Superior coke selectivity and bottoms cracking from a novel single particle

Thanks to our world-class R&D, manufacturing, and processing advances, we created an advanced matrix binding system with more effective matrix surface area in a catalyst designed to withstand high vanadium levels without sacrificing the impressive coke selectivity, attrition resistance, and particle size distribution Grace has already excelled in with traditional catalysts.

Pushing operating constraints to new limits

Take full advantage of opportunity crudes. Process heavier feedstocks containing higher contaminant metals. Increase volume gain, reduce costs, and produce more valuable products with FUSION™ catalysts.

Commercially proven!
Read more about FUSION™ at grace.com/value
An Evolving Industry Demands Innovations

Nathan Ergonul
Vice President, Marketing, FCC
W. R. Grace & Co.

Eboni Adams
Director, Marketing
Advanced Refining Technologies (ART)

At W. R. Grace & Co., we continue to focus on, and remain committed to, serving the refining industry with our broad FCC and hydroprocessing catalyst portfolios. Recent announcements we made about our acquisition of Rive Technology, Inc. and our joint development agreement with TechnipFMC are just a few examples of how we plan to meet the challenges and opportunities our industry faces while continuing to generate value for our customers. See page 17 for more about RIVE® catalysts powered by Molecular Highway® zeolite technology that introduces ordered mesoporosity into zeolite crystals.

One of the biggest changes ahead will be the adoption of global marine fuel regulations requiring lower sulfur fuels. As the new regulations are implemented, we will continue to monitor market dynamics and impacts. Grace and Advanced Refining Technologies (ART) believe IMO 2020 can be an opportunity for refiners to improve profitability. As customers’ objectives evolve, we continue to collaborate with them to provide catalyst solutions and offer our technical expertise to boost value for our customers and meet evolving market needs.

ART is at the forefront of innovation of hydroprocessing catalyst solutions for upgrading, maximizing diesel yield, and managing contaminants, such as sulfur. Read more about ART’s ebulliating bed technology and its implications for IMO 2020 on page 25.

While desulfurization via hydrocracking and hydrotreating are major components of many refiners’ strategies, a key unresolved problem for many refiners remains the FCC bottoms disposition. That’s where Grace’s FCC technology comes in to help refiners maximize profits while complying with IMO 2020 rules. Read about Grace’s MIDAS® catalyst family, a proven technology which has driven bottoms upgrading to LCO at many FCCs, on page 34.

In this issue, we highlight successful innovations in ISODEWAXING® catalyst. See page 38 to read about our achievements in IDW® technology. In addition to investments in technology and innovation, ART has made significant investments in a new hydroprocessing catalyst plant located in Lake Charles, LA, USA. This new, world-class plant will improve our supply network in an evolving market. Watch for our grand opening announcement soon.

Also, you can read about one of our newest FCC catalyst technologies, FUSION™, on page 12. This advanced matrix binding system is designed to withstand high vanadium levels without sacrificing coke selectivity, attrition resistance, and particle size distribution.

Catalagram is designed to keep you informed about what we’re doing to help refiners extract more value from our latest innovations. We’re working very closely with our customers to tailor catalyst solutions to meet their evolving needs. We hope you will find this issue to be enlightening and thought-provoking. We welcome your comments and suggestions on what you would like to see and read in our future issues.

New Executive Co-Editors Named

W. R. Grace & Co. and ART Hydroprocessing are pleased to announce the appointment of two new executive editors for Catalagram. Nathan Ergonul and Eboni Adams will share executive editing responsibilities for Catalagram, representing the interests of their respective business segments.

We would like to thank Catalagram’s previous executive editor, Scott Purnell, who held the title of Vice President, Marketing, FCC until late 2018, when he took on the leadership of Grace’s R&D team and was succeeded by Nathan Ergonul.

Nathan has more than 16 years of experience in the oil and gas industry. He started his career at TOTAL before becoming the General Sales Manager, Middle East and Africa, for Grace and ART. Nathan holds a B.S. in Chemical Engineering from the UK’s Aston University and an MBA from Hult International Business School. He is a Chartered Chemical Engineer and a member of the Institution of Chemical Engineers, UK.

Eboni began her professional career as a Project Engineer at Amoco Chemical Company (now BP) followed by her 22 years of service at Grace and ART, where she has held various roles including Process Engineer, Operations Technical Supervisor, Customer Service Supervisor, Sales Operations Manager, and Transactional Lean Six Sigma Black Belt. She holds a B.S. in Chemical Engineering from University of Illinois at Chicago and an MBA in Marketing from Georgia State University in Atlanta.
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 catalysts systems deliver significant value in today’s challenging refining environment.

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IN THE NEWS

Keeping you up-to-date on Grace FCC and ART Hydroprocessing activities
Grace Sponsors Awards for Advancements in Catalysis

Dr. Javier Perez-Ramirez (center) is presented with the Paul H. Emmett Award in Fundamental Catalysis by Jingguang Chen (left) and Rob Harding (right).

The North American Catalysis Society’s (NACS) biennial meeting in Denver drew over 1,800 leaders in the catalyst industry from 39 countries, including 11 from Grace’s Refining Technologies, Materials Technologies, and Specialty Catalysts businesses.

Rob Harding, Senior Technology Advisor, presented the Paul H. Emmett Award in Fundamental Catalysis to Dr. Javier Perez-Ramirez of ETH Zurich for his innovative catalytic processes that address energy, resource, and environmental challenges.

Sudhakar Jale, Marketing Director, Chemical Catalysts, presented the F.G. Ciapetta Lectureship in Catalysis to Teh Ho of ExxonMobil (retired) for his catalytic process that removes sulfur and nitrogen from hydrocarbons for the manufacturing of clean fuels and petrochemicals.

The Emmett Award is named for Paul H. Emmett, a former Grace Professor of Chemistry at Johns Hopkins University who was also a Grace Advisory Board Member. He is best known for his contributions to the Brunauer-Emmett-Teller (BET) technique for the measurement of surface area. The Ciapetta Lectureship is named after Frank Ciapetta, a former VP, R&D at Grace, for his contributions to catalyst science.

Grace Acquires Rive Technology, Inc.

In June, Grace acquired the business and assets of Rive Technology, Inc., including its Molecular Highway® zeolite technology. As part of the transaction, certain research and development, technical services, and commercial employees will join Grace.

“Over the past decade, we have seen terrific progress and benefits for our customers by incorporating Rive zeolite technology in certain FCC catalyst applications,” said Tom Petti, Grace’s President, Refining Technologies. “As demand for petrochemicals grows, the addition of Rive’s patented technology allows us to offer our customers greater flexibility in converting crude oil to petrochemical feedstocks. That delivers real value to our global refinery customers.” Rive’s technology has broad applicability on different types of zeolites that will allow Grace to continue Rive’s development activities in applications for a wide range of chemical catalysts and processes.

Rive Technology, Inc. was founded in 2006 to commercialize Molecular Highway® zeolite technology for catalytic processes, such as those used in fluid catalytic cracking (FCC) units in oil refineries. Invented at MIT by Dr. Javier Garcia-Martinez, Rive’s technology improves traditional zeolite catalysts through the introduction of novel channels of medium pore size (“molecular highways”), which enhance the diffusivity of these materials leading to higher value product yields, improved process efficiency, and increased refinery profitability.

In 2010, Rive and Grace entered a joint development and commercialization program to combine Rive’s innovative technology with Grace’s market-leading capabilities in FCC catalyst formulation and manufacturing. Grace is currently marketing and selling breakthrough RIVE® FCC catalysts to many of the world’s leading refiners.
ART Launches Hydrocracking Specialist Development Program

ART has successfully launched the first session of an ambitious program to develop Saudi Arabian process engineers into hydrocracking specialists over a period of only 18 months. This exclusive program allows candidates nominated by Saudi Aramco, the official Saudi Arabian national oil company, to work with ART’s technical experts to enhance the nominees’ knowledge of hydrocracking in multiple sessions.

Saudi Aramco’s P&CSD hosted the first session covering the fundamentals of hydrocracking from April 28 to May 1 at the company’s Al Midra Tower in Dahran. It included participants from seven Saudi refineries who approached the program in a highly collaborative way, which allowed for increased knowledge sharing for the benefit of all involved. Participants learned the colorful history of hydrocracking, beginning with the technology’s invention by Chevron, as well as the process layout of each unique Saudi hydrocracker.

Four additional sessions are planned. The next session will cover unit monitoring and is tentatively scheduled for mid-July in The Hague, Netherlands.

The program aims to create a reliable network of specialized professionals in the region who are familiar with ART’s hydproprocessing technology.

ART Teams with Recycling Companies to Reclaim Metals from Spent Catalysts

Recently, ART announced two agreements to reclaim metals from spent catalysts as part of a targeted strategy to foster the sustainable reuse of metals while providing benefits to customers.

ART has teamed with GS EcoMetal Co. Ltd (GSEM) in a multi-year agreement to recover metals from spent catalysts supplied by ART to its refinery customers. GSEM’s processing facility is in Ulsan, South Korea and will serve ART’s customers in Asia Pacific and other regions.

The agreement allows ART and GSEM to address customers’ spent catalysts disposal needs while establishing a pathway to sustainable reuse of metals derived from the catalyst manufacturing and oil refining processes.

GSEM Chief Executive Officer Byung-Rak Lim noted that, “This agreement with ART Hydroprocessing, a global leader in hydproprocessing catalysts, allows GS EcoMetal to expand commercial production and strengthen ART’s impact on protecting the environment through recycling of limited natural resources.”

In a separate agreement, ART announced a Memorandum of Understanding (MoU) with Gladieux Metals Recycling, LLC (GMR) to explore a full-cycle catalyst management service for hydproprocessing catalysts in North America.

The MoU outlines a framework for ongoing collaboration between the two companies to expand the use of recycled metals recovered from spent hydproprocessing catalysts. Under the agreement, ART and GMR agree to identify and partner on certain spent catalyst reclamation services and metals supply arrangements using proprietary processes at GMR’s Freeport, TX facility.

“Partnering with GS EcoMetal and GMR enables ART to provide a convenient and environmentally sustainable solution for our customers,” said André Lanning, “It is part of our targeted strategy for full-cycle catalyst management services.”

“The synergy between ART and GMR will be of great benefit to the environment and our customers,” said GMR President Ruchir Kadakia. “With a true recycling option, customers can better manage their environmental risk and reduce the impact of volatility in the metals market.”

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GRACE IN THE NEWS

Grace and ART Hydroprocessing Attend Leading India Refining Event

Representatives from ART Hydroprocessing and Grace FCC attended the 2019 Global Refining and Petrochemical Congress (GRPC) in India on July 17-18. ART Hydroprocessing sponsored this prestigious event in New Delhi, which is a leading international forum to explore next-generation downstream opportunities and bring together participants to collaborate on emerging and future risks across industry markets.

Vipan Goel, Business Director for ART and Grace in India participated as a conference advisory committee member and chair for a technical session. Ashit Rakshit, Business Manager, ART, presented on "Catalytic Solutions for Increasing Middle Distillate Yields – Resid Hydrocracking and Post Hydrotreating Synergy," which generated great interest in ART’s new Ebullating Bed technology in India.

Grace Emphasizes In-Country Value for Oman at ODEC Event

Ecat Lab Supervisor Rahma Juma Al Badri presents at the Oman Downstream Exhibition and Conference on April 18.

As part of Grace’s commitment to delivering in-country value to the Middle East refining industry, EMEA Marketing Manager, Rafael Gonzalez traveled to Oman to join Grace’s Oman Ecat Labs Supervisor Rahma Tuitan Juma Al Badri and Dr. Hamdan Sulaiman Al Fazari from Sohar University to present at the Oman Downstream Exhibition and Conference (ODEC).

Rahma is one of several Omani women hired and trained by Grace for technical careers in the refining industry as part of a unique collaboration between Grace, Sohar University, and Orpic to establish a world-class material characterization (Ecat) lab in Oman.

Rahma and Dr. Al Fazari detailed this collaboration in keynote presentations for the ODEC audience, emphasizing the in-country value it brings to Oman and Grace’s future plans for the lab. Rahma holds a Bachelor’s degree in Chemistry from the College of Science, Sultan Qaboos University, in Muscat, Oman. She joined Grace in May 2017 as lab supervisor with four years of experience.

Rafael also presented on Grace’s highest activity ZSM-5 additives used to maximize valuable light olefins yields from FCC units and staffed an exhibit at the event to promote Grace’s FCC business.
Commercial Teams Learn from Panel of Top Customers at OneART Annual Meeting

From left: Eithne Traenor, Mr. Ahmed Al-Motawa (KNPC), Pietro Maugeri (RAM), Hee Seok Jeong (GS Caltex) and Raul Adarme (Motiva).

At the OneART Annual Meeting in California, ART spent an afternoon engaging in a free-ranging and often frank discussion of challenges and opportunities in the market and how ART can better serve refiners.

Eithne Traenor, a professional moderator, led the discussion among approximately 100 ART team members and executives from KNPC (Kuwait), RAM (Italy), Motiva (U.S.), and GS Caltex (Korea), which together represent each of the four primary regions into which ART sells (the Americas, Europe, the Middle East, and Asia Pacific).

The panelists praised ART for their products, business relationships, and reputation for expert technical service, but urged the company to be innovative not just in product development, but in all interactions with customers to add value. They stressed the use of data, sharing information via partnerships, and communication. Several panelists spoke at length about the need for catalyst companies to get to know their customers intimately.

The panelists also addressed new, more stringent, environmental regulations such as IMO 2020, which requires the reduction of sulfur in marine fuels, and how those regulations are impacting each region. ART has recently launched a campaign to educate customers about hydrotreating solutions for sulfur reduction.

The panel session ended with a standing ovation from the crowd and a sense that they had received valuable insights from customers. In fact, the insights were used in the innovation working sessions held during the remainder of the OneART meeting.

Upcoming Events

Find Grace and ART at these global industry events this autumn.

UOP FCC Conference (Grace only)
September 17-19
Cheyenne Mountain Resort, Colorado

LARTC
October 1-4
Cartagena, Colombia

MEPEC
October 14-16
Kingdom of Bahrain

AFPM Summit
October 14-16
San Antonio, TX

FCC Technology Workshop (Grace only)
October 28-31
Heidelberg, Germany

ERTC (Grace only)
November 4-7
Warsaw, Poland

ResidHydrotreat (ART only)
November 19-21
Kuwait
Successful FCC Fundamentals Workshop Adds Value to Grace/KMG Relationship

Over a 36-year period of continuous catalyst supply, Grace has developed a very strong partnership with Kazakhstan’s state-owned JSC National Co. KazMunayGas (KMG), including a recently-executed long-term supply agreement through our Grace Kazakhstan joint venture. So, it is not surprising that the KMG’s Pavlodar refinery was selected as the location of the Grace Kazakhstan JV’s first FCC Fundamentals and Operations Optimization Workshop.

The Grace FCC team covering the Commonwealth of Independent States (CIS), formerly Soviet republics along with the Global Customer Technology (GCT) team and Marketing personnel, worked closely with Pavlodar refinery management to design a unique training agenda to fit their needs. One of the key objectives from the refinery's perspective was an educational seminar which would include all FCCU operators (field operators, control room operators, chief operators, and maintenance mechanics). To maximize value, Grace added specific topics and sessions to cover refinery engineers and management interests over a four-day period.

All sessions proved to be valuable to the refinery and interactive exchanges took place discussing Pavlodar-specific challenges and objectives. One challenge that arose after FCC modernization was completed late in 2018, was heat balance closure. So, workshop participants worked closely with the Grace team to develop an actionable technical map to address this key issue, including operational adjustments and catalyst reformulations.

From left: Aleksey Popov, Technical Sales and Service Engineer, CIS; Anastasia Ryzhenkova, Sales Support, CIS; Stéphane Montmasson, EMEA Chief FCC Technologist; and Ilia Filimonov, Technical Sales Engineer, CIS.
For some time, the refining industry has been focused on measuring its environmental footprint—the sum of negative environmental impacts from the operation of the industry’s facilities, and the resources they consume. At Grace, in addition to our footprint, we are looking to measure what has been referred to as our “handprint”—the sum of the positive impact we can make on the environment with our products and processes.

Efforts to improve our global “handprint” are a natural outcome of our focus on customer-driven innovation—the core concept of partnering with our customers to research, develop, test, and commercialize innovations in technology designed to achieve our customer’s goals—including their sustainability goals of increasing the efficiency of their processes or products, enabling compliance with the toughest environmental standards, or reformulating their products to meet consumer demands.

When we understand our customers’ sustainability priorities and business goals, we can co-develop ways to deliver value through more efficient and sustainable products and processes.

In this issue of Catalagram, we highlight strategies for helping our customers adapt to and even profit from new low-sulfur marine fuel regulations set to go into effect in 2020 (Routes to Maximize FCC Profits During The IMO 2020 Phase-in, page 34). We also announce on page 5 a new initiative from ART to contribute to the circular economy by reclaiming and recycling metals from spent catalysts.

Today, our refining technologies contribute to sustainability goals by helping customers produce high-octane gasoline or reduce SOx and NOx emissions from refinery operations. Yet Grace’s “handprint” is not limited to the refining sector. Our Specialty Catalysts and Materials Technologies segments also market technologies that significantly contribute to our customers’ sustainability goals.

Interestingly, most of the innovations that we identify as improvements to our “handprint” emerged not from special environmental or sustainability initiatives, but as part of our normal course of business. As we work closely with our customers to understand what will truly increase the value they realize from our technologies, we forge a path toward a more sustainable future for the industry.

### Our Products Contribute to Our Customers’ Sustainability Objectives

<table>
<thead>
<tr>
<th>2018</th>
<th>Examples of Grace Sales Products and Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>~$0.1B</td>
<td>• High-performing PP catalysts for lightweighting auto parts to improve fuel economy</td>
</tr>
<tr>
<td></td>
<td>• Custom single-site PE catalysts for downgauging packaging to reduce plastics requirements</td>
</tr>
<tr>
<td></td>
<td>• Silicas for tires to reduce rolling resistance and improve fuel economy</td>
</tr>
<tr>
<td></td>
<td>• Zeolites for dual pane windows to reduce energy use</td>
</tr>
<tr>
<td>~$0.5B</td>
<td>• Advanced FCC catalysts to reduce raw material and energy requirements</td>
</tr>
<tr>
<td></td>
<td>• Advanced silica gel for filtration to reduce water use and waste</td>
</tr>
<tr>
<td>~$0.3B</td>
<td>• Hydroprocessing catalysts to meet cleaner fuels standards (e.g., IMO 2020)</td>
</tr>
<tr>
<td></td>
<td>• Additives to reduce SOx and NOx emissions from refinery operations</td>
</tr>
<tr>
<td></td>
<td>• Colloidal silicas for vehicle emission control devices</td>
</tr>
<tr>
<td>~$0.1B</td>
<td>• Non-phthalate PP catalysts for safer packaging and household items</td>
</tr>
<tr>
<td></td>
<td>• Silicas for anti-corrosive coatings that are heavy-metal free</td>
</tr>
<tr>
<td>~$1.0B</td>
<td>• Silicas for high performance paints with low-VOCs</td>
</tr>
</tbody>
</table>

1. Represents revenues aligned to SASB Chemicals Sustainability Accounting Standards definition of products designed for use-phase resource efficiency, including improving energy efficiency, reducing emissions, reducing raw materials consumption, increasing product longevity, and/or reducing water consumption.
This year W. R. Grace & Co.-Conn. ("Grace") signed an agreement with Technip Stone & Webster Process Technology, Inc. ("TechnipFMC") to jointly develop an improved catalyst and process related to the TechnipFMC PMcc™ (PropyleneMAX™ catalytic cracking) technology.

PMcc is a high-severity fluid catalytic cracking process licensed by TechnipFMC and designed to produce very high yields of propylene and other petrochemical feedstocks. The collaboration will leverage Grace’s knowledge as the leading supplier of FCC catalysts and light-olefins additives as well as TechnipFMC’s significant experience in catalytic cracking process technology and mechanical know-how.

“As the demand for petrochemicals grows, processes specifically designed to provide pathways to convert crude oil to petrochemical feedstocks, like PMcc, will become imperative for refiners,” said Tom Petti, Grace’s President, Refining Technologies. “Grace is very excited to partner with TechnipFMC, which is the technology leader in this area having licensed seven units with greater than 18 wt% propylene yields.”

In explaining the rationale for the agreement, Stan Knez, TechnipFMC’s President, Process Technology, offered that “Grace is the world leader in FCC catalysts and more specifically, catalyst solutions for the max propylene segment. We look forward to our collaboration and expect our joint efforts to deliver significant value to current and future licensees.”

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Or
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Or
email FCC@technipfmc.com
SUCCESS STORIES
Introducing FUSION™ Catalyst
The Best of Both Worlds

Superior coke selectivity and bottoms cracking from a novel single particle

Lamy Khodeir
Market Segment Manager, FCC Refining Technologies
W. R. Grace & Co.

One of the keys to optimal FCC catalyst performance is striking the right balance between zeolite and matrix, both in terms of selectivity and activity. Historically, catalyst systems containing (1) a high matrix input to maximize conversion of bottoms and (2) a high zeolite input to impart favorable coke and gas selectivities, has been known to outperform individual catalyst offerings. Grace has successfully commercialized these types of catalyst systems in more than 100 refineries worldwide, and they continue to form a valuable segment of our industry leading catalyst portfolio today.
Until now, however, the mechanism to unlock premium coke to bottoms performance has been achieved through the combination of two complimentary catalyst components with individual matrix technologies. Through world-class R&D, as well as manufacturing and processing advances, Grace has developed a catalyst solution, FUSION™ catalyst, which incorporates a differentiated advanced matrix binding system in a single catalyst particle. By reducing the proximate distance between multiple Grace technologies into the span of a single particle, the synergistic effects are magnified in FUSION™ catalyst to deliver premium catalyst performance for moderate and heavy metals applications.

**A Unique Approach to Catalyst Design**

The FUSION™ advanced matrix binding system deploys a combination of market-leading Grace technologies for intrinsic bottoms cracking and metals trapping into a single catalyst particle. This unique characteristic reduces the diffusion path length compared to alternative catalyst systems or separate particle metals traps solutions. Improved diffusion of heavy feed components facilitates pre-cracking of large feed molecules, and combined with the latest generation of metal trapping technologies, delivers premium coke selective bottoms cracking.

The novel single particle FUSION™ catalyst technology maintains the level of mesoporosity in the 100 to 600 Å range that is found in traditional catalyst systems but has a higher pore volume in the > 1000 Å macropore range. Macropores of > 1000 Å allow large feed molecules to effectively diffuse into the catalyst system, where the feed molecules subsequently reach the active sites and begin the series of cracking reactions. As a result, one of the key benefits of FUSION™ catalyst is additional bottoms cracking.

The pore size related signatures of the FUSION™ catalyst (higher macroporosity while maintaining mesoporosity to provide the ultimate combination of bottoms cracking with coke selectivity) are demonstrated in Figure 1.

**Homogeneous Metals Tolerance**

In addition to the new pore size benefits, FUSION™ technology integrates the latest developments of commercially proven integral metals trapping technology. In many operations, the nickel content of Ecats is systematically growing, which makes it necessary to use catalysts with improved Ni trapping ability to avoid running into wet gas compressor constraints as Ni is known to produce hydrogen.

To confirm the effectiveness of Ni trapping within FUSION™ catalyst, Grace R&D performed lab catalyst deactivation by spray coating Ni on the catalyst surface, followed by CPS deactivation, to give a metal distribution that is more comparable to that of Ecats where nickel is enriched on the outer shell of the catalyst particle. X-ray powder diffraction (XRD) analysis was used as a tool to study the reactivity of γ-Al₂O₃ with nickel species to confirm the presence of the Ni passivator. The XRD pattern of the samples is shown in Figure 2. A broader reflection associated...
with gamma alumina is observed at 67.2° for the sample containing no nickel (Fig. 2a). Upon increasing the Ni level of the lab-deactivated catalyst, a shift of the alumina peak to lower angular values reveals a modification of the alumina. This marks a progressive increasing of the unit cell (UC) of the alumina with increasing Ni content. A progressive enlargement of the unit cell indicates a strong interaction of nickel with γ-Al₂O₃, corresponding to the formation of sub-stoichiometric Ni alumina phase.

**Figure 2:** XRD patterns of a) FUSION™ sample with no Ni b-d) from the bottom: increasing Ni level.

The progressive increase of the unit cell volume of the spinel-like phase of nickel aluminate upon increasing the Ni content on the catalyst is plotted in Figure 3. The unit cell volume increases linearly with the Ni content. The linearity of the expansion of the UCV of the Ni-rich spinel-like phase upon increasing the Ni level follows a Vegard’s type law, which is described to be typical for solid solutions. This finding strongly indicates the preferential interaction of Ni²⁺ with γ-Al₂O₃, forming solid solutions of the formula NiₓAl₂O₃+ₓ.

The Grace self-manufactured Ni-trap present in FUSION™ catalyst makes Ni²⁺ ions essentially non-reducible through the solid-state interaction under FCC conditions, thereby reducing the extent of dehydrogenation reactions catalyzed by Ni metal particles. This Ni trapping technology prevents enhanced coke formation as well as production of hydrogen from Ni induced dehydrogenation reactions.

To provide additional evidence to verify the hypothesis of a strong interaction of nickel with γ-Al₂O₃, electron microprobe analysis was performed. Elemental mapping comparing the Ni with the Al map shows the preferential location of nickel on alumina particles that is clearly seen as Al/Ni hotspots in Figure 4.

**Figure 3:** Variation of the unit cell volume with increasing Ni level on lab deactivated FUSION™ sample.

**Figure 4:** Electron Microprobe Analysis Image of lab deactivated samples showing the presence of Al/Ni hotspots.
FUSION™ catalyst also employs Grace’s latest generation of Integral Vanadium Trap (IVT), which is an integral rare earth based technology known from the IMPACT® and NEKTOR™ product families. While attempts using MgO- and CaO-based V traps may show promise under laboratory testing conditions, silica and sulfur within FCC regenerator conditions can poison the vanadium trap to form Mg$_2$SiO$_4$ (forsterite) and CaSO$_4$ (anhydrite). The incorporation of Grace’s integral vanadium trap enhances stability and activity retention as it protects the zeolite from vanadic acid attack, enhancing stability. Grace resid feed catalysts that contain effective integral rare earth oxide-based vanadium traps provide differentiated performance even in units with low vanadium mobility. Microprobe analysis confirms that vanadium, which is mobile under FCC regenerator conditions, migrates to regions of concentrated RE from the incorporated traps resulting in RE/V hotspots as indicated in Figure 5.

**Step-out Coke-to-bottoms Performance**

An ACE™ pilot plant was used to compare selectivities for FUSION™ catalyst against a corresponding traditional catalyst system. Both catalysts were impregnated with 3000 and 2000 mg/kg vanadium and nickel using spray coating and deactivated at the same conditions using CPS deactivation. At a given conversion, the same bottoms yield was observed for both catalyst solutions, but FUSION™ catalyst offered a significant drop in hydrogen and coke yield as demonstrated in Figure 6. The improved gas and coke selectivity provides improved coke to bottoms performance, confirming that the advanced matrix binding system causes a valuable interaction that outperforms traditional catalyst systems.

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Figure 5: Electron Microprobe Analysis Image of lab deactivated samples showing the presence of RE/V hotspots.
The Pursuit of Value

At Grace, value is defined by our customer’s financial success. FUSION™ catalyst is the latest example of an innovative FCC catalyst solution designed to provide differentiated product yields and physical properties with benefits in unit retention that can withstand dynamic and challenging FCC feed profiles. The combination of the above-mentioned functional qualities and unique catalyst design architecture provides the next step improvement in value to refiners. As product economies shift in 2020 and beyond, FUSION™ catalyst provides another tool to improve our customer’s bottom line. At the time of this publication, we have new trials of FUSION™ catalyst underway in multiple regions. Please contact your local Grace representative for more information regarding FUSION™ catalyst or visit grace.com.

References

RIVE® FCC Catalyst Powered by Molecular Highway® Zeolite Technology

Tony Tavares
Segment Marketing Manager, FCC
Refining Technologies
W. R. Grace & Co.

Grace has a long history of providing innovation in the development of FCC catalysts, as the first company to supply synthetic FCC catalyst in 1942, the first to supply a spray-dried, microspheroidal catalyst, and the first to supply a zeolite-based catalyst to the world’s refiners. Over the years, Grace has continued to develop and commercialize innovative technologies in the FCC catalyst industry including: alumina sol binding technology, integral vanadium trapping technology, coke selective deep bottoms cracking matrix, low coke matrix nickel passivation technology, and the addition of rare-earth metals to stabilize the zeolite Y component of the catalyst, to name a few.

In 2010, Grace embarked on the deployment of another innovation, when we began a joint development agreement with Rive Technology Inc. The company was created to commercialize a step out zeolite technology developed at Massachusetts Institute of Technology (MIT) by Dr. Javier Garcia-Martinez, called “Molecular Highway® zeolite technology”. The breakthrough technology improves traditional zeolite catalysts through the introduction of highly interconnected channels of medium pore size, which enhance diffusion of feed molecules inside zeolite crystals, leading to higher value product yields, improved process efficiency and increased refinery profitability. Combined with Grace’s market leading capabilities in FCC catalyst formulation and manufacturing, Rive Technology Inc. and W. R. Grace & Co. co-developed and commercialized the groundbreaking RIVE® FCC catalysts in the refinery industry.
On June 17, 2019, Grace’s Refining Technologies business acquired the business, patents and other assets from Rive Technology Inc, including its Molecular Highway® zeolite technology. This addition to Grace’s strong portfolio of catalyst technologies makes Grace uniquely positioned to serve the dynamic needs of the refining industry, and it is perfectly aligned with Grace’s focus on catalyst and materials technologies.

**Introducing Ordered Mesoporosity**

The Molecular Highway® Y-zeolite technology is a surfactant-templated post-synthesis zeolite meso-structuring process that introduces ordered, well-controlled, and hydrothermally stable mesoporosity into zeolite crystals. The Molecular Highway® process is engineered to allow a high degree of control in the size and the amount of ordered mesopores created inside the zeolite crystal, resulting in homogeneously distributed and interconnected pores.

RIVE® FCC catalysts powered by Molecular Highway® Y-zeolite (MHY™) technology enhances feed molecules’ access to and from active catalytic sites in the zeolite. This allows refiners to make more primary cracking products, including LPG olefins, and less coke per unit of conversion—both of which are highly valued by many refiners.

**The Molecular Highway® Advantage**

With conventional Y zeolites, molecules with kinetic diameters up to roughly 1 nm (10 Å) can directly enter the Y-zeolite structure. This corresponds to hydrocarbons that boil up to around 950°F (510ºC). Larger hydrocarbons boiling above this temperature are traditionally cracked in the FCC by mesoporous aluminas. These materials have somewhat less selective 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 (3-5 nm; 30-50 Å) in the MHY™ zeolites, larger feed molecules which boil at temperatures in the 950-1100ºF (510-593ºC) range are now able to directly access the strong acid sites in the zeolite. MHY™ zeolites can crack these larger feed molecules more selectively than conventional active matrix materials. This translates commercially into coke-selective bottoms cracking. Additionally, MHY™ zeolite technology rapidly channels 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.
Among the primary and secondary "cracked products", LPG olefins are very reactive, particularly at the high temperatures present within 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. MHY™ zeolite's ordered mesopores 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).

**Molecular Highway® Y-zeolite (MHY™) Technology**

*Y Zeolite*

Too large to enter

Small pores in conventional Y zeolites work well with molecules that boil up to 950°F (510°C).

*MHY™ Zeolite*

Easy way in

Easy way out

MHY™ zeolite technology creates larger pores, allowing zeolites to crack larger molecules that boil in the 950-1100°F (510-593°C) range.

The RIVE® FCC catalyst represents the first and only use of ordered mesoporosity in FCC zeolites or catalysts, and is capable of providing a step change in value for many FCC operations. The result: enhanced diffusion of hydrocarbons both into and out of the catalyst particle.

Refiners around the world have used RIVE® catalyst's signature benefits to increase FCC profitability in several different objective/constraint scenarios. These benefits improve operational flexibility which allows refineries to pursue heavier feedstocks via delta coke reduction, reduce FCC dry gas without loss in LPG, increase volume swell in delta coke limited operations, and alleviate existing unit constraints such as main air blower rate, wet gas compressor rate, and regenerator temperature.

Performance signatures of RIVE® FCC catalysts powered by MHY™ zeolite technology include:

- **Increased Refinery Profitability**
- **Increased LPG Olefinicity**
- **Increased Gasoline Octane**
- **Increased Operational Flexibility**
- **Improved Bottoms Upgrading**
- **Decreased Delta Coke**

Continued on Page 20
**Success Stories**

**Benchmarking between RIVE® Catalyst and Traditional FCC Catalysts**

Grace performed an in-house benchmarking study comparing the effect of standard USY zeolite versus MHY™ zeolite within one of our leading coke selectivity catalyst benchmarks. The tested catalysts were manufactured with equal rare earth, alumina and zeolite content. In addition, all sample preparations, deactivations conditions, and feed profile were the same.

The RIVE® Catalyst provided:
- Significantly better LPG olefinicity, particularly C4= olefinicity
- Improvement in gasoline RON
- Similar or better coke selectivity
- Better bottoms cracking selectivity
Third Party Testing
Recent testing done at an independent lab has confirmed benefits of RIVE® catalyst:

- Greater total liquid volume (C3+)
- Greater amount of LPG olefins (C3= + C4=)
- Lower coke / bottoms
- Lower dry gas

Commercial Success
RIVE® catalysts powered by MHY™ zeolite technology have been used successfully in numerous commercial operations. An excellent example, previously published in AFPM (2017-17-47), is the ongoing operation at a former Motiva (now Shell) refinery in the Gulf Coast of the United States. This FCC unit processes a mix of VGO, heavy coker gas oils, and resid. The feed rate of 10-15 KBPD typically pushed to a maximum air blower / supplemental oxygen limit. The catalyst circulation rate could be increased by approximately 10% over base levels before meeting the maximum allowable circulation rate. API and CCR generally remained in similar ranges as before the trial. The RIVE® catalyst demonstrated notable improvements in coke selectivity, dry gas selectivity, LPG olefinicity, bottoms reduction and C3+ Total Liquid Volume.
SUCCESS STORIES

In another commercial example from a major refiner, the RIVE® FCC catalyst increased the volume of transportation fuels (at constant LPG) and also improved the quality of the slurry. This combination has resulted in a significant increase in FCCU profitability:

### Table 1: Motiva (Shell) Commercial Data Summary

<table>
<thead>
<tr>
<th>Predictions</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease coke selectivity</td>
<td>-10% (rel)</td>
</tr>
<tr>
<td>Increase total liquid volume</td>
<td>+ 2.3 vol% (abs)</td>
</tr>
<tr>
<td>Increase C₃ olefinicity</td>
<td>+ 2% (rel)</td>
</tr>
<tr>
<td>Increase C₄ olefinicity</td>
<td>+ 4%</td>
</tr>
<tr>
<td>Decrease dry gas yield</td>
<td>- 10% (rel)</td>
</tr>
<tr>
<td>Decrease hydrogen in coke</td>
<td>- 15%</td>
</tr>
<tr>
<td>Increase FCC profitability</td>
<td>&gt; $1.00/BBL</td>
</tr>
<tr>
<td></td>
<td>$0.40-$1.20/BBL</td>
</tr>
</tbody>
</table>

In another commercial example from a major refiner, the RIVE® FCC catalyst increased the volume of transportation fuels (at constant LPG) and also improved the quality of the slurry. This combination has resulted in a significant increase in FCCU profitability:
A third commercial example in a “high added-iron” (+0.4 wt.% Fe) operation had the main objective of reducing regenerator temperature for a given amount of vacuum tower bottoms in the feed. Over the course of the trial, the delta coke and regenerator temperature both steadily decreased, as desired. This provided the refinery with increased operating flexibility to process lower cost feeds, while not exceeding unit constraints.

**Overcoming Constraints**

RIVE® FCC catalysts containing MHY™ zeolites provide improved bottoms upgrading, increased olefinicity and octane, 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:

**Main Air Blower Rate**

Increase feed preheat temperature or decrease riser outlet temperature making less coke, and alleviating the air blower constraint. These actions decrease catalyst circulation and bottoms conversion, but RIVE® catalyst’s improved coke selectivity counteracts them. The feed rate can be increased until a new constraint is met.

**Wet Gas Compressor Rate**

RIVE® catalyst’s enhanced diffusion reduces over cracking of valuable hydrocarbon products to dry gas. This allows the feed rate—or operating severity—to be increased until a new constraint is met.

**Regenerator Temperature**

RIVE® catalyst’s improved coke selectivity increases the catalyst circulation rate, lowering the regenerator temperature. This allows the feed rate—or feed residue content—to be increased until a new constraint is met.

This improved operating flexibility allows for increased catalyst circulation via lower delta coke, or the introduction of heavier opportunistic feeds, if increased circulation is not possible.

*Continued on Page 24*
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What’s Next

In addition to deploying MHY™ technology in some of Grace’s global FCC catalyst products and new development pipeline, this technology has broad applicability to different types of zeolites.

Demand for transportation fuels is projected to peak in the next decade, as competing influences of population growth and higher living standards are offset by fuel efficiency trends. Many refiners are considering shifting FCC objectives to produce light olefins for petrochemical feedstocks to best utilize existing FCC assets. It is estimated that the demand for petrochemicals will rise by more than 7 million b/d over the next 20 years, surpassing oil demand from the transport sector. As demand for petrochemicals grows, the addition of MHY™ zeolite technology will allow us to offer refining customers additional solutions and greater flexibility in converting crude oil to petrochemical feedstocks.

Our R&D team, which includes talented scientists from Rive Technology, are already working on new concepts for the deployment of MHY™ zeolite technology in FCC and a wide range of chemical applications. Grace is just scratching the surface of what this technology can do. Stay tuned for new innovative catalyst solutions powered by this exciting technology that will deliver value to our customers now and into the future.

References

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

grace.com/value

GRACE
Talent | Technology | Trust™
**Residuum Oil Hydrocracking: Chemistry and Catalysis**

Balbir Lakhanpal  
Global Technology Lead  
EB Resid  
ART Hydroprocessing

Julie Chabot  
Residue R&D Technical Manager  
ART & CLG Applied Technology

Woody Shiflett  
Manager  
ART & CLG Applied Technology

Significant advances have been made in both understanding the hydrocracking chemistry of residuum oils and in the catalysis and catalytic systems required for deep conversion well above 90% of the vacuum residua.

The hydrocracking of residuum oil fractions has been practiced for nearly six decades, evolving from simpler, single catalyst ebullated bed reactor systems capable of 65-70 wt.% vacuum bottoms conversion to the latest slurry hydrocracking systems that effectively push vacuum bottoms conversion well beyond 90 wt.% up to 97-98 wt.% Deepend conversion of residuum enables the production of ultra-low sulfur (ULS) fuels as well as feed preparation for petrochemicals production.

Throughout this development history, a key challenge has been to maintain robust and reliable operability by mitigating and ultimately controlling what is generically called sediment or sludge formation and deposition. Sediment formation has limited the performance of ebullated bed reactor systems from achieving the potential conversion levels possible with the LC-FINING™ reactor platform. This is also highly dependent on the feed characteristics as shown in Figure 1.
Key to fully utilizing the full reactor potential to maximizing conversion is the types of catalyst utilized in conjunction with appropriate operating conditions and flow scheme. This article will review the understandings in analytical petroleum chemistry and catalysis that have enabled this technology to arrive at this level of success. Success in deep residuum hydrocracking is only possible by understanding the fundamental hydrocarbon chemistry involved and marrying it with the properly designed catalysts and optimized catalyst systems to meet high conversion objectives.

Understanding the Chemistry

Fundamental concepts of the hydrocracking chemistry of residuum fractions have progressed immensely since the 1960s when the heavier components of residuum fractions were characterized by carbon residue measurements relevant to thermal visbreaking, coking operations and fluid catalytic crackers (FCCs) and somewhat ill-defined insolubles in one or more alkanes.

The term “asphaltenes” was associated with alkane (typically heptane) insolubles but poorly envisioned much less understood on a molecular level. They were highly aromatic in nature and deficient in hydrogen, but little more was fundamentally known. Empirically, it was established that sediment formation, for the most part, arose because the catalytic hydrogenation associated with the residuum hydrocracking was overly selective in hydrogenating the hydrocarbon fractions acting as the solvent for the ill-defined asphaltene components. At the same time, cracking of the side chains and naphthenic rings occurs in the asphaltene molecules leaving the aromatic cores mostly unaffected and incompatible with the oil. These changes make the oil product more paraffinic and the unconverted asphaltene cores more aromatic and condensed than those in the feed. In consequence, a disturbance in the asphaltene-resin interactions occurs leading to the precipitation of asphaltene as sediments. Additionally, as temperature increases, the rates of thermal cracking reactions increase more rapidly than the hydrogen addition counterparts. Thus, hydrogen transfer limitations occur which can lead to the growth of aromatic structures in the asphaltenes making them more prone to precipitate once these compounds leave the reactor zone.

Various filtration methods and gradient of solvent experiments led from saturates, aromatics, resins and asphaltene (SARA) characterization to asphaltene solubility profiles. However, empirical characterization progress needed to be matched by a coherent theoretical understanding of the molecular nature of residuum oil components. Prior to the 1980s, theory on the nature and structure of asphaltenes and associated heavier ends focused on them being polymeric in nature and perhaps the result of geological transformations or conversely micellular entities consistent with a colloidal view of petroleum.

However, in the 1980s and 1990s, the extensive effort first by Boduszynski, et al. and extended by Ovalles, Moir et al. at Chevron Energy Technology Company established that the molecular composition of petroleum from light ends through the heaviest residuum components was a continuum in molecular weight (the “Boduszynski Continuum”) and developed more and more advanced means of characterizing the molecular spectrum that framed the species that lead to sediment formation under residuum hydrocracking conditions.

Enhanced asphaltene separation techniques using liquid chromatography apparatus and tailored solvent gradient sequences coupled with in-line filtration developed in the last few years by Rogel, Ovalles, Moir and coworkers now allow asphaltene types to be separated and characterized by their stability and tendencies to precipitate as sediment.

Today, advanced analytical techniques such as ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry enable the mapping of the heavy oil molecular continuum by carbon atom count and aromaticity as indicated by double bond equivalent (DBE). Indeed, it is now possible to track reaction dynamics molecularly by DBE and carbon atom count as shown in Figure 2. Atomic Force Microscopy (AFM) enables us to “see” various asphaltene structures. Such advances better enable the design and optimization of catalyst chemistry, porous structure and multi-catalyst reaction systems in residuum hydrocracking.
The Role of Catalysis

Most of the vacuum residuum conversion in hydrocracking processes is thermal in nature. The catalyst or catalyst system provides a variety of concurrent benefits through various catalytic reactions: removal of sulfur (Hydrodesulfurization or HDS) for Ultra-Low-Sulfur (ULS) fuels, nickel and vanadium (Hydrodemetallization or HDM) reactions to mitigate fouling deactivation of downstream catalyst systems, nitrogen removal (Hydrodenitrogenation or HDN) and removal of micro carbon residue (HDMCR) to mitigate inhibition in subsequent processes such as Vacuum Gas Oil (VGO) hydrocracking, and selective hydrogenation for mitigation of sediment formation plus polynuclear aromatics (PNA) reduction in lighter fractions. Other reactions such as dealkylation of asphaltenes and other higher molecular weight multi-ring aromatics must also be considered in mitigating sediment formation. Because catalysts are concurrently added and removed from both ebullated bed reactors (EBRs) and slurry hydrocracking reactors in such processes as LC-FINING™ and LC-SLURRY™ technology, they also serve the role of transporting deposited nickel and vanadium metals and heavy, carbonaceous coke from the reaction zones.

The upshot of these catalytic reactions is that significant effort must be devoted to developing the proper catalyst chemistry as well as the distinct pore size distribution to address operational needs and targets, and similarly, the utilization of multi-catalyst systems must be understood in order to be optimized. We will review the progress in this area in both ebullated bed (EB) catalysis (“millimeter scale”) and slurry hydrocracking catalysis (“micron scale”). We will also review our findings for purported nano-scale catalysts or co-catalysts in residuum hydrocracking and their subsequent implications for sediment mitigation. Processing considerations have been reviewed in some detail earlier.

Catalyst Development Efforts on a Millimeter Scale

To ensure that state-of-the-art catalyst technologies are commercially available for its ebullated bed and slurry hydrocracking processes, Chevron Lummus Global (CLG), a joint venture between McDermott and Chevron, established a cooperative agreement with Advanced Refining Technologies LLC (ART), a joint venture between Grace and Chevron.

ART is the leading supplier of residuum hydroprocessing catalysts worldwide. Resources, know-how and ideas are shared between the parties to assist in the development of new catalyst technologies to meet various commercial needs. State-of-the-art research units located in Richmond, California, are utilized for ART catalyst screening studies as well as CLG/ART joint catalyst development and process optimization studies.

The extensive database generated from these units as well as CLG’s and ART’s extensive commercial experience ensures the best catalysts are selected to achieve processing objectives. This testing has led to the development of several new and enhanced ‘Catalyst Technology Platforms’ in the last ten years.

This was a natural evolution from the initial formation of both joint ventures. Indeed, shortly after the formation of the ART and CLG JVs in 2001, efforts commenced to integrate each company’s catalyst strengths. All parties contributed significant residue upgrading technology, with Chevron’s 35 years of process and catalyst expertise in residue hydrotreating (including ARDS, VRDS, OCR®, and UFR® technology), CLG’s 23 years of experience with the LC-FINING™ residue hydrocracking process and Grace’s 30 years of background with catalysts for the EBR process.

The sharing of ideas from each party provided leads with respect to new catalyst designs specifically to address sediment formation—a problem common to both residue hydrotreating and hydrocracking.

We have found that to achieve the best performance it is critical to provide the right balance between meso and macro pores. The intrinsic reaction rate, which is inherently related to the catalyst surface area, controls the HDS, the HDMCR, and the residuum conversion characteristics of the catalysts. The diffusivity, which is more related to the macro pores (greater than 25 nanometers), controls the demetallation and the sedimentation functions of the catalyst.

The optimization of the pore volume and pore size distribution (PSD) is critical to the catalyst development:

- Pores in the < 20 nm range are most useful for HDS and HDCCCR activity. Pores in the 25+ nm range are effective in allowing diffusion of the majority of the asphaltenic molecules into the catalyst.

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A select number of pores >25 nm is essential to allow the largest asphaltenes molecules to readily enter the catalyst to achieve maximum HDM, while cracking the molecules with minimum sediment formation.

The above characteristics are established via the proper combination of chemical composition and preparation techniques.

The active metals, both molybdenum and the Group VIII promoters, are also extremely important to get proper catalyst performance. The correct amounts of the two (or more) elements dispersed throughout the extrudate are necessary to ensure full metals utilization. This requires exact control of the metals distribution and dispersion. The optimum catalyst is designed to deliver the maximum residue conversion, with a high level of asphaltenes and CCR conversion to minimize organic sediment formation. In addition to the key role the catalyst plays, the maximum conversion level attainable is dependent on the feedstock characterization. The Colloidal Instability Index (CII) and the characterization of the asphaltenes are important factors in benchmarking various feeds. The CII is a measurement of the ratio of asphaltenes plus saturates to aromatics plus resins. A lower CII is indicative of a feed which is easier to process. In addition, the asphaltenes can be characterized into those which are easier or more difficult to process based on a solvent based analysis. The greater the percentage of easier to process asphaltenes the higher the conversion level that can be attained.

<table>
<thead>
<tr>
<th>EBR Catalyst Platform</th>
<th>Application and Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCS</td>
<td>Maximum Metals Removal; GR-61X</td>
</tr>
<tr>
<td>ECAD™</td>
<td>Metals Removal with Enhanced Catalytic Activity; GR-95X</td>
</tr>
<tr>
<td>HSLS®</td>
<td>Sediment Control with Good Catalytic Activity; GR-82X</td>
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<tr>
<td>HSLS® Plus</td>
<td>Sediment Control with Very Good Catalytic Activity; GR-LS10</td>
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<tr>
<td>LS™</td>
<td>Sediment Control with Enhanced Catalytic Activity; GR-83X</td>
</tr>
<tr>
<td>HCRC™</td>
<td>Maximum Catalytic Activity; GR-73X</td>
</tr>
</tbody>
</table>

Table 1: Features of the ART’s DCS, ECAD™, HSLS®, HSLS® Plus, LS™ and HCRC™ catalyst platforms.

**LS™ Technology Platform**

Developed and commercialized in 2002, the LS™ technology platform continues to be in use in several EB RHC units worldwide in both a standalone and dual catalyst system.

It provides very good sediment control, particularly for highly sediment forming feeds such as Urals.

**HSLS® Technology Platform**

Developed and commercialized in 2007, this catalyst offers superior sediment control in combination with higher demetallation activity. The unique pore structure of this catalyst enables higher metals loadings (i.e. Ni + V), while still providing superior sediment control activity. It has been successfully used in several units, processing a wide range of feedstocks, and offers the most cost-efficient technology for residue hydrocracking. The HSLS® technology incorporates a novel base, along with an advanced and special process technology for efficient metals impregnation. The proprietary alumina, with its unique pore size distribution, provides enhanced access to the active metal sites.

Key performance features of this technology platform include:

- Lower sediment formation (decreased 7-20%), reducing the cleaning frequency of downstream equipment, higher on-stream factor and lower maintenance costs. In some cases, this has allowed for higher residue conversion and/or flexibility to process more difficult opportunity crudes.
- Higher micro carbon residue (MCR) removal – better coker feed quality.
- Improved HDS of the distillate and unconverted residuum.
- Significant reduction (5-15%) in fresh catalyst addition rates with higher metals removals, which also means more value for metals recovery on spent catalyst.

This catalyst is being successfully used in combination with LS™ catalyst in a dual catalyst system in Asian and European units, with superior performance and sediment control. In addition, it is also being used in combination with our high demetallation removal catalyst in a Gulf Coast U.S. unit.

**HSLS® Plus Technology Platform**

Developed in 2012 and commercialized in 2018, this catalyst technology is an enhancement of the HSLS® technology and geared for higher HDS and HDMC conversion, in EB units which are processing high sulfur feeds and are targeting lower bottoms sulfur and MCR in the EB RHC HT Resid and converted products.

Key performance features of this technology platform, in addition to the HSLS® technology platform described above are:

- Higher HDS and HDMC conversion.
- Lower VTB bottoms sulfur and MCR.
- No change in catalyst usage rates.
Technology, even for high-metals feeds. The latest addition to the metals loadings (i.e. Ni+V) for a highly cost-efficient catalyst sediment control could be achieved while retaining very high the HSLS metals capacity. When combined in a dual catalyst system with DCS Catalyst Platform, very little impact to HDS or HDMCR activity is observed. The unique pore structure of the ECAD™ catalyst enables the higher metals loadings (i.e., Ni+V), while providing superior sediment control activity. This new platform is currently in trial in one unit, processing a challenging feedstock, and offers a very cost-efficient technology for residue hydrocracking. The ECAD™ technology incorporates a novel base, along with an advanced and special process technology for efficient metals impregnation. The proprietary alumina, with its unique pore size distribution, provides enhanced access to the active metal sites.

Key performance features of this technology platform include:

- Higher metals capacity than HSL® catalyst platform, and higher activity than EBR Demet Grades.
- In a dual system platform, ECAD™/LS™ catalyst provides improved residuum conversion sediment trade-off, relative to HSL®/LS™.
- Significant reduction in fresh catalyst addition rates with higher metals removals, which also means more value for metals recovery on spent catalyst.

**ECAD™ Technology Platform**

Developed in 2016 and commercialized in 2018, this catalyst platform offers exceptional sediment control in combination with significantly higher metals capacity compared to the HSL® platform. When combined in a dual catalyst system with the LS™ catalyst platform, very little impact to HDS or HDMCR activity is observed. The unique pore structure of the ECAD™ catalyst enables the higher metals loadings (i.e., Ni+V), while providing superior sediment control activity. This new platform is currently in trial in one unit, processing a challenging feedstock, and offers a very cost-efficient technology for residue hydrocracking. The ECAD™ technology incorporates a novel base, along with an advanced and special process technology for efficient metals impregnation. The proprietary alumina, with its unique pore size distribution, provides enhanced access to the active metal sites.

Key performance features of this technology platform include:

- 4% higher residuum conversion (preferentially to distillate).
- 4% higher HDS (lower sulfur in the unconverted bottoms and converted oil products).
- 6% higher MCR removal.
- 3% higher HDN (lower nitrogen in distillate and VGO).

This technology provides the ability to achieve the same or higher residue conversion at lower thermal severity (i.e. lower temperature) at higher cracking activity with comparable sediment formation.

**ECAD™ Technology Platform**

Developed in 2016 and commercialized in 2018, this catalyst platform offers exceptional sediment control in combination with significantly higher metals capacity compared to the HSL® platform. When combined in a dual catalyst system with the LS™ catalyst platform, very little impact to HDS or HDMCR activity is observed. The unique pore structure of the ECAD™ catalyst enables the higher metals loadings (i.e., Ni+V), while providing superior sediment control activity. This new platform is currently in trial in one unit, processing a challenging feedstock, and offers a very cost-efficient technology for residue hydrocracking. The ECAD™ technology incorporates a novel base, along with an advanced and special process technology for efficient metals impregnation. The proprietary alumina, with its unique pore size distribution, offers exceptional access to active sites and superior metals capacity, while retaining physical strength and integrity.

**Dual Catalyst System**

ART was the first catalyst supplier to introduce and commercialize a ‘Dual Catalyst System’ in EB RHC Units in 2009, and remains the only catalyst supplier to offer such an advanced catalyst system option. This innovative concept, based on extensive commercial experience, was developed with the goal of maximizing the performance of front and tail reaction stages while minimizing catalyst addition rates.

The first commercial application of such a dual catalyst system, in a Gulf Coast U.S. unit, was found to be very successful. Since then, additional specific catalyst platforms have been developed to enhance the specific performance of front and tail reaction stages, and various combinations of dual catalyst systems have been tested by ART and CLG in research units and are in commercial use in numerous EB RHC units, including LC-FINING™ units in Asia and Europe, with proven superior performance and sediment control.

The use of a dual catalyst system allows for unique catalyst synergies and has been proven to maximize residuum conversion, HDS, HDMCR and HDM, while retaining superior sediment control, maximizing catalyst metals capacity and minimizing catalyst addition rate and cost (Table 2).

The use of a state-of-the-art dual catalyst system provides a significant technology advantage, including efficient catalyst utilization and operational flexibility in the operation and optimization of the RHC unit performance. While operating in a dual catalyst system mode, these units have benefited from lower sediment formation at equivalent residuum conversion, when compared to single catalyst system operation.

As shown in Figure 3, the use of a dual catalyst system, as opposed to single catalyst system operation, has been reliably proven both in extensive research unit testing and commercial operation to reliably reduce sediment formation at a given residuum conversion. This improved sediment-conversion trade-off leads to reduced fouling and cleaning frequency of downstream equipment, higher on-stream factor, lower maintenance costs, and improved product stability.

The dual catalyst system approach provides reliable sediment-conversion tradeoff enhancement, while also providing improved catalyst metals capacity, therefore directionally reducing catalyst addition rate and handling, as shown in Figure 4. The dual...
catalyst system platform has been proven, in extensive research unit testing, including larger-scale research unit testing, to be far more reliable and economic than relying on the combination of a single catalyst system and the addition of a co-catalyst additive, such as organo molybdenum compounds. Indeed, such co-catalysts have been described as “nano-catalysts,” but the evidence does not support this assertion, and this will be discussed further in our section on micron scale catalysts.

Figure 3: Pushing the performance edge toward higher conversion

ART’s Dual Catalyst Systems

While these challenges are difficult, ART’s pioneering use of dual catalyst systems in EBR units has helped refiners profitably process a wide variety of difficult feedstocks. By staging the catalyst functions in different reactors (Table 4), ART’s dual catalyst systems enable refiners to maximize profitability at minimal catalyst additional rates, with proven catalyst savings of up to 11% (Table 3).

<table>
<thead>
<tr>
<th>Desired Circulating</th>
<th>Rx1</th>
<th>Rx2 / Rx3</th>
<th>Contribution of Rx T</th>
<th>Contribution of Catalyst</th>
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<tr>
<td>Catalyst Quality</td>
<td>Good</td>
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<td>Metal Removal</td>
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<td>HDS</td>
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<td>High</td>
<td>High</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>High HDM &amp; Mod. HDS; Excellent Sediment Control</td>
<td>Good Sediment Control; High HDS/HDCRC; Low HDM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Dual stage balances process and catalytic functionalities. Balancing the process (severity/residence time) vs. catalytic functionality allows breaking through the capacity/activity trade-off.
Dual Catalyst System Case Study

<table>
<thead>
<tr>
<th>Case Summary</th>
<th>Customer A</th>
<th>Customer B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Challenges/Goals</td>
<td>High Ni+V VR feed with limitation on cat addition rates</td>
<td>Increase conversion with minimal impact on sediment</td>
</tr>
<tr>
<td>Dual Catalyst</td>
<td>• ~11% lower catalyst addition rate</td>
<td>• ~6% higher 579C+ conversion</td>
</tr>
<tr>
<td>System Result</td>
<td>• Constant resid conversion, HDS, and HDMCR</td>
<td>• Minimal sediment increase</td>
</tr>
<tr>
<td></td>
<td>• 3% lower catalyst addition rate</td>
<td>• 3% lower catalyst addition rate</td>
</tr>
<tr>
<td>Added Flexibility</td>
<td>Ability to process higher fraction of high metals discounted crudes</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Refiners using ART’s dual catalyst systems were able to meet their complex goals while reducing catalyst addition rates.

<table>
<thead>
<tr>
<th>Technology Platform</th>
<th>Stage 1</th>
<th>Stage 2/3</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Function</td>
<td>DCS (DeMet)</td>
<td>HSL®</td>
<td>In Use</td>
</tr>
<tr>
<td></td>
<td>Very High HDM / Moderate HDS /</td>
<td>High HDS / HDMCR / Excellent Sediment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Excellent Sediment Control</td>
<td>Control</td>
<td></td>
</tr>
<tr>
<td>Catalyst Function</td>
<td>HSL®</td>
<td>LS™</td>
<td>In Use</td>
</tr>
<tr>
<td></td>
<td>Good HDM / Good HDS &amp; HDMCR / Very</td>
<td>High HDS &amp; HDMCR and very good Sediment Control</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Good Sediment Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst Function</td>
<td>ECAD™</td>
<td>LS™</td>
<td>In Use</td>
</tr>
<tr>
<td></td>
<td>High HDM / Good HDS &amp; HDMCR /</td>
<td>High HDS &amp; HDMCR and very good Sediment Control</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Excellent Sediment Control</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4: ART’s Dual Catalyst Systems for EB RHC Units.

As shown in Figure 6, the addition of a costly co-catalyst has not been shown to provide a sediment-residue conversion trade-off benefit or any other performance benefits, including catalytic activity improvements, when tested in CLG’s large state-of-the-art 1 Bbl/day research unit. In fact, during this extensive testing, the addition of the co-catalyst led to slightly increased sediment, not lower sediment, at a given residuum conversion, since the co-catalyst solids were recovered in the unconverted product and contributed to additional inorganic sediments.

In addition to contributing to increased inorganic sediments in the unconverted oil, without reliable improvement in sediment-conversion trade-off or catalytic performance, the use of a co-catalyst presents many key challenges. The use of such costly additives contributes to significant additional catalyst addition costs, and increased operation complexity, requiring additional catalyst supply logistical provisions, handling and injection requirements. Furthermore, such additives have been observed to react and evolve quickly and contribute to problematic equipment and reactor fouling issues that could interfere and limit operation run cycle length.

Because of these key concerns, ART and CLG have favored the more reliable and proven dual catalyst system technology, as opposed to the combination of a single catalyst system plus co-catalyst additive combination. The various combinations of dual catalyst systems, employing the above listed catalyst technology platforms, currently in use or undergoing commercial trials are summarized in (Table 4).

Continued on Page 32
Catalyst Innovation on a Micron Scale

The extension of residuum hydrocracking to the level of 90%+ vacuum bottoms conversion has required significant changes in reaction transport dynamics and catalysis approaches. Fortunately, the historically proven and well optimized LC-FINING™ reactor platform has been demonstrated to have both the flexibility and sustained robustness to meet the needs of deep conversion slurry hydrocracking of residuum embodied in the innovations of the LC-SLURRY™ technology process. The LC-SLURRY™ technology process utilizes the unique ISOSLURRY™ catalyst. ISOSLURRY™ catalyst's unique properties result in efficient hydrogenation activity needed to convert the heavy end to useful products and effectively mitigate sediment formation, thus ensuring the reactor effluent is clean, which means that the fractionation section equipment is not subject to fouling.

CLG’s approach of using a nickel promoted molybdenum slurry catalyst with a defined structure has been found to be far superior to other approaches that have been tried such as using organo-moly liquids as catalyst precursors or conversely employing low activity or no activity solids.

In contrast to the LC-SLURRY™ technology clean system concept, the thermal slurry processes that operate with higher temperatures require large amounts of inactive or low activity solids and cannot produce a high-quality heavy oil product like ISOSLURRY™ does. The combination of a unique nickel-molybdenum slurry catalyst (ISOSLURRY™) with the LC-FINING™ reactor system allows even the most difficult VRs, SDA tars, and other heavy residues to be upgraded reliably and selectively.

The catalytic chemistry, morphology and porous structure of the ISOSLURRY™ catalyst is key to dependable, high performance in residuum hydrocracking that reaches 97% vacuum bottoms conversion. As shown in Figure 7, its micron scale particle size distribution ensures that mass transfer limitations inherent to high conversion are dramatically reduced, and, coupled with a high pore volume, maximizes the access to highly dispersed nickel-promoted MoS\(_2\) active catalytic sites. Furthermore, the high pore volume (particularly pore diameters in excess of 10 nm), high internal surface area and high particle geometric surface area allows for effective deposition of nickel and vanadium sulfides plus heavy carbonaceous foulants and their subsequent transport out of the reaction system.

The nature of the inherent ISOSLURRY™ proprietary synthesis from low-cost raw materials in the LC-SLURRY™ technology process assures high dispersion of the nickel-promoted MoS\(_2\) active sites and their effective pre-sulfiding, activation and optimal particle size distribution. Broad flexibility exists in pre-production, quality control and storage owing to an exceptionally robust shelf life of ISOSLURRY™ catalyst. Its particle size distribution is optimized for subsequent separation and recovery for both economic recycle catalyst operation and active metal recovery.
In the past decade, significant progress has been made in improving the performance of ISOSLURRY™ catalysts through optimizing their morphology. The pore volume has been increased by well over an order of magnitude, and the macroporosity critical to removal of metals and heavy carbonaceous deposits has been increased by over a factor of 15. In terms of the commercial unit opex economics, this has resulted in catalyst addition rates being reduced at a minimum by a factor of 25. This, coupled with efficient catalyst recycle technology, has been pivotal in optimizing process economics to a minimum catalyst cost.

We return to a consideration of the potential for true nano-catalysts for residuum conversion. In the long path to optimizing ISOSLURRY™ catalyst performance in terms of both chemistry and morphology, a number of organo or, generically, soluble molybdenum formulations have been studied. In all cases, rather rapid agglomeration of initially nano-size entities has occurred. Significantly, active catalytic species of 250-400 nm have been clearly identified after less than 15 minutes residence time at 770°F (410°C). Mass balance closure has clearly shown that no measurable quantity of potential molybdenum nano-catalysts survive the rapid agglomeration phase. While the performance of the resultant micron scale catalytic species is by no means profoundly inferior to ISOSLURRY™ catalyst with respect to residuum conversion, they offer no benefits in catalytic performance or mitigation of sediment formation over ISOSLURRY™. This supports the concept that a stable and fully-formed Ni-Mo catalytic entity is highly favored over a rapidly agglomerating singular Mo entity for effectiveness in catalytic reactions such as HDS, HDN and carbon residue reduction in addition to the more operationally critical ability to mitigate sediment formation and reliably transport contaminants out of the reaction system without fouling. This finding is not limited to a specific comparison to ISOSLURRY™ catalysts: we noted the comparable case for ebullated bed Ni-Mo catalyst performance earlier in our discussion of the clear benefits of dual catalyst performance compared to soluble molybdenum co-catalyst coupled with single catalyst performance.

Significant advances in the chemical characterization of residuum petroleum materials coupled with innovation in synthesizing and understanding catalysts and catalyst systems has provided the refiner with an impressive portfolio of solutions for economic residuum hydrocracking. Catalysis and process research and development efforts by CLG and ART, coupled with in-depth analytical efforts at Chevron Energy Technology Company have, to a large part, made this possible. These efforts continue, not only to produce the cleaner vehicle and marine fuels of the future, but also to address the needs for greater petrochemicals production.

Additional Contributors
The authors would also like to thank the following individuals for their contributions to this article:

Dan Gillis, CLG
Bruce Reynolds, CLG
Cesar Ovalles, Chevron

References
Few refining industry issues have been as universally discussed by refiners over the last several years as the upcoming IMO regulations on marine fuel quality. As a critical change for the refining industry, there has been a tremendous amount of discussion around, and process strategy associated with the implementation of IMO 2020.

Grace, along with our partners at ART Hydroprocessing™, has been working for some time to understand the impact of IMO 2020 on refiners, and to identify the most profitable solutions to help refiners adapt to the new environment. While desulfurization via hydrocracking and hydrotreating are major components of many refiners’ strategies, a key unresolved problem for many refiners remains the FCC bottoms disposition.
In most refineries, the FCC bottoms is a reasonably high sulfur stream (1wt%+), and the combination of the high sulfur and the suspended catalyst particulates create a specific challenge for marine fuel blending under IMO 2020. Alternatives which have been discussed include FCC feedstock changes (lower S), routing the FCC bottoms to a resid hydrotreater/heavy oil upgrader, or routing the FCC bottoms to a coker. Each of these comes with their own set of costs and constraints and many refiners do not have multiple options.

At the same time, the value of middle distillates, including FCC LCO, is pushing toward a relative maximum. Figure 1 shows the projection (at the writing time of this article) for the US Gulf Coast price differential between ULSD and Regular Gasoline from Wood Mackenzie’s Product Markets Short Term service, which shows that middle distillates are expected to rise in value under the new IMO regulations, as low sulfur cutter stock is proposed as an option to manage the sulfur in the finished marine fuel blend.

Together, these forces line up to drive the incentive to upgrade FCC bottoms to an all-time high. Luckily, prior to the new IMO regulations, upgrading FCC bottoms to higher value products was often a strong economic driver on the FCC. With the onset of new marine regulations, this incentive is poised to become the most significant economic driver for even more FCCs globally.

**Catalytic Routes to Reducing FCC Bottoms**

There are two basic ways to reduce bottoms in the FCC through catalyst modification. The first is to improve the coke selectivity of the catalyst; due to the FCC heat balance, this will tend to drive higher Cat-to-Oil ratios, which will drive conversion of bottoms and LCO to Gasoline and LPG. The second is to drive higher bottoms destruction via active FCC matrix components; in some cases, these yield effects can be achieved in isolation, but in others, increasing FCC matrix will have additional impacts on the FCC yields.

To illustrate the difference between these approaches, Table 1 summarizes the potential yield shifts possible via catalytic changes pursuant to either route, in an example unconstrained FCC. With these yield patterns, we can examine the effects of either route as we apply varying economic sets to the yield pattern.

In Figure 2, we show the effect on profitability for each route as we increase the difference in price between FCC LCO and FCC gasoline. The modeling shows that a break-even point exists between the coke selectivity route and the bottoms cracking route as this differential is increased (in our case, at about $20/bbl delta); below this price differential, the coke selectivity route is economically favored; above this price differential, it is more profitable for the refiner to crack bottoms into LCO. This difference exists primarily because the coke selectivity route destroys LCO, where the bottoms cracking route increases its yield.

---

<table>
<thead>
<tr>
<th>Yield Component</th>
<th>Drive 1% of Bottoms to LCO via Matrix Cracking</th>
<th>Drive 1% Bottoms Reduction via Coke Selectivity Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas</td>
<td>-</td>
<td>-(0.19 wt%)</td>
</tr>
<tr>
<td>LPG</td>
<td>-</td>
<td>+1.5 vol%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>-</td>
<td>+1.5 vol%</td>
</tr>
<tr>
<td>LCO</td>
<td>+1.1 vol%</td>
<td>-(1.2 vol%)</td>
</tr>
<tr>
<td>Slurry</td>
<td>-1.0 vol%</td>
<td>-(1.0 vol%)</td>
</tr>
</tbody>
</table>

Table 1: Delta Yield Patterns for Coke Selectivity and Bottoms Cracking model cases.
It is critical to distinguish the bottoms cracking route from a traditional “LCO maximization” operation. In many LCO maximization cases, a refiner considers sacrificing FCC volume swell to increase LCO yields; in our model case, there is no volume swell loss. Even with the added volume gain in the improved coke selectivity case (+0.8 vol%), the improved bottoms upgrading case is more profitable when the differential between LCO and gasoline widens.

Therefore, we conclude that while attempting to destroy bottoms in the FCC to manage IMO can be done in several ways, the exact route chosen will have a very large impact on the resulting profitability of the operation. And of course, the model cases above are illustrative in nature; the exact optimization on any particular FCC operation must include a thorough review of unit constraints and all yield objectives (not simply bottoms upgrading). It should also be noted that the cases above do not consider feed quality or other refinery level processing adjustments that could be part of an IMO strategy.

Finally, through recent advances in catalyst technology, improved coke selectivity and matrix driven bottoms cracking are no longer independent catalytic functions; a great example of a combined approach is Grace’s FUSION™ technology (Introducing FUSION™ Catalysts – The Best of Both Worlds, page 12).

**Deploying FCC Matrix in Catalysts - the MIDAS® Catalyst Family**

Grace has deployed FCC catalysts with active matrix technology capable of upgrading FCC bottoms to LCO at hundreds of refineries. Our newest innovations, including our MIDAS® Gold technology, allow for the inclusion of a high degree of our signature mesoporosity, as well as an increased amount of macroporosity to extend the range of benefits that can be delivered by our catalyst solutions.

Figures 3 and 4 present unit data of one such application, where the use of MIDAS® increased FCC LCO by destroying FCC bottoms. In this case, the refiner’s primary target was to upgrade bottoms into LCO, and the catalyst employed was designed for this specific purpose. The baseline catalyst was a high Z/M formulation from Grace, which had previously been used to maximize gasoline + LPG make.

It is important to note that a reduction in FCC bottoms yield of 1 vol% of fresh feed (as in this example), can reduce the amount of FCC bottoms produced by 20-40% overall – significantly reducing the issues associated with blending this difficult stream.
Deploying Coke Selective FCC Catalysts

Since the advent of zeolitic cracking catalysts, a large number of catalytic advances have been aimed at improving coke selectivity. Much of the current expertise of modern catalyst manufacturer technology is aimed at producing higher conversions at lower coke levels. Whether through rare earth zeolite stabilization, metals tolerant FCC catalyst aluminas, integral metals traps in FCC particles, and even new advances like Grace’s RIVE® FCC catalysts (RIVE® FCC Catalyst Powered by Molecular Highway® Zeolite Technology, page 17), there are many examples of improvements in coke selectivity available via properly designed FCC catalyst systems. In most cases, the optimal way to improve coke selectivity in an FCC is a unit specific optimization, and Grace’s technical service team has been working this type of optimization effort at hundreds of refineries for several decades.

Key Conclusion

FCC bottoms can present a challenging stream for many FCC operators as IMO 2020 compliance plans are executed. Catalytic solutions exist to reduce FCC bottoms, and can take the form of solutions based on coke selectivity improvements or matrix driven bottoms upgrading to LCO, or a combination of the two routes. With multiple routes available to reduce FCC bottoms, the value to the refinery will depend on many factors; one critical factor is the price difference between FCC gasoline and FCC LCO, which is projected to widen under expected market conditions around implementation of IMO 2020. Grace’s MIDAS® catalyst family is a proven technology which has driven this bottoms upgrading to LCO at many FCCs around the world, and is a strong part of an IMO 2020 solution at many refineries. Additionally, many of Grace’s other catalyst technologies can deliver improved coke selectivity to FCC operations; and Grace’s new FUSION™ catalyst can deliver both functions in a single catalyst particle solution. ☺
A Revolution in the Lubricant Base Oil Industry

Over One Million Pounds of 5th Generation ISODEWAXING® Catalyst in Service

Kenneth Peinado
Global Lubes Sales Manager
ART

Over 25 years ago, in 1993, the first pound (actually more than 100,000 lbs.) of ISODEWAXING® (IDW®) catalyst was placed in service, which launched a revolution in the lubricant base oil industry. Since then, continuous R&D to improve IDW® catalysts done by Chevron and ART has led to significant breakthroughs, launching new generations of IDW® catalyst.

After many years of R&D, culminating in a rigorous 13 months of continuous testing on six different (and some very challenging) feeds in one of our research units, ART’s 5th generation IDW® catalyst was proven and ready to commercialize. The first pound (also over 100,000 lbs.) of this 5th generation of IDW® catalyst was placed in service at the end of 2016.
ART is very pleased to announce that in the 1st quarter of 2019, the 1,000,000th pound of this 5th generation IDW® catalyst was placed in service! This 1,000,000-pound milestone refers only to our 5th generation IDW® catalyst and does not include the accompanying IDW® guard catalyst or the hydrofinishing catalysts we produce. Currently more than 1.5 million pounds of our 5th generation IDW® catalyst have been (or are in the process of being) made. As of now, about 1.25 million pounds have already been put in service. And the limited amount that has not already been put in service is either on site, in transit, or being manufactured.

This unprecedented, rapid, successful deployment of 5th generation IDW® catalyst is enabled by demonstrated success in our client’s plants where the catalyst has consistently met or exceeded performance expectations, as seen in the following figures.

*ART’s R&D team began work on 6th generation IDW® catalysts before the first pound of 5th generation IDW® catalyst was put in service and we eagerly await its arrival in just a few more years.*

*In the meantime, we invite you to talk with us and learn more about what our 5th generation IDW® catalyst and our other top quality hydroprocessing catalysts can do for you. Get more information at arthydroprocessing.com.*

---

**Figure 1:** Improved Activity for Heavy Neutral (HN) Feed for Client A.

**Figure 2:** Improved Activity for Medium Neutral (MN) Feed for Client B.
SUCCESS STORIES

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Figure 3: Improved Activity for Heavy Neutral (HN) Feed for Client B.

Figure 4: Improved Base Oil Yield for Heavy Neutral (HN) Feed for Client B.
Figure 5: Improved Activity for Medium Neutral (MN) Feed for Client C.
Increasing Customer Sustainability

New FCC Additive Technology for SOx Reduction

Colin Baillie
Environmental Additives Manager
Grace FCC

Grace is proud that our products contribute to our customers’ sustainability objectives, whether the products improve our customers’ products or processes, enable our customers to reformulate their products to meet consumer demand, or help customers meet strict environmental standards. Approximately $0.3B of Grace’s 2018 sales were generated by products that directly enable customers to meet environmental standards. Examples include hydroprocessing catalysts to meet cleaner fuels standards (e.g., IMO 2020), colloidal silicas for vehicle emission control devices, and FCC additives to meet the toughest SOx and NOx emission standards from refinery operations. In this respect, Grace is pleased to announce the development of new FCC additive technology to further drive SOx emission reduction.
Introducing Super DESOX® CV+ Technology

During the process of SOx additive development, it is important to consider that there are three key steps in the SOx reduction mechanism. The first step occurs in the regenerator, where sulfur contained in the coke on the catalyst is oxidized to ca. 90% SO$_2$ and 10% SO$_3$. In this regards, cerium plays a critical role in promoting the full oxidation of SO$_2$ to SO$_3$ in the presence of oxygen. In the second step in the reaction mechanism, SO$_3$ is captured by a magnesium species to form magnesium sulfate in the regenerator. The third and final step occurs in the FCC reactor/stripper section, where magnesium sulfate is reduced to hydrogen sulfide. Here, both the magnesium and vanadium functionalities facilitate this additive regeneration step.

In 2018 Grace made a modification in its SOx additive manufacturing facilities, requiring significant capital investment. This has resulted in an improved version of its Super DESOX® additive for SOx reduction, with improvements to both product properties and performance. The improved SOx additives are being described as CV+ grades, which signifies an improvement in the cerium and vanadium dispersion across the additive particle. Cerium and vanadium dispersion plays an important role in SOx additive performance by enhancing the effectiveness in their key roles described. Figure 1 shows DCR pilot plant testing comparing SOx reduction for SOx additives with lower vanadium and cerium dispersion versus the same SOx additives with higher levels of vanadium and cerium dispersion. The pilot plant testing is initially operated without SOx additive to establish the baseline level of SOx, and then at ‘Time = 0 hours’ the SOx additive is introduced in a single dose to observe the initial level of SOx reduction. The subsequent period of time that it takes for the SOx emissions to increase back to the baseline level of SOx is used as a measurement for the additive’s effectiveness for SOx reduction. The additives with high and low vanadium dispersion were tested at the standard level of 1 wt.% oxygen, and the results highlight that both additives show the same initial level of SOx reduction, but the additive with a higher level of vanadium dispersion retains the SOx reduction activity for a larger period of time. When the additives with high and low cerium dispersion were tested at the standard level of 1 wt.% oxygen, both additives showed a similar profile for SOx reduction. However, when tested at a lower oxygen level of 0.2 wt.% the additive with a higher level of cerium dispersion shows an improved capability for SOx reduction. The testing highlights the importance of vanadium dispersion in full burn operations, as well as the benefits of improved cerium dispersion for lower oxygen or partial-burn applications.

Figure 1: DCR testing highlights the importance of vanadium and cerium dispersion across the additive particle for SOx reduction.

Grace’s Super DESOX® additives are unique in that they incorporate magnesium-aluminate (MgAl$_2$O$_4$) spinel technology. One of the founding SOx additive developmental publications describes that a stoichiometric amount of magnesium-aluminate spinel with free magnesium oxide (MgAl$_2$O$_4$·yMgO; y = 1) provides the maximum SOx pick up activity (Figure 2).$^1$ SOx pick up activity starts to drops off when higher than stoichiometric amounts of free MgO are present (MgAl$_2$O$_4$·yMgO; y > 1). In addition, the effect of reduction temperature in the riser on the sulfated additives was studied, and the results show that the reduction of MgSO$_4$ to H$_2$S is easier and requires lower temperature for the spinel-based additive compared to MgO-based additive (Figure 2). This highlights the importance of spinel technology for maximum SOx reduction performance.
Grace’s Super DESOX® CV+ additive has improved cerium and vanadium dispersion across the additive particle, and has an optimized spinel formation, resulting in improved SOx reduction performance compared to the non-CV+ grades. This is highlighted by the DCR pilot plant testing shown in Figure 3.

**Case Study of Super DESOX® CV+ Additive Performance Versus a Competitor Additive**

Refinery A in North America switched from a competitor SOx additive to Grace Super DESOX® CV+ additive in March 2019. Figure 4 shows the refinery operating data from January 2018 to June 2019. During the period of using competitor SOx additive, the SOx emissions were being maintained at low levels (average value of 9 ppm). Switching to Super DESOX® CV+ exceeded the goal of maintaining the very low SOx levels; in addition, a reduction to an average value of 4 ppm was observed. This reduction in SOx emissions is even more impressive when considering the SOx additive addition rate, which was reduced by approximately 50% with the use of Super DESOX® CV+.

At Refinery A, the base level of uncontrolled SOx (the level of SOx that would be obtained without the use of SOx additive) is calculated based on slurry sulfur levels. This allows the mass of SOx being captured to be calculated, which when divided by the mass of SOx additive being used gives a measure of the SOx additive effectiveness, known as the Pick Up Factor (PUF). Figure 5 highlights that the PUF increased considerably with the switch to Super DESOX® CV+, demonstrating the improvement in SOx reduction performance compared to the previous competitor additive being used.
Figure 4: Lower SOx emissions obtained using Super DESOX® CV+ and lower additive rates required.

Figure 5: Super DESOX® CV+ provided a significant increase in PUF.

The SOx emissions obtained using competitor additive versus Super DESOX® CV+ at comparable operating parameters is shown in Figure 6. The switch to Grace SOx additive provided lower SOx emissions when evaluated against constant levels of additive rate, excess oxygen, feed sulfur, and slurry sulfur.

Continued on Page 46
A summary of SOx additive performance is shown in Table 1. Super DESOX® CV+ provided (and continues to provide) lower SOx emissions at a lower additive addition rate. Some of the key operating parameters that can influence SOx emissions when using additive include feed sulfur, slurry sulfur, and excess oxygen. Table 1 highlights that these variables were in a similar range for both additives analyzed.

The switch from a competitor’s SOx additive to Super DESOX® CV+ has been considered a big success at Refinery A and the refinery continues to use the Super DESOX® CV+ to effectively control SOx emissions while achieving lower OpEx costs due to the reduced additive addition rate.

**Table 1: Summary of SOx Additive Performance.**

<table>
<thead>
<tr>
<th>Average Values</th>
<th>SOx (ppm)</th>
<th>Additive Rate lb/d</th>
<th>PUF</th>
<th>Feed S (wt.%%)</th>
<th>Slurry Sulfur (wt.%)</th>
<th>Excess O2 (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competitor</td>
<td>9</td>
<td>1153</td>
<td>8</td>
<td>0.7</td>
<td>1.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Super DESOX® CV+</td>
<td>4</td>
<td>515</td>
<td>16</td>
<td>0.6</td>
<td>1.4</td>
<td>4.2</td>
</tr>
</tbody>
</table>

**Figure 6:** Comparison of SOx Emissions vs Additive Rate, Excess Oxygen, Feed Sulfur, and Slurry Sulfur.
Case Study of Super DESOX® CV+ Additive Performance Versus Super DESOX®

Refinery B switched from Grace’s Super DESOX® additive to the new improved version (Super DESOX® CV+) in June 2018. As shown in Table 2, average feed sulfur and slurry sulfur levels were very similar during the trial period, resulting in a similar level of uncontrolled SOx as calculated using a refinery correlation. In addition, excess oxygen levels (which can impact additive performance) were also similar.

<table>
<thead>
<tr>
<th>Average Value</th>
<th>Super DESOX®</th>
<th>Super DESOX® CV+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Sulfur (wt.%)</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>Slurry Sulfur (wt.%)</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Excess Oxygen (vol.%)</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>% SOx Reduction</td>
<td>48%</td>
<td>60%</td>
</tr>
</tbody>
</table>

Table 2: Average Values of Key Parameters During Trial Period.

The SOx emissions dropped by 22% with the switch to Super DESOX® CV+. This translates to an improvement in SOx reduction levels from 47 to 59%, as highlighted in Figure 7.

Many refiners have long since used SOx reduction additives as part of their strategy for SOx emission compliance, however, there are an increasing number of applications, partly due to more stringent SOx emission legislation in various regions, as well as heightened interest to reduce WGS caustic costs. Grace was the first company to commercialize SOx additives, and continues to deliver improved performance with the recent commercialization of Super DESOX® CV+ technology. This improved additive provides increased levels of SOx reduction through higher cerium and vanadium dispersion across the additive particle, combined with an optimized spinel formation.

Several refiners are now using Super DESOX® CV+ additive, which is delivering a higher level of SOx reduction, as demonstrated by the two case studies described.

References
Introducing Breakthrough Zeolite Technology

RIVE® FCC catalysts powered by Molecular Highway® Y-zeolite (MHY™) technology enhances feed molecules’ access to and from active catalytic sites. These unique MHY™ zeolites crack larger FCC feed molecules more selectively which allow refiners to make more of what they want and less of what they don’t.

This is the first and only use of ordered mesoporosity in FCC zeolites or catalysts that have been proven to allow rapid transport of highly reactive valuable LPG olefins out of the zeolite, thereby enhancing LPG olefinicity. With enhanced diffusion of hydrocarbons into and out of the catalyst particle, allows refiners to process heavier opportunity feeds, reduce costs, circulate more catalyst, and preserve valuable products increasing operating flexibility.

Find out more about this breakthrough technology today at grace.com/RIVE

Molecular Highway® Y-zeolite (MHY™) Technology

Small pores in conventional Y zeolites work well with molecules that boil up to 950°F (510°C).

MHY™ zeolite technology creates larger pores, allowing zeolites to crack larger molecules that boil in the 950-1100°F (510-593°C) range.

Ask us about our proven, novel approach to:
- Increased LPG olefinicity
- Increase gasoline octane
- Decreased delta coke
- Improved bottoms upgrading
- Increased operational flexibility to the refiner
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