation was also well aligned with the RPTM theme of “Aligning Refineries Towards Sustainable Future.” In addition, CLG presented about Competitive Pathways for Crude to Chemicals.

Bruno Tombolesi, ART General Manager for the Europe, Middle East and India regions, commented “The India market is very dynamic with strong growth. Our presence in the country is perfect for ART to be a major hydroprocessing catalyst and technology player there.”
Remembering Betsy Mettee

On Dec. 10, 2018, long time Grace employee Betsy Mettee passed away while in retirement in Florida. Many customers will remember Betsy as an instrumental part of the success of Grace’s Refining Technologies business during her four-decade tenure leading marketing communications and public relations in that division. Betsy originally came to work for Grace in 1974 and retired in 2014.

Betsy was honored with a memorial service and funeral mass before being laid to rest at the Dulaney Valley Memorial Gardens in Maryland. She is survived by her brother John Wasowicz, son Joseph Mettee, and stepchildren Michael Mettee, Carol Beck, and Donna Mettee.

Betsy may be best remembered for her big personality and masterful organization of important Grace customer events such as the Grace Golf Tournament and annual Mardi Gras celebration. She focused a tremendous amount of her energy on building and maintaining excellent personal relationships with customers and business partners. She also played a large role in the development and publication of Catalagram.

In addition to her daily duties for the Refining Technologies team, Betsy became the point person for Grace’s partnership with Meals on Wheels of Central Maryland in 2006 and personally delivered some of the hundreds of meals provided to Grace’s Columbia, Maryland, community over eight years.

On March 17, 2019, Grace’s Refining Technologies commercial team will remember Betsy at the event which she was most proud to have created, the annual AFPM Brunch, during the AFPM Annual Meeting in San Antonio, TX. ©
More Profit From Your FCC? Rive May Be Your Solution

Chris Haynes
Chief Operating Officer
Rive Technology, Inc. Princeton, New Jersey, U.S.A.

Adrian Humphries
VP, Technical Services
Rive Technology, Inc. Princeton, New Jersey, U.S.A.

Rive Molecular Highway™ Technology

Founded in 2006, Rive Technology is a material science company focused on the development and commercialization of Molecular Highway™ mesoporous zeolite technology originally discovered at the Massachusetts Institute of Technology.

Molecular Highway™ mesoporous zeolite technology is a highly patented (41), zeolite meso-structuring process that introduces ordered, well-controlled, hydrothermally stable, mesoporosity into zeolite crystals. As opposed to random irregular zeolite mesopores, Rive’s Molecular Highway™ technology allows for control of the order, size of and the amount of mesopores incorporated into the zeolite which leads to consistent structures and thus performance.

Since 2010, Rive has been commercializing Molecular Highway™ zeolites in FCC catalysts with W. R. Grace & Co. and Grace/Rive is currently supplying multiple FCC units around the world with the first, and only, use of ordered mesoporosity in FCC catalysts capable of providing a step change in value for many FCC operations.

The Molecular Highway™ Advantage

With conventional FCC catalysts, molecules with kinetic diameters up to roughly 1 nm (10 Å) can directly enter the Y zeolite structure. This corresponds to hydrocarbons which boil up to around 950°F (510°C). Larger hydrocarbons are traditionally subjected to matrix aluminas. These materials have somewhat weaker acid sites and the goal is to cleave off hydrogen-rich side chains which can subsequently enter the zeolite cage.

With the vast network of ordered mesopores in Rive zeolites, larger feed molecules are now able to directly access the strong acid sites in the zeolite. Rive zeolites are able to crack these larger feed molecules much more selectively than conventional active matrix materials. This translates commercially into coke-selective bottoms cracking. Additionally, these Molecular Highways rapidly channel the valuable cracked products out of the zeolite before they succumb to potentially undesirable reactions such as over-cracking, hydrogen transfer, or condensation reactions to form coke within the catalyst pores.

Typical “signatures” of Grace FCC catalysts containing Rive zeolites include improved bottoms upgrading, decreased delta coke and decreased dry gas production. Refiners have used these trademark benefits to increase FCC feed throughput by alleviating existing unit constraints such as maximum air blower rate, wet gas compressor rate, and regenerator temperature. Improved operating flexibility allows for increased catalyst circulation via lower delta coke, or alternatively heavier feed can be introduced if increased circulation is not possible.

Figure 1: Mesopores are integral to the zeolite crystal.
LPG olefins are very reactive, particularly at high temperatures present in the FCC riser and reactor. If these valuable, reactive molecules spend too much time inside the catalyst, they can become saturated through hydrogen transfer reactions into less-valuable LPG paraffins. Rive’s ordered mesopores have been commercially proven to allow rapid transport of valuable LPG olefins out of the zeolite. Preservation of primary products in conjunction with reduced hydrogen transfer also leads to a boost in Research Octane Number (RON), while more efficient bottoms upgrading results in higher MON.

Grace FCC catalysts with Rive’s Molecular Highway™ technology have been used successfully in numerous commercial operations. There has been no increase in catalyst losses or stack opacity with any commercial sales or trials at any of these locations, confirming the excellent physical properties of the Rive catalysts supplied. Several sets of commercial results (including stack opacity comments) have been published through AFPM (see rivetechnology.com).

An excellent example, as previously published through AFPM (2017-17-47), is the ongoing operation at a Motiva (now Shell) refinery in the USA Gulf Coast, where this commercial operation has demonstrated noticeable improvements in coke selectivity, dry gas selectivity, LPG olefinicity, bottoms reduction and C3+ Total Liquid Volume.

In another commercial example from a major refiner, Rive has been able to increase the volume of transportation fuels (at constant LPG) and also improve the quality of the slurry. This combination has resulted in a significant increase in FCCU profitability (as depicted in graphs on right).

A third commercial example in a high added iron operation had the primary objective of reducing regenerator temperature for a given amount of vacuum tower bottoms in the feed. Over the course of the trial, delta coke and regenerator temperature both steadily decreased. This provided the refinery with increased operational flexibility to process lower cost feeds while not exceeding unit constraints.

As refiners around the world continue to face new challenges on a daily basis, Rive’s Molecular Highway™ technology has demonstrated a novel approach to the design of FCC catalysts. These modified zeolites can be introduced into the entire range of Grace’s FCC catalyst portfolio in order to provide an increased level of operating flexibility to the refiner.

The resulting enhanced diffusion of hydrocarbons, both into and out of the catalyst particles, provides the refiner options to process heavier feeds or circulate more catalyst, while preserving valuable products and reducing delta coke and dry gas from less over-cracking.

Please contact your local Rive and Grace representative to learn more about the benefits of ordered mesoporosity through Rive’s exclusive Molecular Highway™ technology. ☺️
SUCCESS STORIES
Industry Leaders Weigh In on the Future of Refining

Moderator:
Eithne Treanor
Media and Communications Specialist

Panelists:

Stephane Morin
Manager, TAKREER TRC
Experimental R&D Department

Pappu Sundaramoorthy
General Manager, Technical Services, ORPIC

Alfredo Barbaro
Senior Vice President, ENI

Tom Petti
President, Refining Technologies
W. R. Grace & Co.

Alan Gelder
Vice President, Refining, Chemicals and Oil Markets, Wood Mackenzie

In October 2018, Grace convened a panel of refining industry experts to discuss present and future challenges to FCC operation as part of its FCC Technology Conference in Rotterdam in the Netherlands. More than 140 delegates, from 55 companies including refiners and other FCC shareholders attended the conference and participated in a broad technical program. The panel discussion is transcribed here and edited for length and clarity.

More than 140 delegates from 55 companies joined us in Rotterdam in October to discuss the challenges facing FCC operations. Thanks to our distinguished speakers and panelists.
Combined from Page 11

**Moderator:** Considering the bigger picture of the direction that refining and specialty chemical industry is taking, currently being the sector that everybody is looking at with urgency for potential new investments to move forward, what is the good news for the refining sector?

**Alan Gelder:** The industry had a good couple of years. With the crude oil price drop in 2014 and 2015, the refining and chemicals industry moved from a poor position to be the main value driver. The situation now is that there is an energy transition going on, and maybe new projects upstream might not be the way to go. The growth in fuels and petrochemicals is still expected to be from the refining sector. If you look at the oil majors now, most of their CEOs are from refining, which would be highly unexpected ten years ago. This is because they understand the sector and they know how to make money out of it.

**Moderator:** With the understanding that adding value is about monetizing every sort of molecule in the barrel and that this is where the focus is, what can you and customers do to ensure that this is a win-win for everyone?

**Tom Petti:** A refinery is a factory that converts raw materials into different products, historically refineries have been thought of as very narrowly focusing only in transportation fuels and throughput that drove all the economics. This way has to change into getting less expensive raw materials. The growth in fuels and petrochemicals is still expected to be from the refining sector. If you look at the oil majors now, most of their CEOs are from refining, which would be highly unexpected ten years ago. This is because they understand the sector and they know how to make money out of it.

**Moderator:** If we look at the situation in different countries, we see that it is not equal. Specifically in Europe, we are currently seeing a lot shift. Alfredo, can you please give us a feel for what the industry is facing, especially in Europe?

**Alfredo Barbaro:** More than 25-30 refineries have been shut down in Europe in the last years. Also ENI converted two refineries into biorefineries. So our vision is to focus more on biofuels moving forward to support gasoline and diesel demand. In other parts of the world, the situation is different with big investments planned for new, big refineries. In Europe we are facing legislation on emissions control that is much more stringent than other places, which is a more challenging situation for Europe.

**Moderator:** From a chemical engineering perspective, how can we maximize value and profit?

**Pappu Sundaramoorthy:** We talk about 4 Ps: plant, process, people, and performance. Plants are getting bigger so there is economy of size. In terms of process, with the help of hardware and catalysts it is improving along the way. In the past we used to have operators with just a diploma, nowadays they possess higher degree education. With this new scenario, one thing is to assume that one cannot know about everything so partnerships are required with parties like manufacturers, sharing the best of each other to go to the next level. Especially when talking about RFCC, one key element is to maximize the run length, so if the refinery is going to run 4-5 years how long will our RFCC unit operate during this period? Run length for a hydrocracker in the past was 12-24 months between catalyst bed change, while now is going to four years. Big changes are happening in catalyst performance. How to do this in the RFCC is the challenge. So, we can add Partnership as the fifth P.

**Moderator:** Looking at the tremendous expansion taking place in the Middle East, and in particular with ADNOC leading it, it has the mission to become an global National Oil Company with huge investments in refining sector, but not only ADNOC but also all companies working with it.

**Stephane Morin:** ADNOC has a very good geographic position in the Middle East. First the local market is increasing consistently, and just next to it there’s India, China, and south-east Asia, which is a very big market. Recently the ADNOC CEO announced a $45 billion investment in downstream for the Ruwais refinery to become the first integrated petrochemical-refining centre in the world. This big investment responds to the thinking that there is value behind this big market. Integration is a key part of the project, increasing to triple the capacity of the petrochemical plant. To maximize efficiency the integration should be built in a new plant from the scratch. The real value comes from this integration and products diversification beyond classic transportation fuels to plastics and chemicals.

**Moderator:** Talking about integration, Alfredo, you previously mentioned biofuels, but looking at the bigger picture, does ENI think that integration is the key to add value?

**Alfredo Barbaro:** We believe that integration is key to deliver value, but in Europe it is going to be very difficult to compete with companies like ADNOC, trying to produce the same product at lower price, because, for instance,
their energy costs are much lower than ours. Besides integration, feedstock quality is going to worsen. But above all, the production of specialties will be key rather than production of gasoline or diesel. Specialties are more difficult to produce, so there might be room for differentiation here, hence ENI efforts in R&D and company focus is moving towards this.

**Moderator:** We see the difficulties in Europe, but companies can also invest abroad, at locations where it makes sense...

**Alfredo Barbaro:** Yes, ENI is looking for partnerships in places like the Middle East. We believe that refining will still be profitable for some more time, but not particularly in Europe. In Europe there is no clear support to the industry but rather increasing regulations that hinder competitiveness. Besides people do not want industry in their backyard.

**Stephane Morin:** Indeed. ADNOC is looking for partnering with other companies who have the knowledge and the technology.

**Moderator:** Alan, looking at the wider picture, it seems that partnerships among suppliers and the knowledge sharing is where the industry is changing or has to change. Is this a huge opportunity that we see with different players like Saudi Aramco and others?

**Alan Gelder:** You see the partnership concept as revolutionary in the last years, even within a company. We saw Total putting refining and chemical departments together, two groups that used to compete with each other, and now they collaborate.

**Moderator:** Tom, what are you finding with your customers when you look at that? Given the tag line for Grace is Talent, Technology, Trust, obviously you play a big role with refiners, but has this role changed in the last years embracing the concept of partnership?

**Tom Petti:** It has changed. We work very closely with our customers. That is something we have done historically, but the strength of this collaboration has never been as tight as today. But there are also new problems to solve which create opportunities. The same solutions we came with to solve past problems are not as valuable as they were at some point in time. There have to be new things developed. We have a toolbox of technologies we can apply, but it has to expand to be able to solve new problems. For instance, there is a gap today in Europe of propylene, that’s an opportunity for refiners. In the short-term refineries in Europe should focus on how to capture this demand. If you look at how U.S. refining has developed in the complexity scheme, we had some closures there as well, so the complexity and the investment will create the opportunities. Also, the new IMO regulations will bring shifts, so the mentality of how to improve profitability through investments is on what we should be working together.

**Moderator:** Morty, you’ve got a long history of working with the majors like Shell, working in Singapore, India, Saudi Arabia, and now in Oman. How do you see the industry changing over the years, when it comes to the concept of working in a partnership instead of competing?

**Pappu Sundaramoorthy:** People changed their mind when they came to bigger plants. Equally, there are things we can do and we can’t do as refiners. I really do like the word from Grace’s tag line, “Trust”. People have been apprehensive to share data with suppliers, now the world is flat: if you do not share you are going to suffer. Two things are happening: oil companies are sharing the information, second there has been progress on the service side as people realized that it’s not only about costs but about what can be provided in terms of technology and talent. There is a big appetite to share the problems to find solutions.

**Moderator:** Stephane, one of the areas of partnership that is an easy win is knowledge sharing and the research concept. This is technology driven and there is probably more attention to make things more efficient and better. From the R&D perspective, where are you focusing?

**Stephane Morin:** We are a very young research center. How do you want a center with 70 people and 8-9 years history to be very efficient? This is not possible at all. All our jobs are through partnerships, so we are continuously finding win-win situations, like for instance with catalyst suppliers. We want to test their catalyst properly to find the best one for us, and for that we share all our data from the tests. We had a complicated issue recently and we were working for several months with different catalyst suppliers, we learned a lot during this time of catalyst selection. But it also happens with troubleshooting or FCC software simulation tools. This is what is efficient for our research center.

**Alfredo Barbaro:** I fully agree with Stephane. When we thought about partnership we used to think about an oil company with an engineering company or a catalyst supplier to be more efficient. Now we are trying to open new windows because something new is happening, which is digitalization. So now we are also partnering with companies which only do software, differently from in the past.

Continued on Page 14
SUCCESS STORIES

Continued from Page 13

Moderator: When we look at digitalization, which is across the industry, everyone is looking at it and being afraid of it, without a doubt. This industry has been very good at gathering data, but it is about what we do with this data. Tom, there’s something you are looking at in terms of where you are going to be positioned?

Tom Petti: Our industry is probably behind a lot of industries in this topic. We generate a lot of data, like Ecate analyses for everybody in the industry, but frankly we don’t know if we are getting as much value out of that data as we possibly could. We share unit data with most of our customers and we do thousands of tests using ACE™ and DCR™. This is an opportunity but there is no clear strategy yet so it must be taken seriously.

Moderator: Alan, what are you hearing about this?

Alan Gelder: Very similar things. The refining industry has a huge amount of data, if you think of all the units recording data in almost real time. There is also advanced process control. Many software engineers have access to platforms to play and see. We have seen something about augmented reality to make your operator more efficient or the idea of taking operators out of the plant and making life a bit safer. We are also seeing the ability to accurately forecast corrosion of an installation, which is a huge part of a plant shut down.

Moderator: Actually, a thing like that could have prevented an accident like the one in the Exxon plant in Torrance. Particularly in safety when it comes to gathering that data, this is something that refiners are focusing on. It also gives assurance to people discontented with industry, as Alfredo pointed out, with people not wanting industry in Europe or Italy. Why? Because they are afraid it is going to blow up, and they look at it as a dirty industry. That has to shift. Morty, what are your views on digitalization?

Pappu Sundaramoorthy: It is one of biggest changes in the industry. The expectations for the process engineers will be less, and more on the data. Data collection is more efficient today with more powerful computers, we can analyze trillions of data in a short time and do the predictions. In terms of profitability, the question now is “Are we able to get the additional profitability?” For a normal refinery with 200k-250k barrel production, you can get another $40-60M in profit with digitalization, just working with the data.

Stephane Morin: We have been working a lot with catalyst testing. Fifteen years ago it was typical to work with 2-3 reactors, and the high throughput labs came with 15-16 reactors in parallel. Some of the people at the time integrated this in a different way in the process and they were successful. Something similar will happen with digitalization. It is not going to work by putting a bit of digitalization here and a bit of it there. The key is to have the picture of how this will be integrated into the system so we are going to work completely different than today, a transformation.

Moderator: Let’s talk about the fear of the electric car, what can you say about the electric car, is it a real fear?

Tom Petti: It is a real fear, but for instance in the U.S., gasoline has been declining even though the driven miles went up. Combustion engine efficiency will continue to get better and it has to, it needs to be more competitive. Electric vehicles will eventually come and we need to continue to get more efficient, so gasoline is going to go down as a result of both. But the electric vehicle does not make sense in some parts of the world, if you look at emissions per km driven. When you need coal to generate this electricity, it is a loser. Politics is going to drive this more than science. It is going to come and the question is when, so we are going to be ready as an industry to help our customers to increase profitability in a phase change.

Alfredo Barbaro: I think in the short term it is not going to have a big impact if, as pointed out by Tom Petti, the energy source has to be coal or similar. In Europe it will have to be alternative sources, which may take time. I think, however, that the different lifestyles of people may have bigger impact. People living in cities, they do not have a car anymore, people tend not to use them in cities, and this might have a bigger impact than electric vehicles.

Pappu Sundaramoorthy: Our estimations indicate that from total energy produced by the Oil & Gas industry, more than one third is for cargo transportation like ships, another third is about heavy vehicles like trucks and less than one third is for small vehicles. The diesel car will have an impact on the gasoline demand, but the electric vehicle will be around 3% of the 30%, which is limited. The real impact will take time, at least two decades to have a significant impact.

Moderator: Tom, talking about regulations, how do you, as a global company, deal with the implications of regulations being different depending on the location, as there is no global standard?

Tom Petti: I think it’s a matter of applying technologies. If you look how regulations are shifting in general, taking gasoline sulphur as an example, it’s not consistent around the world. But there are different choices that customers can make to comply. It is affecting
hydroprocessing capacity and, also, we see impact on the FCC. Basically, we need to be aware of what is going on and make sure that our customers understand what is possible from the technology side.

Alan Gelder: I think it’s key for the regulators to understand what they are doing. If you want to decarbonize the transport fleet, it has to be just electric vehicles. If you look at the carbon cost of the electric vehicle it goes to $1000/ton. Regulators need to think a bit more holistically and not necessarily regulate an industry that innovates because it is actually much more successful.

Moderator: Where is the future? What needs to be done in the short term to be sure there is a long term in this industry?

Stephane Morin: To find the value everywhere through diversification, we are looking for aromatic specialties and other high value products.

Pappu Sundaramoorthy: Size and integration will be the key moving forward over the next years.

Alfredo Barbaro: Size and specialties, looking for something different, with the main challenges being regulations in Europe and other areas.

Tom Petti: Oil is going to be an important raw material and will be an important source of energy, we just need to navigate through this phase change, and all projects are focusing on that. There might be painful transitions but our goal is to help our customers to navigate successfully through this change.

Alan Gelder: Industry in Europe will need to track innovation. Doing nothing is not an option. Let’s try to maintain what we are good at, thinking about different solutions and outlooks, but there is going to need for investment in people and technology.

Coming Soon

Launch of a Redesigned e-Catalysts.com® Website

Soon, Grace’s FCC customers will be able to take advantage of an upgrade to the industry’s first and most successful Sample Analysis & Technical Service portal, e-Catalysts.com.

The freshly redesigned site will offer customers a mobile friendly, modern user experience with more intuitive navigation, a new data dashboard, and new communication tools on top of the existing services they have come to expect from e-Catalysts.com and Grace.

Visit e-Catalysts.com to log in or apply for membership and look for more information coming to your inbox soon.
LUKOIL Neftochim Burgas Refinery JSC (Neftochim) commissioned an H-Oil Vacuum Residue Ebullating Bed Hydrocracker in 2015 that led to a significant deterioration of the FCC unit VGO feedstock quality. Consequently, a significant drop of conversion was observed that negatively affected FCC unit profitability. Grace and Neftochim went through the challenge successfully by means of a strong collaboration that included state of the art catalyst technology implementation together with a variety of tailored services, resulting in a gain of +1.6 wt. % conversion and 0.86 wt. % gasoline in the new more challenging scenario. In this article Neftochim and Grace explain how a strong technology partnership can deliver value to customers far beyond than simply the supply of FCC products.
The H-Oil VGO Challenge

The Neftochim FCC unit typically processed desulphurised VGO as main feedstock contributor. The FCC unit objectives are typically:

- Maximize FCC unit conversion
- Maximize gasoline yields and gasoline octane
- Optimize C3= and C4 cut
- Increase FCC feed throughput

Feedstock properties are the most dominating factor determining FCC conversion levels and yields of high margin key products like naphtha, C3=, C4 cut or LCO. In 2015 Neftochim commissioned an H-Oil Vacuum Residue Ebullating Bed Hydrocracker and, since then, the Neftochim FCC unit is processing approximately 20-30% range of a blend of HVGO and LVGO from the H-Oil unit. As this VGO feedstock is already cracked, its nature is very aromatic and heavy – it can exhibit densities as high as 973 kg/m³. Its introduction into Neftochim’s FCC feedstock blend had a huge impact in feed crackability as shown in Table 1.

Given the expected negative impact of the processing of the H-Oil VGO with losses of conversion between 2-6 wt.% FF, the Neftochim refinery asked Grace to provide technology solutions to cope with this new very challenging scenario. To provide the highest increase in unit profitability to Neftochim, Grace proposed to engage both parties in a collaboration to find the optimum catalyst technology and services with a focus on the following value generators:

- Continuous state-of-the-art FCC catalyst and additives technologies implementation
- FCC unit operations optimization and debottlenecking
- FCC unit reliability monitoring and improvement

NADIUS™ 4G* Technology Platform – A Story of Value Creation

In the current challenging ever-changing refining market, it is vital to build strong long-term strategies to maintain the highest levels of competitiveness. Neftochim and Grace have been collaborating very closely in the last decade to achieve remarkable increases of FCC unit performance throughout the period. Indeed, as shown in Figure 1, continuous implementation of newly developed catalyst technologies delivered consistent unit conversion growths and additional value to FCC operations.

Grace has been continuously delivering value through different technologies since 2012. Due to the rare earth hyperinflation experienced in 2011, Grace introduced its rare earth free REsolution** technology to help Neftochim alleviate its operating costs with no debit in catalyst performance. Indeed, Grace’s proprietary Z-21 RE-free zeolite stabilization delivered 1 wt.%FF conversion increase versus the incumbent competitor catalyst at the time. Once this price inflation period ended, Grace introduced the NADIUS™ 4G Technology Platform with NADIUS™ 545 catalyst, which provided further benefits in unit conversion by additional 1 wt.%FF conversion.

Table 1: Impact of feedstock properties on commercial FCC unit conversion levels.
NADIUS™ 4G technology is the latest generation of Grace’s market-leading NADIUS™ catalyst family for hydrotreated and straight-run VGO feed applications. NADIUS™ 4G technology, which is branded as AURORA® in Australia, Canada, India, Mexico, and Singapore, incorporates new technologies that were developed during the extensive Grace R&D programme that was initiated as a result of the tight oil boom in North America and the new challenges faced by European refineries. This R&D programme resulted in advances to key catalytic functionalities; NADIUS™ 4G technology features the higher zeolitic activity with a tailored hydrogen transfer specific for this particular application (Figure 2).

The new catalyst technologies resulted in successive improvements in FCC unit operating profitability, as expected. Nevertheless, Neftochim challenged the status quo and trialed an alternative FCC catalyst supplier in 2015 together with the commissioning of the H-Oil unit. The resulting conversion levels were about 2 wt.%FF lower than the Base level of 2011. This massive drop of conversion was at the time partly attributed to the change in FCC feedstock quality due to its lower crackability.

Meanwhile, Neftochim encouraged Grace to find new technology solutions to maximize conversion in the new scenario. Grace conducted extensive research to develop the new NADIUS™ 865 ZP catalyst. Subsequent ACE™ pilot plant testing with representative feedstock for the new scenario (Table 2) against the base catalyst NADIUS™ 983 confirmed the superior performance according to Neftochim objectives as shown in Fig 3-5.

Following the promising performance benefits identified in the ACE™ pilot plant for NADIUS™ 865 ZP catalyst, Neftochim conducted a commercial FCC unit trial employing this technology. FCC unit results showed in Table 3 revealed that NADIUS™ 865 ZP catalyst provided superior performance achieving +1.6 wt.%FF conversion and 0.86 wt.%FF gasoline at 25 wt.% H-Oil VGO level versus base case.

Table 2: Feedstock properties for ACE™ catalyst selection.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, 15°C [g/cm³]</td>
<td>0.928</td>
</tr>
<tr>
<td>API Gravity</td>
<td>20.9</td>
</tr>
<tr>
<td>Refractive Index, 60°C</td>
<td>1.509</td>
</tr>
<tr>
<td>Sulfur [wt.%]</td>
<td>0.50</td>
</tr>
<tr>
<td>Conradson Carbon [wt.%]</td>
<td>0.15</td>
</tr>
<tr>
<td>UOPK Factor</td>
<td>11.69</td>
</tr>
</tbody>
</table>

Table 3: Conversion results for NEFTHOM® case versus NADIUS™ ZP catalyst.

<table>
<thead>
<tr>
<th>Conversion [wt.%ff]</th>
<th>NEFTHOM® Case</th>
<th>NADIUS™ ZP catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.5</td>
<td>Base</td>
</tr>
<tr>
<td>4</td>
<td>2.7</td>
<td>NADIUS™ ZP catalyst</td>
</tr>
<tr>
<td>5</td>
<td>2.9</td>
<td>NADIUS™ ZP catalyst</td>
</tr>
<tr>
<td>6</td>
<td>3.1</td>
<td>NADIUS™ ZP catalyst</td>
</tr>
<tr>
<td>7</td>
<td>3.3</td>
<td>NADIUS™ ZP catalyst</td>
</tr>
<tr>
<td>8</td>
<td>3.5</td>
<td>NADIUS™ ZP catalyst</td>
</tr>
</tbody>
</table>

Figure 1: Overview of FCC conversion through FCC catalyst technologies.

Figure 2: NADIUS™ 4G technology main performance functionalities.

Figure 3: NADIUS™ 865 ZP catalyst ACE™ pilot plant activity vs base.
ACE™ Ecat Testing Results Validates Improved Selectivity

A change of FCC catalyst represents a significant step for refiners. Grace provides a risk mitigation plan and performs a range of activities to support refineries, both before and during the catalyst change-out with the express purpose of minimizing those risks and ensuring a smooth and successful transition. A key part of this reinforced technical support is the close monitoring of the circulating inventory change out coupled with an ACE™ pilot plant Ecat performance evaluation using Ecat samples received on a weekly basis. It is generally accepted that most of the impact on yield shifts from a new catalyst can be observed when circulating inventory reaches ≥ 60% change out level of the new catalyst. As ACE™ pilot plant operating conditions and feedstock are constant, the ACE™ unit allows a selectivity assessment without the influence of ever-changing operating variables of the FCC commercial unit.

Results from ACE™ Ecat testing from Figures 6-7 revealed that NADIUS™ 865 ZP catalyst provided higher gasoline yields at constant conversion while preserving the LPG selectivity.

A common issue when searching for improved gasoline selectivity is the potential bottoms cracking selectivity debit when catalyst design does not have the optimum balance between required high intrinsic activity and balanced hydrogen transfer. Therefore, it is vital to check that no deterioration of bottoms upgrading performance at constant conversion is occurring. As shown in Figures 8-9, NADIUS™ 865 ZP catalyst maintains superior bottoms cracking selectivity at constant conversion, while Figure 10 shows an improved FCC bottoms destruction at constant gasoline production.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base</th>
<th>Case 1 – H-Oil VGO</th>
<th>Case 2 – NADIUS™ 865 ZP</th>
<th>Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrotreated VGO, wt.%</td>
<td>100</td>
<td>75</td>
<td>75</td>
<td>–</td>
</tr>
<tr>
<td>H-Oil VGO, wt.%</td>
<td>0</td>
<td>25</td>
<td>25</td>
<td>–</td>
</tr>
<tr>
<td>Conversion, wt.% FF</td>
<td>Base</td>
<td>-3.1</td>
<td>-1.5</td>
<td>+1.6</td>
</tr>
<tr>
<td>Gasoline yield, wt.% FF</td>
<td>Base</td>
<td>-1.8</td>
<td>-0.95</td>
<td>+0.9</td>
</tr>
</tbody>
</table>

Table 3: NADIUS™ 865 catalyst performance with 25% H-Oil VGO feedstock blend.
SUCCESS STORIES

Continued from Page 19

Figure 6: Ecat gasoline selectivity.

Figure 7: Ecat LPG selectivity at constant gasoline yield.

Figure 8: Ecat bottoms selectivity.

Figure 9: Ecat LCO selectivity.

Figure 10: Ecat bottoms yields vs gasoline production.
Delivering Value Through Partnership

Delivering maximum benefits and economic profit to customers requires a profound understanding of customer needs and value drivers. Establishment of a long-term partnership with the Neftochim refinery enabled Grace to identify the value opportunities for Neftochim operations and objectives, and to build a tailored Technical Services proposal fit to the customer’s needs. Some of the successful outcomes are listed below:

- **Improved Energy Efficiency:** Grace and Neftochim managed to increase profitability in excess of 1.3 M€/y using FCC Simulation Modeling to optimize unit steam injections into the unit.

- **Feedstock Optimization and Prediction:** Grace supports Neftochim using simulation and statistical models coupled with ACE™ pilot plant tests to monitor LPG make in the new propylene strategy as well as helping with estimates to the Neftochim refinery crude selection strategy.

- **Troubleshooting and Unit Inspection Services:** Grace provided support to identify the root cause of a particle loss episode and its solution (Picture 1). Grace also provided Neftochim with a complete FCC unit inspection service with a technical report during TAR (Picture 2).

By means of the latest NADIUS™ 865 ZP technology, Neftochim was able to significantly increase FCC unit conversion and gasoline yield by 1.6 wt.%FF and 0.9 wt.%FF, respectively, after introducing the heavy, poorly crackable H-Oil VGO into the feedstock blend. Although being challenged with a competitive technology trial, NADIUS™ 4G Platform demonstrated again its superior performance for VGO maximum conversion applications. Additionally, a dedicated technical support team delivered a list of opportunities for value creation including unit operations and feedstock optimization, FCC simulation models, TAR inspection or specific logistic services that helped Neftochim to extract further profitability from their FCC unit.

To stay competitive in the current increasingly challenging refining market, it is vital to both utilize highest performance catalyst and additives in the market as well as continuously identify value opportunities from the FCC operations. LUKOIL Neftochim Burgas JSC refinery and Grace demonstrated that, through a strong, long-term partnership far beyond the mere supply of FCC products, it is possible to create an environment of collaboration to maximize profits in the FCC unit.

Q&A from the 2018 AFPM Operations and Process Technology Summit

The following questions and answers are based upon a Q&A panel session that took place at the American Fuel & Petrochemical Manufacturers (AFPM) Operations and Process Technology Summit in October 2018. The answers appearing here may vary from the event transcript in order to provide context and/or clarity.

Ann Benoit
Senior Principal FCC Technologist
W. R. Grace & Co.

Steven Gremillion
Technical Sales Manager, FCC Technical Sales
W. R. Grace & Co.

Ken Bryden
Manager, Catalyst Evaluations Research and Services
W. R. Grace & Co.

Bob Riley
Marketing Manager, Americas
W. R. Grace & Co.

Michael Federspiel
Senior Director, Global Customer Technology, FCC Technical Sales
W. R. Grace & Co.
Are there any operational parameters that can be manipulated to improve the operation of the slurry circuit and minimize fouling? Can you outline the slurry exchanger circuit recommended design practices to minimize fouling, plugging and erosion?

Answer from Michael Federspiel:

Slurry exchanger fouling comes in several forms, which can be broken down into either organic or inorganic fouling. Inorganic fouling can be caused by corrosion products, precipitated metals, or catalyst particulates in the slurry circuit. Organic fouling, which is more common, can be caused by coke deposits or asphaltenes that have precipitated from the slurry.

Understanding and addressing the root causes of the different types of fouling can help minimize their impact on FCC operations. Using the correct metallurgy in the main fractionator and slurry circuit will significantly reduce corrosion. By closely monitoring antimony injection, a refiner can reduce the risk of antimony accumulation in the main fractionator.

By maintaining cyclone physical integrity and operating at proper cyclone inlet velocities, a refiner can reduce the contribution of catalyst particles to slurry fouling. It is also worthwhile to pay attention to catalyst and additive attrition index and particle size distribution as these can both impact losses to the main fractionator.

Time, temperature, and composition of the slurry all contribute to coke formation and steps can be taken with each of these parameters to help minimize slurry fouling. Ensuring close proximity of slurry exchangers and avoiding unnecessarily long slurry piping runs can reduce the amount of time slurry spends at elevated temperature. The temperature in the slurry circuit can be reduced using slurry quench. It is recommended to calculate and monitor the bubble point temperature of the slurry while using slurry quench as an indication of the slurry composition. Ensuring good distribution of the slurry circuit return to the main fractionator, and maintaining a slurry pumparound rate such that the wash trays are always sufficiently wetted will also reduce the chances of coke formation. Finally, undercutting LCO into the slurry product will both reduce the temperature and lead to a directionally lighter slurry composition.

Asphaltene precipitation can occur when the asphaltene concentration increases (which can be due to feed type) or if the solubility of those asphaltenes is reduced. Asphaltenes are more soluble in highly aromatic environments, while the presence of more saturated compounds reduces this solubility and leads to fouling. Loss of conversion due to lower catalyst activity or reactor severity can lead to more saturated compounds in the slurry, so addressing loss of conversion is a solid strategy for reducing slurry fouling.

Grace published a thorough paper titled “Understanding and Minimizing FCC Slurry Exchanger Fouling” in Catalagram Number 101, Spring 2007. In it, the causes of the above types of fouling are discussed in more detail, along with mitigation strategies and design considerations. It can be found on grace.com/catalysts-and-fuels/en-us/catalagram.

Reference

What is the range of activity for FCC catalysts in the FCCUs? When is catalyst activity considered too low? When do you decide to reformulate versus changes in operating conditions in order to increase unit conversion?

Answer from Bob Riley and Michael Federspiel:

FCC catalyst activity is conventionally defined as 100 – (LCO, wt.% + Bottoms, wt.%), and is most often measured in microscale laboratory units. “Activity” refers to the propensity for the catalyst to upgrade heavier products into higher value, higher volume products. The absolute numbers measured will depend on several factors, including the specific testing unit and conditions, the choice of feedstock, and the quality of the catalyst being tested. There is no standard range or universally accepted testing equipment for FCC catalyst activity (although MAT and ACE™ pilot plant are popular designs), and each testing lab measures catalyst activity on a different scale, because of the reasons cited above.

In Grace’s database, since 2014, the range of microactivity measured on individual samples has been between 48 and 85, with the overall average of 71.7 (Figure 1). This includes over 62,000 individual measurements, and the shape of the distribution is skewed right of normal because conversion reactions in the FCC are empirically approximated by 2nd order kinetics. To correct for this, one can look at Kinetic Conversion (defined as Conversion / 100-Conversion); these data are

Continued on Page 24
Continued from Page 23

centered on a Kinetic Conversion of 2.6 over the same period, and much more closely resembles a normal distribution (Figure 2). It is important to note that the 48 to 85 Ecat activity range represents individual sample activity results; industry average Ecat activity typically ranges from low 80s to low to mid 60s.

Catalyst activity requirements are a function of the objectives and constraints of any given FCC, which means that each unit likely requires a unique catalyst activity (or range of activity) to meet its goals. Catalyst activity is a function of the fresh catalyst composition, the catalyst addition/replacement rate, in-unit conditions (temperatures, residence times, and potential for thermal or hydrothermal deactivation), and the metals level and type on the FCC equilibrium catalyst.

Optimizing catalyst activity requires an intimate understanding of objectives and constraints; it is highly desirable to define the quantitative difference between today’s performance and the desired unit performance as opposed to the qualitative direction of desired shifts from current operation.

Symptoms of low catalyst activity can include low conversion, low regenerator temperatures, high cat to oils, and erratic regenerated slide valve delta P. These symptoms often represent the constraints present in low activity FCC operations. Feedstock, upstream units, and refinery flexibility will often dictate the operating window necessary for FCC catalyst activity.

In a typical VGO or resid operation, low catalyst activity leads to low regenerator temperatures and higher cat to oil ratio, often up to the limit of control as established by the stability of the slide valve differential pressure. In this scenario, the lower limit of catalyst activity is often set by circulation limits as manifested by low slide valve delta P. Higher cat to oil ratio is generally desirable for units pursuing maximum conversion. However, in some instances the higher cat to oil may not compensate for the lower catalytic activity which could result in lower conversion. Catalyst additions, reactor temperature, and even feed temperature can all be used as control handles to maintain an adequate differential pressure or a sufficient level of conversion.

In contrast, a highly hydrotreated feed operation is likely to see low catalyst activity manifest as low regen dense bed temperatures, often near the point where combustion is not adequate to fully regenerate the catalyst. The lower activity limits in these operations are typically much higher than those in VGO service, and in this scenario, catalyst additions or catalyst reformulation are

Figure 1: Equilibrium catalyst activity as measured in Grace’s Ecat program since 2014.

Figure 2: Kinetic (2nd order) conversion as measured in Grace’s Ecat program since 2014.
typically the best handles for managing regenerator temperature. Other methods, including torch oil injection, slurry recycle, fired air heater use, or even reduction in stripping steam, often cost more in lost products or in catalyst deactivation than they gain in unit operating stability. Routine use of these “other methods” for heat balance control should be viewed as an indicator of catalyst activity being too low.

Regarding reformulation versus changes in operating conditions, catalyst reformulations are recommended to manage sustained changes in refinery operating requirements. Whether for increasing conversion, or managing virtually any new requirement on the FCC, the timing is a critical factor in the decision between the use of catalyst versus the use of operating conditions. Examples of sustained changes that could merit a catalyst change include adjacent units nearing end of run conditions, sustained use of new feedstock, degradation of the mechanical condition of the FCC equipment, or market trends which require long term production of a modified yield slate. Because of the timing required to properly design, deploy, and turn over new FCC catalyst formulations, the main drivers for reformulation should be matched to the time scale of the unit’s ability to realize the benefits. For shorter term needs, it is often more desirable to consider changing operating conditions, or using FCC additives to modify yield selectivities or manage short term refinery requirements. Operating conditions which can increase conversion include increased reactor temperature, reduced feed temperature, increased catalyst additions, reduced carbon on catalyst (partial burn units), and removal of low conversion feed components (slurry recycle, other low hydrogen content feeds, etc.).

As the demand for higher octane gasoline components increases and lobbying for a 95 RON gasoline standard continues, how are you adjusting your operations to meet the market demand? What FCC specific changes do you make to produce higher octane gasoline components?

Answer from Ken Bryden and Bob Riley:

Octane is a relative measure of the knocking characteristics of a fuel in an internal combustion engine. Knocking is caused by auto-ignition of fuel ahead of the flame front. Different hydrocarbon molecules have different resistance to auto-ignition, related to their role in hydrogen peroxide formation under combustion conditions\(^1\). Hence, gasoline octane is governed by the types and relative concentrations of the individual hydrocarbon molecules that comprise the fuel. Figure 1 presents octane trends by hydrocarbon type and carbon number based on data from API Research Project 45\(^2\). As seen in the graphs, lighter molecules have higher octane. RON and MON values trend by hydrocarbon type as follows:

Aromatics ~ Olefins > Naphthenes > Iso-Paraffins > Paraffins.

Figure 1: Octane Trends by Hydrocarbon Type
Continued from Page 25

Also, for olefins and iso-paraffins, octane increases as the degree of branching increases. To increase gasoline octane, the composition of the molecular types in the stream must be changed. Changes that can be made specific to the FCC to produce higher refinery gasoline octane fall into two main categories: (A) changes inside the FCC unit that change the composition of the FCC gasoline, and (B) adjustments to FCC operation that improve overall refinery gasoline pool octane.

(A) Changes Inside the FCC Unit

Gasoline Cutpoints

Changing the distillation range of the gasoline from the FCC can influence octane. Butane is part of the light end of the gasoline and possesses a high octave number. Increasing amounts of butane will increase RON. However, this must be balanced against vapor pressure considerations. For the heavy end, the effect of increasing gasoline endpoint on octane can vary. For aromatic gasolines, increasing end point will generally increase octave as higher boiling point aromatic molecules are included in the gasoline. For other gasolines, the effect of endpoint on octave will vary with the feedstock to the unit, the conversion level and the catalyst. Detailed hydrocarbon analysis of FCC gasoline via gas chromatography and application of gasoline octave prediction models can be used to simulate how octave will change with gasoline endpoint.

Feedstock

The feedstock to the FCC will have a major effect on octane. Feedstock paraffins generally crack to form low octave gasoline range paraffins. Feed naphthenes crack to form high octave gasoline range aromatics and olefins. Aromatics with side chains present in the feed generally crack to form high octave gasoline range aromatics. As the feed becomes less paraffinic, octane increases. As a rule of thumb, a 0.2 number decrease in the UOP K factor of the feed will result in a 1 number increase in RON. Similarly, a 0.1 number increase in the ratio of naphthenic to paraffinic carbons (Cn/Cp) in the feed will generally result in a 1 number RON increase.

Operating Variables

Increasing riser outlet temperature will increase RON by increasing the amount of olefins in the gasoline. As a rule of thumb, at a base RON of 90, an 18°F increase in riser temperature will result in a 1 number increase in RON. The octane gains with increasing riser outlet temperature will diminish as reactor temperature is increased. More precise values can be determined by cat cracker operators through observations made on their own units.

Increasing conversion will increase octane. As conversion increases, cracked products increase, which means that the amount of olefins and aromatics in the gasoline increases. As a rule of thumb, a 10 LV% increase in conversion will result in a 1 number increase in RON at constant riser outlet temperature.

Decreasing hydrocarbon partial pressure will increase FCC gasoline octane. Gasoline olefin content increases when the rate of bi-molecular hydrogen transfer reactions drops – which happens as hydrocarbon partial pressure drops.

Catalyst and Additives

The molecular composition of FCC gasoline is governed by the relative rates of cracking and hydrogen transfer reactions. Lowering zeolite unit cell size will lower hydrogen transfer and increase gasoline range olefins and thus increase octane. Increasing matrix content of the catalyst will help to crack side chains off of aromatic cores and increase octane by increasing gasoline range aromatics. Dual-zeolite catalysts that incorporate both faujasite and pentasil type zeolites will lead to increased rates of isomerization and result in higher octane from the greater amount of branched hydrocarbons.

ZSM-5 based additives and butylene selective additives can also be used to increase octane. These additives can increase isomerization reactions. Also, by cracking some gasoline range olefins to LPG olefins, they concentrate aromatics in the FCC gasoline, resulting in increased octane.

(B) FCC Adjustments to Improve Overall Refinery Gasoline Pool Octane

Increasing Alkylate Production

With a typical RON of 95+, alkylate is one of the highest octave blend streams in the gasoline blending pool. For refineries with alkylation capacity, FCC adjustments that increase the amount of LPG olefins used as alkylation feedstock will increase alkylation production and refinery gasoline pool octane. LPG olefins from the FCC can be increased by adjustments to reactor conditions, base catalyst, and use of ZSM-5 based additives. For units desiring a higher ratio of butylene to propylene in their LPG, butylene selective additives can be used instead of conventional ZSM-5 type additives. Variables that affect LPG olefin production in the FCC have been covered in detail in previous AFPM Q&A sessions.

Reducing FCC Gasoline Hydrotreating Severity

Refiners report losses between 1 and 5 numbers of octane when FCC gasoline is hydrotreated to remove sulfur. Hydrotreater severity can be lowered when the FCC gasoline contains less sulfur. Lower FCC gasoline sulfur can be achieved through use of gasoline sulfur reducing catalysts and additives that convert gasoline range sulfur to hydrogen sulfide. A detailed discussion of preserving octave with gasoline desulfurization technology can be found in Reference 10.
In summary, there are many ways FCC operations can be adjusted to increase octane. Inside the FCC unit, octane can be increased through feedstock selection, choice of operating conditions, tuning of base catalyst properties, and use of specialty additives. Outside of the FCC, the amount of alkylation feed derived from the FCCU can be increased through careful FCC catalyst and additive selection, and octane loss during FCC gasoline hydrotreating can be reduced by lowering FCC gasoline sulfur through use of gasoline sulfur reducing catalysts and additives.

As always in FCC, changes to influence one variable (octane), will result in changes to other FCC unit yield objectives. Refiners should work closely with their catalyst supplier to understand the options available to increase octane and how to balance these with other yield objectives. Grace has a wide portfolio of catalyst and additive solutions and would be happy to engage with refiners to discuss options to increase gasoline octane.

References

**Question:** Butylene demand and prices in relation to other refined products reached a record level in 2017. What caused it and what can we do in the FCC to produce more butylenes?

**Answer from Ann Benoit and Ken Bryden:**

Increase in butylene price is most likely attributed to keeping the refinery alkylation unit full to produce high octane low sulfur gasoline blendstock to help in the era of tight oil processing and TIER 3 regulations. The lower fraction of 650°F+ material in tight oils compared to many other crudes tends to result in less FCC feedstock production from the crude distillation unit. The paraffinic nature of many tight oils results in lower FCC gasoline octane. Reduced FCC feed rate can cause alkylation units to run at lower rates while the lower FCC octane reduces overall octane in the refinery. It has become more important for refiners to keep the alkylation unit full so that it can produce a high octane, lower sulfur blend component to help meet octane and TIER 3 requirements. Since C4 olefins are the preferred feedstock for alkylation units, refiners are looking at ways to produce more from the FCC. The answer will first address the formation mechanism of C4 olefins and then discuss how to increase the C4 olefin production by the FCCU. Feedstock, operating conditions, catalyst effects and the role they play in C4 olefin production will be discussed afterwards.

To maximize C4 olefins in the FCCU, one first needs to understand the mechanism of their formation. Figure 1 summarizes the fundamentals of butylene selectivity and maximization. The cracking pathways involved can be thought of as four stages. In Figure 1, the desired pathway for maximizing butylene is depicted with green arrows and the undesired pathways with red arrows. The first stage is cracking of the feed to naphtha range olefins. These cracking reactions can occur on zeolite or on matrix surfaces. In the second stage, these naphtha range olefins can further react to form naphtha range paraffins by hydrogen transfer (an undesired pathway), or crack to form C3 and C4 olefins. The rate of cracking of gasoline range olefins to C3 and C4 olefins is faster and more selective on ZSM-5 zeolite than Y-zeolite. The C3 and C4 olefins that are produced in stage 3 can further form propane, iso-butane and butane (via H-transfer reactions), which are undesired when maximizing butylene. These H-transfer reactions occur much faster on zeolite than on matrix. Based on this fundamental reaction scheme, butylene can be maximized by decreasing the hydrogen transfer activity and by minimizing the cracking of naphtha olefins to propylene.

**Feedstock Effects**

Even though feedstock is typically not a controlled variable for refinery process engineers, it does impact butylene production and thus warrants a brief discussion. The chemical nature of the starting feedstock will affect its reaction products. As a feed becomes more aromatic, the olefinicity of the LPG stream will drop. As a feedstock becomes more

Continued on Page 28
naphthenic, LPG olefin production drops. This is because naphthenes are good hydrogen donors and react with gasoline range olefins to form aromatics and gasoline range paraffins. Since gasoline range olefins are the precursors to LPG olefins, this depletes the pool of available precursor molecules required to form LPG olefins and reduces LPG olefinicity.

Operating Condition Effects

Typically, total C4 production depends on conversion, regardless of whether the conversion is achieved by reactor temperature or catalyst to oil ratio. Figure 2 shows data from a Grace DCR™ pilot plant study that demonstrates the relationship between total C4s and conversion. As conversion increases the total C4s will increase which, in turn, can increase butylene yield. One thing to note is that the ratio of isobutane to butylene is strongly influenced by reactor temperature. Since hydrogen transfer has higher activation energy than cracking, the rate of cracking increases faster with temperature than the rate of hydrogen transfer. Thus, as reactor temperature increases, the ratio of iC4/C4 decreases.

Catalyst Effects

The base catalyst can be reformulated to increase butylene by reducing the rate of hydrogen transfer. Reducing hydrogen transfer can be done by lowering the rare-earth on zeolite or by adjusting the zeolite/matrix ratio. Lowering the zeolite/matrix ratio of the base catalyst will increase the gasoline range olefins and thus the amount of butylene produced from these precursors. This is a consequence of the lower intrinsic hydrogen transfer activity on matrix surfaces relative to that on zeolite surfaces.

ZSM-5 based additives also increase butylene production. ZSM-5 cracks the C6+ gasoline range olefins to propylene and butylene. Figure 3 shows the effect of ZSM-5 on the olefins distribution. Adding ZSM-5 additive will consume gasoline range olefins and produce both propylene and butylene. The increased propylene yield with ZSM-5 additives is not always desirable. There are specific catalysts and additives that are tailored to increase butylene yield in the FCC. Grace’s butylene selective catalyst (ACHIEVE® 400 catalyst) is formulated with dual zeolites with tailored acidity to deliver an optimum level of butylene to keep the alkylation unit full and maintain refinery pool octane. With traditional ZSM-5 technology, cracking of gasoline olefins extends beyond C7s and into C6s and thus generates a disproportionate amount of propylene relative to butylene (Figure 4). The dual-zeolite technology works synergistically with a high diffusivity matrix to selectively enhance olefinicity, preferentially cracking C7 and above gasoline olefins into butylene.

Continued from Page 27

![Diagram showing stages of cracking and hydrogen transfer](image)

**Figure 1: Octane Trends by Hydrocarbon Type**

![Graph showing relationship between conversion and total C4s](image)

**Figure 2: Relationship between conversion and total C4s.**
The result is a higher ratio of C4 to C3 olefin yield than traditional light olefin additives. Figure 5 illustrates the butylene selectivity improvement of this catalyst compared to a system using conventional ZSM-5 based additive. In addition to increasing butylene selectivity, the catalyst also increases octane of FCC naphtha.

Similarly, there are butylene selective FCC additives that allow refiners to achieve a higher butylene to propylene ratio than that obtained with traditional light olefin additives. This allows refiners to increase their butylene yields from the FCC without committing to a full-fledged FCC catalyst reformulation. Figure 6 shows the results from an ACE™ evaluation comparing Grace’s butylene selective GBA™ additive to conventional light olefin additives. Results show at increasing additive use both types of additives increase total LPG olefins. However, GBA™ additives achieve both a higher butylene-to-propylene ratio and a higher boost to FCC gasoline RON compared to the traditional ZSM5 additive. The increased octane is driven by improved isomerization activity.

In summary, increasing butylene can be achieved by changing feedstock, operating conditions, catalyst reformulation, or additive use. Proper choice of catalysts and additives based on operating objectives and unit constraints is critical in maximizing butylene selectivity. Grace’s technical service team has the experience and resources to help refiners evaluate feed, operating condition and catalyst shifts to maximize butylene selectivity.

Figure 3: Effect of ZSM-5 additive on olefins distribution (from Reference 4).

Figure 4: Selectivity from cracking gasoline range olefins over ZSM-5 additive and ACHIEVE® 400 catalyst.

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

Continued on Page 30
Continued from Page 29

Figure 6: ACE™ evaluation of Grace’s GBA™ additive versus conventional light olefin additives.

References:


How are you optimizing the use of Wet Gas Scrubbers caustic use and SOx additives?

Answer from Steve Gremillion:

SOx emission control continues to be an important topic for many refiners, particularly in regions and countries where more stringent environmental emission targets will come into effect. Two of the most common approaches utilized by refiners for complying with SOx emission targets are the use of wet gas scrubbers (WGS) and the application of FCC SOx reduction additives. While WGS’s are typically very effective for SOx control, they can result in high OPEX costs, particularly those associated with caustic soda price. A recent analysis of the US market shows that more than 50% of refiners operating WGS’s are also using SOx reduction additives to optimize WGS caustic usage.

Over the past two years, global caustic pricing has increased considerably. Figure 1 highlights caustic pricing in various regions of the US and EMEA. While the pricing varies by region, a consistent increase in caustic price has been observed over the last two years in all regions. This increase in caustic pricing has a significant impact on OPEX costs for refineries operating a WGS and provides economic incentive for the optimization of WGS caustic usage via the application of SOx reduction additives.

Figure 1: Caustic Soda Market Pricing
Because SOx reduction additives are a well-established method of reducing FCC SOx emissions, it is possible to make an accurate estimation of the potential cost savings associated with using an optimum combination of WGS caustic and SOx reduction additive to meet SOx emission limits.

Key factors affecting the available cost savings are the uncontrolled SOx emissions (i.e. the SOx level that would be obtained without the use of any SOx reduction technology), targeted SOx emission level, caustic soda pricing, SOx reduction additive performance, and SOx additive price.

Figure 2 shows an example of the daily OPEX cost of using SOx reduction additive compared to WGS caustic to control SOx emissions.

SOx reduction additive performance is typically represented by the PUF (lbs SOx removed/ lbs of additive). Observed PUF is unit specific and varies significantly across industry due to differences in regenerator operating conditions and regeneration kinetics, target SOx removal percentage, and specific additive type.

It is also important to note that PUF decreases as the percentage of SOx reduction increases. Due to this fact, there is a breakeven point where the additive cost and the caustic cost have the same OPEX. This is shown in Figure 2 when the additive cost (green line) and the caustic cost (blue line) intersect. Using additive to obtain a level of SOx reduction anywhere to the left of the breakeven point will reduce operating cost. Maximum OPEX reduction is achieved when using SOx reduction additive at the point where the distance between the two lines is greatest and then using WGS caustic to obtain additional SOx reduction beyond that point.

Based on these factors, it is very important for the refinery to work closely with their additive supplier to develop an accurate economic evaluation to understand where this breakeven point is for their specific operation and determine the optimum combination of caustic use in the WGS and SOx reduction additives for meeting SOx emission targets.

**Contributors Biographies**

**Ann Benoit, Senior Principal FCC Technologist, W. R. Grace & Co.**

Ann Benoit is the Senior Principal FCC Technologist in the Global Customer Technology team. She holds a B.S. degree in Chemical Engineering from Tennessee Technological University. Ann joined Grace in 2008 as technical sales representative supporting customers in the U.S. Gulf Coast and Rocky Mountain regions. In addition, she held the position of Technical Sales Leader supporting technical service activities for North America and Latin America. Prior to joining Grace, she worked at CITGO’s 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 over 15 years of refinery and catalyst experience.

**Ken Bryden, Manager, Catalyst Evaluations Research and Services, W. R. Grace & Co.**

Ken 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 11 peer-reviewed journal articles and numerous trade press publications.

**Michael Federspiel, Senior Director, Global Customer Technology, FCC Technical Sales, W. R. Grace & Co.**

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 in the Gulf Coast. Currently, Michael leads Grace’s Global Customer Technology team, a group of specialists dedicated to improving our customer’s profitability through superior technical services. 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.

Figure 2: OPEX Comparison Example
**Continued from Page 31**

**Steven Gremillion, Technical Sales Manager, FCC Technical Sales, W. R. Grace & Co.**

Steven joined Grace in 2012 as a Technical Service Manager supporting customers in the U.S. Gulf Coast region. Prior to joining Grace, Steven worked as an FCC engineer at CITGO Petroleum and then as a process design engineer for a private engineering consulting firm. Steven brings a wide range of experience to the Technical Sales Team from process simulation and design to FCC optimization and troubleshooting. He holds a Bachelor of Science in Chemical Engineering from McNeese State University and is a professional engineer in the state of Louisiana.

**Bob Riley, Marketing Manager, Americas, W. R. Grace & Co.**

Bob joined Grace in 1998 as a Technical Service Representative, FCC Additives, and over the last twenty years, has held a wide variety of positions in FCC technical service, FCC Marketing, Process Quality & Assurance, FCC Sales, and Global Commercial/Business Development for Renewable Fuels and Chemicals. Currently, Bob holds the position of Marketing Manager for the Americas for Grace’s FCC business, where he follows key market trends and areas where Grace can add value to FCC customers. Bob holds a Bachelor of Science in Chemical Engineering from the Johns Hopkins University, and a Master of Business Administration from the University of Illinois at Urbana-Champaign. Bob is also a certified Six Sigma Black Belt, and serves on the Steering Committee for the AFPM OPT Summit. 🌐
Navigating a New Course Under IMO Rules

Don’t let IMO’s 2020 lower global sulfur regulations capsize your FCC bottoms strategy. Grace leads the catalysts industry in helping steer potential problems to profitable solutions. Let us show you how to turn the challenges of blending FCC bottoms into an opportunity to create more valuable FCC LCO.

Grace has partnered with hundreds of refineries to provide comprehensive catalyst solutions and we’re leading the way into 2020 with current and new technologies designed to provide advantaged bottoms cracking and increased FCC fuels and petrochemical production.

Ask Us How We Do It