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Catalyst Courier

Tier 3 regulations and their impact on refineries

Best practices for using simulation models in FCC catalyst bids

New catalyst, Ketjenfine® 780 STARS®, leads the way for clean fuels hydrotreating

ALBEMARLE®

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EVENTS DIARY 2017

March

19–21	AFPM Annual Meeting, San Antonio, TX, USA
29–30	ARTC 20th Annual Meeting, Jakarta, Indonesia

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 (formerly Q&A), Austin, TX, USA

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SILVIO GHYOOT
PRESIDENT,
REFINING SOLUTIONS

THE CASE FOR CAUTIOUS OPTIMISM IN UNCERTAIN TIMES

The past few years have seen a significant supply–demand imbalance in the oil and gas industry and a dramatic fall in oil prices associated with slowing economic growth. The refinery sector could do with a period of increased stability and predictability, but is that what the future holds?

Three main factors are driving the market for refinery catalysts: global megatrends such as rising populations and increased personal mobility; the continuing emphasis on environmental protection and more-stringent fuel specifications; and an industry-wide shift towards larger and more-complex refinery and petrochemical facilities.

The adoption of more-stringent limits for fuel emissions is a crucial issue in the hydroprocessing arena. In many parts of the world, the 10-ppm level for sulfur has become the norm and western environmental standards are being taken up more widely. There are changes too in FCC, which has long been a crucial part of the gasoline economy but is now making a larger contribution to petrochemicals and olefins.

Regional differences, price changes and greater crude complexity

Future demand and the prospects for long-term growth center on emerging markets such as South East Asia, the Middle East and China. The situation will be very different across the West, where a continuing shift to alternative energy sources and improving fuel efficiency will be the controlling factors.

Oil prices clearly influence refinery margins. We think that oil will remain at its current range in 2017 and that we will see slight growth, but any sudden price change would be disruptive because it will cause uncertainty. Another challenge for refiners is how to convert more-complex crudes into ever-more-tightly specified products.

The outlook for 2017 suggests that refiners should be cautiously optimistic. We expect gasoline to grow, though not as much as it did from 2015 to 2016 when the market was in recovery. As the industry moves through another period of transition, Albemarle's top priority is to provide customized products that help refiners to address current requirements, deliver products to specification and adapt to what could be an unpredictable future.

SILVIO GHYOOT
PRESIDENT, REFINING SOLUTIONS

NEWS
FROM ALBEMARLE

LITHIUM OPERATIONS TO EXPAND IN CHILE

Atacama Desert, Chile

After discussions with the Chilean Economic Development Agency and with legal approval from the appropriate authorities, Albemarle's lithium production rights agreement in Chile has been amended.

The ideal place to support the growing global demand for lithium, the Atacama Desert holds enough lithium to supply the world for decades. However, this strategic mineral is subject to strict extraction quotas from the Chilean government.

Stephen Elgueta, vice president of Albemarle's lithium resources group, says, "We believe the Salar de Atacama is the best lithium brine reserve in the world and we have a responsibility to ensure this strategically important resource is properly managed so that it can continue to provide value for all stakeholders."

Albemarle's Planta La Negra in Antofagasta will expand and its quota for authorized lithium extraction at the Salar de Atacama facility will increase. Effective from December 30, 2016, the amended agreement provides Albemarle with sufficient lithium to produce more than 80,000 t/y of technical- and battery-grade lithium salts over the next 27 years.

John Mitchell, president of Albemarle's Lithium and Advanced Materials Global Business Unit, adds, "We are proud to be part of this transformational agreement that allows for broad collaboration, value sharing and sustainable development of important lithium-based advanced materials within the country of Chile."

The extended agreement also supports links between Albemarle and the local indigenous communities while creating significant funding for research and development for energy storage, renewable energy and advanced battery materials.

FAREWELL TO CHEMETALL SURFACE TREATMENT

The $3.2 billion sale of Albemarle's Chemetall surface treatment business and related assets to German chemicals group BASF is complete.

Luke Kissam, Albemarle's chairman, president and chief executive officer, comments, "We are very pleased to complete this transaction, which will accelerate our transformation into a company focused on powering increased energy efficiency around the world through our leading lithium and refinery catalysts businesses. We appreciate the contribution that the Chemetall surface treatment team has made to Albemarle over the last two years and we are certain that BASF will be an excellent steward of this outstanding business."

> "We are proud to be part of this transformational agreement that allows for broad collaboration, value sharing and sustainable development of important lithium-based advanced materials within the country of Chile."

CMO AWARD WINNER

Our Fine Chemistry Services group was a multi-category winner in the 2017 CMO Leadership Awards. The team won awards in all six of the core categories: quality, reliability, capabilities, expertise, compatibility and development.

Life Science Leader developed the CMO Leadership Awards in 2011 to support the vetting of outsourcing partners, which is a time-consuming and complex process. The winning contract manufacturing organizations (CMO) are chosen through third-party, impartial market research based on feedback from sponsor companies that utilize outsourcing services, so, very well done to the Fine Chemistry Services team.

CORPORATE FOCUS

As Albemarle continues to grow, we must not forget our responsibility to the environment. Here is a sample of the initiatives we follow.

Our marshes

We help to protect the environment through two unique wastewater treatment facilities at our Magnolia, USA, plants. The marshes at the south and west plants remove low levels of toxic chemicals from large quantities of water using aquatic plants. Treating an average of one million gallons a day of noncontact water and storm-water runoff, the project is a result of 20 years of research by National Aeronautics and Space Administration on wastewater treatment and reuse in space.

Albemarle employees are on daily duty at the marshes where their responsibilities include feeding wildlife and monitoring the health of the marshes.

Responsible Care

Responsible Care is the US chemical industry's award-winning performance initiative. It has resulted in a 70% reduction in emissions and an employee safety record that is four times better than the average in the US manufacturing sector.

As a member of the American Chemistry Council, Albemarle is committed to achieving the principles of Responsible Care, including minimizing the footprint from its operations; distributing products safely; providing excellent training; auditing its carriers and distributors; understanding and communicating the hazards of its products though testing; and being responsible contributors to the communities where it operates.

Corporate responsibility

Our Pasadena, USA, plant has adopted Jackson Intermediate School as a partner in education. Albemarle employees participate in book drives, science fair judging, monthly mentoring programs and tutoring algebra and environment education workshops. We also have employees serving on the education subcommittee and the community relations and environment committees.

Our employees also partake in volunteer opportunities such blood drives and the Trash Bash and Hazardous Waste Collection Day.

EPA ENERGY STAR® partner

ENERGY STAR is a voluntary program run by the United States Environmental Protection Agency (EPA) that helps businesses and individuals to save money and protect the climate through superior energy efficiency. Albemarle is a partner in ENERGY STAR and is committed to protecting the environment through continuous improvement of its energy performance. We believe that an organization-wide energy management approach helps us to enhance our financial health and to preserve the environment for future generations.

> “As a member of the American Chemistry Council, Albemarle is committed to achieving the principles of Responsible Care.”

LUKE KISSAM ELECTED CHAIRMAN

On November 7, 2016, Luke Kissam was elected as Albemarle's chairman in addition to his other responsibilities. Kissam became chief executive officer in 2011, joined the board of directors in 2011 and became president in 2013.

Kissam succeeded Jim Nokes, who continues to serve on the board of directors as lead independent director. Nokes commented, “It has been my honor to serve as chairman of the board of directors. I am confident in Luke's ability to lead this board, as he can help ensure leadership continuity through Albemarle's continued growth.”

HELPING REFINERS DRIVE DOWN SULFUR CONTENT

Striking the balance between investment costs, sustainability of operations and long-term profit

DAVE CLARY
VICE PRESIDENT, HEAVY OIL UPGRADING

The United States Environmental Protection Agency (EPA) Tier 3 regulations came into force on January 1, 2017. These rules, which are designed to reduce air pollution from passenger cars and trucks, require most US refiners to reduce the average level of sulfur in gasoline from 30 to 10 ppmw, with a maximum of 80 ppmw sulfur in any gallon of gasoline.

According to the EPA, the new gasoline sulfur standard will make emission control systems more effective for existing and new vehicles, and will enable the application of more stringent vehicle emissions standards, as removing sulfur enables a vehicle's tailpipe catalytic converter to work more efficiently. The EPA estimates suggest that the new sulfur standard will increase fuel manufacturers' production costs by about 0.65¢ per gallon.

Small refining companies and low-volume refineries have more time to comply with the 10-ppm annual sulfur average. Refiners that meet a range of criteria, including having fewer than 1500 employees company-wide and having produced less than 155,000 bbl per calendar day during 2012, will have until January 1, 2020, to comply. The EPA has also defined provisions that allow some companies to petition for delayed compliance on a case-by-case basis for situations of extreme hardship or extreme unforeseen circumstances.

But, for most US refinery operators, the new targets are an immediate and significant challenge. Some industry commentators are looking to Japan and Europe as models for achieving the 10-ppm annual sulfur average, but the configurations and capacities of oil refineries in these regions are often very different from those in the USA. Any comparison must acknowledge the fact that US refiners have made major investments in infrastructure to maximize gasoline production from the refining of heavy sour crude oil. This oil can be sourced from foreign markets at a significant discount compared with sweeter crudes. Switching to sweeter feedstocks might carry substantial cost implications and, although it would help to ensure compliance, it would probably be no more than a short-term solution.

The challenge is to strike the right balance between investment costs, sustainability of operations and long-term profit under the constraints of the Tier 3 regulations. This balance varies from refinery to refinery and may change over time as feedstocks, processes, catalysts and regulations evolve. There is a further dimension to the issue of compliance. Although gasoline regulation changes generally focus on product sulfur, they also affect octane quality.

Focusing on FCC for sulfur removal

The reformer and the FCC unit are the

biggest contributors of volume to the overall gasoline pool (Table 1), and FCC gasoline is, by far, the biggest source of gasoline pool sulfur. Consequently, naphtha hydrotreating before the reformer, FCC pretreatment (FCC-PT) and FCC naphtha post-treatment have the most significant impacts on gasoline pool sulfur. It seems likely that FCC-PT and FCC naphtha post-treatment will be the main focuses when seeking to comply with Tier 3 gasoline regulations. Isomerization and alkylation are, by comparison, minor processes in terms of their volume contributions to the overall gasoline pool, but they essentially produce sulfur-free, high-octane gasoline components.

FCC gasoline accounts for 35–40% of the US gasoline pool and averages 60–80 ppmw sulfur, with the exact value depending on the sulfur content of the feedstock. Consequently, significant reductions in sulfur content will be required to meet Tier 3 regulations.

For US refineries where the existing infrastructure is insufficient to deliver the 10-ppm annual average, capital investments may be required to achieve compliance. Modifying facilities can be a time-intensive process with extended periods being required for planning, construction and commissioning. This is particularly true when the proposed modifications require air permits or shift the focus toward more-expensive sweet crude sources rather than continuing with the conventional FCC approach to maximizing gasoline production.

Complying with the Tier 3 regulations and achieving the 10-ppm annual sulfur average will not be a simple task. Refinery operators will have to adjust their operating strategies and, in some cases, commit to capital investments for new or upgraded process equipment.

The main options include
- more severe hydrotreating of the FCC feed
- hydrotreating of FCC gasoline
- undercutting heavy naphtha, which contains a disproportionate amount of sulfur, from the FCC unit into the distillate pool
- using fuel-sulfur reduction additives in the FCC
- increasing the fraction of the gasoline pool coming from other units, for example, alkylate and reformate
- mercaptan removal from light gasoline.

	SULFUR, PPM	TYPICAL PROPORTION OF GASOLINE POOL, %	CONTRIBUTION TO SULFUR, %
FULL-RANGE FCC NAPHTHA[1]	2000	45	99
LIGHT STRAIGHT-RUN NAPHTHA	150	3	<1
BUTANES	10	5	«1
ALKYLATE	3	10	«1
REFORMATE	1	32	«1
C_5/C_6 ISOMERATE	3	5	«1

[1]Range can be 300–3000 ppm sulfur, depending on the crude source and degree of FCC feed hydrotreating

Table 1: Typical gasoline pool blending components.

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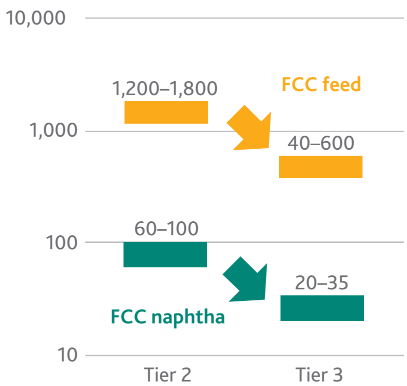

Figure 1: The transition from Tier 2 to Tier 3 in terms of sulfur content.

These possible solutions offer a range of potential advantages and disadvantages. The option chosen will depend on factors such as capital costs and specific operating constraints.

Complying with Tier 3 specifications

Under the Tier 2 regulations, the FCC naphtha values were generally in the range 60 to 100 ppmw sulfur and the FCC-PT hydrodesulfurization (HDS) requirement was 90–95%. For Tier 3, the FCC naphtha values will be 20–35 ppmw sulfur and the FCC-PT HDS requirement will be over 97% (Figure 1).

The change to Tier 3 gasoline specifications will result in a slight increase in operating stress for FCC naphtha post-treatment units and a more significant stress on FCC-PT units that lack any post-treatment capabilities.

Tight oils have displaced conventional crudes in many cases and this trend is expected to continue. Tight oil (also known as shale oil or light tight oil) is a light crude oil produced from low-permeability formations such as shale or tight sandstone. The use of tight oils reduces the severity of operations required to meet HDS and hydrodenitrification targets, but often requires more guard catalysts.

Albemarle has examined numerous case studies and conducted simulations to assess the likely impact of Tier 3 regulations. For refineries without FCC naphtha post-treatment, the effects will be substantial. These companies will have to shorten their cycles and increase hydrogen consumption at start of run. For constant HDS mode, refiners could face a 20–40% cycle length reduction if they continue to rely on the same feeds.

Tier 3 will also lead to higher annualized catalyst costs and make the integration of FCC-PT–FCC unit turnarounds more complicated. Selecting higher activity catalysts could help to extend cycle lengths, as could switching to easier feeds.

Added cost 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 companies 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.

More severe hydrotreating of the FCC feed

Hydrotreating the FCC feed is an attractive option because it provides an effective way to remove sulfur (typically lowering FCC feed sulfur content by 70–90%) and delivers other substantial benefits: greatly improved yields from the FCC unit with a relatively small negative impact on octane. This is probably the best long-term answer for refineries, though it may require substantial lead time to introduce and some operators may be reluctant if significant new capital were to be required. Where feasible, the use of more effective catalysts within existing PT units is the quickest and most cost-effective solution.

Gasoline sulfur additives

The use of gasoline sulfur additives such as Albemarle's Resolve technology may assist in lowering the sulfur content of FCC gasoline by up to 35%, but this will depend on the specifics of the refinery's operations.

Hydrotreating the FCC gasoline

Refiners may need to hydrotreat their FCC gasoline or increase the severity of existing hydrotreatment units to meet the new requirements. An unfortunate side effect of this operation is the reduction in gasoline octane due to olefin saturation. This octane reduction adds to the value of alkylate, which is both high octane and low in sulfur, and so increases the need for C_4 streams with high olefinicity to feed the alkylation unit.

Catalysts such as ACTION® from Albemarle offer octane relief for refiners by increasing the FCC gasoline octane and the production and olefinicity of butylene from the FCC unit, thereby enabling increased production of high-octane, low-sulfur alkylate.

A recently published joint paper with Marathon Petroleum discussed how the FCC unit at the Galveston Bay refinery switched to Albemarle's ACTION technology.[1] The benefits went straight to the bottom line. After data normalization using KBC's powerful FCC SIM kinetic model to adjust for feed and operating changes, ACTION catalyst was shown to deliver a 2.3 vol% increase in butylene yield, a butylene olefinicity increase of more than 4% and an incremental improvement in product octane. These benefits, combined with higher conversion, volume gain improvement and better bottoms upgrading, resulted in a benefit of $1.60/bbl.

A key role for catalysis

Catalyst choices will play a crucial role in the drive towards compliance, particularly new-generation catalysts for PT and hydrotreating processes. Albemarle offers solutions for refiners facing profit constraints from the new Tier 3 regulations, including optimized hydrotreatment and isomerization catalysts, gasoline-sulfur reduction additives and butylene-maximizing and octane-enhancing FCC catalysts.

FCC-PT catalysts such as Albemarle's Ketjenfine® (KF) 907 STARS® and KF 905N STARS have been specially designed for FCC-PT applications. KF 907 STARS is a very high activity Type I hydrotreating catalyst that can be used for a wide range of feedstocks. It is particularly well suited for FCC-PT applications where its very high desulfurization levels can deliver low-sulfur FCC gasoline without sacrificing denitrogenation and hydrogenation performance.

KF 905N STARS is a high-activity NiCoMo catalyst that uses STARS technology to ensure near 100% Type II active sites. In addition to a high desulfurization capability, it offers excellent stability in high-severity operations and with metal-containing feedstocks.

Octane has become a key issue for many refiners with the advent of tight oil, more-efficient car engines, the almost worldwide ban on the use of lead as a gasoline additive and continuing pressure on octane blending components. The drive to ever-lower sulfur specifications is making this even more of an issue because most PT designed to remove sulfur from gasoline also reduces its octane.

Albemarle's ACTION FCC catalysts provide higher-octane gasoline and a higher yield of valuable C_4 components with excellent olefinicity, which enables refiners to maximize operation of the alkylation unit and increase gasoline pool octane.

New zeolite technology

Following a detailed study of FCC reaction mechanisms, which crucially centered on the way that higher olefins are broken down, Albemarle scientists developed a new zeolite technology, ADZT™ 100. This provides unique cracking chemistry and, when used in combination with high-accessibility catalyst technology, enhances gasoline octane and butylenes while preserving transportation fuels.
When formulated into an FCC catalyst, the new zeolite shifts the balance between isomerization and cracking toward the former. What occurs, therefore, is branching of the longer-chain FCC naphtha components, as opposed to cracking. The result is increased octane with minimal conversion of gasoline to LPG. Moreover, the isoparaffins that contribute much of the octane gain are unaffected by any PT processes to remove sulfur.

HDS activity and octane selectivity

Conventional hydrotreating to reduce sulfur in gasoline has the unfortunate side effect of saturating olefins and thereby reducing octane. In preparation for Tier 3 regulation and optimization of performance, Albemarle proposed its next-generation catalyst for selective gasoline hydrotreating process: RT-235. This catalyst was a joint development by ExxonMobil and Albemarle resulting from test screening of about 500 catalyst formulations to ensure optimized support structure and metals distribution.

The aim was to develop a catalyst that

- 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.

RT-235 has excellent selectivity to desulfurization reactions while significantly boosting overall desulfurization activity. The extra desulfurization activity can provide significant economic benefits, especially on units that require a relatively high level of desulfurization.

Rising to the challenge

The Tier 3 regulations will present a significant challenge to many US refinery operators. Some that had planned to rely on sulfur credits, which can be used during the period 2017–2018, are finding that this may not be a straightforward solution. Each refinery needs to develop a long-term strategy that will meet its specific needs in terms of productivity, upfront investment and operating costs.

Albemarle has an extensive toolkit for addressing environmental compliance challenges while enhancing customer profitability. Contact us for help and advice about overcoming your sulfur and octane challenges.

Reference

[1]Skurca, M. et al.: An action plan to improve FCC unit performance at the Marathon Galveston Bay refinery," paper AM-17-48 presented at the AFPM Annual Meeting 2017, San Antonio, TX, USA (March 19–21, 2017)

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HELP WITH OPTIMIZING YOUR REFINERY OPERATIONS

Useful advice for refiners

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. The first discusses operating and catalytic changes to FCC for lowering gasoline sulfur while retaining octane and the second looks at options for optimizing the C_4 olefin yield of an alkylation unit.

Q1: What FCC operating and catalytic changes can lower gasoline sulfur while retaining octane? How would feed hydrotreatment affect these options? How would the FCC operating and catalytic changes affect gasoline post-hydrotreating?

A1: The strategy for reducing gasoline sulfur and preserving octane has to be, by necessity, customized to the specific configuration, the feeds being processed and the octane needs of the refinery. While the octane lost by gasoline hydrotreating can be 2 to 3 road octane numbers (RON) or more, most of the loss comes from RON reduction due to olefins hydrogenation, whereas the motor octane number (MON) reduction is less.

It is important to map the sources of gasoline sulfur and the streams that feed into the naphtha hydrotreater carefully. In general, if the FCC feed contains highly paraffinic tight oils or severely hydrotreated feeds, the cat naphtha will be lower in sulfur and thus require less-severe hydrotreating, which will result in a smaller octane loss. Consequently, the whole train of cat feed hydrotreater, FCC unit and naphtha hydrotreater should be optimized in terms of its operation and the catalysts being used in order to identify the most advantageous operating scheme.

As the heavier and most aromatic portion of the gasoline contains most of the sulfur and this sulfur is the hardest to remove, the sulfur level can be reduced without significant RON loss by undercutting the gasoline. This method was in frequent use before gasoline hydrotreating became common. It does have the obvious drawback of decreasing gasoline yield, but it can be utilized if the economics favor directing the heavy cut naphtha to the distillate stream.

Gasoline octane loss during hydrotreating can be reduced by separating out the light cat naphtha portion of the gasoline before hydrotreating it. As light cat naphtha is the most olefinic and the highest in RON fraction, hydrotreating it has the largest negative impact on RON. Examples include treating the gasoline in a selective hydrogenation unit; separating a lower-sulfur light cat naphtha stream and using a Merox unit to remove the sulfur from the light cat naphtha, and then, if needed, hydrotreating the light cat naphtha less severely.

It may be possible to decrease the octane loss and improve the overall profitability by redirecting some of the streams. For example, it may be better to drop the heavy cat naphtha into the LCO and send it to a hydrocracker, if one is available, while sending

more straight-run distillate to the FCC unit. However, the impact of more distillate in the FCC feed on the yields, including the gasoline octane, must be considered.

If the refinery has an alky unit that is not fully utilized, the refiner could consider increasing the production of alky feed from the FCC unit in order to make more low-sulfur, high-octane alkylate. As additional alky feed production from the FCC unit often comes at the expense of gasoline, the lower cat naphtha contribution to the gasoline pool may enable a reduction in the hydrotreating unit's severity, thereby decreasing the octane loss.

Catalyst technologies for naphtha hydrotreaters continue to evolve, so re-examining the catalyst in the unit and the operating conditions, could facilitate a decrease in octane loss.

Another option is to start with a higher cat naphtha octane. There are several strategies that can help to increase gasoline octane. Each one should be considered in conjunction with the other FCC unit and the refinery objectives to arrive at the overall economic impact before its adoption:

- Increasing the riser temperature will increase octane, conversion, LPG make and olefinicity.
- Using a catalyst containing a lower amount of rare earth and/or increased matrix activity will help to raise the gasoline octane. However, less rare earth may mean that the catalyst is less active and, thus, necessitate an increase in catalyst additions. It will also affect the amount of gasoline and LPG being made.
- ZSM-5 additives are well known to increase gasoline octane and the concentration of high-octane aromatic components. However, ZSM-5 additives can decrease gasoline production, as they convert most of it to propylene.
- Catalyst suppliers are also marketing catalysts that are formulated to help increase gasoline octane.

Gasoline sulfur reduction technologies have been around for more than two decades. If they are effective at decreasing gasoline sulfur, they reduce the need for more-severe operation of the naphtha hydrotreater and, therefore, decrease the octane loss. However, the performance history of gasoline sulfur additives is uneven. Multiple factors, including the feed properties and composition, and the unit configuration and operation, can affect their performance. In addition, the efficacy of these additives at low levels of gasoline sulfur (less than 30 ppm) has not been fully ascertained. Where they have been shown to work, they have decreased gasoline sulfur by as much as 30%. Figure 1 shows a summary of the performance of Albemarle's RESOLVE family of gasoline sulfur reduction additives.

Q2: What operational and catalytic changes can be implemented to optimize the C_4 olefin yield of an alkylation unit?

A2: In recent years, the production of C_4 olefins from FCC units has been negatively affected by the feeds being processed, including tight oils produced by fracking. These crude oils are highly paraffinic and

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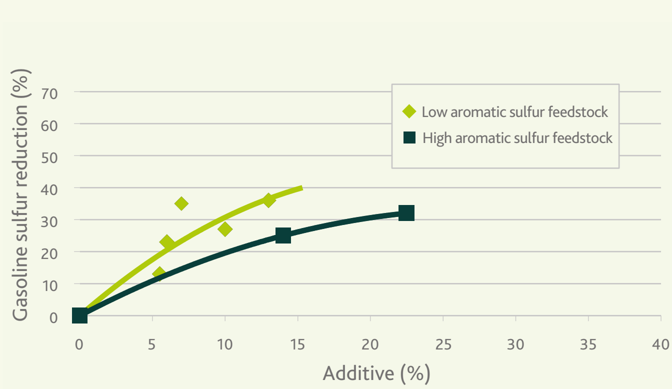

Figure 1: Summary of a RESOLVE gasoline sulfur reduction additive's performance.

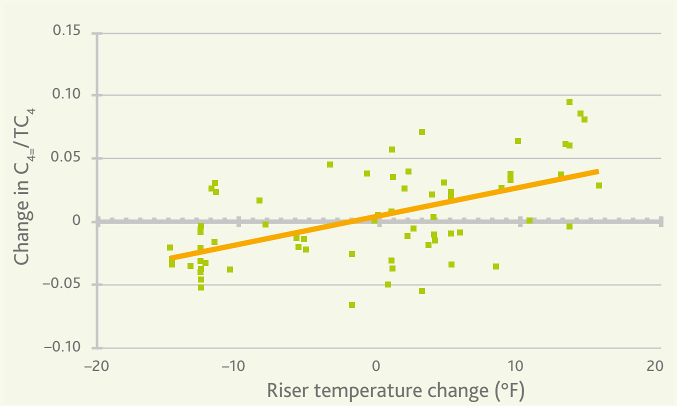

Figure 2: Example of C_4 olefinicity change with riser temperature.

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result in a decrease of both LPG olefinicity and gasoline octane. This trend has happened at the same time that the values of alkylate and gasoline octane have been at their highest in the last two decades. Consequently, many refiners are looking for ways to increase alky feed production from the FCC, mostly C_4 olefins.

There are several operating options that can result in an increase in the C_4 olefins yield.

Increasing the riser temperature is an effective option that increases the LPG make and improves olefinicity, including the C_4 olefins yield, as Figure 2 shows. However, if this is implemented, it will also increase conversion and dry gas, as the riser temperature is the strongest operating driver for dry gas make. If the unit is operating in distillate maximization mode, increasing the riser temperature may not be a good option.

If tight oils are being processed, efforts should be made to try to minimize the amount of light straight-run distillate going to the FCC unit, as this is quite paraffinic and has the largest negative impact on LPG olefinicity.

If possible, the refiner could attempt to decrease the hydrocarbon partial pressure in the riser. The hydrocarbon partial pressure is a key driver of the reactions converting LPG olefins into paraffins. Decreasing the hydrocarbon partial pressure in the riser can be accomplished by decreasing the unit pressure or increasing the inerts. However, in Albemarle's experience, a significant change in hydrocarbon partial pressure cannot be achieved without undertaking a unit turnaround. This option is easier to implement with a grassroots unit. Because decreasing the hydrocarbon pressure will also decrease conversion, the catalyst will have to be redesigned to help recover some of the lost conversion.

Decreasing the residence time in the riser and the reactor, and improving stripping will also decrease the secondary reactions and improve olefinicity. However, this option may require a new short contact time riser, riser termination devices and/or a new stripper. None of them are readily available options and all of them require significant capital investment.

For increasing the C_4 olefins production of an alky unit, catalytic options are typically easier to implement and likely to be cheaper.

In addition to increasing the riser temperature, the refiner can use a more-active catalyst and/or more catalyst in the unit in order to push the unit conversion higher, as shown in Figure 3.

Unless the catalyst is specifically designed with low hydrogen transfer and high matrix activity, this option will typically require higher rare earth content in the catalyst, which will decrease the olefinicity. In addition, the conversion is high enough in many units that the C_4 olefinicity will likely decrease even if the yield increases, see Figure 4.

The combination of decreasing the rare earth content and/or increasing the matrix activity and overall accessibility is, in many cases, the most effective option, as it will increase both the LPG olefins yield and the olefinicity by increasing olefin production and decreasing hydrogenation reactions. Unless the catalyst is redesigned to maintain the activity, decreasing the rare earth content can make the catalyst less active, thus requiring an increase in catalyst additions, and it will affect the amount of gasoline and LPG being made. The gasoline olefinicity will also increase.

ZSM-5 additives are well known to increase the LPG olefins make in the FCC unit at the expense of gasoline. However, traditional ZSM-5 additives primarily convert gasoline to propylene: butylenes are secondary products. Thus, they are inefficient options for increasing C_4 olefins production for use in an alky unit unless there is also room to use the extra propylene being made or propylene is a high-value product for another application.

Albemarle also has catalysts and additives available that promise to increase C_4 olefins production selectively. In Albemarle's experience, catalyst technologies specifically formulated to increase C_4 olefins production are currently quite popular in North America. Figure 5 show an example of the C_4 olefinicity improvement that can be expected with Albemarle's ACTION™ catalyst technology. This technology is discussed in greater detail in Yaluris and Kramer (2014).[1]

Reference

[1]Yaluris, G. and Kramer, A.: "Take ACTION™ – To maximize distillate and alky feed from your FCC unit," paper AM-14-26 presented at the American Fuel & Petrochemical Manufacturers 2014 Annual Meeting, Orlando, FL, USA (March 23–25)

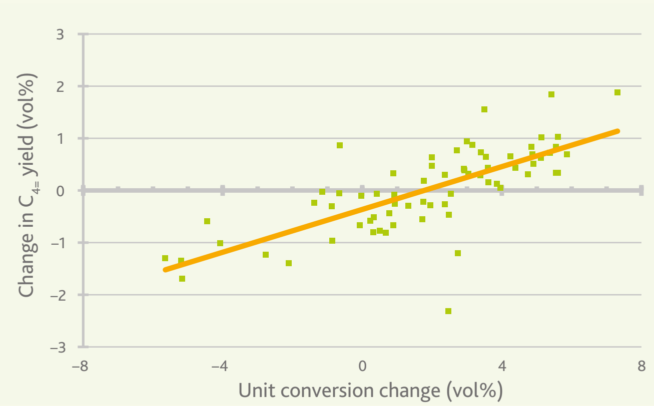

Figure 3: Example of C_4 olefins yield change with unit conversion.

> ALBEMARLE HAS CATALYSTS AND ADDITIVES AVAILABLE THAT PROMISE TO INCREASE C_4 OLEFINS PRODUCTION SELECTIVELY. IN ALBEMARLE'S EXPERIENCE, CATALYST TECHNOLOGIES SPECIFICALLY FORMULATED TO INCREASE C_4 OLEFINS PRODUCTION ARE CURRENTLY QUITE POPULAR IN NORTH AMERICA.

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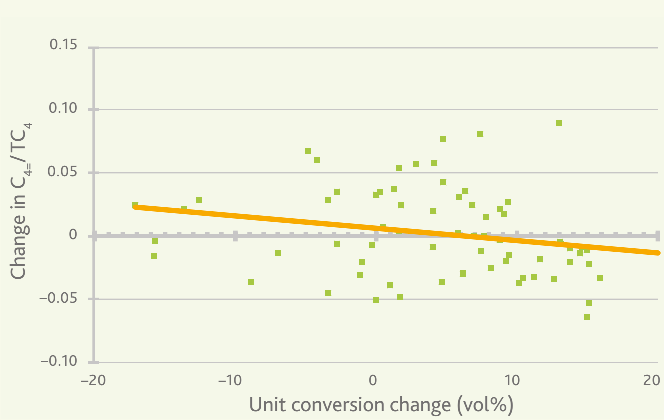


Figure 4: Example of C_4 olefinicity decrease with unit conversion.

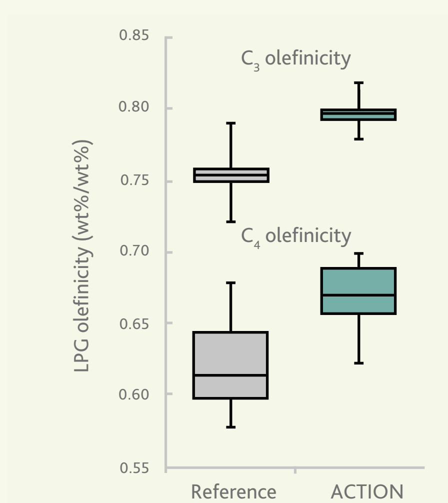


Figure 5: C_3 and C_4 olefinicity increases in an FCC unit using Albemarle's ACTION catalyst technology after normalizing for feed and operating differences.

OPTIMIZING VENDORS' BIDS

Best practices for using FCC simulation models in the catalyst bid process

At Albemarle, we have noted an increase in the number of refiners including model results as part of the FCC catalyst bid package requirements, especially in the past two years. Although a variety of FCC models has been developed over the past few decades, the industry is coalescing around the FCC-SIM model developed by KBC Advanced Technologies. This model combines the level of sophistication and accuracy required by those of us in the industry, along with a large user community.

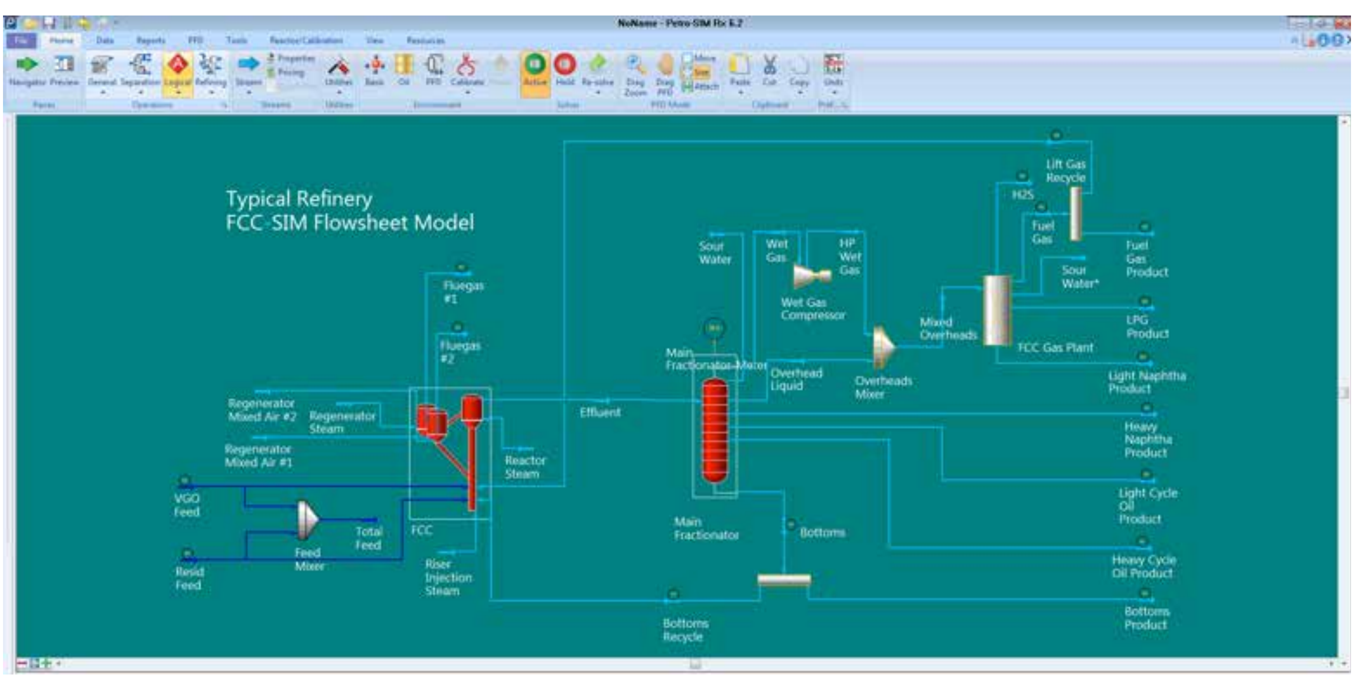
Refiners have given us many reasons for requiring model results as part of the overall bid package. These reasons fall into three groups:

- Some believe the model results provide an increased level of understanding and a reduced level of risk associated with the catalyst change. Comments such as, "I want to make sure all vendors' projections hydrogen balance," and "If I give everyone the same starting point and same model, it should be easy to pick the winner," define this group.
- Some have been instructed by upper management to use models. "The refinery manager believes in models," and "We invested heavily and want to see returns on that investment," are statements we have collected from refiners in this situation.
- Finally, some refiners wish to investigate the catalyst's performance in other situations. "We want to know how different catalysts compare if conditions change from those given in the bid package," and "We want to compare catalysts in another operating mode [such as comparing results from a maximum gasoline operation with a maximum distillate operation]," are typical comments from these users.

Regardless of why refiners choose to use process modeling, it is clear that these models are becoming permanent fixtures. The challenge, and focus of this article, becomes how to get the most benefit from the process model when using it as a tool in the FCC catalyst bid process.

Be realistic

Be realistic in setting your expectations. The most common issue we see is engineers underestimating the amount of work required to define the base case and to make sure that the model can predict correctly. Learning how to use the FCC model can be a tremendous learning experience, but using the catalyst bid process as the entry point into one's foray into modeling may be akin to jumping straight into the deep end of a pool. We recommend that engineers first become versed in using the model for regular monitoring of their FCC unit and can



undertake predict cases for operational and feed changes without difficulty before evaluating a catalyst.

Choosing the base case and verifying the model's abilities are undoubtedly the most important and probably the most time-consuming parts of the process. The quality of a bid projection will only be as good as the quality of the base case and the tuning of the model you give to the catalyst vendors.

As a catalyst bid is a forward-looking process and you are choosing the catalyst for a future expectation of operations, perhaps with a different feed or product demand scenario, you will likely want to use the expected future conditions as the base case for the catalyst vendors. However, this creates a problem in setting up the model. You can only calibrate the model to existing (past) data. So, how do you then create an accurate base case for future conditions? Answering this question is where most of the work in setting up the catalyst bid lies.

An accurate base case

First, identify the calibrated cases available. It is wise to collect as many as possible because the vetting process may quickly whittle down the number of usable cases. The following are a few of the best practices Albemarle has established for identifying whether you should include or eliminate a calibration case:

- The cases must all be for the same catalyst formulation. Avoid cases
  - during catalyst transition periods
  - where purchased E-cat is used at a rate 25% outside the typical amount
  - where the purchased E-cat properties are clearly atypical.
- The cases should all be within 20% of the typical feed rate.
- The feed density should fall within approximately 0.02 kg/l or 2 API of typical feed.
- The cases should all be for the same combustion mode and the same as the base case for your catalyst projection. For refineries with a single regenerator that operates either partial or full burn, segregate the cases according to combustion mode.

Once you have identified the initial pool of calibration cases, evaluate the quality of each case. A good, quick option is to trend every single variable entered on the calibration input sheet graphically to find cases with flyers or atypical values, trends over time or high variability in the input data. Correct flyers whenever possible; otherwise, eliminate the case. If you find trends, investigate whether the trend correlates with a trend in any calibration factors possibly related to that independent variable. If a correlation exists, investigate the data further for quality issues. Either manual tuning of the model or the elimination of some cases may be required.

The next recommended step is to create trend plots of the calibration result dataset. Check the results for reasonableness, but pay particular attention to the hydrogen balance, the hydrogen content of the coke, the heat of cracking, the catalyst-to-oil ratio and the estimated core aromatics content and distribution.

Finally, the calibration factor values often provide the best insight as to the quality of the raw data and the ability of the model to assimilate the data. Albemarle recommends plotting the “important” calibration factors and noting any flyers, trends or variability in these factors. As with the input and result data, you should thoroughly investigate, understand and correct any anomalies noted in the calibration factor plots or discard the case, as applicable. You can obtain a list of the most-important calibration factors for the FCC-SIM model, their typical values and the impact of catalyst formulation on these factors from Albemarle. An example of an important calibration using “fake” data is shown in Figure 1.

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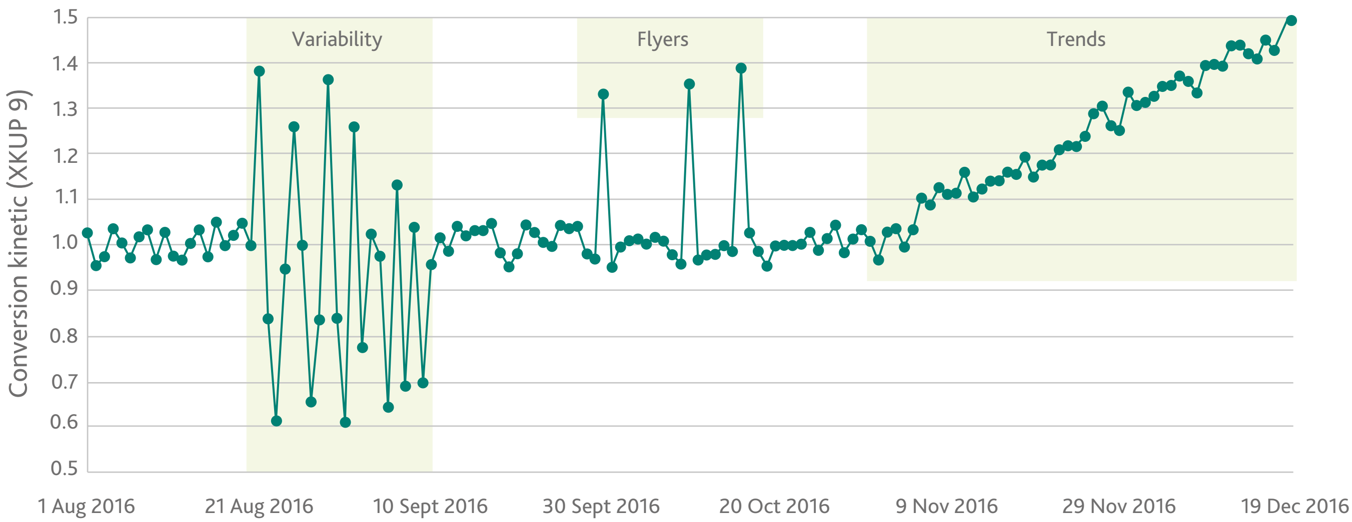

Figure 1: The conversion kinetic value is an important calibration factor.

> PROCESS SIMULATION MODELS SUCH AS FCC-SIM ARE GAINING TRACTION IN THE INDUSTRY AS VALUABLE TOOLS FOR SUPPORTING DECISION-MAKING PROCESSES. THIS IS EVIDENT IN THE GROWING USE OF THESE MODELS AS AN INTEGRAL PART OF REFINERS' FCC CATALYST BID PROCESS.

After vetting the calibration input data, results and factors, you should use as many cases as possible of those that remain to establish the base case for the catalyst bid. Although the process is simpler, Albemarle does not recommend merely selecting a single day, known as a "super day", from the candidate cases. Investigations have found that predictions based on a single super day chosen at random from a collection of high-quality super-day candidates can vary by a surprisingly large amount.[1] Rather, it is recommended that the base cases' variables be appropriately averaged to yield a single case. You should then calibrate this new averaged case and compare the input data, results data, and calibration factor data as before against the individual cases comprising it.

Unfortunately, creating the averaged case for the calibration set is not the end-point; it is only the halfway point of the bid preparation process. The second step, which is often neglected, is to verify, and correct, as necessary, the underlying predictive accuracy of the model.

Verifying predictive capability

To verify the validity of the model's predictive capability, you should use the averaged calibration case as developed up to this point. To establish the predictive accuracy of the model, copy the averaged calibration case into the predict sheet, along with its calibration factors. Key independent operational variables such as riser and feed temperatures, feed rate and individual feed properties should be varied individually across their range of experienced and expected values. Then compare the results from these single variable step-out cases with actual experience to gauge the predictive accuracy of the model. If you find a disconnect between the model's results and experience, use the manual tuning factors to tune the model to align it with observations.

You should establish the predict scenario for the FCC catalyst bid base case before submitting it to the vendors. Now is the time to change the feed properties of the base case if you desire the catalyst to optimize the unit under a different feed than run in the average calibration case. You should also specify the predict targets options to be used for the stripper, spent catalyst recycle, regenerator, oxygen enrichment and pressure balance, as applicable. The catalyst vendor should be responsible for ensuring the correct catalyst and metals balance target is used so that the catalyst addition rate, activity, and E-cat metals are correct.

Preparing for deployment

When preparing the bid base case for deployment, run the bid base case to verify smooth operation of the model. You should provide each catalyst vendor with identical workbooks and FCC-SIM flowsheets. To ensure consistency in results and an apples-to-apples comparison, we recommend specifying the version of FCC-SIM that the catalyst vendor(s) should execute.

KBC Technologies currently supports version 4.1 through version 6.2 of the FCC-SIM model. Older versions are neither supported nor available for download. We recommend refiners utilize the most up-to-date and technically advanced version of the model available. Also, vendors typically license only the FCC-SIM reactor model. If your process flowsheet include objects not included with the FCC-SIM license, such as crude distillation units, feed or product hydrotreaters, other reactor models or feed assays, the vendor will be unable to execute the model. The flowsheet should only contain the FCC unit, the main fractionator, the naphtha distillation columns and the component product splitters representing the FCC unit gas plant.

Valuable tool

In conclusion, process simulation models such as FCC-SIM are gaining traction in the industry as valuable tools for supporting decision-making processes. This is evident in the growing use of these models as an integral part of refiners' FCC catalyst bid process. As with any model, the benefit strongly depends on the quality of data input and the care taken to ensure that the model is tuned to provide accurate predictive results. The best practices offered in this article can be used as a guide to help ensure the best results possible when utilizing a process simulation model in conjunction with your upcoming catalyst bid.

Reference

[1]Kramer A., "How can I use FCC-SIM to monitor my FCC unit regularly?" KBC Users' Group Conference, Houston, Texas, USA (September 2015)

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SMOOTHFLOW™: CIRCULATION CURE-ALL

SMOOTHFLOW fluidization aid extends operations having damaged cyclones and helps post-repair start-up

The modern FCC unit is a complex harmony of physical and chemical processes for upgrading low-value hydrocarbons. The harmony depends substantially on the reliable retention and transportation of fluidized catalyst through the reaction and regeneration zones. When fluidization deteriorates or becomes erratic, the FCC unit may shut down completely, violate environmental permits or reduce profitability. Albemarle's SMOOTHFLOW fluidization aid (Table 1) can mitigate these problems and help refiners continue operations until a planned maintenance period.

FCC unit fluidization basics

The fluidization of FCC catalyst is a well-studied subject. The key, influencing factors are illustrated in Equation 1:

$$\frac{U_{mb}}{U_{mf}} = \frac{2300\rho_g^{0.126}\mu^{0.523}\exp(0.716F_{45})}{d_p^{0.8}\left[(\rho_p-\rho_g)g\right]^{0.934}}$$

Equation 1.

As gas is passed through the FCC catalyst, it first flows through the interparticle voids of a packed bed. At a minimum velocity (U_{mf}), drag forces overcome gravity and interparticle friction, and the bed expands to a fluid, free-flowing state. Such a state is ideal for smooth, steady transfer of catalyst from one part of the FCC unit to another. At a higher velocity (the minimum bubbling velocity, U_{mb}), distinct bubbles form in the fluid catalyst. These bubbles can restrict catalyst transfer or flow.

The ratio of the minimum fluidization velocity (U_{mf}) to the minimum bubbling velocity (U_{mb}) is a key parameter for fluidization. Refiners operating with a higher ratio of U_{mb} to U_{mf} have a wider operating window for stable catalyst circulation. Equation 1 shows that the ratio depends on the gas density (ρ_g), the gas viscosity (μ), the particle density (ρ_p), the particle size (*dp*) and gravity (*g*). The influence of fines (percentage <45 µm, F45) and *dp* is of utmost importance. Albemarle's SMOOTHFLOW additive has a high value of F45 and a lower value for *dp*; both of which increase the ratio of U_{mb} to U_{mf} and facilitate stable operation.

SMOOTHFLOW: Solutions

Cyclone damage

Within cyclones, the capture efficiency is directly related to the particle size, among other factors. When holes form in the cyclone, the F45 fraction and even larger particles can be rapidly lost. Increased catalyst additions are a suboptimal solution, as such action does not preferentially restore the smaller-sized particles vital to fluidization and lost most rapidly. The superior solution is SMOOTHFLOW fluidization aid, which contains a very large fraction of particles in the 30–80-µm range (Figure 1).

Dipleg malfunctions

The cyclone diplegs are responsible for returning captured particles to the bulk, fluidized bed. Some diplegs are finished with flapper valves that prevent ingress of gas and fluid catalyst (a short circuit). If these valves become stuck, the cyclone overloads and the FCC unit loses catalyst to the overhead. Smaller particles are lost most rapidly. SMOOTHFLOW additive assists operability by preferentially restoring this particle size range.

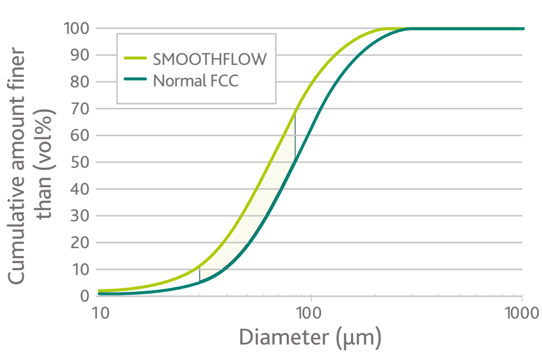

Figure 1: SMOOTHFLOW fluidization aid has a large amount of 30–80-µm particles that tangibly benefit circulation and fluidization.

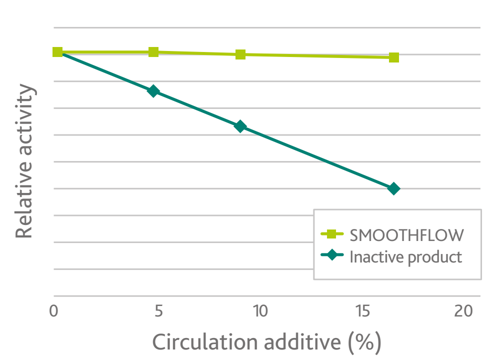

Figure 2: SMOOTHFLOW fluidization aid contains active matrix and zeolite components to prevent activity loss in units requiring higher amounts of additive to correct the particle size distribution.

Standpipe stress

Many refiners use aeration taps along standpipes to aid catalyst flow from reactor to regenerator. When these taps become plugged, flow may become erratic and lead to an unstable ΔP across the slide valves or physical stress (for example, standpipe movement). Since SMOOTHFLOW fluidization aid fluidizes more easily and deaerates more slowly than normal catalyst, it can provide immediate relief.

Start-up difficulties

When a refinery shuts down an FCC unit to repair the cyclones and other critical hardware, it may have difficulty restarting on the exceptionally coarse E-cat. In one case, a refiner's catalyst de-fluidized in the diplegs, bridged the cross section and created a plug. With SMOOTHFLOW fluidization aid, this refiner recovered stable operations within a day.

SMOOTHFLOW: Fluidization with activity

A key advantage of SMOOTHFLOW additive compared with competitive products is its tangible cracking activity. It includes Albemarle's proprietary ADM-20 bottoms upgrading matrix and proprietary zeolite technologies. It can be used very aggressively without worry about dilution effects or significant yield alterations. Some competitive products have little or no cracking activity. Although these other products may relieve some circulation issues, they can significantly lower the activity of the circulating catalyst and create new problems (Figure 2). The active ingredients in SMOOTHFLOW fluidization aid make it the preferred solution for units needing significant additive to correct the particle size distribution.

References

[1]Geldart, D. and Radtke, A. L.: "The effect of particles on the behaviour of equilibrium cracking catalysts in standpipe flow," *Powder Technology* (1986), 47(2), 157–165
[2]"A fine solution to FCC unit start-up problems," *Catalyst Courier* 76, 15

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TYPICAL PRODUCT PROPERTIES	
ADDITIVE NAME	SMOOTHFLOW
APPLICATION	**Fluidization additive**
SURFACE AREA, M²/G	**205**
PARTICLE SIZE DISTRIBUTION (0–40), %	**24**
PARTICLE SIZE DISTRIBUTION (0–20), %	**6**
ATTRITION INDEX, WT%	**4.7**
SURFACE AREA, M²/G	**0.71**

Table 1: Typical properties for SMOOTHFLOW fluidization aid.

KETJENFINE® (KF) 780 STARS®: AN INTELLIGENT OPTION FOR FCC PRETREATMENT (FCC-PT) APPLICATIONS

Meeting the challenges of clean fuel hydrotreating needs

As discussed in a previous *Catalyst Courier* article[1], refiners increasingly need to produce ultra-low-sulfur gasoline and more diesel fuel, which can be challenging. Therefore, FCC-PT units are increasingly more important in helping to overcome this challenge, so they require robust and reliable catalyst systems for high activity and good stability.

Albemarle's VGO STAX®–FCC-PT is the preferred technology solution to enable customers to meet the FCC-PT challenges in their refineries. Albemarle has wide-ranging global refinery operational insights that help it to identify customers' needs, constraints and opportunities. Strong process and technology application expertise enables the company to advise customers on the preferred catalyst systems and operating tactics for meeting their operating objectives. To bolster this technical expertise, Albemarle uses a proprietary computer process modeling capability, which gives highly reliable performance estimates, to generate and assess catalyst loading design recommendations for customers.

Unlike processes that produce clean fuel products directly, the economic value of FCC-PT is largely from how well it improves FCC unit product yields, product qualities and operations. Depending on the refinery, the key objectives for FCC-PT operations may be to

a) maintain a low product sulfur level with high hydrodesulphurization (HDS) to meet environmental regulations on gasoline sulfur content and FCC unit SOx emissions

b) reduce nitrogen and aromatics levels by maximizing hydrodenitrogenation (HDN) and hydrodearomatization (HDA) for improving FCC unit product yields, selectivities and operations

c) increase the conversion of VGO to diesel-range products.

In addition, controlling FCC-PT catalyst fill costs and achieving target cycle lengths are generally high priorities.

No single FCC-PT unit is representative of this process application: units are designed and operated to fit specific refinery operating strategies and objectives. Consequently, FCC-PT units cover a broad range of feed properties and operating variables. These units can be characterized by operating objectives and hydrogen partial pressures (ppH_2) ranging anywhere from low (inlet ppH_2 <55 bar, <800 psi) to "high" (inlet ppH_2 >90 bar, 1300 psi). Units in Europe, the Middle East and India are mostly in the low- to moderate-pressure range and are typically operated to achieve deep HDS and, in some cases, to increase conversion of VGO feed to diesel product. North American units tend to fall primarily in the moderate- to high-pressure range. Although many of these units focus on HDS, others focus on maximizing HDN and HDA.

Albemarle's viewpoint

In recent years, product sulfur targets have become even lower and the need for more active and stable catalysts has increased. In addition, for moderate- to high-pressure catalytic feed hydrotreating (CFHT) units, the need for deeper HDN and greater HDA to improve FCC yields and selectivities has increased.

To meet these market needs, Albemarle has researched extensively across its customers' operations to determine how best to help them meet their needs. It became clear that variations in FCC-PT operating conditions, feeds, unit objectives and unit constraints often make it impractical for a single catalyst to fulfill all a refiner's needs and wants. Albemarle concluded that STAX technology solutions for FCC-PT are preferable for enabling customers to meet the challenges encountered in almost all their CFHT applications.

KF 780 STARS – an intelligent catalyst addition

KF 780 STARS is the latest CoMo catalyst addition to Albemarle's hydroprocessing portfolio. It is a Type II catalyst suitable for FCC-PT and diesel hydrotreating applications, which makes it ideal for cascading between different refinery applications. This high-activity HDS catalyst can be a standalone catalyst or a key component in a STAX configuration for FCC-PT.

The defining feature of KF 780 STARS catalyst is its extremely high metals efficiency. This step out was achieved through improved metals dispersion and tailored distribution of active sites coupled with better pore accessibility. This combination of almost 100% Type II active sites and superior metals efficiency gives this catalyst exceptional activity and stability in even the most-demanding VGO hydrotreating applications. These enable it to help refiners overcome constraints and exploit opportunities.

Figure 1 shows the typical application regimes for KF 780 STARS catalyst in conjunction with Albemarle's overall FCC-PT catalyst portfolio. Each catalyst is available in two or three sizes to provide solutions for any refining objective in terms of activity, stability, hydrogen consumption and/or avoiding pressure drop issues. Each catalyst can be deployed in various ways using VGO STAX FCC-PT technology.

Figure 2 illustrates how KF 780 STARS catalyst provides value to refiners. A high activity and relatively low loading density give this catalyst superior FCC-PT performance without increasing fill costs. It also enables refiners to upgrade lower value feeds and/or to achieve deeper HDS to decrease the sulfur in FCC products and reduce SOx generation. This is especially important for enabling North American refiners without FCC naphtha post-treatment capabilities to meet Tier 3 ultra-low sulfur gasoline regulations. Finally, KF 780 STARS catalyst has also been successful for those refiners trying to increase VGO conversion and increase diesel fuel production.

KF 780 STARS catalyst – Commercial examples

KF 780 STARS catalyst is now in 11 different VGO commercial hydrotreating units (Table 1). Two FCC-PT cases follow to illustrate how this catalyst can provide increased operating benefits to refiners. In both cases, KF 780 STARS catalyst was originally selected on the basis of in-house pilot plant testing; its superior commercial performance justified its selection for subsequent cycles also.

Commercial Case A is a low-pressure FCC-PT unit (ppH_2 inlet ~42 bar, 610 psi) operating in constant HDS mode. The unit has two reactors in series treating a blend of heavy VGO and middle distillates, including cracked stock, to about 600-ppmw sulfur (current cycle) in the total liquid product (TLP). The TLP is sent to the FCC unit without fractionation. The bottleneck in the operation is the product sulfur of the FCC naphtha (25–35 ppmw), which determines the operating weighted average bed temperature (WABT) of the FCC-PT process. Hence, the operating

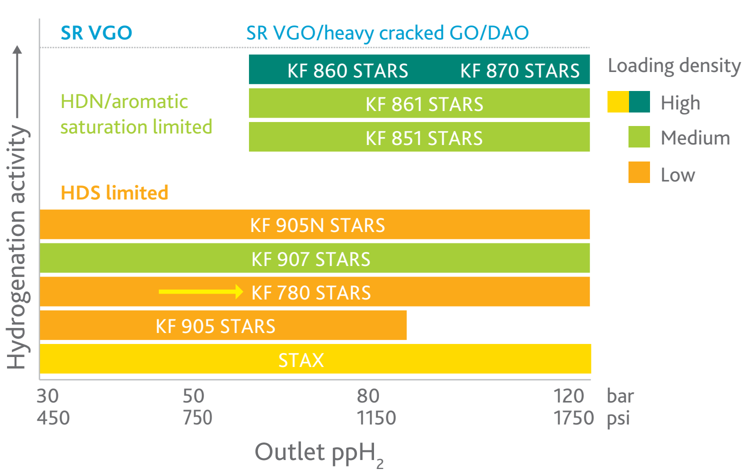

Figure 1: Albemarle's FCC-PT catalyst portfolio.

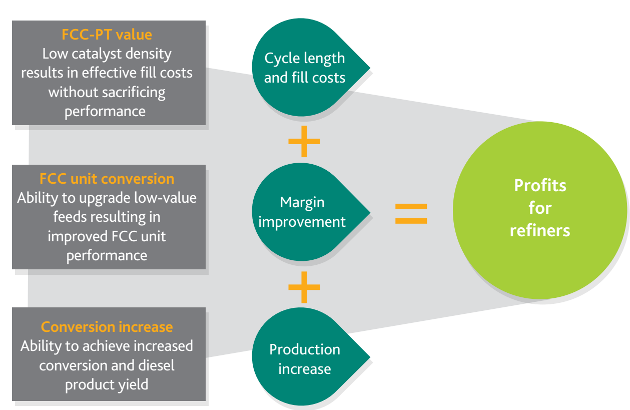

Figure 2: KF 780 STARS catalyst gives value to refiners at all ppH_2 levels.

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COUNTRY	SERVICE	AMOUNT (T)	NUMBER OF UNITS
AUSTRIA	**Mild hydrocracking-PT**	67	1
FINLAND	**FCC-PT**	305	1
GERMANY	**FCC-PT**	221	1
LITHUANIA	**FCC-PT**	109	1
UNDISCLOSED	**FCC-PT**	83	1
SPAIN	**FCC-PT**	409	2
INDIA	**FCC-PT**	448	1
COLOMBIA	**FCC-PT**	17	1
CANADA	**FCC-PT**	133	1
USA	**FCC-PT**	49	1

Table 1: KF 780 STARS catalyst sales to VGO hydrotreating units.

	CYCLE 1 (PREVIOUS)	CYCLE 2 (CURRENT)
MAIN CATALYST	**KF 905 STARS catalyst + KF 757 STARS catalyst**	**KF 780 STARS catalyst**
P_{TOT}/PPH_2 INLET, BAR	48/43	47/41
FEED RATE, M³/H	352	368
HYDROGEN/OIL RATIO, NL/L	258	220
AVERAGE FEED PROPERTIES (FIRST 280 DAYS ONSTREAM)		
SULFUR, WT%	1.44	1.35
NITROGEN, PPMW	1184	1076
DENSITY AT 15°C, G/ML	0.903	0.899
BROMINE NUMBER, G/100 G	2.8	2.8
AVERAGE FEED PROPERTIES (FIRST 280 DAYS ONSTREAM)		
SULFUR, PPMW	786	585 (~200 lower)
START OF RUN WABT, °C; °F	~357; 675	~360; 680
NORMALIZED WABT AT 786-PPMW SULFUR, °C; °F	357; 675	352; 666 (–5°C; –9°F)
CYCLE LENGTH, MONTHS	18	18 (projected)

Table 2: Commercial Case A: Comparison between commercial cycles 1 and 2.

incentive is to boost HDS as much as possible. The cycle length requirement is typically 18 months to satisfy the refinery's turnaround schedule.

In the previous cycle, in view of the very low ppH_2 and necessity for very high HDS activity, the unit was loaded with a combination of KF 905 STARS catalyst (Reactor 1) and KF 757 STARS catalyst (Reactor 2), which achieved a successful run. In the current cycle, supported by very positive customer test results, the unit's catalyst system was improved by replacing the KF 757 STARS catalyst in Reactor 2 and much of the KF 905 STARS catalyst in Reactor 1 with KF 780 STARS catalyst.

The main value proposition was to reduce product sulfur in the FCC naphtha while treating a similar FCC-PT feedstock. Table 2 compares the first 280 days of operation of the previous (Cycle 1) with the current cycle with KF 780 STARS catalyst (Cycle 2). The feed properties were similar for the two cycles (slightly more difficult for Cycle 1), but the operating conditions in Cycle 2 were more demanding to achieve deeper HDS: on average, ~4.5% more feedstock was treated over the same period in Cycle 2 and the inlet ppH2 (41 versus 43 bar, or 595 versus 625 psi) and hydrogen-to-oil ratio (220 versus 258 Nl/l, or 1300 versus 1530 scf/bbl) were lower.

KF 780 STARS catalyst has consistently delivered 200-ppmw (~25%) lower TLP product sulfur in Cycle 2 for the derived benefit of lowering the FCC naphtha sulfur concentration by at least 7 ppmw and probably by ≥10 ppmw. If the WABT at the start of run is normalized for the difference in feed and product properties and for the main operating conditions, the WABT advantage that KF 780 STARS catalyst provided was approximately 5°C (9°F) compared with the KF 905 STARS–KF 757 STARS system for a 800-ppmw sulfur level in the TLP.

Normalized deactivation in this cycle was lower, i.e., less than 1.5°C/month (2.7°F/month) compared with 1.8°C/month

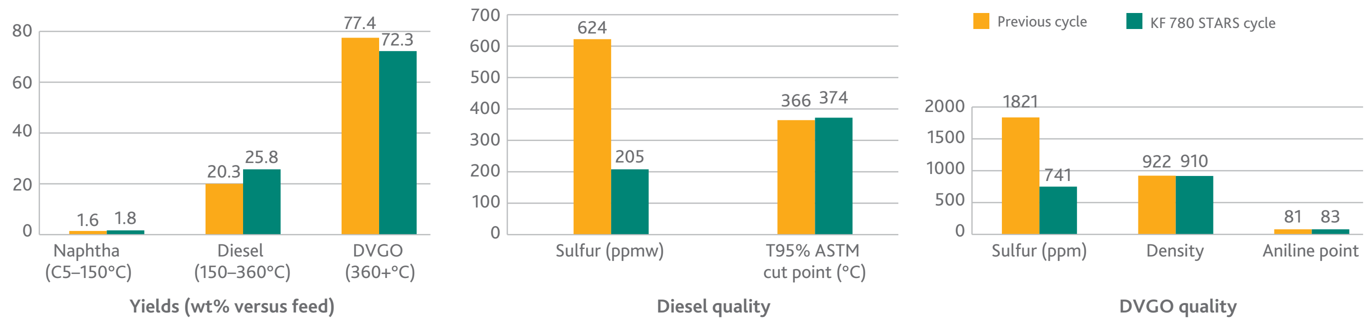

Figure 3: Commercial Case B: yields and qualities for the KF 780 STARS catalyst cycle versus the previous cycle.

(3.2°F/month) over the same period in the previous cycle. This result testifies to the better stability of KF 780 STARS catalyst, despite the more demanding operating conditions.

Commercial Case B is an FCC-PT unit operating at moderate pressure (ppH_2 inlet ~53 bar) and on oil for more than 18 months, even though the original cycle length target was 12 months. The primary objective for this unit at Repsol's Petronor refinery in Spain was to increase VGO conversion (third objective in Figure 2) from ~25 to ~30 wt% while ensuring that the FCC feed sulfur content remained below 700 ppmw throughout the run. The overall reactor loading consists of 28 vol% regenerated NiMo catalyst and 72 vol% KF 780 STARS catalyst. The feed is a blend of straight-run VGO and heavy coker gas oil with >3.0 wt% sulfur, >2300 ppmw nitrogen and ~0.94 g/ml specific gravity (19 API).

Repsol conducted pilot plant tests before selecting a catalyst for this unit. In these tests, KF 780 STARS catalyst gave 4.6 wt% higher net conversion than the base case catalyst system, with a 0.8 wt% higher naphtha yield and a 3.4 wt% higher diesel yield. Because of the higher conversion and better FCC-PT product qualities, the company selected KF 780 STARS catalyst for the commercial unit.

The commercial operations have exceeded Repsol's expectations. The unit was run in low-temperature, constant-product-sulfur mode for the first two months onstream and produced ultra-low-sulfur diesel (ULSD). After switching to the higher-temperature, higher-conversion operating mode, the catalyst deactivation rate remained low (2.1°C/month, 3.8°F). Net VGO conversion was 5.1 wt% higher than for the previous cycle, with only a 0.2 wt% higher naphtha yield and a 5.5 wt% higher diesel yield, see Figure 3. The figure also shows that the diesel product for this cycle contained significantly less sulfur, which enabled the refinery to make an 8°C (14°F) higher cut point.

The DVGO feed to the FCC unit has significantly lower sulfur, lower nitrogen and aromatics levels, a slightly lower density and a slightly higher aniline point than the DVGO for the previous cycle. These feed improvements enabled the FCC unit to generate better yields than during the previous FCC-PT cycle.

Through its positive experience with this cycle, Repsol chose KF 780 STARS catalyst again for the next cycle and for a similar CFHT unit in another refinery.

Summary

In conclusion, KF 780 STARS CoMo catalyst is a more intelligent catalyst for FCC-PT applications, as it spans all pressure regimes and all operating objectives, with particular benefits in low- and moderate-pressure applications. It features high activity and stability through step-out improvements in active site dispersion and utilization efficiency. The performance and economic benefits can be achieved in stand-alone applications and as a key component in VGO STAX FCC-PT catalyst systems that are tailored to achieve customers' needs and objectives.

This catalyst has shown very good performance in customer pilot unit testing and its first eight commercial applications. It is too early to report on the other three commercial units because they have either not yet started up or are very early in their cycles. KF 780 STARS catalyst is available in both 1.3Q and 3Q sizes, and is also showing good performance in initial ULSD applications. That usage will be the subject of a future *Catalyst Courier* article.

Reference

[1]Anderson, G.: "Flexibility for FCC pretreatment," *Catalyst Courier* 84, 22–24

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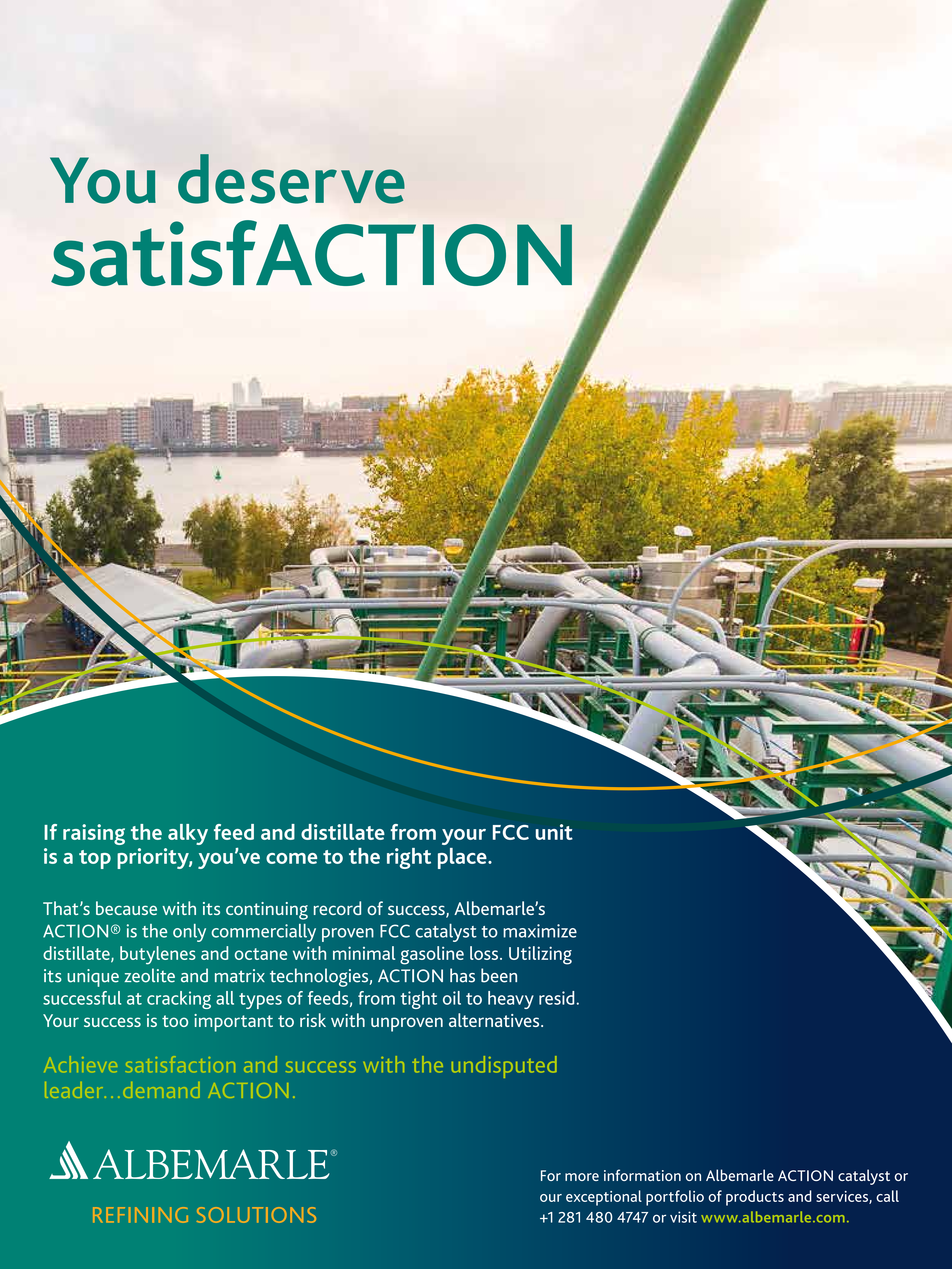
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