ISSUE 87 | 2017

Catalyst Courier

In this issue

Alkyclean® adds value for refineries

Driving new profit ambitions for existing hydrotreaters with Nebula® catalyst

Addressing the ULSG challenge with Ketjenfine® (KF) 907 and RT-235

ALBEMARLE®

INSIDE THIS ISSUE…

4	NEWS FROM ALBEMARLE
6	CATALYST SELECTION STRATEGY: COSTS TO BE MINIMIZED OR OPPORTUNITIES TO BE GRASPED?
8	ALKYCLEAN® – ADDING VALUE FOR REFINERS
11	INCREASE YOUR REFINERY PROFITABILITY WITH NEBULA® CATALYST
16	KETJENFINE® (KF) 907 FOR VGO HYDROTREATING
20	MAXIMIZING OCTANE BARRELS WHILE PRODUCING ULTRA-LOW-SULFUR GASOLINE

EVENTS DIARY 2017

September
18–19 5th Refining India Conference, New Delhi, India
18–20 Abu Dhabi International Downstream, Abu Dhabi, UAE

October
2–4 AFPM Operations & Process Technology Summit, Austin, TX, USA

November
6–8 ResidHydroTreat, Kuwait City, Kuwait
13–15 ERTC, Athens, Greece
27–29 Annual GPCA Forum, Dubai, UAE

December
6–7 Middle East Catalyst Technology Conference, Bahrain

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

Correspondence and distribution for *Catalyst Courier*
Brooke Robertson
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

SILVIO GHYOOT
PRESIDENT,
REFINING SOLUTIONS

FRESH THINKING AND A NEW FOCUS ON VALUE CREATION

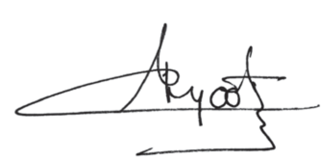
Albemarle provides customized products that help refiners to address their current requirements and to meet increasingly demanding product specifications. But, beyond that level of support, we are also committed to developing and offering products that enable operators to adapt, adjust and maximize the performance of their hydroprocessing and FCC units. This focus on value creation can help to boost performance right across a refinery.

Traditionally, efforts to increase margins have been constrained by a drive to minimize capital and operating expenditure. This cautious approach often becomes a refuge for all operators when there is a downturn in the market. Today, with the market appearing to have stabilized after a period of extreme uncertainty, forward-looking businesses are starting to consider new ways to sustain or increase production.

For example, Albemarle's existing bulk metal catalysts such as Nebula® and a soon-to-be-released new generation of bulk metal catalysts can play a crucial role in helping refiners to balance the technical and commercial challenges. The full benefits of Nebula catalyst are realized by careful consideration of how the catalyst is deployed. The potential for added value extends far beyond the performance of a single hydroprocessing unit, so, by focusing on this bigger picture, customers can unlock much greater value.

To conform to ever-more-stringent specifications, refiners are turning to higher-activity catalyst solutions such as Albemarle's Ketjenfine® (KF) 907 catalyst. Designed to deliver high hydrodesulfurization activity and very high stability throughout the operating cycle in extremely demanding conditions, this catalyst can help refiners to meet the challenges that implementing the new Tier 3 gasoline regulations imposes.

Increasingly, refinery operators are looking for dynamic new ways to add value. One of the key enablers for this will be taking a strategic view of the process of catalyst selection and ensuring that catalyst change-outs are managed to maximize value rather than merely to provide continuity. We have vast experience of fresh thinking here at Albemarle and are already helping those operators who want to break the mold.



SILVIO GHYOOT
PRESIDENT, REFINING SOLUTIONS

NEWS FROM ALBEMARLE

ALBEMARLE ACHIEVES RECOGNITION AS 2017 KIRKPATRICK AWARD FINALIST

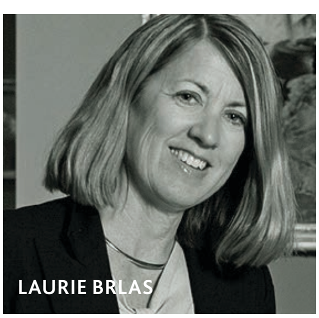
Albemarle and its technology partner CB&I have received recognition as 2017 Kirkpatrick Chemical Engineering Achievement Award finalists for the breakthrough AlkyClean® process technology. This technology, which applies the proprietary Albemarle AlkyStar® catalyst, eliminates the use of liquid acids in producing motor fuel alkylate and thus removes the hazards and environmental and operating issues associated with handling liquid acids.

This world-first solid catalyst alkylation process was commercialized in Zibo, Shandong Province, China, in August 2015. The AlkyClean process offers environmental benefits owing to the reduction of waste streams such as spent acids and acid-soluble oils, and is inherently safer when compared with technologies using liquid acids.

The Kirkpatrick Award honors the most noteworthy chemical engineering technology commercialized anywhere in the world over the past two years. There are only six finalists out of the many submissions to *Chemical Engineering* magazine. A board of judges will review the detailed packages for each nomination and select the most noteworthy. Criteria for winner selection include the novelty of the technology, the difficulty of the chemical engineering problem that was solved and the overall engineering excellence. The winner will be announced at Chem Show in New York in November.

The AlkyClean process technology was the recipient of the 2016 Presidential Green Chemistry Challenge Award by the U.S. Environmental Protection Agency in cooperation with the American Chemical Society.

NEW BOARD MEMBER


LAURIE BRLAS

The former executive vice president and chief financial officer of Newmont Mining Corp., Laurie Brlas, has joined Albemarle's board of directors.

"Laurie brings extensive operations, strategy and financial experience to our strong board of directors," Luke Kissam, Albemarle chairman, president and chief executive officer, says. "We are excited to have her join our team. With over 20 years' experience as a leader in various industries, including natural resources, she will serve Albemarle and our shareholders well."

"I am also very pleased to welcome Laurie to the Albemarle board of directors. In addition to her industry experience, her financial background and prior experience as a director complement the diverse skills of our board and make her an excellent addition to the committees on which she will serve," Jim Nokes, Albemarle's lead independent director, adds.

With previous experience in various leadership roles at Cliffs Natural Resources Inc., an iron ore producer, Brlas has also served as vice president and chief financial officer for STERIS Corp. She currently also sits on the director's boards for Perrigo Co. and Calpine.

INVESTOR DAY IN NEW YORK CITY

Albemarle presidents Silvio Ghyoot, Raphael Crawford and John Mitchell, and chairman, president and chief executive officer Luke Kissam led a successful set of talks at this year's investor day in New York City, USA. Topics ranged from refining solutions through bromine specialities and lithium to a financial overview.

As Albemarle is in the Standard & Poor's Index Top 500, investor days are key steps to ensuring that shares continue to grow at such a successful rate.

To see highlights from Albemarle, please watch the video.

CLICK HERE TO SEE VIDEO

LEED CERTIFICATION FOR HEAD OFFICE

Developed by the U.S. Green Building Council, the Leadership in Energy and Environmental Design (LEED) rating is a leading system for recognizing the best green building practices.

Albemarle has achieved LEED certification for implementing practical and measurable strategies at its Charlotte head office aimed at reaching high performance in energy use and atmosphere; materials and resources; water efficiency; and indoor environmental quality.

Luke Kissam, Albemarle chairman, president and chief executive officer, comments, "We are proud to receive this designation. From the beginning, our goal was to create a workplace that would inspire creativity, foster collaboration and generate pride for our employees. Thanks to our dedicated project team, we have accomplished this goal, and we have done so in a way that demonstrates Albemarle's commitment to sustainability."

The project, completed in June 2016, features two floors of office space totaling 47,000 ft^2 in South Park, Charlotte, NC, USA.

This certification joins April 2016's achievement for the South Tower building.

DOUBLING PRODUCTION OF LITHIUM CONCENTRATE

As Albemarle's customers' requirements for lithium grows, its previously announced lithium output expansion plans continue.

According to John Mitchell, president, lithium and advanced materials for Albemarle, the "expansion of mine and ore upgrading facilities is a key deliverable in our supply strategy to grow total combined lithium carbonate equivalent production to approximately 165,000 MT/y early in the next decade."

Expansion at the Greenbushes mine in Western Australia aims to more than double the lithium carbonate equivalent capacity: from 80,000 to more than 160,000 MT/y. Of this, Albemarle has a 50% interest in the offtake. Commissioning for the expansion is expected to start in the second quarter of 2019.

ALBEMARLE EXECUTIVE TOP "WOMAN IN BUSINESS"

Running for its 21st year, *Charlotte Business Journal*'s Women in Business Achievement Awards recognizes women who make significant contributions to their professions and communities throughout the year.

Karen Narwold, Albemarle's executive vice president, chief administrative officer and general counsel, was honored among 25 outstanding businesswomen in the region that includes Albemarle's headquarters.

Joining Albemarle in September 2010 as general counsel and corporate secretary, Narwold has assumed roles of increasing responsibility ever since. Luke Kissam, Albemarle chairman, president and chief executive officer, comments, "As a senior leader in our organization, Karen has a profound impact on both our businesses and our employees. We are continually inspired by her commitment to power the potential of Albemarle, and I am pleased to congratulate her on this noteworthy accomplishment."

> "As a senior leader in our organization, Karen has a profound impact on both our businesses and our employees."

KAREN NARWOLD

ANNEMIE DONKERS
DIVISIONAL VICE PRESIDENT

BOB LELIVELD
BUSINESS DIRECTOR, LICENSED CATALYSTS

CATALYST SELECTION STRATEGY: COSTS TO BE MINIMIZED OR OPPORTUNITIES TO BE GRASPED?

Taking a wider view of catalyst selection can pay dividends.

When you change the oil in your car, you cannot expect a dramatic change in performance, but if you were to change its engine, your driving experience could be very different. When it comes to refinery operations, and the never-ending quest to increase profitability, operators are starting to realize that it pays to think of their catalysts as the engine, not the oil.

The factors that influence a refinery's profitability are its size, configuration, location and the extent to which it can access disadvantaged crudes. Acknowledging these, refiners generally accept that they can only achieve stepwise improvements in profitability through making major capital investments. But what if there was another way to boost profitability: a method that did not require major capital expenditure, rather one that involved a more holistic and strategic approach to catalyst selection? Consider, for example, hydrotreating catalysts.

Installed hydroprocessing capacity has grown exponentially over the past two decades across all application segments, ranging from straight-run naphtha through producing ultra-low-sulfur diesel (ULSD) and upgrading vacuum gas oil (VGO) and resid cuts. However, once a hydrotreating unit has been designed and constructed, its operating parameters are defined and unlikely to change. Feed quality and diet, product specifications, available hydrogen and other process conditions are all defined and "set in stone" by the time the operator starts the selection process for a catalyst refill.

Efforts to improve operations or boost the profitability of a unit through a catalyst change-out are viewed as being incremental and this is reflected in the catalyst selection process. New and higher-activity catalysts are used to bring down costs per month of cycle length or, exceptionally, to push throughput above design conditions because this is what is expected. Catalyst performance forecasts are expected to meet or marginally exceed the request-for-quote conditions but not to challenge them. This limits the opportunities for value creation through optimization.

Improving the catalyst selection process

This is why refiners often miss the value of breakthrough catalysts during the first few years after their market introduction. The catalyst selection process measures the new higher-activity catalyst against a fixed set of feed, process and product conditions. The catalyst has to fit in with fixed parameters that constrain its potential for boosting refinery profitability. The true value is only revealed when the refiner acknowledges that the new catalyst may enable the unit to operate more effectively.

Some refiners do continuously seek margin improvements through taking different approaches to catalyst selection. Their focus is not on the unit, but on what the unit could do for refinery profitability and how the new catalysts and innovative technology could help deliver this. By discovering new opportunities, rerouting feed streams, cutting deeper into certain fractions or producing higher-quality products, they can enhance profit by millions of dollars. Instead of selecting a catalyst based on current unit conditions, catalyst selection should be part of a refinery margin improvement program that extends beyond the extension of run length and reducing operating costs for the unit.

Pathways to profitability

There are many routes to stepwise improvements. Intelligent stacking of catalysts (Albemarle's STAX® technology) or introducing new functionalities such as catalysts containing a mild hydrocracking functionality or a superb hydrogenation function can all be game changers for performance and profitability. This concept has potential beyond the level of the individual hydroprocessing unit and can achieve meaningful margin improvements for the whole refinery.

Here are just a few examples of the benefits that refiners have achieved by selecting high-end catalysts such as Nebula® and RT-235 and adjusting their operations to maximize value.

Nebula catalyst

In its fifth consecutive cycle with Nebula catalyst, a European refiner managed to process twice the amount of LCO, light VGO and aromatic extract feedstocks from its ULSD unit compared with pre-Nebula levels. This delivered additional profits of more than €20 million and payback on the catalyst system within two months.

In another hydrocracker, Nebula catalyst enabled the operator to increase the throughput of distressed feedstock by 20% while increasing the cycle length by 45%. This delivered exceptional profitability and a payback period of less than four months.

Another European refiner used Nebula catalyst to produce a premium diesel fuel and provide the company with a unique competitive advantage. The return on investment was so rapid that the refiner decided, on the basis of pilot plant testing, to anticipate loading Nebula catalyst, despite there being residual activity in the incumbent system.

More than 90% of customers that have selected Nebula catalyst have retained this product for subsequent cycles.

RT-235 catalyst

A North American refinery that was making ultra-low-sulfur gasoline used RT-235 catalyst to boost its annual profits by $12 million thanks to increased octane savings. Another refiner used RT-235 catalyst to achieve additional profits by pushing the operational boundaries of the unit. Making the right catalyst choice enabled it to increase throughput with a more severe feedstock while maintaining octane retention and meeting new regulations.

In every case where operators have selected high-end Albemarle catalysts such as Nebula and RT-235, the refiners have reached the breakeven point within three or four months. On cycles that last two or three years, that represents a long period of increased profitability.

The key concept is to recognize that new catalysts and catalyst systems offer opportunities to operate units differently. Rather than defining a box that sets limits on catalyst operation, refiners should use the catalyst to define, or even redefine, the operational box.

AlkyClean® technology

Technology can play a key role in the drive towards greater refinery profitability. AlkyClean gasoline alkylation technology, for example, is an advanced solid catalyst alkylation process for the production of motor gasoline alkylate. As the world's only commercial solid catalyst alkylation technology, it provides a safer and more environmentally friendly alternative for operators that are seeking to replace liquid acid methods, such as those that rely on hydrofluoric acid.

> “Some refiners continuously seek margin improvements through taking different approaches to catalyst selection. By discovering new opportunities, rerouting feed streams, cutting deeper into certain fractions or producing higher-quality products, they can enhance profit by millions of dollars.”

The first commercial AlkyClean unit, in Zibo, Shangdong Province, China, started up in August 2015. Throughout its two years of operation, it has safely and successfully produced an alkylate product of a quality on a par with existing technologies and meeting or exceeding all the process guarantees.

This edition of *Catalyst Courier* will highlight Albemarle's catalyst solutions and technology for increasing refinery profitability as a whole. Their value goes beyond the unit and helps refiners to achieve new levels of profitability. Albemarle firmly believes that looking through the wider lens of refinery profitability is a more rewarding way of catalyst selection. It opens up a world of possibilities and enables Albemarle and its customers to define jointly what catalyst system is best to maximize value in the short and long terms.

FOR MORE INFORMATION, CONTACT:
Bob Leliveld or Annemie Donkers
Email: bob.leliveld@albemarle.com or annemie.donkers@albemarle.com

ALKYCLEAN® – ADDING VALUE FOR REFINERS

Solid catalyst alkylation technology offering a giant step forward in safety and operation

AlkyClean gasoline alkylation technology is an advanced solid catalyst alkylation process for producing motor gasoline alkylate. With AlkyClean technology, light olefins from typical refinery sources such as FCC units or methyl tertiary butyl ether extract react with isoparaffins to produce alkylate. Of primary interest is the reaction of butylenes with isobutane to form high-octane trimethylpentane isomers.

Technology that adds value and improves safety

For decades, scientists have been trying to replace liquid acid technologies with safer and more environmentally friendly solid acid catalyst technology. Hydrofluoric acid, in particular, is especially toxic and, on release, forms clouds that can be lethal for long distances. Based on refinery risk management plans, in the USA alone, more than 17 million people currently live within such danger zones. Although mitigation options have been developed, they can be very costly and have not been universally adopted. Significant risks still exist, especially during unit repair and maintenance or when process accidents occur in adjacent units. An example of what happened during a hydrofluoric acid release at a non-Albemarle site is given in the text box below.

Previous attempts to use a solid acid catalyst for alkylation have failed because of poor product selectivity or excessively rapid catalyst deactivation associated with either the formulation of the catalyst or the lack of an effective catalyst regeneration procedure. In some cases, these catalysts also used leachable corrosive components such as halogens, trifluoromethanesulfonic acid, boron trifluoride or sulfuric acid that could migrate into the product.

CB&I and Albemarle have developed and offer a catalyst–process combination that removes these drawbacks. Furthermore, neither acid-soluble oils nor spent acids are produced, and there is no need for product post-treatment. Without these waste streams and the need for post-treatment, alkylate yield is higher and corrosion is eliminated in the downstream fractionation section. With the use of a particulate catalyst, liquid acids such as sulfuric or hydrofluoric acid with their health, safety and environmental risks are no longer required.

Incident in Gumi, South Korea

During unloading to storage tank at a chemical plant in Gumi, 8 t hydrofluoric acid was released on September 27, 2012. As a result:

- 5 people died
- 18 people were injured, including workers and emergency personnel
- more than 3000 people were evacuated
- the site was difficult to decontaminate
- there was agricultural damage
- there was vehicle damage
- livestock were affected.

AlkyClean technology adds value to refiners by producing clean and high-quality alkylate and by, more importantly, minimizing the risks through eliminating the use of conventional liquid acids and their associated hazards and operational complexity in manufacturing gasoline alkylate. A true solid alkylation catalyst, AlkyStar®, was developed for exclusive use in an innovative process employing multiple fixed-bed reactors operating in cyclical mode to produce high-quality alkylate continuously while regenerating in off-line reactors. CB&I and Albemarle's AlkyClean process is the world's only solid catalyst alkylation technology to be commercialized successfully.

Albemarle's AlkyStar catalyst (Figure 1, right) uses a zeolite that is well proven in the industry and has a low concentration of a noble metal component.

First successful commercialization

The first commercial AlkyClean unit was successfully started up in August 2015 in Zibo, Shangdong Province, China, by Shandong Wonfull Petrochemical Group Co., Ltd. This 2700-bbl/d unit (Figure 2, overleaf) has now been operating safely and successfully for close to two years producing an alkylate product at a quality on a par with existing technologies and meeting or exceeding all the process guarantees. The research octane number (RON) of the alkylate product is typically 95–97, as shown in Figure 3 (overleaf). With the successful commercialization of the first unit, there is growing interest from refiners worldwide in this inherently safer technology and how it can add value to refineries.

Why produce alkylate?

Motor gasoline alkylate consists of clean-combusting isoparaffin with a low vapor pressure and a very high octane value. Furthermore, it contains no environmentally unfriendly or toxic components such as aromatics, olefins and sulfur compounds. Alkylate is the preferred gasoline blending component for compliance with ever-stricter environmental regulations, for example, Tier 3 gasoline specifications in the USA and Sino VI gasoline specifications in China. Alkylate is also crucial in meeting the higher octane requirements for performance engines that will enable vehicle fleet mileage efficiency targets to be met, for example, Corporate Average Fuel Economy (CAFE) standards in the USA, and overall gasoline consumption to decrease.

As background, the motor gasoline pool contains, on average, nearly 8% alkylate on a global basis and nearly 13% in the USA, see Figure 4 for details. Ample quantities of light olefins are currently available to increase the world's alkylate production capacity substantially over the next few years and to replace motor gasoline blend streams that are less environmentally friendly.

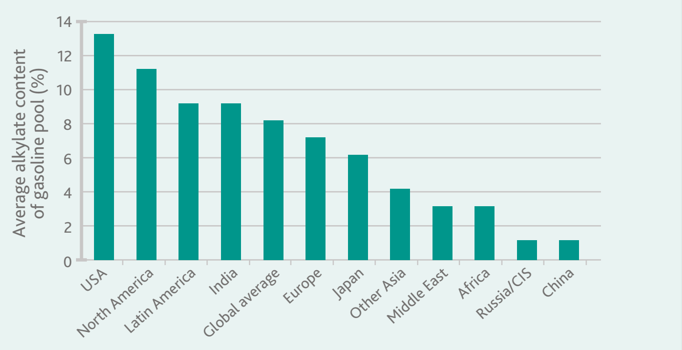


Figure 4: Average alkylate content of gasoline pool.

> Alkylate is crucial in meeting the higher octane requirements for performance engines that will enable vehicle fleet mileage efficiency targets to be met.

Figure 1: Albemarle's catalyst manufacturing facility in Amsterdam, the Netherlands, where AlkyStar catalyst is made.

>>>

>>>

Figure 2: The AlkyClean unit in Zibo.

Through the collaborative efforts between CB&I and Albemarle, the world's first true solid catalyst gasoline alkylation process has been developed and successfully commercialized. The process–catalyst combination (AlkyClean and AlkyStar) solves a long-standing problem of how to recover catalyst activity fully while producing an excellent quality alkylate and thus makes the technology commercially attractive and economically viable.

To find out more about the first successful AlkyClean unit, watch the video about the construction of the unit in Zibo for Shandong Wonfull Petrochemical Group.

CLICK HERE TO SEE VIDEO

The benefits

AlkyClean technology is a true solid acid catalyst alkylation process. This technology produces a high-quality alkylate and the hazards associated with liquid acid use are absent, as are the measures necessary to mitigate them. This gives economic benefits and, above all, confidence that the interests of refinery personnel and the public are being served through the high standards of safety and environmental protection:

- The in-situ regeneration procedure ensures a long catalyst life; the hydrogen off-gas stream from the regeneration is suitable for recovery or for use by other refinery applications.
- The alkylate product is free of acids and halogen compounds, so requires no further treatment. The AlkyClean process does not produce acid-soluble oil, a by-product from the liquid acid processes that must be incinerated.
- Downstream treatment and waste disposal are eliminated because there is no need for washing and neutralization procedures to remove acids, thus no liquid wastes.
- The active noble metal component in spent catalyst can be reclaimed.

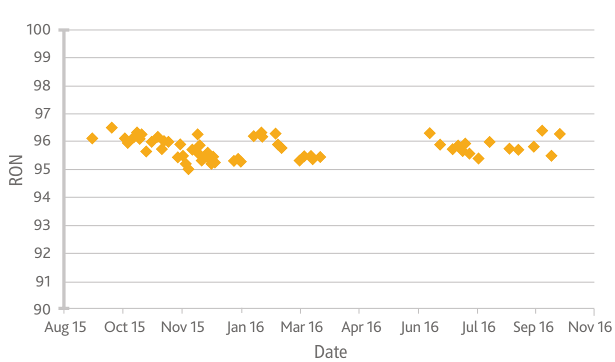


Figure 3: The RON of the alkylate product during the first 14 months of operation.

> "Through the collaborative efforts between CB&I and Albemarle, the world's first true solid catalyst gasoline alkylation process has been developed and successfully commercialized."

FOR MORE INFORMATION, CONTACT:
SeckLeong Lee
Email: seckleong.lee@albemarle.com

INCREASE YOUR REFINERY PROFITABILITY WITH NEBULA® CATALYST

A proven route for driving new profit ambitions for existing hydrotreaters

Those refiners challenged to stretch the targets for their hydroprocessing units and ambitiously and continuously seeking refinery margin improvements have adopted Albemarle's Nebula catalyst. Nebula catalyst affects the hydroprocessing unit in which it is applied and a complex of units in the entire refinery. Over a period of 10 years, Albemarle and its Nebula customers have gained a wealth of commercial experience on how to utilize the unique nature of the catalyst and extract value from it.

Features of Nebula catalyst

- A super high activity bulk metal catalyst jointly developed with ExxonMobil
- Denitrogenation and hydrogenation activity compared with those of conventional catalysts typically more than double and the highest available in the market
- Higher (150–200%) desulfurization relative volume activity compared with conventional catalysts
- Extremely high hydrogenation activity for outstanding nitrogen removal. Nebula catalyst is always loaded more towards the bottom of the reactor in a sandwich configuration with conventional catalysts. By tuning the position and amount of Nebula catalyst, it is possible to satisfy different targets. Nebula catalyst is exceptionally good at removing specific classes of refractory nitrogen species present in high concentrations in cracked stocks.

Customers have calculated that the payback times for the application of Nebula catalyst are on average two to three months. Customer satisfaction is extremely high, which is evidenced by the repeat orders from almost all users.

Nebula in the market

- Deployed globally in a wide range of challenging hydroprocessing applications
- Proven: more than 60 individual users with over 5000 MT sold
- Market acceptance is growing, as evidenced by repeat orders of Nebula: 85–90% of customers buy Nebula again. It gains one new customer every two months (Figure 1).

Unlocking hydroprocessing value

Each refinery has its own unique configuration, feed and product slate, so can benefit in different ways by applying Nebula catalyst. They can

- avoid capital investment for a new reactor, most often in combination with new product specifications, for example, sulfur targets
- increase feed end points or process lower-quality feeds or more cracked feeds such as LCO, vacuum bottom gas oil or coker gas oil (CGO)
- increase throughput
- deploy Nebula's unique hydrogenation activity to produce high-quality, low-aromatic fuels or solvents
- increase volume swell and cetane uplift in ultra-low-sulfur diesel operations if they have a hydrogen surplus
- move conversion capacity into the pretreatment stage by deep aromatic saturation and drive both volume swell and better yield structure in hydrocracking pretreatment
- reduce furnace firing and extend cycle lengths.

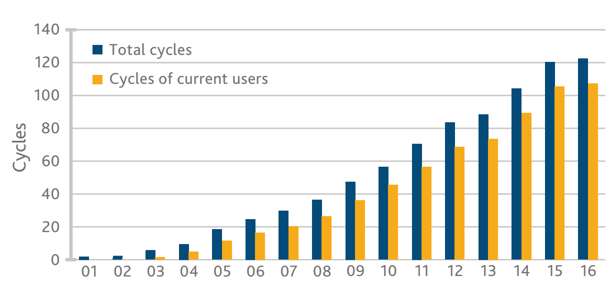


Figure 1: Nebula catalyst has a growing customer base.

>>>

>>>

Nebula catalyst offers unique advantages best exploited by carefully considering its deployment. Its true value proposition reaches further than a single hydroprocessing unit. Albemarle works with its customers to unlock Nebula's value by looking beyond the boundaries of the application of the catalyst based on an enquiry about a single unit.

Naphtha, kerosene and distillate applications

Naphtha application

In naphtha units, Nebula catalyst is loaded to either upgrade distressed feeds or reduce the nitrogen and sulfur slip of the product that will be sent to, for example, a reformer. Albemarle has a commercial reference in this application available with a partial outlet pressure of 10 bar (145 psi). This operation was onstream for seven years targeting product nitrogen below 0.2 ppmw.

Kerosene application

A kerosene unit is operating at a pressure of 130 bar (1885 psi) to produce an almost nitrogen- and sulfur-free, high-value specialty product with a <0.5 wt% aromatic content. The client selected Nebula catalyst after pilot plant testing. An optimum of 50% Nebula catalyst in STAX® loading with NiMo catalysts was consequently defined. The unit started up in 2011 and has been onstream for more than eight years with flawless performance.

Distillate application

The move from Sino IV (50-ppmw sulfur in diesel) specification to Sino V (10-ppmw sulfur in diesel) has required many Chinese refiners to increase their installed catalyst activity by revamping existing units. One of Albemarle's Chinese customers wanted to produce Sino V diesel without a unit revamp. This 77-bar (1117-psi) unit processes 80% cracked material (LCO, CGO and coker naphtha) and is characterized by a high liquid hourly space velocity (LHSV) of 2 h^{-1}. The unit was limited by the capacity of the makeup gas compressor.

To avoid a revamp, the unit was loaded with Ketjenfine® (KF) 860 STARS® and Nebula catalyst with KF 767 STARS catalyst at the bottom. The processed feed contains 0.66-wt% sulfur and 645-ppmw nitrogen. The sulfur in the diesel product has been reduced to less than 5 ppmw and the nitrogen is less than 1 ppmw. The unit started up in May 2014 and has been onstream for three years with a deactivation of 0.3°C/month. A density uplift of 20 kg/m^3 has been obtained.

Another customer has two identical units (catalyst volume, pressure, etc.) in the same refinery running the same feed (straight-run gas oil, light CGO and diesel from a cat feed hydrotreater). Unit A is loaded with 100% KF 848 STARS (conventional NiMo) catalyst and Unit B is loaded with a combination of 78 vol% NiMo and 22 vol% Nebula catalyst. Data from a performance test run after three months onstream showed that Unit A had obtained a density improvement of 16 kg/m^3 (3.8 API) whereas Unit B reached a density uplift of 31 kg/m^3 (6.1 API). Unit B also obtained three points more cetane improvement (based on D4737A). The payback time for the investment in catalyst, including Nebula, was four and a half months.

By loading Nebula catalyst, a third refiner has been able to increase the feed rate for a diesel application by 60%, double the feed nitrogen to 600 ppmw, increase the CGO intake from 12 to 30 wt% and decrease the inlet pressure from 68 to 62 bar (986 to 900 psi). The product properties have also improved: the product sulfur has fallen from 50 to 10 ppmw and the density gain has improved from 8 to 17 g/l, on average.

The current catalyst system, Nebula catalyst in a STAX load with Type II NiMo catalysts, has enabled increased operating severity while reaching the required product properties and a cycle length of two and a half years. The unit is currently finishing its fourth cycle in a row with Nebula catalyst in the system with outstanding performance. For the next cycle, the amount of Nebula has been optimized to increase the cycle length up to three years for higher severity feed, namely higher nitrogen intake and increased feed cut points.

HIGHEST ACTIVITY

The highest activity hydrotreating catalyst on the market: over 2–3 times more active than traditional catalyst

SHORT PAYBACK

Nebula offers improved margins and a short payback period of 2–3months, which leads to more profits for refiners

MARKET ACCEPTANCE

Exceptional customer loyalty and market acceptance: 90% repeat customers plus 1 new customer every 2 months

THE TOTAL PACKAGE

Nebula affects a complex of units across the entire refinery in addition to optimising the individual unit

Deep aromatic saturation

Ultra-deep saturation of aromatics can help refiners to produce new fuels such CARB diesel in California, USA, with a maximum aromatic content of 10 vol%. Sweden has a local diesel product MK1 that contains a maximum of 5 vol% total aromatics.

Traditionally, deep aromatic saturation was obtained by using a dedicated aromatic saturation reactor based on a noble metal catalyst. However, loading Nebula catalyst at the bottom of the pretreatment reactor can eliminate the use of a noble metal catalyst reactor.

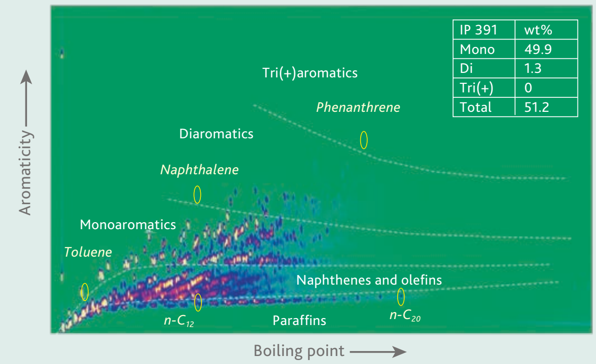


Figure 2: Gas chromatography measurements of LCO hydrocracker products at 83 bar (1200 psi).

Volume swell and cetane uplift

Loading Nebula catalyst will lead to more volume swell and cetane uplift. Figure 2 shows a typical aromatic distribution of product obtained from an LCO hydrocracker and indicates the distribution between paraffins, naphthenes, olefins and mono, di- and tri(+) aromatics. Figure 3 shows that almost all di- and tri(+) aromatics are saturated, but hardly any monoaromatics are saturated when the feed is post-treated over a reactor loaded with a conventional NiMo catalyst system. Saturation of monoaromatics is kinetically unfavorable and barely occurs with a conventional catalyst system.

To obtain a higher product cetane number and a higher density reduction, monoaromatic saturation is required. This can be achieved by applying Nebula catalyst to the reactor. Figure 4 shows the aromatic distribution of the same stream with Nebula catalyst loaded in the post-treatment reactor for two and a half times more saturation of aromatics compared with a NiMo load.

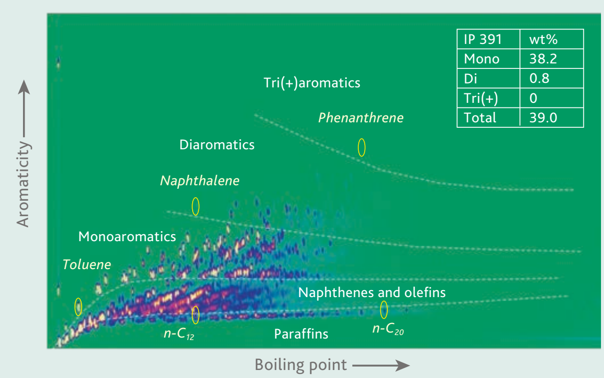


Figure 3: Gas chromatography measurements of post-treated (loaded with conventional NiMo catalyst) LCO hydrocracker product.

> “NEBULA CATALYST ADDS VALUE FOR ALMOST ANY TYPE OF HYDROPROCESSING APPLICATION, FROM NAPHTHA TO HEAVY VGO FEEDS.”

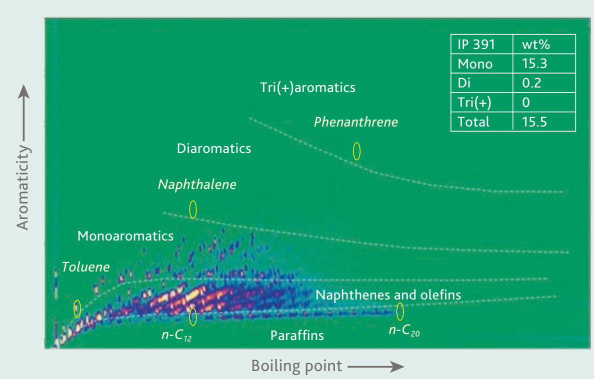


Figure 4: Gas chromatography measurements of post-treating (loaded with Nebula catalyst) LCO hydrocracker product.

>>>

>>>

Hydrocracking

In hydrocracking, Nebula catalyst has been used commercially to improve the yields and product qualities of multiple units significantly. In hydrocracking pretreatment operation, most unit operators tend to think primarily of the nitrogen slip to the cracking catalyst but Nebula catalyst can debottleneck hydrocracking units in multiple ways that can radically increase their profitability.

The most straightforward way to use Nebula catalyst in a hydrocracking unit is to lower the nitrogen slip. When the nitrogen slip to the cracking catalyst is reduced from, for example, 50 to less than 10 ppmw, the operating temperature required to achieve the same level of conversion decreases substantially. This lower operating temperature reduces the unselective thermal conversion, thereby decreasing gas and naphtha yields, and increasing middle distillate yields and thus profitability. With just this simple operational change, middle distillate yields can be increased by 0.5–1 wt% with minimal payback times.

This effect is multiplied if the refinery uses the lower nitrogen slip to the cracking catalyst to opt a more-selective hydrocracking catalyst for the cracking reactor of the unit. The lower nitrogen slip Nebula catalyst achieves enables the more-selective but often lower-activity catalyst to achieve the same conversion at comparable operating temperatures (and thus the same cycle length) to the previous higher-activity cracking catalyst but with significantly improved yields.

A refinery can also elect to use the additional pretreatment activity Nebula catalyst provides to increase the feed severity by either extending the end points of the current feed streams or finding orphan streams in the refinery that are currently being downgraded to fuel oil or coker feed. The exceptional pretreatment activity of Nebula catalyst enables a refinery to process these orphan streams in the hydrocracker and convert them to transportation fuels. Payouts of two to three weeks have been achieved commercially in refineries that have used the opportunities that Nebula catalyst offers. On heavy feeds, Nebula catalyst has proven to show the same high stability as conventional systems.

Using Nebula catalyst in a hydrocracker can be profitable in many ways. Optimized solutions come from detailed discussions between the refinery team and Albemarle on the overall objectives and the constraints of the refinery. By combining resources and inputs, Albemarle has shown that it can find profit improvements in a unit that are limited only by imagination.

Hydrocracker pretreatment application

A hydrocracker operates at 161 bar (2300 psi) and processes 50% material from a residue hydrodesulfurization unit with a LHSV of 0.8 1 h^{-1}. Loaded with a conventional pretreatment catalyst, it had a cycle length of 12 months while targeting 5-ppmw nitrogen slip to the cracking catalyst. Loading a sequence of stacked beds of NiMo and Nebula catalyst was 30°C (54°F) more active and has resulted in a cycle length of two and a half years. The unit is now in its fifth cycle and the cut point of VGO has been deepened further by +10°C (18°F) to a T95 of 550°C (1022°F).

Conclusion

The examples discussed in this article show that Nebula catalyst adds value for almost any type of hydroprocessing application, from naphtha to heavy VGO feeds. For heavy feeds, Nebula catalyst is proven to show the same high stability as conventional systems.

Despite the higher initial investment compared with conventional hydrotreating catalysts, the economic payback time for Nebula catalyst is very short because of the significant economic advantages that its application brings. For each refinery, the profit potential is different. It might be necessary to look beyond just one hydroprocessing unit and looking at the whole refinery scheme.

Nebula catalyst is a drop-in solution in terms of catalyst fill, but it requires ambition and willingness from refineries to challenge and change the status quo around a particular unit. Through its kinetic STAX model and commercial references, Albemarle has a great deal of knowledge and experience in a wide range of applications and related value proposition. The company is ready to work with its customers to look into optimizing the changing demands in refinery products.

To find out more about Nebula catalyst and the value it brings to refiners, please watch the video.

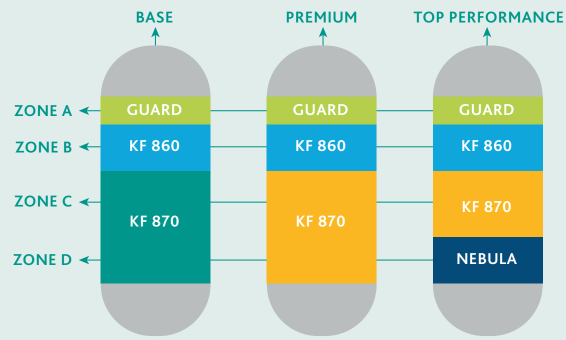
CLICK HERE TO SEE VIDEO

Exceptional activity

Owing to its exceptional hydrogenation activity and by controlling its hydrogen consumption according to Albemarle's STAX principles (see Figure 5), Nebula catalyst can have a profound effect of the qualities of hydrocracker product. These include lower density products and, therefore, increased volume yields, and improvements in other product properties associated with a lower aromatics content such as the viscosity index of base oil feed, the cetane number of diesel and the smoke point of kerosene.

FOR MORE INFORMATION, CONTACT:
Barbara Slettenhaar
Email: barbara.slettenhaar@albemarle.com

Figure 5: Overview of applying Nebula in hydrocracking pretreatment applications.



VALUE PROPOSITION	BASE NIMO	PREMIUM NIMO	TOP PERFORMANCE
Cycle length	Base	+20–30%	+40–50%
Distressed feed intake	Base	+5–10%	+10–20%
Diesel yield	Base	+0.5–10%	+1.0–2.0%
API uplift	Base	+1 API	+2° API
Density reduction	Base	5 kg/m³	10 kg/m³

KETJENFINE® (KF) 907 FOR VGO HYDROTREATING

A high-activity, high-stability catalyst solution

Refiners are increasingly being challenged to produce ultra-low-sulfur gasoline (ULSG). To do so, fluidized catalytic cracking pretreatment (FCC-PT) units are more important than ever and these units require high-activity catalyst systems with good stability to achieve their operating goals. This is especially true for refineries that do not have FCC naphtha post-treatment units, but it is also true for octane-constrained refineries that do have post-treatment units.

KF 907 catalyst is a new addition to Albemarle's FCC-PT catalyst portfolio. It is applicable as a standalone catalyst and as a key component in various STAX® configurations utilizing Albemarle's proprietary reactor loading technology. It is a Type I NiCoMo catalyst specifically designed to achieve high hydrodesulfurization (HDS) activity with very high stability throughout the operating cycle, even in the most demanding conditions. This catalyst also has high hydrodenitrogenation (HDN) activity. It is suitable for use in FCC-PT applications ranging from low- to high-pressure operations.

Higher-activity catalyst solutions help refiners to overcome constraints and exploit opportunities. Thus, KF 907 catalyst can help refiners to meet the challenges imposed by implementing the new Tier 3 gasoline regulations. It can also help refiners to overcome constraints related to unit start-up limitations.

VGO STAX FCC-PT solutions

FCC-PT operations typically only have two reaction zones that vary in length and position during the operating cycle. The catalyst application strategy must account for reaction Zone 1 growth and Zone 2 shrinkage throughout the cycle, as well as the feed properties, the operating conditions and objectives, and the unit constraints, see Table 1.

	ZONE 1 (30–60 VOL%)	ZONE 2 (40–70 VOL%)
Hydrogen partial pressure (ppH_2)	Higher	Lower
Main HDS reaction Main HDS inhibitor	Direct Hydrogen sulfide	Direct + hydrogenation Organic nitrogen
Main HDN/(hydro de-aromatization(HDA) reaction Main HDN/HDA inhibitor	Hydrogenation Organic nitrogen, aromatics	Hydrogenation Organic nitrogen, aromatics
HDS reaction rate HDN/HDA reaction rate	Fast Very slow	Slow Slow
Preferred catalyst types (guidance may vary for specific cases)	CoMo (low to medium pressure) NiCoMo (med. to high pressure) NiMo (high pressure)	CoMo (<60 bar ppH_2) NiCoMo (>50 bar ppH_2) NiMo (>90 bar ppH_2)

Table 1: VGO STAX FCC-PT system design for robust operations.

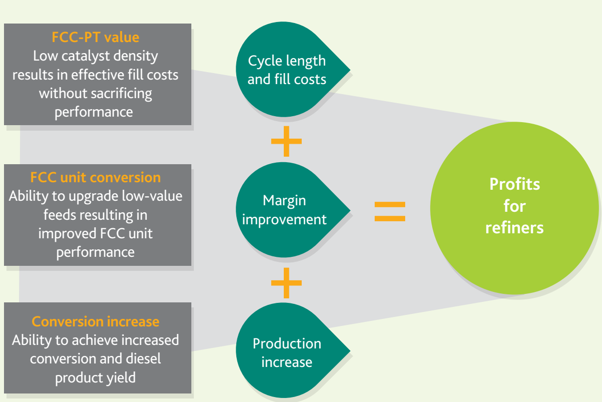


Figure 1: KF 907 catalyst gives value to refiners at all ppH_2 levels.

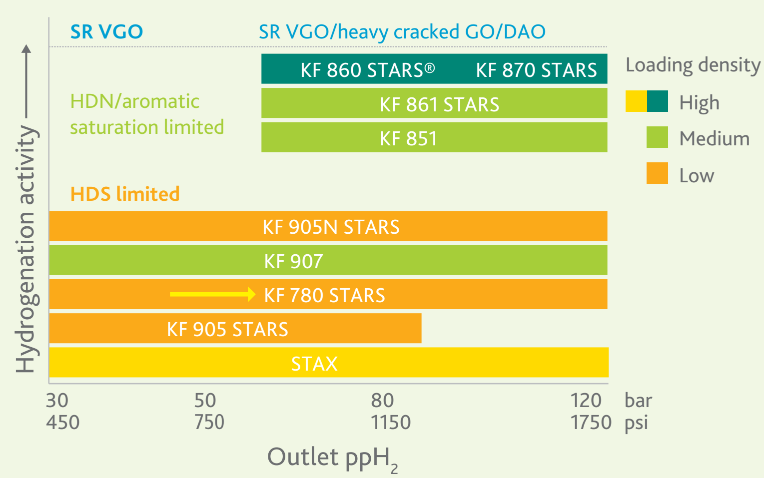


Figure 2: FCC-PT catalyst portfolio.

NiCoMo catalysts, with their balance of HDS and HDN activities, are well-suited for use in zones 1 and 2 of low- to medium-pressure units and for Zone 1 of high-pressure units that are challenged to achieve Tier 3 gasoline sulfur and cycle length targets. The high activity and stability of KF 907 catalyst help refiners to achieve these goals.

Superior performance; higher profitability

Through the superior activity and stability of KF 907 catalyst, refiners can achieve higher profitability. As shown in Figure 1, most of the value is added in the FCC-PT process and by enabling a lower sulfur content in the FCC products. The FCC-PT added value derives from the moderate catalyst loading density and cost coupled with strong HDS/HDN performance throughout an extended cycle. For some refiners seeking higher FCC-PT conversion to diesel products, KF 907 catalyst can also promote this benefit. Additionally, the catalyst can enable upgrading of lower value feedstocks to suitable FCC feeds to improve overall margins for the refiner.

FCC-PT catalysts for any refining objective

Albemarle's portfolio for FCC-PT includes several different catalysts, each available in at least two different sizes. This array of catalysts provides solutions for meeting any refining objective in terms of activity, stability, hydrogen consumption and pressure drop.

These catalysts can be deployed in many different ways according to Albemarle's proprietary VGO STAX FCC-PT technology to generate tailored solutions for specific customer requirements. The overall FCC-PT catalyst portfolio is shown in Figure 2 and the application of the catalysts as standalone solutions or as part of a STAX system is illustrated in Figure 3.

KF 907 catalyst – A proven FCC-PT performer

KF 907 catalyst is a strong performer in pilot plant tests and commercial unit applications operating across the operations spectrum from low- to moderate- and high-pressure FCC-PT applications.

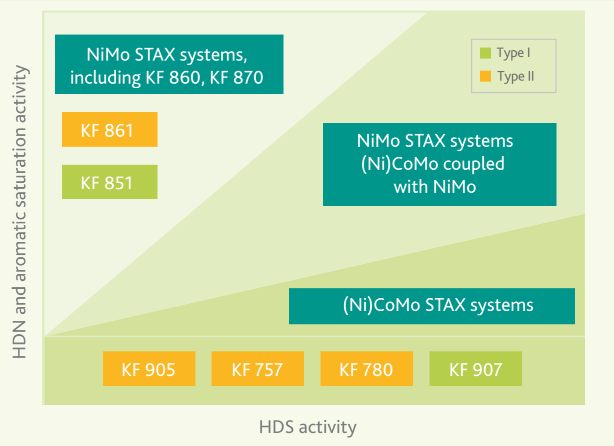


Figure 3: FCC-PT catalyst portfolio applications.

The HDS and HDN relative volume activity (RVA) benefits of KF 907 catalyst are high in reaction Zone 1, and they increase further as the HDS and HDN severities increase in reaction Zone 2. Thus, for low- and moderate-pressure applications, KF 907 catalyst can often be used as a standalone catalyst solution. For high-pressure applications where deep HDS and deep HDN/HDA are the objectives, KF 907 catalyst can be applied in Albemarle's proprietary VGO STAX configurations.

Up to 20% HDS RVA benefit

Extensive pilot plant testing covering a range of feeds and operating conditions has shown KF 907 catalyst to have up to 20% HDS RVA advantage compared with KF 905 STARS® catalyst in FCC-PT applications. These tests covered ppH_2 values ranging from low to high.

One pilot plant test example is shown in Figures 4a–c. This test was conducted at 870 psi ppH_2, 680°F weighted average bed temperature (WABT) and varying liquid hourly space velocity (LHSV) with VGO feed containing 2.0 wt% sulfur, 1600 wppm nitrogen and 21.4 API gravity.

Figures 4a and 4b plot product sulfur and product nitrogen, respectively, against 1/LHSV on a semi-log chart. In essence, they show how these product properties respond to increasing "residence time" in the reactor. Figure 4c plots RVAs for HDS and HDN against 1/LHSV. These RVAs are estimated with a process model using 1.65 reaction order kinetics for the HDS reactions and 1.0 reaction order kinetics for the HDN reactions. Figures 4a and 4b can be used to assess RVAs directly for any product sulfur and nitrogen level by comparing the ratio of LHSVs for the two catalysts at constant product quality.

>>>

>>>

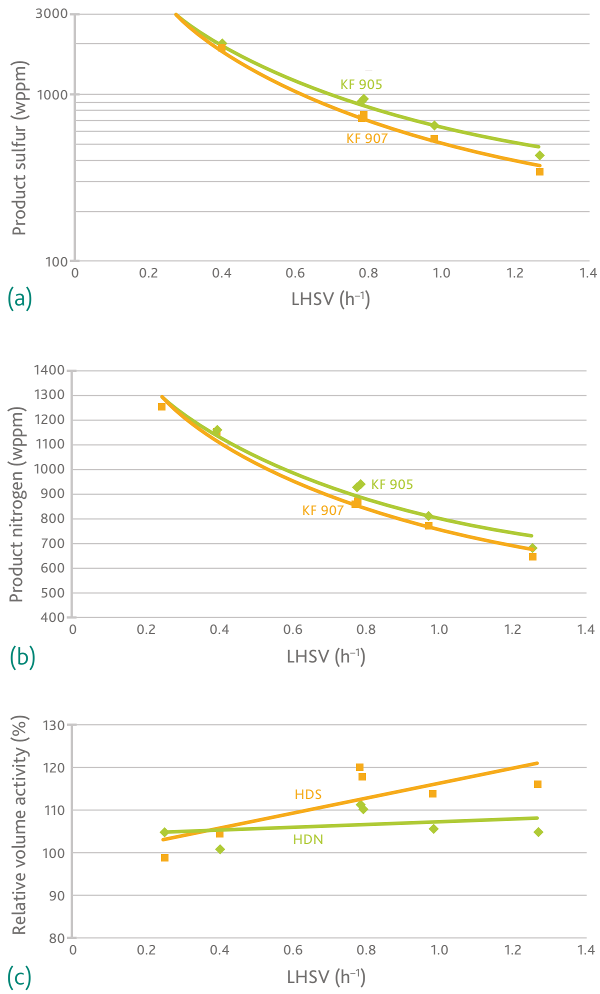


Figure 4: KF 907 catalyst performance benefits for FCC-PT applications compared with using KF 905 STARS catalyst: (a) product sulfur; (b) product nitrogen; and (c) HDS/HDN RVA.

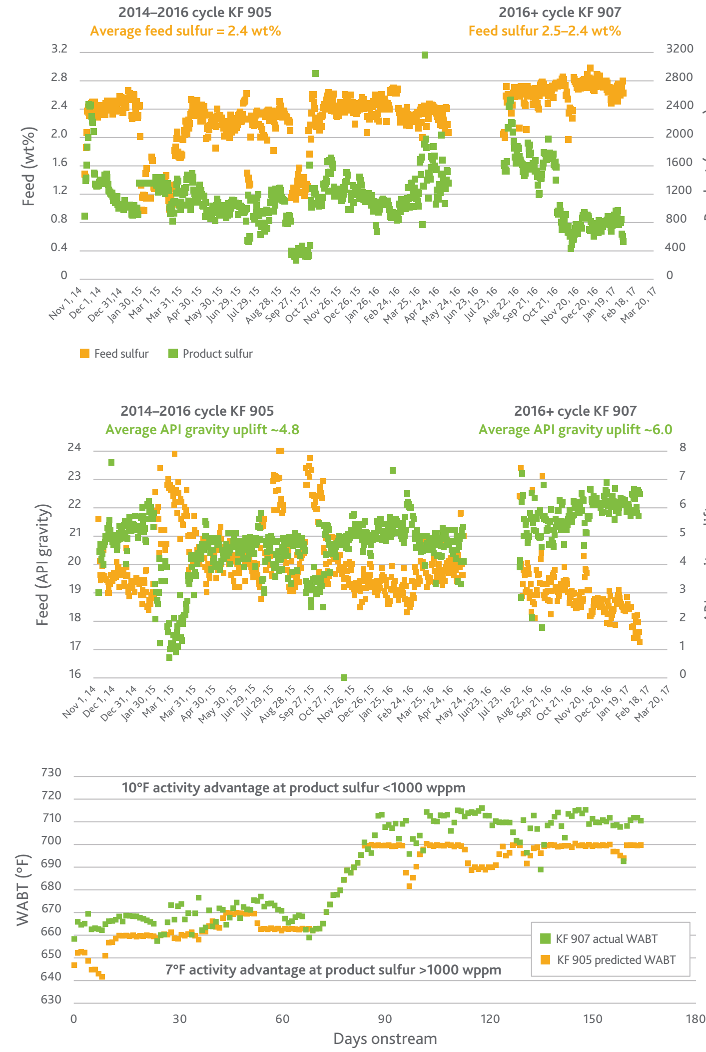


Figure 6: Comparison of KF 907 catalyst's performance with KF 905 STARS catalyst in a high-pressure FCC-PT application: (a) product sulfur; (b) feed API and API uplift; and (c) activity benefits.

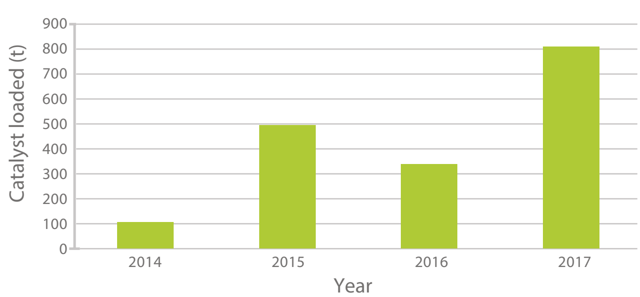


Figure 5: KF 907 FCC-PT catalyst loaded into commercial units.

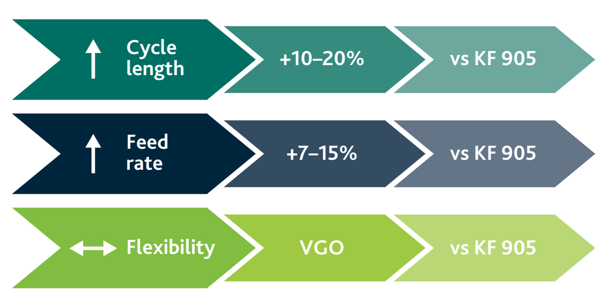


Figure 7: Value propositions for FCC-PT applications of KF 907 catalyst.

TYPICAL CATALYST PROPERTIES							
SHAPE/SIZE	SCS, lb/mm	Abrasion, wt%	Nominal size, mm	Average length, mm	Sock loading density, g/ml (lb/ft³)	Dense loading density, g/ml (lb/ft³)	Sulfur uptake, wt%
1.3Q	>4.0	<2.0	1.2 × 1.4	2.8–4.5	0.66 (41.0)	0.77 (48.0)	12
2Q	>5.0	<2.0	1.8 × 2.1	3.5–6.5	0.66 (41.0)	0.77 (48.0)	12
1.5E	>2.5	<2.0	1.4	2.8–4.5	0.72 (45.5)	0.83 (52.0)	12

Table 2: Typical properties of KF 907 catalyst.

Commercial performance confirms pilot plant results

KF 907 catalyst has been successfully applied in 10 commercial FCC-PT cycles, including two units operating at >1200 psi ppH_2 in the USA. As shown in Figure 5, more than 1600 t of KF 907 catalyst have been installed in commercial units since its introduction in 2014.

The commercial FCC-PT example highlighted in Figure 6 compares KF 907 catalyst's performance in the current cycle against the previous successful cycle with KF 905 STARS catalyst. This unit treats a nominal 50,000-bbl/d feed that is a blend of heavy VGO and heavy coker gas oil (HCGO). As shown in Figure 6, the API gravity and sulfur and HCGO content of the feed are all worse for the current cycle, whereas the product sulfur is lower and the density uplift is higher.

The 7–10°F lower WABT for KF 907 catalyst translates into a 15–20% HDS RVA advantage for KF 907 catalyst compared with KF 905 STARS catalyst, which is consistent with pilot plant test results. The deactivation rate for the KF 905 STARS catalyst was 1.1°F/month, and the deactivation rate for the KF 907 catalyst is averaging 0.8°F/month.

KF 907 catalyst properties and overall value proposition for refiners

The typical catalyst properties reported on the KF 907 data sheet are shown in Table 2. As implied by the information in Figure 2, this catalyst has a moderate loading density typical of many FCC-PT catalysts. Because it is a Type I catalyst, its loss on ignition is very low and its as-received loading densities are very close to the loading densities shown on a dry basis.

This catalyst can be ordered in asymmetric quadralobe (either 1.3 or 2 mm) or cylindrical (1.5E) shapes. Packaging can be large bags or steel drums.

Figure 7 shows the most probable value propositions for KF 907 catalyst compared with KF 905 STARS catalyst in typical FCC-PT applications. The HDS RVA benefit for KF 907 catalyst can be expected to be up to 15%; higher benefits are achievable as the HDS severity increases. This HDS RVA benefit is typically accompanied by an HDN RVA benefit of up to 10%. Depending on feed characteristics and operating conditions, cycle length can generally be extended by at least 10%; ≥20% cycle length benefits can often be expected.

For refiners opting to regenerate and reuse FCC-PT catalyst, KF 907 catalyst can provide even more value because it recovers >90% of the fresh catalyst activity with regeneration only. It also helps resolve the start-up constraints that sometimes result from the temperature at which VGO feeds are introduced to the unit. KF 907 catalyst is amenable to gas phase sulfiding procedures.

Summary

KF 907 NiCoMo catalyst is a high-activity, high-stability FCC-PT catalyst with superior performance proven in commercial applications. It can be successfully applied across the full range of FCC-PT operating pressures and as a standalone catalyst solution or as a key component in a VGO STAX configuration. As a result, KF 907 catalyst is a valuable resource for helping refiners to meet the challenges of ULSG regulations.

FOR MORE INFORMATION, CONTACT:
George Anderson, Brian Muegge or Luca Moraca
Email: george.anderson@albemarle.com, brian.muegge@albemarle.com or luca.moraca@albemarle.com

“KF 907 CATALYST IS A VALUABLE RESOURCE FOR HELPING REFINERS TO MEET THE CHALLENGES OF ULSG REGULATIONS.”

MAXIMIZING OCTANE BARRELS WHILE PRODUCING ULTRA-LOW-SULFUR GASOLINE

Taking advantage of the industry's best-performing catalyst for selective gasoline hydrotreating processes: RT-235.

Over the past decade, the refining industry has taken major steps toward accommodating the increasingly stricter regulatory requirements that aim for a low-sulfur world. Europe has generally been the frontrunner on regulations for low-sulfur, "clean" transportation fuels, but the rest of the world is also gearing up to accommodate changes in maximum sulfur limits in gasoline over the next few years. While reducing emissions from existing vehicles, the lower gasoline sulfur limits will also enable more-stringent vehicle emission standards and make emission control systems more effective.

Several operational and performance unknowns are associated with reducing the average sulfur content of gasoline to ≤10 ppmw. To address this challenge and meet regulatory requirements, refiners are carrying out extensive technical and economic studies of the various catalyst drop-in solutions available in the market to assess which would provide maximum profitability and performance for their refineries.

The processing of FCC naphtha takes on an even more important role in meeting the new regulatory changes. Table 1 shows typical gasoline pool blending components before treating.

	SULFUR, PPM	PERCENTAGE OF GASOLINE POOL, %	CONTRIBUTION TO SULFUR, %
FULL-RANGE FCC NAPHTHA*	2000	45	99
LIGHT, STRAIGHT-RUN NAPHTHA	150	3	<1
BUTANES	10	5	<<1
ALKYLATES	3	10	<<1
REFORMATE	1	32	<<1
C5/C6 ISOMERATE	3	5	<<1

*Range can be 300 to 3000-ppm sulfur depending on the crude source's degree of catalytic feed hydrotreating

Table 1: Typical gasoline pool blending components.

Although the gasoline pool comes from various sources in the refinery, full-range FCC naphtha typically accounts for 30–50% of the overall gasoline blend and is the biggest contributor to sulfur. Operating selective hydrodesulfurization (HDS) gasoline units to process FCC naphtha effectively generally entails lower investment and operating costs compared with the alternatives available for meeting the regulatory changes.

Although process configurations and operating constraints vary between refineries, the chosen catalyst has a large impact on the level of HDS activity and selectivity for octane retention. Refiners judge that they can achieve maximum refinery economic benefits by increasing operating severity and the yields of higher-octane products. Robust catalyst stability, improved performance with aging and the ability to cope with significant variations in feed components are all important catalyst parameters for reliably producing ≤10-ppmw, ultra-low-sulfur gasoline while maximizing octane barrels and profitability.

Owing to strong gasoline margins, some refiners are focusing on developing a strategy to maximize gasoline production while also preparing for the upcoming regulatory changes.

Octane demand and refiner profitability

Demand for octane remains high

Although changes to gasoline regulations generally focus on product sulfur, they also concern octane quality. Gasoline with a higher octane number enables greater engine efficiency and performance. The US gasoline octane market has varied over the years and has typically been affected by changes in gasoline grade demand, crude oil quality, crude and gasoline prices, gasoline specifications and octane enhancers.

To track pricing and historical demand for octane better, Albemarle has developed a correlation for octane barrel value that combines market data from the U.S. Energy Information Administration with commercial customer data over the last two decades. Figure 1 summarizes the trend in the value of the road octane number, which is the average of the research octane number (RON) and motor octane number (MON).

The data show that octane values rose between 2004 and 2006 when the market was also seeing an expansion in refinery gasoline production. Crude and product prices were rising and methyl tertiary butyl ether was being phased out of the gasoline pool owing to concerns over its solubility in water and consequent contamination of water resources. From 2007 to 2011, there was a slowdown in octane demand because of the increased use of ethanol as an octane booster and lower refinery octane targets. The time frame also coincides with severe economic recessions in the global market.

However, the octane barrel value, which fluctuated periodically from 2012 to 2016 and increased to historic highs, has now plateaued. Some nontraditional drivers leading to the increased octane value include high-compression engines, premium share increase, ethanol growth decline and processing more light tight oils.

The high cost of octane is expected to continue, as regulations for lower sulfur levels are already in effect. Added costs will come in the form of new refining equipment or higher-severity hydrotreating of gasoline. Additionally, the lower sulfur requirements will also cause refiners to blend less light naphtha into the gasoline pool owing to its low sulfur and octane values. As refiners look for new ways to improve octane quality while meeting sulfur regulations, catalyst drop-in solutions for existing selective HDS gasoline units are effective ways for them to capitalize on the market changes without large capital investments.

Profitability: Octane is still the name of the game

With the demand for octane remaining high, refiners have an opportunity to capitalize on profit margins by maximizing octane barrels while producing ultra-low-sulfur gasoline. Figure 2 captures the impact of better octane retention from an existing selective HDS gasoline unit. Using data from the gasoline octane market and Albemarle's correlation for octane barrel, the plot uses an estimated value of $1 per octane barrel for the valuation. However, the cost of octane will vary for each refiner based on the octane target, among other factors relating to refinery operations.

For example, if a refiner has a single-stage unit that is processing 30,000 bbl/d from a selective HDS gasoline unit, an improvement of 0.5 in the RON for the product could lead to approximately $5 million a year in additional profits. However, a two-stage unit processing the same feed rate could expect to achieve a RON improvement greater than 1, which would lead to correspondingly larger profits for the refinery (upward of $10 million a year).

Catalytic solutions

Conventional hydrotreating to reduce sulfur in gasoline has the unfortunate side effect of saturating olefins and consequently reducing octane. In preparation for more-stringent regulation and performance optimization, some refiners have carried out an extensive study of the various catalyst drop-in solutions available in the market for their selective HDS gasoline units. Outside the general catalyst performance characteristics a refiner typically looks for when selecting a catalyst system, the refiners wanted to challenge the status quo and strive for a solution that offered

- improved selectivity to save additional octane
- increased HDS activity to handle more-severe feedstocks with higher sulfur levels
- improved carbon monoxide tolerance to prevent octane loss.

To help the refiners reach their vision of optimum performance and profitability, Albemarle proposed its next-generation catalyst for selective gasoline hydrotreating process: RT-235. This industry-leading catalyst was a joint development by ExxonMobil and Albemarle, and the result of screening about 500 catalyst formulations by testing to ensure an optimized support structure and metals distribution.[1]

RT-235 catalyst has excellent selectivity to desulfurization reactions while significantly boosting overall desulfurization activity. The extra desulfurization activity can provide significant economic benefits, especially for units requiring a relatively high level of desulfurization. The performance improvement enabled the refiners to enhance the operation of their selective HDS gasoline units by capitalizing on greater octane retention and processing more-severe feedstock without additional octane loss. Both modes of operation significantly improved profitability while enabling the units to produce ultra-low-sulfur gasoline.

The performance of RT-235 catalyst has been a major milestone in the selective FCC gasoline hydrotreating process. This catalyst has a proven track record. It has been applied in more than 20 commercial applications and resulted in exceptional overall profitability for its users. These operations confirm the benefit of RT-235 catalyst with octane retention from 0.1 to more than 1 RON, depending on unit configuration and feed severity. Catalyst stability and resistance to upsets have found to be excellent and enabled users to run reliable operations with long cycle lengths.

>>>

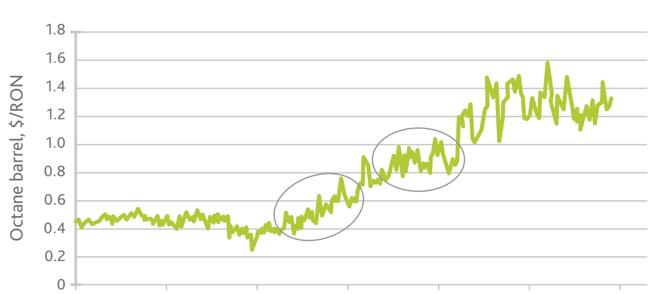


Figure 1: Albemarle correlation for octane barrel.

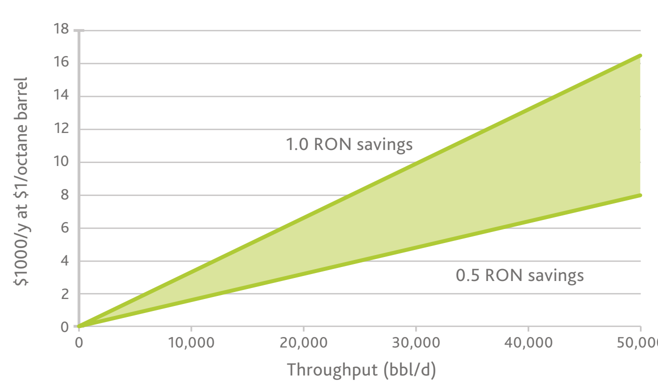


Figure 2: Profitability from increased octane retention.

>>>

Commercial case studies

Processing more-severe feedstock while retaining octane

Refinery A has a single-stage gasoline reactor and a FCC pretreatment unit upstream of the gasoline unit. This unit meant that the average feed sulfur to the gasoline reactor was on the low side, 350–400 ppmw. The feed to the unit was a mixture of light catalytic cracker naphtha (LCN), heavy catalytic cracker naphtha (HCN), light, straight-run naphtha, delayed coker gasoline and platformer pentanes. The previous cycle was not loaded with Albemarle catalyst and the current cycle was short-loaded with RT-235 catalyst because of its exceptional activity.

The main objective for the refiner was to improve profitability across the unit by processing more-severe feed while retaining octane. Owing to the new regulations being implemented and the need to produce gasoline with less than 10-ppmw sulfur, the amount of HDS across the gasoline unit was hard to increase.

Figure 3 shows the feed rate for the current cycle. For most of the cycle, the unit has consistently been processing at about 20–25% above the design feed rate. The refiner was able to operate at this rate by specifically processing more HCN feedstock. On the previous cycle, the unit was processing 5% HCN of the total feed. Now, however, the unit is processing 20–25% HCN.

Figure 3 clearly shows that this refiner was able to push the boundaries of the current cycle by increasing the feed rate and by processing more-severe feedstock in the form of HCN. One way the refiner was able to increase the HCN feed to the unit so drastically was by taking a deeper cut of the HCN feedstock, as shown in Figure 4.

Figure 4 shows the difference between the HCN T90 boiling point on the previous cycle and the current cycle. The current cycle is processing a 40–50°F deeper cut into the HCN T90 boiling point to increase the HCN feed. One of the key objectives of this refiner was to maximize gasoline production because of the favorable margins of gasoline over diesel. However, a main drawback of taking a deeper cut into the HCN feed is that it introduces more-complex sulfur species that need treating, which requires increased operating severity from the unit to reduce the product sulfur to less than 10 ppmw.

A typical HCN feed consists of mercaptans, thiophenes and benzothiophenes. To understand the breakdown of the HCN feed components better, Albemarle completed sulfur speciation testing of the HCN feed with the lower cut point from the previous cycle and compared it with the HCN feed with the deeper cut point on the current cycle, see Table 2.

Table 2 shows the HCN feed from the previous cycle consisted mostly of thiophenes and about 40% benzothiophenes. However, the sulfur distribution of the HCN feed from the current cycle shows a shift to mostly benzothiophenes. This shift causes the unit and catalyst system to work harder to treat the more-complex sulfur species to drive product sulfur below 10 ppmw.

As the main objective of this refiner was to improve profitability across the unit by processing more-severe feed while retaining octane, Figure 5 shows the average octane loss across this unit as the operating severity increased. This refiner was able to limit the octane loss across the unit to between 2 to 3 numbers and to process more-severe feedstock while producing 5–10-ppmw-sulfur product. Utilizing RT-235 catalyst enabled the refiner to achieve additional profits by pushing the boundaries of this gasoline unit while retaining octane and meeting the regulatory changes.

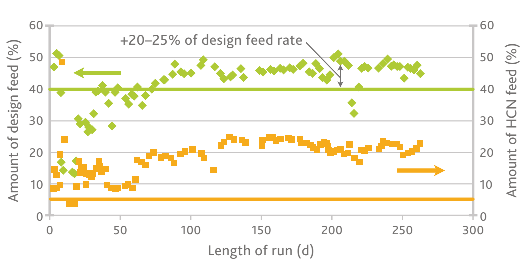


Figure 3: Feed rate operating strategy on current cycle.

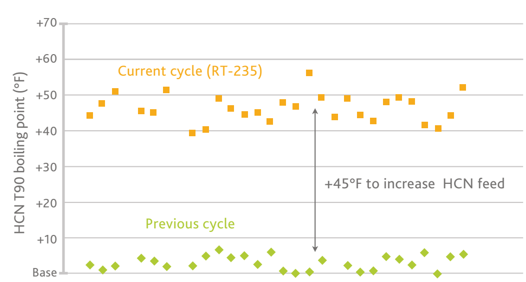


Figure 4: HCN T90 boiling point (D86)

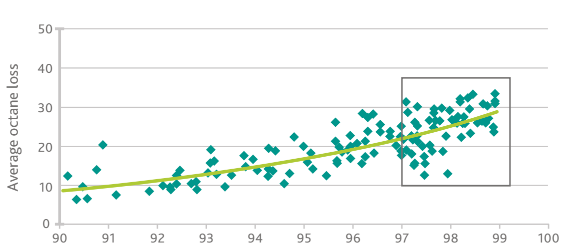


Figure 5: Average octane loss.

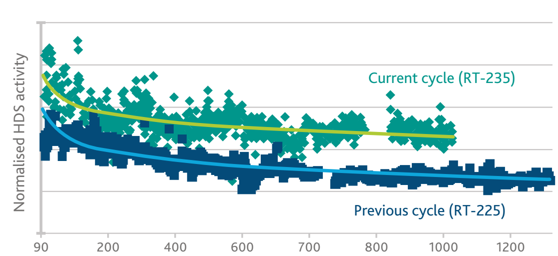


Figure 6: HDS activity comparison between the two cycles.

SULFUR COMPOUND	SULFUR IN FEED, % PREVIOUS CYCLE	CURRENT CYCLE
MERCAPTANS	1	3
THIOPHENES	60	17
BENZOTHIOPHENES	39	90

Table 2: HCN feed sulfur speciation.

Pushing the boundaries without sacrificing cycle length

Refinery B has a two-stage gasoline reactor and the feed sulfur is about seven times higher, averaging 2700 ppmw on the current cycle, than Refinery A. This refinery has a long history of operational excellence with Albemarle catalysts, as two generations of catalyst has been utilized in the unit with a combined experience of over 10 years.

Before the change to 10-wppm-sulfur requirements, Refinery B's preferred solution was to produce low-sulfur gasoline using RT-225, a premium, low-density catalyst. For the current cycle, this refiner wanted to increase the feed rate by 15% and the feed sulfur content by 600 ppmw while improving profitability from maximum octane retention. The unit primarily processes a mixture of LCN and HCN. To meet the objective, RT-235 catalyst was short-loaded for the current cycle. The performance benefits are shown in figures 6 and 7.

Figure 6 shows the normalized HDS activity of the previous cycle loaded with RT-225 catalyst over the first four years of operation. Using the same normalization factors, the RT-235 cycle shows a clear advantage in activity, up to twice as much as the previous cycle. Even with the current cycle processing at increased throughput and feed sulfur levels, and at higher operating severity to reduce product sulfur, the stability or deactivation rate across the cycle remains consistent with the previous cycle. This is another example of how a refiner was able to push the boundaries of a gasoline unit with RT-235 catalyst without sacrificing target cycle length for improved profitability.

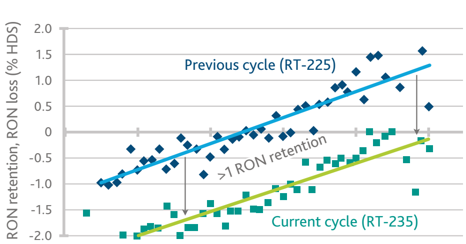


Figure 7: Octane retention by current cycle with RT-235 catalyst.

Figure 7 shows a slightly different way to highlight the average octane loss across the unit as operating severity is increased. To make comparing the two cycles easier, the data were normalized to a target operating severity. The data from the previous cycle show that operating below the target severity leads to octane retention, whereas operating above the target severity leads to additional octane loss. So, normalizing the current cycle data to the same conditions clearly shows the octane retention from the RT-235 catalyst system versus the previous cycle. Even with increased operating severity, RT-235 catalyst maintained its greater than 1 RON advantage. Based on the refinery's economics and valuation of octane, this refiner was able to achieve an additional $12 million a year in profits from greater octane retention by utilizing RT-235 catalyst.

Conclusion

With more stringent gasoline regulations being implemented worldwide, refiners are looking for solutions with minimum investment to reduce the average sulfur content of gasoline. To address this, some refiners have carried out an extensive technical and economic study of various catalyst drop-in solutions available in the market for selective HDS gasoline hydrotreaters.

With the value of octane gasoline barrel at an all-time high, these refiners wanted to challenge the status quo and strive for a solution that enabled them to reach optimum performance and profitability. For the units at refineries A and B, the refiners selected Albemarle's latest-generation catalyst for selective gasoline hydrotreating processes: RT-235. This catalyst has excellent selectivity to desulfurization reactions while significantly boosting overall desulfurization activity. RT-235 catalyst has a proven track record in numerous applications and provided exceptional overall profitability for users.

At Refinery A, RT-235 catalyst was utilized to optimize performance when making ultra-low-sulfur gasoline while introducing a more-severe feedstock and controlling the octane loss across the unit to between 2 to 3 RON. At Refinery B, the transition to RT-235 catalyst resulted in a twice as much HDS activity. The improved selectivity with RT-235 catalyst for octane retention enabled Refinery B to save more than 1 RON in comparison with the previous cycle, which resulted in extremely favorable refinery economics and profitability.

Reference

[1]Mayo, S., Greeley, J. and Wellons, M.: "RT-235: Commercial performance of next generation SCANfining™ catalyst," paper AM-11-58 presented at the 2011 NPRA Annual Meeting, San Antonio, TX, USA (March 20, 2011)

FOR MORE INFORMATION, CONTACT:
Jignesh Fifadara
Email: jignesh.fifadara@albemarle.com