

ISSUE 88 | SPRING 2018

Catalyst Courier

Innovative times: How Albemarle meets
complex technical and commercial challenges

GRANITE™: step-out advances in our line of
FCC products

Under the microscope: Looking at the impact
of metal contaminants on catalysts

 ALBEMARLE®

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EVENTS DIARY 2018

March

- 6–7 ERTC: Ask the Experts, Budapest, Hungary
- 11–13 AFPM Annual Meeting, New Orleans, LA, USA
- 20–22 FCC Course, Houston, TX, USA
- 25–27 AFPM International Petrochemical Conference, San Antonio, TX, USA

May

- 22–24 13th China International Battery Fair (CIBF), Shenzhen, China
- 22–24 FCC course, Amsterdam, the Netherlands

August

- 15–17 HPC Course, Galveston, TX, USA
- 21–22 AFPM Cat Cracker Seminar, Houston, TX, USA
- 23–24 FCC Course, Houston, TX, USA

September

- 10–12 Abu Dhabi International Downstream Summit, Abu Dhabi, UAE

November

- 27–29 ERTC, Cannes, France

Managing editor
Brooke Robertson
E: brooke.robertson@albemarle.com

Correspondence and distribution for *Catalyst Courier*
Hailey Cobb
Albemarle Corporation
4350 Congress Street, Suite 700, Charlotte, NC 28209, USA
www.albemarle.com
E: catmaster@albemarle.com

For North and South America, contact:
Albemarle Corporation
T: +1 281 480 4747
E: catmaster@albemarle.com

For Europe, the Middle East, CIS and the Indian subcontinent, contact:
Albemarle BV
T: +31 20 6347300
E: catmaster@albemarle.com

For Asia Pacific, contact:
Albemarle Chemicals (Shanghai) Co., Ltd
T: +86 21 6103 8666
E: catmaster@albemarle.com

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SILVIO GHYOOT
PRESIDENT,
CATALYSTS



ADAPTING TO CHANGE: ANTICIPATE, INNOVATE AND COLLABORATE

The oil and gas industry is changing. For example, 10 years ago no one would have believed that the USA could be a major producer and exporter. Meanwhile, in the Middle East, the emphasis has shifted from selling crude to refining and selling finished or semifinished fuels and petrochemical products.

Our response to ongoing changes is to anticipate customers' needs, to create innovative solutions and to find collaborative ventures that deliver what our customers need.

At the start of 2018, we renamed our Refining Solutions global business unit; it is now known as Catalysts and contains all Albemarle catalysts in a single business unit. We believe this reflects better the changing needs and priorities of our customers.

One of the challenges in developing effective catalyst products is striking the right balance for a variety of performance and physical property parameters. Catalyst technologies that provide greater formulation flexibility enable solutions offering higher refiner profitability, as catalyst performance can be tuned to meet customers' needs more precisely. In this issue of *Catalyst Courier*, we take a look at GRANITE™, a new technology that gives FCC catalysts outstanding coke selectivity, increased formulation flexibility and improved physical properties. Refiners can use GRANITE-based catalysts to achieve a variety of objectives, from increased bottoms upgrading to an improved product slate.

We also examine the factors that influence metal poisoning in catalysts. Joint studies with customers help us to understand the challenges demanding oil feedstocks pose. By knowing how our catalysts digest these oils and understanding the mechanisms of metal poisoning, we can fine-tune our products. This enables us to protect the catalyst and helps our customers to maximize profit through continuous, trouble-free operations.

At Albemarle, we believe that innovation helps our customers to meet the demands of the market and comply with new regulations. We are adopting a new approach – evidenced by the development of new products such as EVEREST™, PEAK™ AND DENALI™ – where our emphasis is on developing and moving rapidly to market. This will involve bringing customers into the loop for early discovery and fine-tuning of the products. Rather than doing everything all at once by ourselves, we are developing corporate partnerships with customers or co-producers to combine skills and knowledge.

A stylized, handwritten signature in black ink, appearing to read 'S. Ghyoot'.

SILVIO GHYOOT
PRESIDENT, CATALYSTS

ALKYCLEAN® TECHNOLOGY WINS KIRKPATRICK CHEMICAL ENGINEERING AWARD



AlkyClean technology has won the 44th Annual Kirkpatrick Prize, as announced at the Chem Show in New York on 1 November 2017. This award honors the most noteworthy chemical engineering technology commercialized anywhere in the world over the past two years.

The winning technology applies the proprietary Albemarle AlkyStar® catalyst. Developed jointly with CB&I and Neste, it eliminates the use of liquid acids for the production of motor fuel alkylate. This eliminates the hazards, and environmental and operating issues associated with handling liquid acids.

Only six finalists were selected from the many submissions to *Chemical Engineering* magazine. The criteria for winning include novelty, difficulty of the chemical engineering problem being solved and overall engineering excellence.



This award honors the most noteworthy chemical engineering technology commercialized anywhere in the world over the past two years. ”

ALBEMARLE WELCOMES NEW CHIEF STRATEGY OFFICER



ERIC W. NORRIS

Eric W. Norris has joined Albemarle as chief strategy officer. Norris has over 20 years of experience in corporate development and business leadership, including 15 years at FMC Corp.

Most recently, he served as president, FMC Health and Nutrition, and before that, he spent five years in FMC's lithium segment, first as global commercial director and then as vice president and global business director. His other roles at FMC included director, corporate development, and director, healthcare ventures in its biopolymer segment.

"We are delighted to welcome Eric to Albemarle," said Luke Kissam, chairman, president and chief executive officer, Albemarle. "We look forward to the leadership and contributions his wealth of experience will bring to us. I am confident that his business experiences and insights, combined with his leadership skills, will allow him to make significant contributions to Albemarle's future success."

NEW GRANITE™ TECHNOLOGY FOR FCC

Albemarle has launched GRANITE, a new technology for the FCC catalyst market. Its novel matrix-binder system increases the flexibility of the formulation window. This enables refiners, whether they focus on fuel or petrochemical production, to maximize profitability through better bottoms upgrading and yields, improved coke selectivity and higher zeolite stability. GRANITE technology brings additional value to refiners' operations through new options, and reinforces Albemarle's long-standing position as an FCC market leader.

"Albemarle is proud to offer new technologies that give our customers operational flexibility and higher profits. We are committed to developing superior catalyst solutions that our customers can use to meet their toughest challenges," says Dave Clary, vice president, FCC.

The first catalyst product lines under the GRANITE technology platform are PEAK™, EVEREST™ and DENALI™.



THE ALBEMARLE FOUNDATION: 10 YEARS OF SUPPORT IN OUR COMMUNITIES

Since its inception in 2007, the Albemarle Foundation, a private nonprofit organization and Albemarle's primary vehicle for philanthropy, has granted over \$28,500,000 to the communities in which Albemarle employees live and operate.

The foundation focuses on education, health and social programs, and cultural initiatives. Employees play critical roles in directing funds and leveraging support to give back in a way that is meaningful to their communities. To encourage their charitable efforts, the Albemarle Foundation also offers a matching gift and volunteer grant program that matches employee donations over \$50 to nonprofit organizations. In addition, it donates \$500 for every 35 hours' volunteering to honor the incredible efforts of each engaged employee.

The projects that the Albemarle Foundation has supported are varied. For example, through Habitat for Humanity, the Albemarle Foundation has funded and built more than five homes in the Houston area.

Our employees volunteered with building tasks, including construction, painting and clearing debris.

Bayport, Clear Lake and Pasadena employees have also had positive impacts on local schools, including providing a grant to bring a bilingual book series into the La Porte school system through La Porte Education Foundation for elementary school children throughout the school district. Programs such as these help to inspire the pupils who will lead Houston's future.

Mentoring lunches also take place throughout the school districts. "I often see students who are not always thinking about their future, but going through some of the mentor lunches with the Albemarle Foundation broadens their horizons. They talk more about: 'I do want to go to college because that's something I could do.' That, to me, is impactful because we have just totally changed the track of someone's life," explains one schoolteacher.

Baton Rouge employees support local schools by tutoring and mentoring as well as providing monetary support to volunteers in schools, City Year Baton Rouge and Teach For America. "I sort of see Albemarle as a guardian angel," a local school employee remarks. "I believe the Albemarle Foundation has absolutely helped us grow."

Other key projects in Baton Rouge involve helping Cancer Services of Greater Baton Rouge, Habitat for Humanity and the regional burn center. One employee talks highly of these projects, enthusing, "You gain more than you give."

Our Magnolia employees helped to fund the South Arkansas University summer enrichment camp, the Mulerider Kids College. This camp provides the opportunities for children to learn without the pressure of grades, homework or tests. With the Albemarle Foundation's support, the Mulerider Kids College was able to provide scholarships, additional supplies and a great summer experience, and even to cater for teens in its new program, Mulerider Teen College.

Among many other donations, employees' dollars went to the local boy scouts troop and the fire station to help fund a new truck.

We are proud of our employees and retirees alike for their charitable giving and would like to thank them for their continuing efforts and for Growing the Good!

For further information on our projects and how you can get involved, please contact **Sandra Holub, executive director**, sandra.holub@albemarle.com.





DAVE CLARY
VICE PRESIDENT,
HEAVY OIL UPGRADING

INNOVATION IN A TIME OF CHANGE

Driving product development to meet complex technical and commercial challenges

Today's energy market can be a volatile and uncertain arena characterized by sudden shifts in supply and demand dynamics. To remain competitive and to achieve their business goals, refiners are constantly looking for ways to increase operational efficiency, maximize the volumes of high-value products and reduce costs. Every refinery has its own unique configuration and constraints. This makes the needs of each facility different, but there are several fundamental challenges that every refiner faces: coping with feedstock variability, managing product quality and maintaining process efficiency and reliability. For many refiners, ultimate profitability depends on how they address and manage these challenges.

In North America, for example, we find refiners having to adjust to changing feedstock compositions; widening price differentials for gasoline products; and regulatory changes that pose increasingly complex challenges to operational decision making. Currently, the focus is very much on the octane content of gasoline. Back in 2000, the price difference between premium octane and regular grades was about 18¢ a gallon, but this has increased year on year. In 2017, it averaged 50¢ a gallon. There are several reasons behind this rise in the value of high-octane gasoline.

One aspect is changing regulations. Engine manufacturers are pushing toward improved engine efficiency, which requires fuel with higher octane ratings, while the deep desulfurization processes needed to produce Tier 3 gasoline cuts octane content. Traditional octane boosters, such as methyl tert-butyl ether and lead, have been banned in the USA and been mostly replaced with ethanol. Ethanol has a high

octane rating but cannot be blended into gasoline at concentrations above 10% owing to concerns about the formation of ground ozone.

The increasing use of light tight oil is another factor. This has resulted in higher yields of naphtha with a high paraffin content. However, naphtha has a low octane content and paraffins tend to depress refinery stream octane levels. One solution adopted by many refiners is to maximize the production of alkylate, a high octane, low-sulfur blend component. This approach requires increased production of C₄ olefins, typically from the FCC unit.

In a complex picture such as this, refiners can find the optimal solution and boost their profits by optimizing multiple operational variables together. In this case, the solution might involve the FCC pretreat catalyst (in a hydrotreating operation), the FCC catalyst and the operation itself to maximize gasoline octane directly and to make C₄s to feed the alkylation unit,



consideration of gasoline-sulfur reduction additives for the FCC unit, and optimizing the catalyst and operations for the naphtha hydrotreater to minimize octane loss while meeting sulfur-reduction targets.

Albemarle offers established industry-leading products and a selection of new products to address the issues facing North American refiners, as outlined above. In FCC pretreating, for example, we can help refiners reduce sulfur in FCC feed (maximum hydrodesulfurization) with a combination of Ketjenfine® (KF) 780 STARS® catalyst and STAX® technology solutions. This includes providing tailor-made catalyst systems to help customers meet tough Tier 3 targets. Our ACTION® catalyst for FCC is the leading product for C₄s and octane, and we are currently commercializing a new gasoline-sulfur reduction additive, R-950+, which outperforms the previous industry standard: Albemarle's R-950.

Our RT-235 catalyst for naphtha hydrotreating is a market leader in octane retention and is delivering increased margins for refiners in more than 20 commercial applications. It offers superior hydrodesulfurization activity that means it can handle severe feedstocks with high sulfur levels while enabling refiners to meet more-stringent sulfur specifications.

Other industry trends

Whatever feedstocks they choose or operational and regulatory challenges they face, our customers all have one thing in common: a desire to maximize the profitability of their operations and the return from their investments. One way that leading refiners stay competitive is by adopting the latest catalyst technologies. We have a long-established commitment to research and development and the focus of these efforts has always on been helping customers respond to and thrive in changing conditions.



“Our ACTION catalyst for FCC is the leading product for C₄s and octane, and we are currently commercializing a new gasoline-sulfur reduction additive. Our RT-235 catalyst for naphtha hydrotreating is a market leader in octane retention and is delivering increased margins for refiners in more than 20 commercial applications.”



There are several global business trends that present a direct challenge to refinery operators and to the catalyst systems that they choose. The most significant of these trends are

- regulations designed to lower emissions
- new clean fuel specifications
- new maritime regulations: the introduction of the International Maritime Organization's 2020 fuel sulfur cap
- electrification: the shift in land transportation toward electric vehicles
- integration with chemical plants.

These trends have compelled many refineries to adapt their operations. Refiners have also focused on improving energy efficiency, enhancing reliability and improving contaminant removal to reduce their environmental footprint, which makes it easier to achieve the required product specifications.

New transport specifications

Adapting products to meet new fuel specifications is always a challenge. The International Maritime Organization is tightening the regulations for marine fuel oil by lowering the maximum permissible sulfur content from 3.5 to 0.5%. This change will require a coordinated response from the shipping industry and from refiners. Ship owners and operators will have to change over to low-sulfur fuel oil systems, install onboard scrubbers or switch the vessel to liquefied natural gas fuel. For refiners, the challenge will be to reduce the sulfur levels in their fuel oil drastically by means of desulfurization or conversion processes or by blending with ultra-low-sulfur diesel.

In land transport, the trend toward vehicle electrification will clearly have a major impact on demand for transport fuels. This trend is well-established in some parts of the world, notably Europe, where the German government has set an official deadline for a ban on gasoline-powered cars: all new cars are mandated to be electric by 2030.

Across Europe, governments have been encouraging energy saving for many years and promoting public transportation and renewable resources to combat climate change. Motor vehicles are becoming more and more efficient and using less and less fuel. Future trends toward driverless cars and the expected switch to fleet-owned cars that users hire as needed should significantly reduce the number of vehicles needed.

For refiners, this trend toward vehicle electrification and the reduced demand for traditional road traffic fuels will mean a shift in the market for the products they produce, with greater emphasis on aromatics or chemicals, kerosene for jet fuel, petrochemical feedstocks and fuels for power generation.

Enhancing performance and reliability in FCC units

Faced with the need to adjust production in response to changing market conditions, refiners are looking for technologies that offer flexibility and can deliver specific improvements in the operation of FCC units. In November 2017, Albemarle provided a new solution in this area and expanded its FCC product portfolio with the launch of the GRANITE™ catalyst technology platform.

GRANITE technology uses a novel matrix-binder system to increase the flexibility of the formulation window for maximum catalyst customization. This enables refiners to maximize profitability through better bottoms upgrading and yields, improved coke selectivity and higher zeolite stability. The technology is designed to help refiners' operations by delivering enhanced performance and reliability.

Modern catalyst technologies should help operators in their quest to minimize the volumes of low-value products and boost the yield of valuable products. The launch of the GRANITE technology platform reinforces Albemarle's long-standing leadership position in the FCC market and its continuing focus on improving both fuels and petrochemicals. The first catalyst

products available under the new platform are PEAK™ ACTION® and EVEREST™ ACTION, both of which are designed to deliver superior butylene and octane.

PEAK ACTION catalyst uses our new ADM™-80 binder technology. It offers improved physical properties that open a wider catalyst formulation window and enables the inclusion of higher levels of premium active components. The significant improvements in butylene yield, butylene selectivity with liquefied petroleum gas yield and gasoline octane and the marked increase in the product LCO-to-bottoms ratio, makes PEAK ACTION catalyst an effective option for refiners seeking to maximize octane barrels and achieve high butylene yields and the highest possible bottoms conversion.

The other product currently available within the GRANITE platform is EVEREST ACTION. This product relies on Albemarle's novel matrix-binder system ADM-85, which expands the formulation window and provides enhanced coke selectivity and zeolite stability. Catalysts formulated with ADM-85 consistently exhibit coke yields 8–15% lower than analogous formulations without ADM-85, and relative zeolite surface area retentions more than 30% higher in laboratory deactivations.

Thanks to the superior binding that ADM-85 offers, EVEREST ACTION catalyst can raise the maximum level of ADZT-100 system in the formulation, which provides a ceiling on butylene yield that is even higher than that obtained with PEAK ACTION catalyst.

Ready for a new business landscape

One of the main challenges in catalyst research and development is the time it takes to test potential products and assess their suitability for commercialization. At Albemarle, we make use of our high-throughput unit to accelerate the process. This unit plays an important role in the development of our new technology platforms. Bringing products to market more quickly enables us to respond to

the needs of customers and help them to achieve their operational objectives. Developing and maintaining close links with our customers helps us to understand more clearly what the challenges are in a specific refinery and to ensure that we match the appropriate catalysts to customers' needs.

The scientists and engineers at Albemarle are already developing additional products within the GRANITE technology platform. For example, work is under way to develop products that will improve bottoms cracking and deliver further reductions in coke make. The principle behind this research is to give refiners the tools they need to achieve continuous improvement in the economic value of their FCC products and make it easier for them to handle and generate value from difficult crudes.

We are also actively developing products for the chemical-driven FCC market with the major focus being to develop methods that will increase propylene production.

Future refineries will probably have very different configurations, constraints and priorities compared to those in operation today. Albemarle is preparing catalysts and additive technologies that will enable refiners to make the journey and to protect their commercial performance in a new business landscape.

FOR MORE INFORMATION, CONTACT:

Dave Clary

Email: dave.clary@albemarle.com



At Albemarle, we make use of our high-throughput unit to accelerate the process. This unit plays an important role in the development of our new technology platforms. Bringing products to market more quickly enables us to respond to the needs of customers and help them to achieve their operational objectives.



PEAK™ ACTION® AND EVEREST™ ACTION: ALBEMARLE'S INNOVATIVE GRANITE™ FCC TECHNOLOGY

A novel matrix–binder system provides enhanced butylene and gasoline octane

Albemarle understands that refiners are facing an array of challenges to profitable operation in the form of difficult feeds, frequently changing market conditions and increasingly stringent environmental regulations, all of which exert downward pressure on margins. Consequently, the company has introduced GRANITE technology into this highly competitive environment to provide the most flexible and effective portfolio of tunable catalyst and additive products available.

Utilizing a novel matrix–binder system, GRANITE catalysts feature a wide and flexible formulation window with enhanced binding and improved zeolite stability. This enables Albemarle to formulate catalysts in a highly specific, focused manner so that FCC unit operators can optimally target the most-valuable products. GRANITE technology includes several new products: PEAK ACTION and EVEREST ACTION are the first catalyst options in this bold and innovative technology. They represent step-out advances in Albemarle's commercially proven and highly successful ACTION line of products.

	ACTION CATALYST	PEAK ACTION CATALYST
C ₄₊ , vol%	8.7	+1.5
C ₃₊ , vol%	9.6	+0.9
ΔC ₄₊ /ΔC ₃₊ (v/v)	Base	+1.7
C ₄₊ /LPG (v/v)	Base	+14% (relative)
LCO/BOTTOMS	Base	+12% (relative)
RON	Base	+0.8
MON	Base	+0.5
CAR	Base	Base

Table 1: Comparison of a PEAK ACTION with conventional ACTION catalyst in a commercial operation.

Enhanced butylene and gasoline octane with superior bottoms upgrade

Employing the newly unveiled ADM™-80 binder technology, PEAK ACTION catalyst exhibits improved physical properties that open a wider catalyst formulation window and enable the inclusion of higher levels of premium active components than in standard ACTION catalysts. It also leverages ADZT™-100, the shape-selective zeolite technology system associated with Albemarle's commercially proven ACTION product line. Consequently, PEAK ACTION catalyst can deliver even better butylene yields and gasoline octane through a highly active formulation for overall conversion and bottoms upgrading.

Table 1 shows the differences between a PEAK ACTION and a conventional ACTION catalyst in an application with a full-burn unit processing a 2.5-wt% Conradson carbon residue feed with a combined E-cat nickel plus vanadium level above 5000 ppmw.

PEAK ACTION catalyst significantly improves butylene yield, butylene selectivity with LPG yield and gasoline octane, and provides a marked increase in the product LCO-to-bottoms ratio. It is a powerful and effective option for refiners seeking maximized octane barrels, high butylene yields and the highest possible bottoms conversion.

Enhanced butylene and gasoline octane from a highly coke selective catalyst

EVEREST ACTION catalyst is built on ADM-85, Albemarle's novel new matrix–binder system, which provides enhanced coke selectivity and zeolite stability in addition to expanding the formulation window. Catalysts formulated with ADM-85 consistently exhibit coke yields 8–15% lower than analogous formulations without ADM-85 and relative zeolite surface area retentions 10–30% higher in laboratory deactivations.

	CONVENTIONAL ACTION CATALYST	EVEREST ACTION CATALYST
Fresh surface area, m ² /g	266	311
Fresh matrix surface area, m ² /g	139	134
Fresh zeolite surface area, m ² /g	127	177
Fresh attrition index	2.9	3.0
Fresh rare earth oxide, wt%	2.73	1.4
Deactivation	CD	CD
Deactivated surface area, m ² /g	166	196
Deactivated matrix surface area, m ² /g	97	90
Deactivated zeolite surface area, m ² /g	69	106
Surface area retention, %	62	63
Fresh matrix surface retention, %	70	67
Fresh zeolite surface area retention, %	54	60

Table 2: Properties of fresh and deactivated conventional ACTION and EVEREST ACTION samples.



The catalyst exploits the superior binding power of ADM-85 to raise the maximum level of ADZT-100 system in the formulation further compared with conventional ACTION catalysts to provide an even higher butylene yield ceiling.

In addition, higher levels of other active components are also achievable. This capability, along with the enhanced zeolite stability, enables the formulation of a high-activity EVEREST ACTION catalyst at a significantly lower rare earth level than would be possible otherwise, with the attendant butylene and octane bonuses that result.

In the following case study, a conventional ACTION and an EVEREST ACTION catalyst are compared with a typical UPGRADER™ catalyst containing a conventional ZSM-5 additive. The properties for the fresh and deactivated ACTION and EVEREST ACTION catalysts are shown in Table 2.

The EVEREST ACTION catalyst exhibits a significantly higher fresh zeolite surface area than the conventional ACTION

catalyst, which reflects its higher zeolite content. Furthermore, the zeolite retention of the EVEREST ACTION catalyst is better, which is a consequence of the stabilizing presence of the ADM-85. Note the lower total rare earth oxide content of the EVEREST ACTION catalyst and the even more marked difference in the rare earth oxide on zeolite. Despite the lower rare earth oxide content, more of the zeolite is preserved for the EVEREST ACTION catalyst during the deactivation process. In ACE testing, the activity for the EVEREST ACTION catalyst was identical to that of the conventional ACTION catalyst within the natural variations of the test, despite the lower rare earth oxide content.

Also note that the attrition indices for the two samples are almost identical, even though the EVEREST ACTION catalyst contains a higher proportion of functional components. Conversely, if desired, the EVEREST ACTION catalyst could have been provided at a more similar formulation to the conventional ACTION catalyst but with a significantly higher attrition resistance.

The results from ACE testing also showed the significant advantage associated with EVEREST ACTION catalyst for butylene production. In Figure 1, EVEREST ACTION catalyst is referenced against a conventional UPGRADER catalyst and compared with an UPGRADER catalyst containing ZSM-5 additive and a conventional ACTION catalyst formulation. The remarkable butylene increase is clear: ~1.5 wt% more for the EVEREST ACTION catalyst.

EVEREST ACTION catalyst also represents a step-out improvement in gasoline octane barrels. Figure 2 compares the octane gain per unit of gasoline lost for each catalyst relative to the UPGRADER reference. Both ACTION catalysts show a distinct benefit relative to the UPGRADER/ZSM-5 additive, but the EVEREST ACTION catalyst shows a marked improvement even relative to the conventional ACTION catalyst, itself a widely recognized and employed premium gasoline octane catalyst.

In addition to these yield improvements, EVEREST ACTION catalyst also exhibits

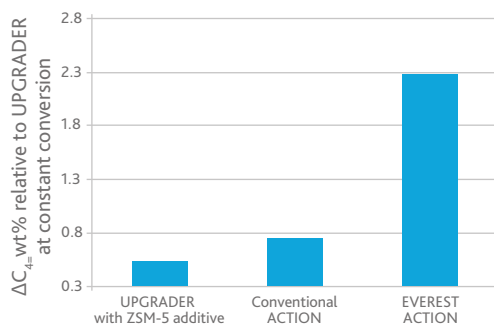


Figure 1: Butylene production at constant conversion relative to UPGRADER catalyst.

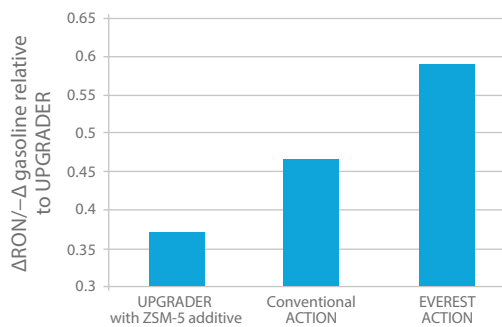


Figure 2: Δ RON/-Δ gasoline relative to UPGRADER catalyst.



improved coke selectivity. This is clearly seen in Figure 3, where the UPGRADER and conventional ACTION catalysts exhibit comparable coke yields, but the EVEREST ACTION catalyst with ADM-85 shows a 15% relative decrease.

Finally, EVEREST ACTION catalyst features the same recognized superior bottoms upgrading that characterizes the existing UPGRADER and ACTION catalyst lines. Combined with the enhanced coke selectivity provided by ADM-85, this results in a marked advantage for the EVEREST ACTION catalyst relative to the conventional UPGRADER and ACTION samples, as shown in Figure 4.

EVEREST ACTION is the catalyst of choice for targeting high butylene yields and octane barrels, while providing superior bottoms upgrading with excellent coke selectivity.

GRANITE technology: Improved economics; greater flexibility

PEAK ACTION catalyst adds premium value through

- increased production of alky unit feedstock
- superior butylene selectivity per LPG gain, which is critical for wet-gas-limited operations
- higher octane with minimum gasoline loss
- the highest possible bottoms upgrading.

EVEREST ACTION catalyst augments these advantages through

- an even wider formulation window that pushes the attainable butylene yields even higher
- the highest octane barrels
- excellent bottoms upgrading
- enhanced zeolite stability
- improved coke selectivity
- improved attrition resistance for comparable formulations.

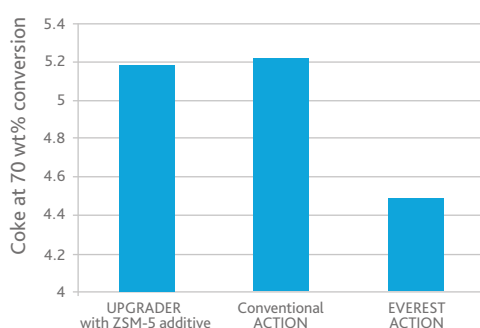


Figure 3: The coke benefit of EVEREST ACTION catalyst relative to UPGRADER and conventional ACTION catalysts.

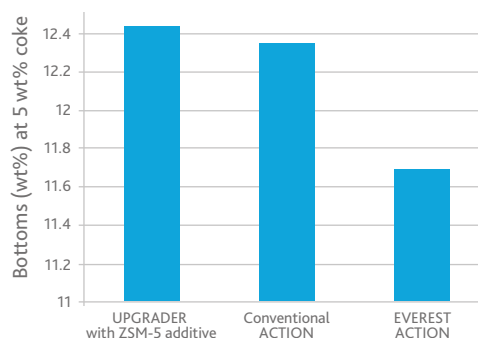


Figure 4: The bottoms upgrading benefit of EVEREST ACTION catalyst relative to UPGRADER catalyst at constant coke.

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GRANITE technology includes several new products: PEAK ACTION and EVEREST ACTION are the first catalyst options in this bold and innovative technology. They represent step-out advances in Albemarle's commercially proven and highly successful ACTION line of products. ”



PIONEERING INSIGHTS INTO METAL POISONING OF FCC CATALYSTS

Albemarle collaborates with Utrecht University and SLAC National Accelerator Laboratory to understand the impact of metal contaminants on catalysts at the microscopic level

The effects of contaminant metals on catalysts are key issues for any refiner operating an FCC unit.¹ Of the many effects, metals lead to collapse of the active zeolite, sintering of the active matrix, pore blocking and increased dehydrogenation reactions. To facilitate the development of future catalysts, Albemarle has collaborated with Utrecht University in the Netherlands and the SLAC National Accelerator Laboratory in the USA to study the impact of contaminants on catalyst architecture. The collaborative team has leveraged X-ray nanotomography techniques to the next level to create 3D maps of both the macropores and the contaminant metals within an FCC catalyst, thereby creating new insights into the fundamentals of metal poisoning of FCC catalysts.

X-ray nanotomography for measuring metals in FCC catalysts

This breakthrough X-ray nanotomography characterization method utilizes advanced software to reconstruct 3D images of whole FCC catalyst particles from a collection of 2D images taken using synchrotron-based, full-field, transmission X-ray microscopy. Figure 1 shows a schematic representation of the apparatus.

The transmission X-ray microscope works much like an optical microscope but using X-rays rather than visible light. Special optics (a) focus the X-rays onto a sample and illuminate its entirety with a large field of view. After the X-rays penetrate the sample, they strike a scintillator screen (e) that converts them into visible light recordable by a camera chip (like those used in smart phones and similar devices but more advanced). Image magnification is achieved using a zone plate (d), which is a Fresnel lens similar to a lens that might be found in a lighthouse but for X-rays.

The catalyst particle is mounted in a transparent capillary that holds it securely and permits rotation (c).

Typically, more than 100 projection images are acquired for each sample at different angles. The 2D resolution of these projection images is better than 50 nm with a 32-nm² pixel size. Advanced mathematical algorithms then combine these 2D images to create a complete 3D representation of the catalyst particle (f). The resultant 3D data are downsampled to 64 nm³ voxels to achieve a 3D resolution of about 300 nm at the 95% confidence level, i.e., the technique captures macropores in this size regime. The final images show the fine details of the sample's inner structure, including regions of higher or lesser material density. Macroporous features such as holes or pores are clearly visible.

The collaborative team leveraged this technique in a remarkable way to reveal the distribution of individual metal contaminants within a FCC catalyst particle, as each element absorbs X-rays

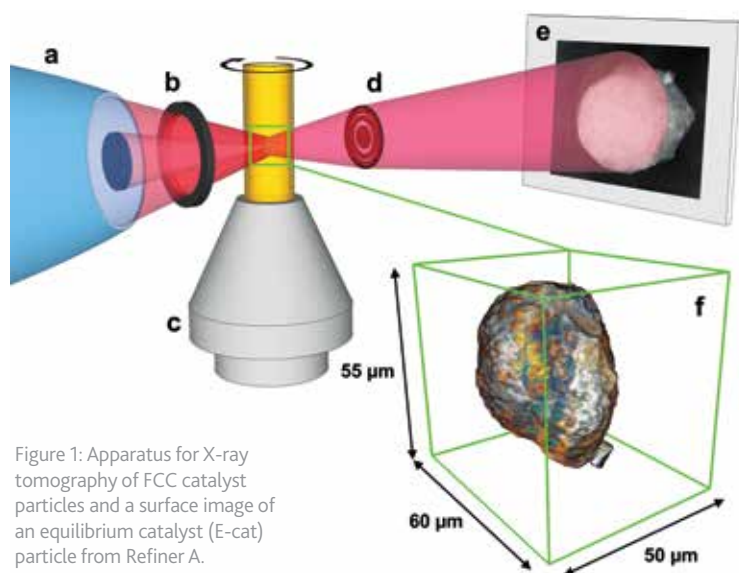


Figure 1: Apparatus for X-ray tomography of FCC catalyst particles and a surface image of an equilibrium catalyst (E-cat) particle from Refiner A.

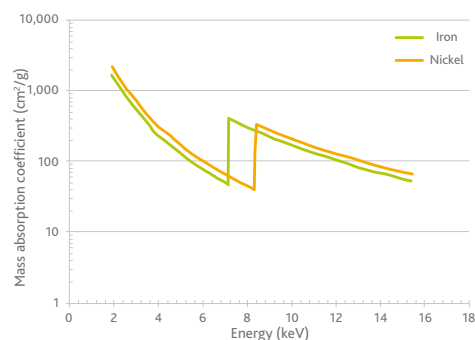


Figure 2: Absorption versus energy (absorption edges) for iron and nickel.³



differently. At a specific energy level, an individual element will absorb X-rays much more strongly than other elements. This abrupt increase in X-ray absorption is called the X-ray absorption edge of an element (Figure 2). To reveal the distribution of the individual elements, such as iron or nickel, the team took two X-ray images: below and above the absorption edge, i.e., strong metal absorption “on” and “off” respectively. The differential absorption contrast between the two images provided an image showing an individual metal’s distribution. The team then assembled these 2D images into a 3D image, this time of the contaminant metal. Reference 2 gives additional details of this advanced tomography technique.

Pore network morphology: Case study for Refinery A

Results from fresh and E-cat taken from Refinery A illustrate the salient capabilities of the method. Bulk analysis showed the

E-cat having 0.65 wt% added iron(III) oxide (Fe_2O_3) and 0.59 wt% added nickel(II) oxide (NiO). Figure 3 shows the remarkably detailed macropore morphology within a segment of a catalyst particle from Refiner A. Figure 3(a) shows a virtual slice through the particle based on tomography data recorded using transmission X-ray microscopy. The red and green color maps show the 3D distributions of iron and nickel respectively.

A sub-volume indicated by the red frame is enlarged to show the distribution of metals in the catalyst’s pore space. In Figure 3(b) (iron switched off), the pore space is displayed with and without a “network mesh” to show the pore connectivity, as generated from the measured pore distribution. In Figure 3(c) (iron switched on), the pore network is again displayed showing the influence of iron on the network. The pore size, tortuosity, location and overall complexity are readily visible.

Using advanced simulation methods, one can select any point of ingress in the particle and move virtually throughout the particle while making observations. These methods powerfully illustrate the morphology of the pore network in FCC catalysts and the actual locations of metal poisons.

3D assessment of particle accessibility

Perhaps the most insightful information comes from quantifying the macropores on a particle’s surface and the impact of contaminant metals on these same macropores. Surface macropores are extremely important to catalyst performance, as they provide pathways into the particle’s interior, which contains substantial amounts of active ingredients. Most people are familiar with the elongated, oval maps that are often used to represent the Earth. These same Mollweide projections can illustrate 3D tomography data on a 2D surface.

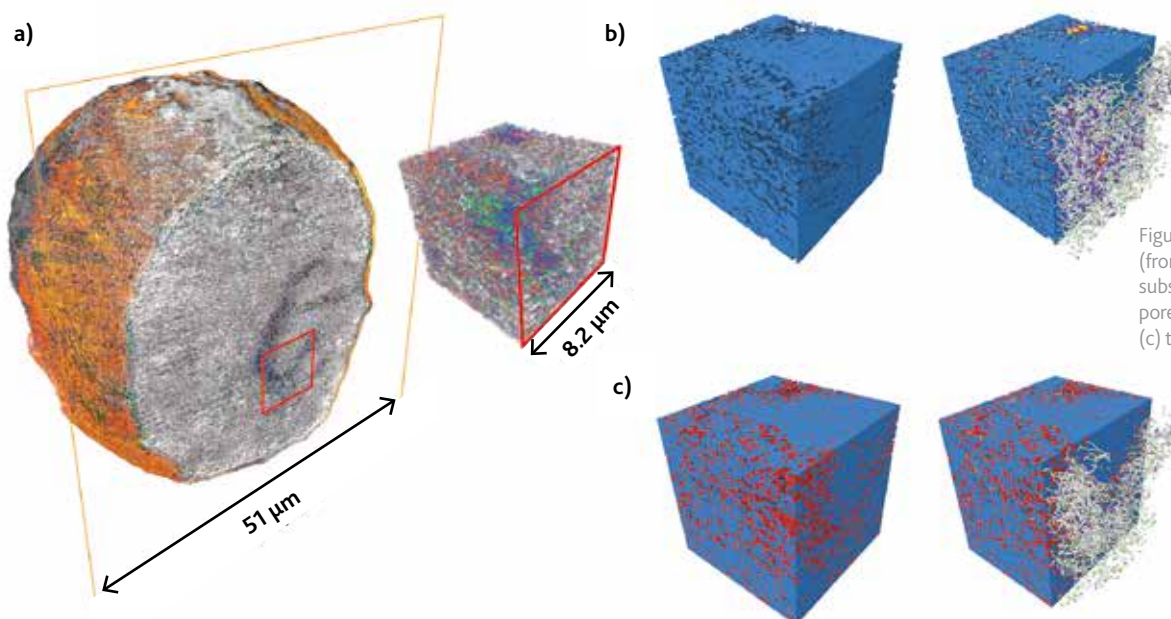


Figure 3: E-cat particle (from Refiner A) with subsection showing (a) pore space, (b) network and (c) the influence of iron.

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In Figure 4, each colored point (not grey) represents an individual surface macropore opening on the fresh catalyst analyzed from Refinery A. Regions in grey do not have surface macropores. From the detailed tomography data, the team determined the connectivity between each surface macropore opening and the underlying pore network. Remarkably, the team found that a single, contiguous network occupied 95% of the total pore volume in the particle. Surface nodes connected to this dominant network are marked in black. Points marked in other colors simply represent additional surface openings (nodes) connected to much smaller macropore networks occupying a small percentage of the total macropore volume.

The decision to image either below or above the absorption edge determined the “visibility” of each contaminant metal. Figure 5(a) shows the distribution of surface macropore openings in a heavily contaminated E-cat with the iron turned off (below the absorption edge). With the iron invisible, the particle shows a wide spread of surface nodes with most again being connected to a single, dominant macropore network. Interestingly, the particle looks remarkably similar to the fresh catalyst in Figure 4.

With the iron switched on (Figure 5(b)), the team observed a significant reduction in the number of surface openings connected to the main network (95% of the pore volume). In fact, less than 7% of the original surface openings of the primary network remained connected to it. These openings are now connected to smaller networks comprising less than 5% of the pore volume. Using the analysis in Reference 2, the team calculated that the contaminant metals have a penetration depth that is insignificant beyond 2 μm . Contaminant metal has substantially deposited near the particle’s surface and thus cut off the surface openings from the bulk of the pore volume. Overall, the team observed a catastrophic loss of connectivity from the surface to the pore volume, and thus the interior active sites, within a catalyst.

A similar analysis for nickel showed a remarkably similar loss of surface nodes and pore connectivity. Figure 6 gives the results for the old catalyst fraction; zero remaining surface nodes are connected to the primary pore network (no black points), which represents 98% of the measured macropore volume. Consequently, less than 2% of the macropore volume is now accessible from the surface.

The loss of a surface node or connectivity to the primary macropore network may not be absolute. The resolution of this analytical method is limited to macropores. Contaminant metal may fully close a pore or reduce its size into the mesoporous range (2–50 nm). In the latter case, a pore actually remains open but is now a mesoporous pathway into the observed primary macropore network. Such a situation appears as a closed pore in this analysis.

From laboratory to commercial application

3D X-ray tomography brings a breakthrough level of insight into the structure of FCC catalyst and the deleterious changes associated with exposure to iron and nickel. For the first time, an analytical method can thoroughly map the internal macropore network. A key finding is that one contiguous macropore network dominates the structure of FCC catalyst. Past work has shown that iron and nickel concentrate on the outer surface.⁴ The present technique, shows, in a quantifiable way, that these metals quickly sever the primary pore network from surface access points. As metals accumulate, over 90% of the surface openings become connected to less than 5% of the total pore volume.

The collaborative team inferred that this remaining pore volume accessible from the surface is most important for performance.

Refiners requiring excellent bottoms upgrading should use a “high-accessibility” catalyst. Such a catalyst contains a pore architecture that maximizes the diffusion of reactants and products

within the outermost catalyst layer. For routine checks of commercial operations, Albemarle’s unique AAI (Albemarle Accessibility Index) test provides a quick, bulk measurement of accessibility or diffusional capacity in catalyst.⁵ AAI monitoring is often important for FCC units operating with high levels of contaminant metals. Refiners should work with their technical service representatives to determine which catalyst will maximize metal tolerance, accessibility and performance in their FCC units, as there is no universal solution.

This article was adapted from a presentation at the AFPM Annual Meeting 2016.⁶

REFERENCES

- ¹Vogt, E. T. C. and Weckhuysen, B. M.: “Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis,” *Chemical Society Reviews* (2015), 44, 7342–7370
- ²Meirer, F., Kalirai, S., Morris, D. et al.: “Life and death of a single catalytic cracking particle,” *Science Advances* (2015), 1(3), e1400199–e1400199
- ³Chantler, C. T., Olsen, K., Dragoset, R. A. et al.: “X-ray form factor, attenuation and scattering tables,” www.nist.gov/pml/x-ray-form-factor-attenuation-and-scattering-tables, National Institute of Standards and Technology, Gaithersburg, MD, USA
- ⁴Lappas, A. A., Nalbandian, L., Iatridis, D. K., Voutetakis, S. S. and Vasalos, I. A.: “Effect of metals poisoning on FCC products yields: Studies in an FCC short contact time pilot plant unit,” *Catalysis Today* (2001), 65(2–4), 233–240
- ⁵Nickell, R.: “Albemarle’s accessibility advantage,” *Catalyst Courier* (2016), 85, 18–19
- ⁶Nickell, R., Mesu G., Liu, Y., Meirer, F. and Weckhuysen, B. M.: “Breakthrough characterization methods for evaluation of metals poisoning in FCC catalyst,” paper AM-16-18 presented at the AFPM Annual Meeting, San Francisco, CA, USA (March 13–15, 2016)

FOR MORE INFORMATION, CONTACT:
Ryan Nickell
Email: ryan.nickell@albemarle.com

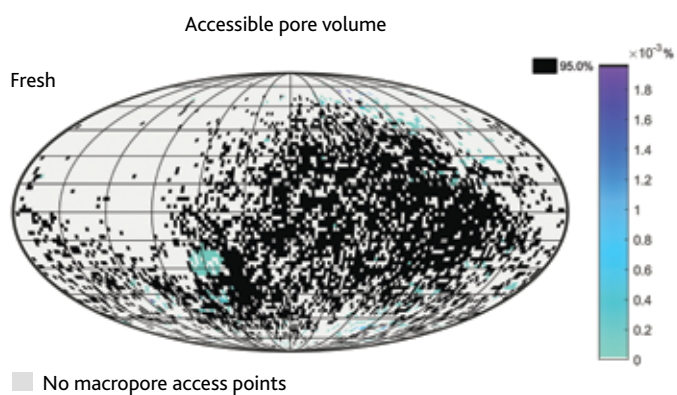


Figure 4: Surface pores in fresh catalyst and percentage connectivity to pore volume.

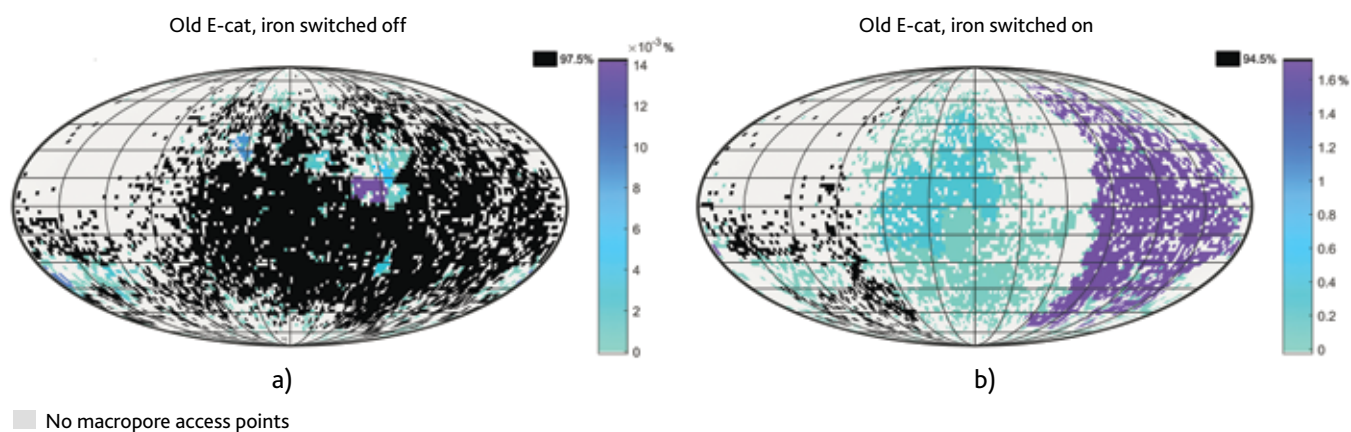


Figure 5: Surface pores in E-cat and iron's influence on percentage connectivity to pore volume.

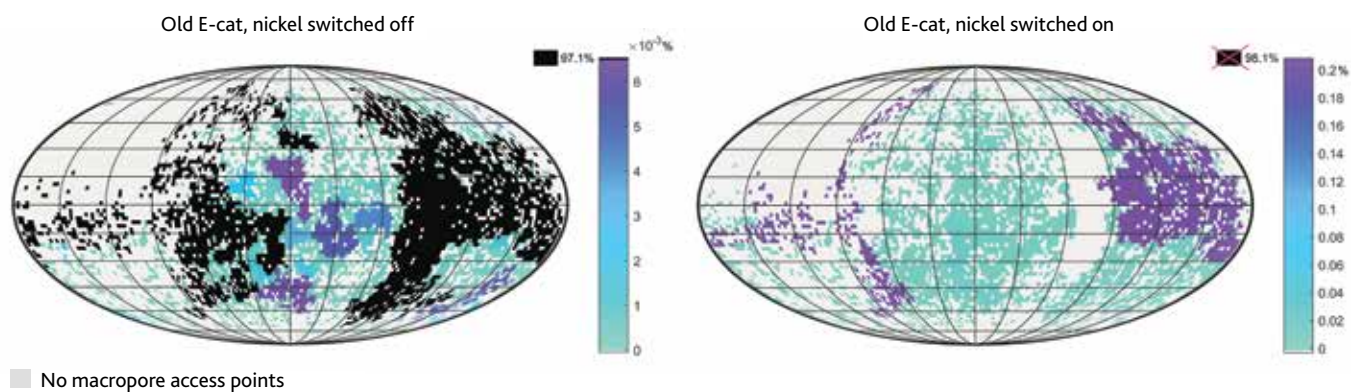


Figure 6: Surface pores in old catalyst and nickel's influence on percentage connectivity to pore volume.

HELP WITH OPTIMIZING YOUR REFINERY OPERATIONS

Useful advice for refiners Part 2

George Yaluris's answers to the following questions, which were posed during the FCC session at the 2016 American Fuel & Petrochemical Manufacturers Q&A and Technology Forum in Baltimore, USA, on September 25–28, 2016, offer useful advice for refiners.

Q1: We have run a full-burn FCC unit for many years. We are considering processing more resid and operating in a partial carbon monoxide (CO) combustion mode. What is a carbon runaway and how can we address it?

A1: A carbon runaway is the accumulation of coke on a regenerated catalyst at levels well above what is common for the E-cat of an FCC unit operating in partial burn, for example, ~0.5 wt%. A carbon runaway can occur when there is insufficient air to burn the coke deposited on the catalyst during each cracking cycle and/or because oxygen (O_2) is consumed catalytically to convert CO to carbon dioxide (CO_2) rather than coke to CO. Figure 1 shows an example of a carbon runaway in an FCC unit.

There are several common causes of carbon runaway.

Attempting to process more resid, heavier and/or higher Conradson carbon resid in a partial burn unit will push the FCC unit deeper into partial burn, increase the CO: CO_2 ratio in the flue gas, decrease the O_2 availability in the regenerator and increase the carbon on regenerated catalyst. The carbon on E-cat may increase rapidly if the change in feed quality is sudden and dramatic.

Some units operating in partial burn can tolerate the use of a combustion promoter and may even need some to control afterburn. However, if the promoter is

used in a unit operating in deep partial burn or the use of lower-quality feed pushes the unit deeper into partial burn, the promoter will catalyze the reaction of CO with O_2 to CO_2 , thereby decreasing the availability of O_2 to remove carbon from the catalyst and potentially causing a carbon runaway.

Using E-cat that contains a CO combustion promoter can cause carbon runaway. Even if the refiner is careful not to use combustion promoter, it is important to ensure that any purchased E-cat used to flush metals from the unit does not contain CO promoter. This includes purchased E-cat, which may be used to start the unit after a shutdown.

Certain contaminant metals deposited on the E-cat have the potential to add CO promotion to the catalyst inventory, push the unit deeper into partial burn and increase the carbon on the E-cat. Increasing nickel (Ni), vanadium (V) and iron (Fe) levels, especially when the change is rapid, can increase the delta coke and, when combined with factors such as limited air availability, increase the carbon on the E-cat. All three metals can add combustion promotion to the catalyst inventory and increase O_2 consumption to convert CO to CO_2 , thereby further increasing the carbon on the E-cat. Doolin et al.¹ studied the effects of Ni, V and Fe on CO promotion and concluded that the oxidative effect increases from Fe to V to Ni. They also showed that antimony (Sb) can be used to passivate the CO oxidation activity of Ni. In an FCC unit, the effects of these metals will depend on how much active Ni, V and Fe have been added to the E-cat and the average age of the E-cat and the metals on it.

High Fe, cerium (Ce) and titanium (Ti) levels in the fresh catalyst are not known to have negative effects on catalyst performance. However, they may be implicated in promoting CO conversion to CO_2 . Theoretically, Fe with high levels of Ti or Ce on the catalyst may act as a CO promoter. Although this does not happen for most catalyst technologies, it is unknown whether there is a threshold above which the presence of these metals can cause a problem.

Some emission control additives are known to operate via a mechanism that includes an oxidation step and, when used in sufficiently large amounts, can potentially increase CO promotion and cause the carbon on the E-cat to increase.

The CO to CO_2 reaction is temperature dependent. At lower regenerator bed temperatures (about <1230°F), increases in delta coke have directly resulted in increased carbon on the E-cat. In some cases, where the average catalyst age is high (>150 d), the carbon has fused onto the E-cat with little opportunity to burn off. Attempts to burn off the carbon on E-cat samples in a laboratory oven have been unsuccessful. A fresh catalyst change can increase

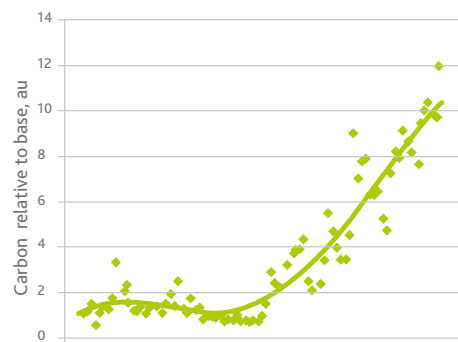


Figure 1: Example of an FCC unit carbon runaway.



the delta coke if the new catalyst is improperly designed, is too active and/or has poor coke selectivity, accessibility or strippability. In a partial burn unit, the increased delta coke can push the unit deeper into partial burn, decrease the air availability and potentially cause a buildup of carbon on the E-cat.

If a carbon runaway occurs, Albemarle recommends addressing it as soon as possible. In most cases, this will require decreasing the feed rate and/or removing some or all of the resid feed that caused it from the combined feed to the unit to make more air available. If purchased O_2 is available and there is room to increase it or to increase airflow, these options can also be used to slowly burn off the carbon from the catalyst.

If contaminant metals are contributing by increasing coke make, they can be reduced using a flushing catalyst such as a purchased E-cat without a CO promoter. Alternatively, the unit can switch to a lower-activity, fresh catalyst, thereby enabling it to increase catalyst additions without increasing E-cat activity. Flushing catalyst is also recommended if the carbon is fused onto the E-cat.

If CO promotion is suspected to be the cause, having been added to the unit by any of the modes discussed above, and as long as the unit can be operated safely, the refiner can

- allow the source of the CO promotion to decay and manage the increased carbon on the E-cat by decreasing the feed rate and the amount of resid being processed
- attempt to flush the promoted inventory with a purchased E-cat

known to be free of CO promoter

- change the cracking catalyst to a lower Fe, Ti, and Ce catalyst to decrease the chance that any of these metals is promoting CO combustion
- remove any additives (in addition to CO promoter) that are known to have some oxidation activity, for example, certain types of SOx additive containing Ce.

If the unit is shut down during a carbon runaway, it is important to develop a plan for slowly burning off the coke before the catalyst is heated during start-up to temperatures that can ignite the carbon. If coke on the E-cat starts burning off during start-up, it may cause an exotherm that can result in rapid catalyst deactivation. For example, if it is safe to do so, the catalyst can continue to circulate in the unit with air during the shutdown until the coke is burned off. If the operator suspects that catalyst high in coke may have deposited downstream of the regenerator, they should consider removing these deposits. This will avoid the risk of creating hot spots in the flue gas line and the downstream equipment should O_2 -rich air reach these deposits during start-up and cause the coke to burn.

Q2: As distillate demand is decreasing, current economics favor maximizing gasoline and octane. What operating and catalyst changes do you recommend for increasing octane barrels?

A2: Octane barrels can be increased by increasing the gasoline yield without decreasing the octane or by increasing the octane without a large decrease in the gasoline yield. The latter approach is, in most cases, the most effective. The various operating options for increasing

gasoline octane include increasing the riser temperature. This will increase the gasoline olefinicity and has the largest effect on increasing gasoline road octane number (RON). However, if implemented, it will also increase conversion and dry gas. If the unit is operating in distillate maximization mode, increasing the riser temperature may not be a good option.

Minimizing the amount of straight-run distillate going to the FCC unit, if processing tight oils, is another option, as the distillate is quite paraffinic and can have a large negative impact on octane.

Separating out the light cat-cracker naphtha portion of gasoline, the most olefinic, and highest in RON can also be effective. If there is the capability, for example, a gasoline splitter, separate this fraction before the hydrotreater and process it separately so that the octane loss decreases across the hydrotreater.

There is also a variety of catalytic options for increasing gasoline octane, including decreasing the hydrogen transfer activity of the catalyst by reducing the rare earth content and/or increasing the catalyst's accessibility and matrix activity. Implementing this will increase the gasoline octane and olefinicity, and affect the amount of gasoline and LPG make. Unless the catalyst is designed with sufficient matrix to maintain overall activity, decreasing the rare earth content could make the catalyst less active, which means an increase in catalyst additions to maintain E-cat activity.

ZSM-5 additives are well known to increase octane and were originally commercialized as octane additives. They



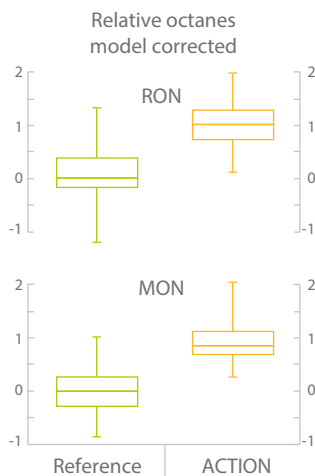


Figure 2: Octane increase in an FCC unit using Albemarle's ACTION catalyst technology after normalizing for feed and operating changes.

work by removing from the gasoline low-octane, straight-chain olefins and paraffins, and concentrating the higher-octane components such as aromatics and multibranched paraffins. However, traditional ZSM-5 additives will decrease gasoline yield and increase LPG make.

Various catalysts and additives are marketed as helping to increase gasoline octane. Albemarle presented its technology for maximizing gasoline octane and C₄ olefins at the 2014 Annual AFPM meeting.² Figure 2 shows an example of octane increase achieved using Albemarle's ACTION® technology.

Q3: What is your experience with processing raw crude in the FCC unit? What types of crude have you tried to process in the FCC unit? What are the yield impacts? Are there any corrosion issues associated with this mode of operation?

A3: Albemarle knows that at least half a dozen refineries have attempted to process crude in the FCC unit, although the actual number is probably larger. In specific cases where crude is being used in the FCC

unit, the types of crudes involved were domestic or Canadian.

Usually a refiner considers processing crude in the FCC unit because typical FCC feedstocks are unavailable, there is a lack of fractionation capacity for the crude or the FCC feedstock is too expensive to purchase. Although the light components of crude (LPG, gasoline and light distillate) could be expected to increase volume traffic through the feed injection nozzles and reactor cyclones, and thus potentially increase the operating velocity, this has not happened. Perhaps this is because the lighter crude components are less reactive under FCC conditions, which results in a lower volume gain that partially offsets the increase in vapor volume due to the lower molecular weight of these same components. When processing crude, Albemarle has seen increased variability in E-cat metals loading and increased sodium, chloride and calcium salts due to a lack of desalter capacity or changes in the desalter operation through raw crude variability.

When refiners started using tight oils, they found out that, as these paraffinic crudes are blended with aromatic heavier feedstocks, they can cause asphaltenes to precipitate and cause fouling. The same phenomenon can happen when some of the domestic crudes are used directly in the FCC unit. Therefore, potential feedstock incompatibilities need considering before deciding to process any specific crude. If no FCC feed desalter is available, the salts and chlorides present may increase catalyst deactivation and chloride salt formation and, thus, cause corrosion in the main fractionator overhead section.

Usually the combined FCC feed containing crude will have properties that, on first assessment, look better, for example, higher API gravity and lower Conradson carbon resid, than the combined feed it replaces, partly because of the

light components present. This can create expectations of improved unit performance and yields. Although the presence of light components in the feed can improve dispersion, feed vaporization and nozzle performance, yields tend not to improve. This is because the light components of the crude in the feed do not convert as much and the remaining feed has not really changed.

The mostly unconverted gasoline in the crude is similar to straight-run material that is quite paraffinic and low in octane. The LPG made from any gasoline and light distillate is often more paraffinic than LPG made from gas oil cracking. As a result, the overall gasoline octane can decrease by 1–3 points, while LPG olefinicity can drop by 5–10 points and perhaps more. Thus, when paraffinic domestic crudes are processed in the FCC unit, both the operation and the catalyst should be reviewed for modification to remedy any negative effects on yields and product quality.

References

- ¹Doolin P. K., Hoffman, J. F. and Mitchell, M. M.: "Role of metal contaminants in the production of carbon dioxide during the regeneration of cracking catalysts," *Applied Catalysis* (1991), 71(2), 233–246
- ²Yaluris, G. and Kramer, A.: "Take ACTION® to maximize distillate and alky feed from your FCC unit," paper AM-14-26 presented at the AFPM Annual Meeting 2014, Orlando, FL, USA (March 23–25, 2014)

FOR MORE INFORMATION, CONTACT:
George Yaluris
Email: george.yaluris@albemarle.com

DENALI™ CATALYSTS: REAL PERFORMANCE WHERE IT COUNTS

The latest FCC catalyst family from Albemarle

To help refiners' profitability climb to new heights, Albemarle has introduced its latest catalyst family: DENALI. The competitive landscape and challenges to profitability have never been greater. More refined products are being distributed by an increasing number of refiners to every region of the globe and squeezing margins. Feedstocks are becoming more difficult and growing in molecular complexity and diversity. New regulations demand new approaches to integrating refinery operations and know-how. Even FCC, the heart of a refinery, is being tested to maintain its dominant position in the refining hierarchy. A key tool for conquering these challenges is new technology. Albemarle's latest technological discoveries are manifested in DENALI catalysts and are made using the company's next-generation GRANITE™ technology platform, which is also the foundation for PEAK™ and EVEREST™ catalysts.

Novel matrix-binder and zeolite technologies

Two innovative technological advances drive the improved performance of DENALI catalysts. First is ADM™-85, a proprietary matrix-binder specially developed to both improve performance and work complementarily with Albemarle's proven ADM™-20 (bottoms cracking) and ADM™-60 (Ni tolerant, coke selective) matrices. One function of ADM-85 is to provide additional binding without pore plugging, thereby enabling DENALI to maintain the same high accessibility with additional active components. The extra binding increases formulation flexibility and, together with high accessibility, increases the ability to disentangle activity from hydrogen transfer, which is critical for maximizing olefins and preserving primary products.

Another key deliverable of ADM-85 is improved matrix-generated cracking. This matrix is inherently coke selective with an improved pore size distribution (Figure 1) that facilitates cracking efficacy and access to larger molecules. Furthermore, ADM-85 also arrests the formation of zeolite defects, which increases the zeolite's stability to enhance selectivities and activity further.

The second pioneering advancement in DENALI catalysts is ADZT™-600, a cutting-edge zeolite technology providing multiple benefits. One benefit is higher intrinsic zeolitic stability and retention, which provides a second tool for extricating and controlling activity versus hydrogen transfer. In addition, acid sites have been optimized with less non-framework alumina for fewer undesired reactions, particularly lower coke and gas. Lastly, more mesoporosity has been incorporated (Figure 1) to increase zeolitic contact with reactants and result in fewer secondary reactions owing to faster disengagement. Overall, ADZT-600 delivers improved yields, especially improved coke selectivity and more selective cracking of larger molecules to assist in bottoms cracking.

Two innovative products employing these new technologies are DENALI and DENALI ACTION®.

Best coke selectivity and lowest bottoms at constant coke among Albemarle catalysts

One catalyst in this new family is DENALI, the next-generation product to succeed Albemarle's UPGRADER™ and AMBER™ catalysts. Utilizing Albemarle's inventive ADZT-600 zeolite technology and ADM-85 matrix-binder, DENALI has demonstrated exciting success in laboratory testing using a full range of feedstocks and various deactivation conditions.

Table 1 shows the improved catalyst properties for DENALI compared with UPGRADER after cyclic deactivation and the addition of 3000 ppmw each Ni and V. In this example, more active ingredients (indicated by the higher surface area) were added to DENALI yet its attrition index was 40% lower than UPGRADER's. Moreover, even with additional binding via the new ADM-85 matrix-binder, pores were not plugged and the industry-leading high accessibility was maintained. Even more impressive is the large improvement in zeolite retention, which manifests itself in a much improved yield slate. (It should be noted that the matrix surface area retention is lower; however, the total matrix surface area for DENALI remains higher and mechanistically some ADM-85 is expended protecting the zeolite.)

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	UPGRADER	DENALI
Fresh surface area, m ² /g	220	270
Fresh matrix surface area, m ² /g	112	141
Fresh zeolite surface area, m ² /g	108	130
Surface area retention, %	57	67
Matrix surface area retention, %	66	58
Zeolite surface area retention, %	47	76
Fresh rare earth oxide, wt%	2.6	3.3
Fresh attrition index	Base	0.6 × base
Albemarle Accessibility Index	12	12

Table 1: Catalyst properties illustrate positive effects of novel technologies.



Moreover, even with additional binding via the new ADM-85 matrix–binder, pores were not plugged and the industry-leading high accessibility was maintained. Even more impressive is the large improvement in zeolite retention, which manifests itself in a much improved yield slate. (It should be noted that the matrix surface area retention is lower; however, the total matrix surface area for DENALI catalyst remains higher and mechanistically some ADM-85 is expended in protecting the zeolite.)

The first notable yield benefit with DENALI is a much improved coke selectivity (ACE testing), as shown in Figure 2. The unique zeolite and matrix technologies combined with the ability to formulate more aggressively without deterioration

in attrition enable a nominal 15% improvement in coke selectivity for DENALI versus UPGRADER.

DENALI also delivers significantly lower bottoms yield at constant coke, as shown in Figure 3. The improved pore size distribution combined with the selective cracking from ADM-85 and ADZT-600 drive this improved performance.

DENALI ACTION for superior butylene yields, best coke selectivity and lowest bottoms at constant coke with Albemarle catalysts

DENALI ACTION, another catalyst employing this new technology platform, merges the new ADZT-600 zeolite

technology in DENALI catalysts with the shape-sensitive, butylene-selective zeolite technology system (ADZT-100) used in conventional ACTION catalysts to generate even higher levels of butylenes. Moreover, the binding power of ADM-85 permits the application of increased levels of zeolite technologies to increase butylenes and other targeted yields further.

In a laboratory example shown in Figure 4, DENALI ACTION delivers higher activity with lower rare earth and a lower (better) attrition index, as detailed in Table 2. As with DENALI, these activity and attrition benefits are enabled by ADM-85, which permits the inclusion of more active components without an attrition or accessibility penalty, and ADZT-600 for improved zeolite stability.

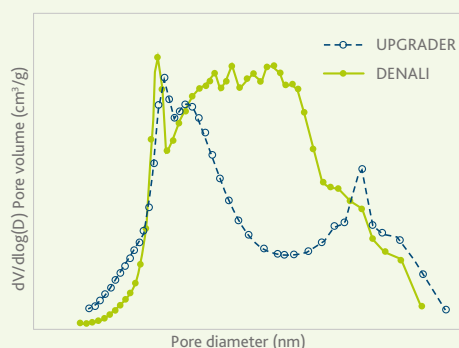


Figure 1: DENALI catalyst's pore size distribution has favorable implications for better selectivities.

	ACTION	DENALI ACTION
Fresh surface area, m²/g	269	314
Fresh matrix surface area, m²/g	142	153
Fresh zeolite surface area, m²/g	127	161
Surface area retention, %	59	67
Matrix surface area retention, %	70	63
Zeolite surface area retention, %	46	70
Fresh rare earth oxide, wt%	0.7	0.5
Fresh attrition index	Base	0.8 x base
Albemarle Accessibility Index	11	11

Table 2: Catalyst properties prove formulation flexibility.

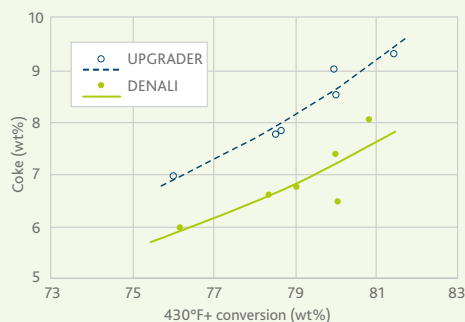


Figure 2: Coke selectivity improves by 15% with DENALI.

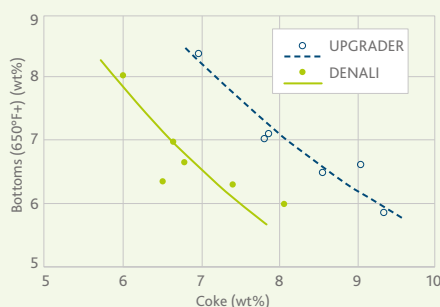


Figure 3: Bottoms make is 20% lower at constant coke with DENALI.

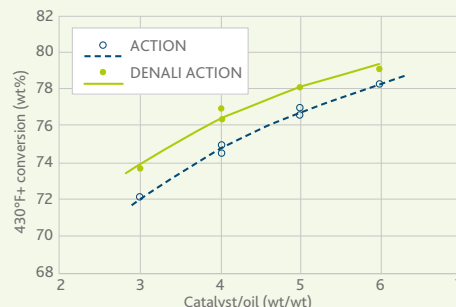


Figure 4: DENALI ACTION has a higher activity with less rare earth than conventional ACTION.

ACTION is recognized as the industry leader in butylene production and selectivity. Now, even higher butane-butylene olefinicity (Figure 5) and improved butylene-to-propylene selectivity (Figure 6) are achievable with DENALI ACTION. This impressive performance demonstrates the step-out change in hydrogen transfer control when assimilating the clever, novel zeolite and matrix technologies in the DENALI family of catalysts with the innovative butylene-generating zeolite technology in ACTION catalysts. Specifically, combining the increased use of more-stable, acid-site-optimized, larger-pore ADZT-600 zeolite technology bound with the selective, highly accessible ADM-85 matrix-binder and integrated with butylene-discriminating zeolite technology creates superior butylene yields.

Finally, for the technological reasons described earlier for DENALI, DENALI ACTION also offers the same improved coke selectivity (Figure 7) and low bottoms at constant coke.

DENALI catalysts deliver superior performance

Albemarle has developed the DENALI catalyst family incorporating innovative zeolite and matrix technologies. This breakthrough provides new catalyst solutions to help customers increase profitability and fortifies Albemarle's leadership position in the FCC catalyst market.



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Compared with other Albemarle catalysts, DENALI and DENALI ACTION increase value through

- the best coke selectivity
- the lowest bottoms make at constant coke
- the highest leading butylene yields
- an expanded formulation window
- greater control of hydrogen transfer
- a lower (better) attrition index
- high accessibility.

FOR MORE INFORMATION, CONTACT:

Ken Bruno
Email: ken.bruno@albemarle.com

DENALI catalyst is available for commercial use; initial FCC unit trials are expected in the second quarter of 2018.

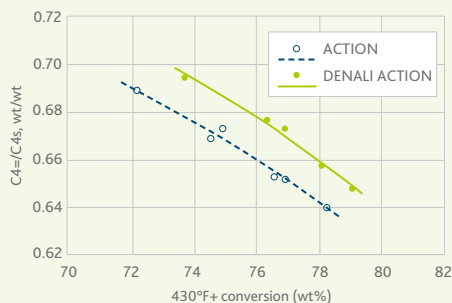


Figure 5: DENALI ACTION increases butylenes beyond the industry-leading ACTION.

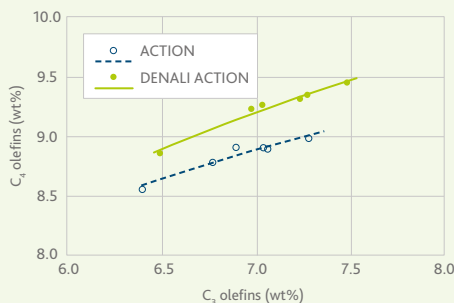


Figure 6: Higher butylene-to-propylene selectivity with DENALI ACTION.

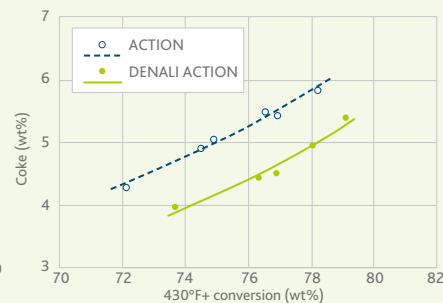


Figure 7: The superior coke selectivity of DENALI ACTION.

SCALE NEW HEIGHTS OF PERFORMANCE AND PROFITABILITY.

Albemarle is proud to introduce its innovative FCC GRANITE™ technology, which provides the most flexible portfolio of catalyst products available in the marketplace. With the constantly changing market conditions, difficult feeds and stringent environmental regulations, refineries are faced with major challenges to create both superior performance and increased profitability.

With Albemarle's GRANITE technology, you can do both. Utilizing its novel matrix-binder system, GRANITE catalysts can be custom tailored to unique refinery requirements. Enjoy better bottoms upgrading, improved coke selectivity, more zeolite stability, maximized higher margins and higher profitability. To learn more about Albemarle's new FCC GRANITE, contact us today.

