

Catalyst Courier

ISSUE 90 | FALL 2022

 ALBEMARLE®

Catalyst Courier

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RAPHAEL CRAWFORD
PRESIDENT,
CATALYSTS

COLLABORATION: FROM RESEARCH AND DEVELOPMENT THROUGH TO CUSTOMER SUPPORT

Welcome to the latest issue of *Catalyst Courier*

Safely delivering for our customers is the Albemarle Catalysts business's mantra, a constant that defines our relationship with refiners and the communities we serve.

Another constant is change. During Albemarle Investor Day in September 2021, Albemarle announced a strategic review of the catalysts business to determine the best path forward for the business's continued success. On August 29, 2022, Albemarle announced plans to move the Catalysts business to a separate, to-be-named business entity, which will function as a wholly-owned subsidiary of Albemarle.

I would like to reiterate the Catalysts business's commitment to the oil and petrochemical industries. Our customers, employees, joint-venture partners, and vendors are important members of our catalysts family. These relationships remain stalwart as we undertake the transition to becoming a wholly-owned subsidiary, with a new name and brand identity.

When I took over the leadership of the Catalysts business in 2018, I was impressed by its commitment to safety and delivering for its customers. This has not wavered, despite the weather, pandemic, and supply chain challenges that have gripped the industry. That should not be a surprise.

Ours is a global business with an entrepreneurial heritage that includes ties to Dutch chemicals producer Ketjen and the US-originated Filtrol Company of California. It is our goal, and expectation, to continue to produce and provide best-in-class catalyst products and technologies into the next century.

As proof, I offer the latest two technologies, **ACTION+™** and **KF 774 PULSAR™**, which we launched in 2021. These are being introduced worldwide, and additional new products are in development and customer trials.

It excites me to announce the results of collaborations between our R&D teams and our refining customers. Creating new, high-performance refinery catalysts while working to ensure the industry flourishes and becomes increasingly sustainable is crucial to what we do. Being the technology leader in this sector requires daily commitment – and resources to fund that leadership.

Our transition to a wholly-owned subsidiary supports our goal of growing the business to anticipate our refining and petrochemical customers' requirements. We will have the independence to fully dedicate our efforts to them, along with the parent organization funding necessary for developing and delivering

the innovative solutions they need to align strategically with their sustainability goals.

Therefore, we are proud to present this issue of *Catalyst Courier* on the theme of sustainability. It includes a discussion of the future of the refining industry and the pivotal role that catalysts will play ([Thought Leadership, p. 6](#)); highlights additional catalyst technologies through a technical paper focusing on renewables coprocessing ([KG 56 etc., p. 12](#)); and emphasizes the collaborative solutions ([Celestia, p. 18](#)) we are bringing to your operations today.

I also want to introduce you to Tina Craft, our new Chief Commercial Officer ([News, p. 4](#)). Many of you are familiar with Tina's work at Albemarle in the bromine and lithium segments, and we are thrilled to have her expertise in catalysts. She understands the oil and petrochemical sectors and the challenges that refiners face from market shifts and supply chain issues.

With that, I hope you enjoy this issue of *Catalyst Courier*. I look forward to your feedback and hope to hear from you soon.

A handwritten signature in black ink that reads "Raphael Crawford". The signature is fluid and cursive.

RAPHAEL CRAWFORD
PRESIDENT, CATALYSTS

CHEERS FOR 100 YEARS: 2022 MARKS 100 YEARS OF ALBEMARLE CATALYSTS IN THE REFINING INDUSTRY



For Albemarle's Catalysts business and our partner refiners, 2022 marks 100 years of collaboration.

Our genesis can

be traced to 1922, when the Filtrol Company of California was founded. An early research and development company, Filtrol developed and sold chemically activated clay products for 'bleaching' crude oil to make it more suitable as a lubricant.

In the late 1930s, French chemist Eugène Jules Houdry discovered that

heavy crude oil could be cracked into aviation gasoline using Filtrol's activated clay. During World War II, the demand for fuels and the construction of catalytic cracking units escalated. At the same time, Filtrol's catalyst supply business soared. By the end of the 1940s, Filtrol had become the largest producer of natural clay catalysts.

Over the years, Filtrol changed ownership several times, but its dedication to the continuous improvement and development of premier catalyst technology persisted. Sulfur-resistant catalysts emerged in the 1950s for treating sour feeds, and the first commercial zeolites were

delivered in the 1960s. In 1985, the first dealuminated zeolites were introduced.

In the late 1980s, Akzo acquired Filtrol and, in 2004, Albemarle Corporation acquired AkzoNobel's catalysts business, resulting in the Albemarle Catalysts business that we know today.

To join us in celebrating 100 years of partnership, pick up the next issue of Catalyst Courier and stay tuned to our social media channels. As in the past, the Albemarle Catalysts business remains dedicated to our customers in the refining industry.

KF 774 PULSAR™: THE NEXT-GENERATION CATALYST FOR CLEAN FUELS TECHNOLOGY

The commercial availability of a next-generation hydrotreating catalyst, KF 774 PULSAR™, was recently announced by Albemarle Corporation. The newest in a growing family of Clean Fuels Technology catalysts, Albemarle's KF 774 PULSAR has been developed collaboratively in a joint venture with Nippon Ketjen to solve the future challenges that the world's refiners will encounter and to support the industries that are critical to the global economy.

The KF 774 PULSAR catalyst offers extended hydrodesulfurization,

hydrodenitrogenation, and aromatic saturation activity, with additional stability for medium and medium-to-high pressure diesel hydrotreaters. At its heart, the catalyst utilizes a novel active-phase technology with extremely high metals dispersion and efficiency. This provides added flexibility in today's refinery operations. Additionally, the catalysts in the PULSAR family, KF 787 and KF 774, can be used in combination as part of Albemarle's STAX® capability to tailor performance to specific refinery operational needs.

"As a catalyst technology leader and innovator, Albemarle routinely gets tough questions with high expectations from our customers," says Raphael Crawford, President, Catalysts. "We welcome the challenges from our refining partners to develop Clean Fuels Technologies that will benefit the environment today and tomorrow. That customer understanding and the tenacity of our scientists, researchers, and operators has resulted in another novel, creative solution."



ALBEMARLE'S 2021 SUSTAINABILITY REPORT RELEASED

Sustainability is key to the long-term strategies of all Albemarle's businesses. In keeping with our company core value of transparency, Albemarle released its 2021 Sustainability Report to the public in June 2022.

The report includes Albemarle's initial assessment of its Scope 3 greenhouse gas (GHG) emissions, which will be used to reduce emissions across the supply chain. Also included are updates on progress against existing targets for GHG emissions and the intensity of freshwater usage. Additionally, readers will find newly set targets for promoting diversity, equity, and inclusion as part of the fabric and culture of Albemarle.

Visit the [report](#) for a closer look at Albemarle's sustainability performance, our sustainability targets, and our plans for enabling a sustainable

future, both for our refining customers and beyond.

"Our products and services make the world safer and more sustainable, and we pride ourselves on doing the right things, the right way, with the right resources. ... For the sixth consecutive year, EcoVadis, a leading sustainability ratings agency, has awarded Albemarle gold medal status. This recognition places us in the top six percent of more than 75,000 companies worldwide."
Kent Masters, CEO.



REFINING CATALYSTS WELCOMES NEW CHIEF COMMERCIAL OFFICER



Tina Craft, former Chief Commercial Officer (CCO) for Albemarle's Lithium global business unit (GBU), has transitioned to her new role as CCO, Refining Catalysts. Tina joined the Catalysts GBU on November 2, 2021. She is a familiar face to many across Albemarle, and to our customers, and is very excited about the future of the catalysts business.

Tina brings considerable leadership experience to our team. Before serving as CCO for Albemarle's Lithium GBU, Tina served as Vice President of Commercial Operations for Bromine Specialties. In addition to her support for Women Connect, Tina's responsibilities have included sales, marketing, and new business development.

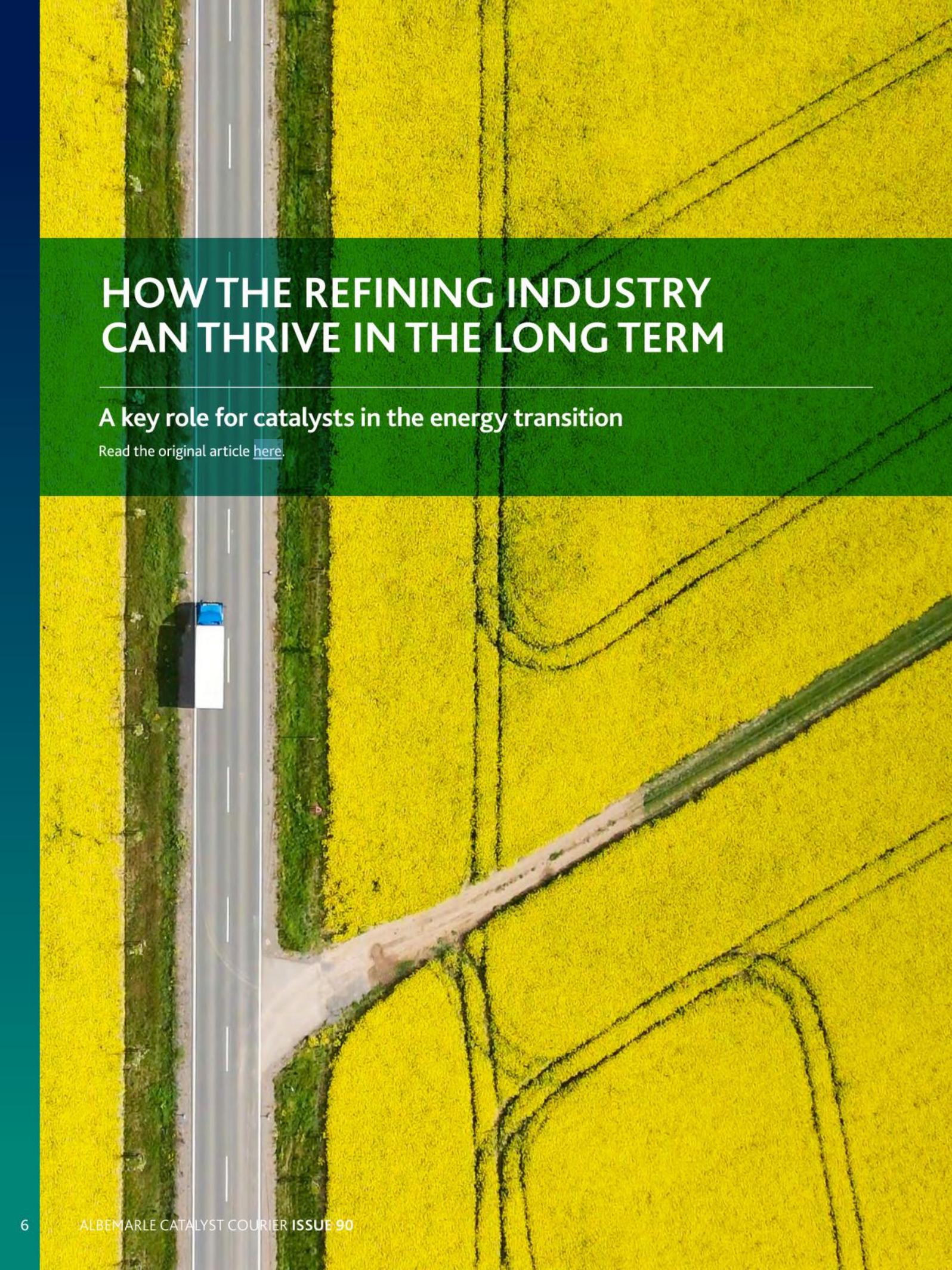
We are incredibly lucky to have Tina's expertise onboard, and we welcome her to the team.

ACTION+™ CATALYST TECHNOLOGY JOINS THE FOLD

ACTION+™ Catalyst Technology is set to join the cornerstone ACTION® FCC catalyst line after successfully completing two commercial trials. Since 2007, Albemarle's ACTION Catalyst Technology has delivered best-in-class performance to refiners around the world. The new ACTION+ Catalyst Technology builds on that success, offering next-generation butylene yields and gasoline octane. The technology was revealed recently at the two-day 2021 American Fuel & Petrochemical Manufacturers summit.

The shape-selective ZT-400 core technology of the ACTION catalyst is leveraged in ACTION+ with ZT-500, a new, innovative Y-zeolite stabilization system. Using ZT-500, hydrogen transfer reactions are minimized, thus providing maximum LPG olefinicity with unrivalled butylene/propylene selectivity. The new technology also preserves the type of species that maximize gasoline octane in an FCC.

"Albemarle understands that today's refiners face new, diverse, and daunting obstacles to profitable FCC operation in an extremely challenging and competitive business environment," says Raphael Crawford, President, Catalysts. **"Our goal is to continue to provide novel, creative solutions for shaping and optimizing product yield slates to ensure maximum returns".**

An aerial photograph of a road and surrounding fields. The road is a two-lane asphalt road with white dashed lines, running vertically through the center. To the left of the road is a narrow strip of green grass. To the right is a large field of bright yellow rapeseed flowers, with dark lines indicating the rows of plants. A dirt path or driveway branches off from the road to the right. The overall scene is bright and clear, suggesting a sunny day.

HOW THE REFINING INDUSTRY CAN THRIVE IN THE LONG TERM

A key role for catalysts in the energy transition

Read the original article [here](#).



RAPHAEL CRAWFORD
PRESIDENT,
CATALYSTS

Today's global energy system has been shaped by consumers, energy suppliers, and governments over many decades. It reflects the need for reliable access to affordable energy and a traditional reliance on fossil fuels. Oil and gas make up about half the world's primary energy mix, and coal provides a further 30%. Global demand for energy is rising but meeting increasing energy demand from these fossil sources would also mean more greenhouse gas emissions.

What is the ideal energy mix for the planet? This is a vitally important question and as someone closely involved with the refining industry, I believe it is essential to understand the world's energy needs today and in the future. For companies that serve the refining industry, this should be a time of serious reflection about the world's energy needs and how they will change in the mid and long terms.

In the current energy landscape, the demand for petroleum-based transportation fuel remains strong. Though environmental policies will evolve, it seems likely that the internal combustion engine will remain a substantial part of global transportation through my grandchildren's generation and perhaps beyond. Nonetheless, a plateau in fossil fuel demand is to be expected and, when it arrives, it will apply increasing revenue pressure on the industry. This change is inevitable.

At Albemarle, we are developing new ways to help customers align their operations with the shift towards cleaner fuels, greener use of petroleum-based products, and lower greenhouse gas emissions. Our focus is on developing and implementing ideas that can preserve livelihoods, extend the return on existing capital investments, and help position customers for long-term success.

Our customers understand that, as an industry, they need to

- extract more useful products from crude oil
- remove unnecessary contaminants from petroleum-based products
- improve the production of biofuels
- turn crude into non-fuel products more efficiently
- refine synthetic crude from waste plastics.

Fuel peaks and fresh opportunities

As the world moves away from hydrocarbon-based fuels towards renewable energies and low-carbon energy carriers, the business realities of the energy transition will come into sharp focus for refiners and their suppliers. Efforts to address climate change concerns and increase sustainability, coupled with changes in consumer habits, will have unprecedented impacts on the industry. Reducing the use of fossil fuels and minimizing the carbon footprints of all human activities will lead to a peak in fuel consumption that will start with gasoline and then other fuels, before finally affecting crude oil demand.

In recent years, some refineries have shut down and others have transformed into logistics terminals, but there are further strategies that refiners might consider as they strive to remain competitive in a changing business landscape.

Seeking out new opportunities: Petrochemicals and synthetic crude

Demand for transportation fuels looks certain to decline, but the market for chemical derivatives is expected to continue to grow. This trend is a response to population growth and rising standards of living in rapidly developing parts of the world. One option for countering lost fuel demand is to transform refining output from unwanted hydrocarbon fuels into petrochemical feedstocks. This can be achieved by different technologies, some of which are available now and others that are under development.

Petrochemicals include raw materials for industrial chemicals, durable plastics, synthetic fibers, dyes, and detergents. As these could provide long-term growth in demand for oil, the industry is making large investments in the crude-to-chemicals value chain. New refineries are being built with petrochemical manufacturing facilities on-site and others are being retrofitted to support the process. Catalysts are playing a pivotal role in making these new builds and retrofits efficient and cost-effective.

Switching refining yields to petrochemicals seems like an obvious way to increase margins and achieve growth.

However, the refining and petrochemical markets are vastly different in scale, and increasing petrochemical production from refineries could easily flood product markets. Also, the investments required to make the switch involve significant capital commitment, at scales or with operations that may not be feasible at every refinery.

Processes for producing synthetic crude oil from waste plastic have been demonstrated by some refiners. This approach provides an opportunity to increase circularity: short-chain crude oil is turned into long-chain plastics that are then turned back into short-chain crude. In principle, a barrel of oil can be used multiple times. It would mean less waste plastic incineration and greenhouse gas emissions.

Switching to biofuels production

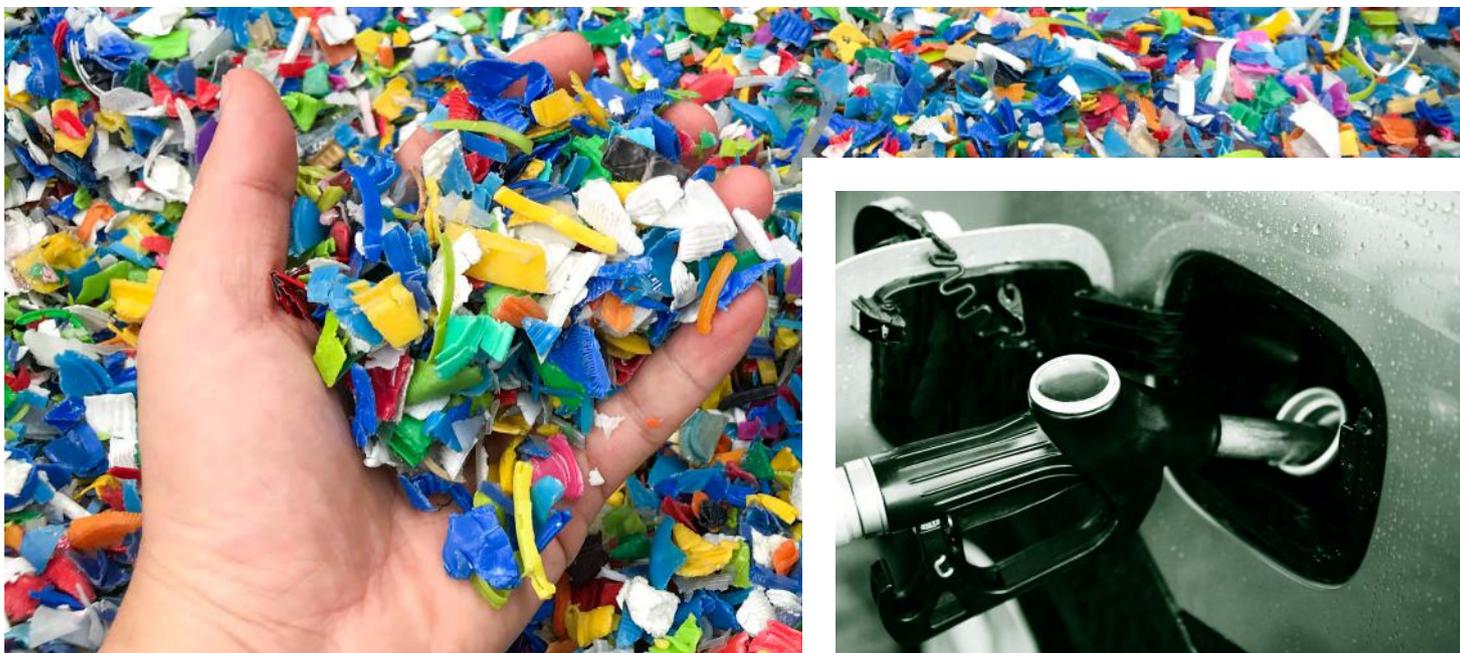
Refiners across Europe are converting some of their refining assets into biorefineries. This improves environmental sustainability and satisfies demand for cleaner fuels. Enhancing biofuel production as part of the journey to net-zero carbon presents new opportunities for refiners and catalyst manufacturers.

The biofuels process relies on catalysts to convert various biomass into high-quality fuels. These catalysts enable refiners to efficiently turn biofeeds (like seed oil and used cooking oil) into renewable diesel and sustainable aviation fuel. The biofuels market forecast reflects sustained growth over the next few years. As we move into the energy transition, Albemarle researchers continue to develop further catalyst grades for the co-processing of biofeeds.

Finding long-term markets by location or sector

Some oil and gas companies are expanding their fuel marketing activities in key growth regions, thereby enabling integration with their operations elsewhere and providing a long-term outlet for refinery products.

In addition to markets defined by geography and transportation development, there are some industrial sectors where the use of hydrocarbon fuels may persist. Demand for jet fuel, for example, may grow over the long term in reflection of the difficulty of finding a replacement fuel for long-haul aviation. Refiners with established connections to airports will be well placed to meet this demand.



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Retaining high-grade assets and making selective investments

Larger companies will likely look to strengthen and streamline their portfolios by divesting standalone facilities to focus on their most efficient and profitable assets. Some oil majors have begun to make selective investments that upgrade their main refining assets and protect their position.

But, if the energy transition and existing viable technology trends accelerate, there is the possibility of much faster cuts in carbon emissions. The adoption of electric vehicles and the switch to cleaner fuels could substantially reduce oil demand and lead to extensive capacity rationalization.

A key role for catalysts

Although most everyone wants to see a more sustainable energy mix,

transformations like these require time. While the transition to a low-carbon future will unfold at different rates regionally, it must, ultimately, encompass all sectors of economic activity, which will create new risks and opportunities. Innovative catalyst technologies, new business models, and partnerships supported by policy and regulatory frameworks will be necessary for the refining industry to thrive.

Albemarle's refining and petrochemical catalyst technologies will play a key supporting role as we transition to the new energy market. There will be very few innovations, whether in biofuels, recycling, or economic circularity, that will not involve catalysis. Our goals are to protect the planet and to help our customers, wherever they are today, and wherever they need to go.

Sources

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The Energy Transition: 5 energy-transition survival strategies for refiners. Dec 2018

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ALBEMARLE HYDROTREATING CATALYST TECHNOLOGY FOR PROCESSING RENEWABLES

Overcoming operational challenges with KG 56, ReNewFine™, and ReNewSTAX™

LUCIA BASILE, ANDREA BATTISTON, AND STEFANO MELIS

Driven by legislative requirements to reduce CO₂ emissions, renewable fuels are rapidly becoming a core part of European and US refiners' hydrotreating operations. Albemarle's long-standing experience in renewables hydrotreating covers more than 50 cycles completed in commercial practice. Working with its customers and research and development teams, Albemarle has introduced guard and active catalysts dedicated to renewables hydrotreating: Ketjen Guard (KG) 56 and the ReNewFine™ 100 and 200 series. These grades demonstrate major advantages when applied according to the principles of ReNewSTAX™, Albemarle's catalyst loading design technology for processing renewables.

Legislation drives the shift to renewables co-processing

The use of renewables in hydrotreating is part of regulators' global strategy for sustainably reducing CO₂ emissions. In this scenario, legislation is playing a leading role. In the USA, the Renewable Fuel Standard 2 (RFS 2) demands an increase in the volume of renewable fuel blended into transportation fuels to 36 billion gallons by 2022.¹ In Europe, the Renewable Energy Directive (RED II) sets the minimum amount of total fuel from renewable sources for road and rail transportation at 14% by 2030.² To ensure the sustainability of biofuels and limit the repurposing of land for biomass production, RED II also stipulates that a minimum of 3.5% of fuels must come from advanced biofuels produced from biomass such as algae and tall oil. The directive also promotes the use of waste-derived fuels from animal fats and used cooking oil (see Figure 1).

Refiners need to adapt quickly and take timely measures to comply with these regulatory obligations. For renewables co-processing, this entails adjusting a hydrotreater's catalyst loading design and potentially revamping existing equipment to cope with the challenges introduced by renewable feedstocks.

Operational challenges in renewables co-processing

Co-processing of renewables brings significant operational challenges, including shorter cycle length, higher hydrogen consumption, and pressure drop control issues.

Today's biofuels consist mainly of triglycerides. In a hydrotreater, these components undergo saturation of their double bonds, which results in the cracking of the triglyceride chains into free fatty acids (Figure 2).

EU regulation RED II stimulates use of sustainable biofeeds:



Limit palm oil

Limiting use of palm oil (down to 0% in 2030)



Limit land utilization

Limiting biofeed with impact on land utilization (down to 7%)



Promote advanced biofuels

Examples are algae, tall oil, and nut shells (3.5% mandatory by 2030)



Promote animal fats and UCO

Double counting UCO (used cooking oil)

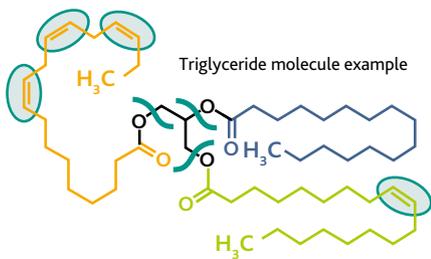
REFINERS NEED TO SWITCH FROM OIL TO ANIMAL FATS, USED COOKING OIL (UCO), AND ADVANCED BIOFUELS

Figure 1. RED II stimulus for sustainable renewable feedstock utilization.

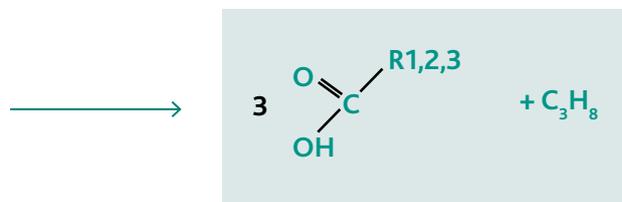
¹RFS 2: <https://www.epa.gov/renewable-fuel-standard-program/renewable-fuel-standard-rfs2-final-rule>

²RED II: <https://www.europex.org/eulegislation/renewable-energy-energy-directive>

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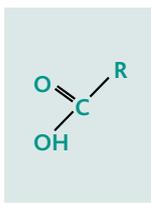


Saturation of double bonds



Triglyceride cracking to carboxylic acid

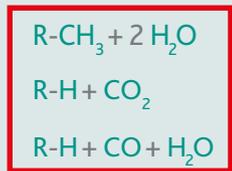
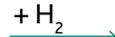
fatty acids
reactions to
n-paraffins



HDO Hydrodeoxygenation

DCX Decarboxylation

DCN Decarbonylation



Loss of 1
C-atom

Figure 2. The main reactions of biofeeds in a hydrotreater.

TECHNICAL FOCUS

These fatty acids further decompose to n-paraffins by three different mechanisms: hydrodeoxygenation (HDO), decarboxylation (DCX), and decarbonylation (DCN).

The DCX and DCN reactions produce CO₂ and CO. CO is particularly detrimental for the operational efficiency of hydrotreaters, as it inhibits hydrodesulfurization (HDS) reactions: treating 5% biofeed causes up to 10°C penalty in the weighted average bed temperature (WABT), depending on the type of catalyst applied. This significantly shortens the cycle length and results in the loss of one carbon atom in C18 paraffins, leading to a 5% yield loss.

The effect of CO on the operating temperature of a commercial hydrotreater is shown in Figure 3. The response of the WABT to the increase in CO concentration resulting from the additional vegetable oil is striking. Thus, to maximize cycle length and product yield, it is necessary to maximize the

catalyst selectivity to HDO reactions, which do not produce CO, while taking care to preserve enough reactor volume for HDS and the other operational targets.

In addition, biofeeds contain solid impurities, unsaturates, and metals. Impurities tend to accumulate in the voids between catalyst particles, thereby increasing the risk of pressure drop at the reactor top. Unsaturates, owing to their very high reactivity, can condense and form gums in a relatively thin reactor layer, thereby also potentially causing pressure drop issues in the upper section of the reactor.

The phospholipids found in biomass have the highest impact on unit performance. They consist of triglycerides in which one of the fatty acid chains has been replaced by a phosphate group. The phosphate group is typically coupled with an (alkaline) metal (see Figure 4).

As phospholipids decompose in a hydrotreater, the phosphate group tends to deposit in the catalyst pores. Alternatively, the phosphate group can react to form phosphoric acid, which promotes polymerization and, ultimately, leads to the formation of carbon deposits. In both cases, the result is pore blockage leading to a lower feed diffusion rate and less feed penetration into the catalyst pores. This allows metals to penetrate deep into the bed and deactivate the catalyst further down the reactor. Overall, the presence of phospholipids in the hydrotreater can result in severe pressure drop issues and increased catalyst deactivation deep in the reactor.

To limit the impact of the impurities, metals, unsaturates, and phosphorus in renewable feedstocks, it is necessary to optimize the design of the guard section of the reactor without sacrificing too much of the main catalyst volume.

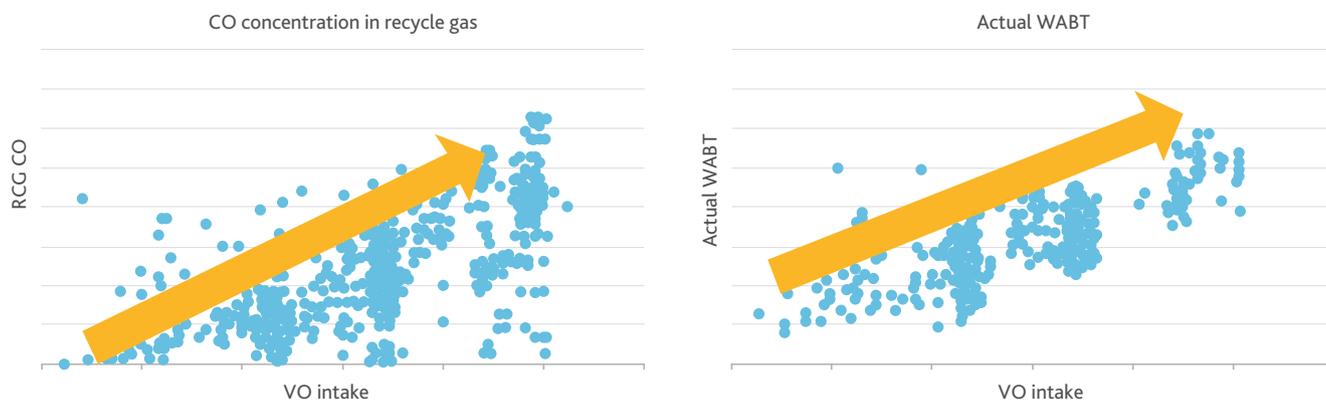
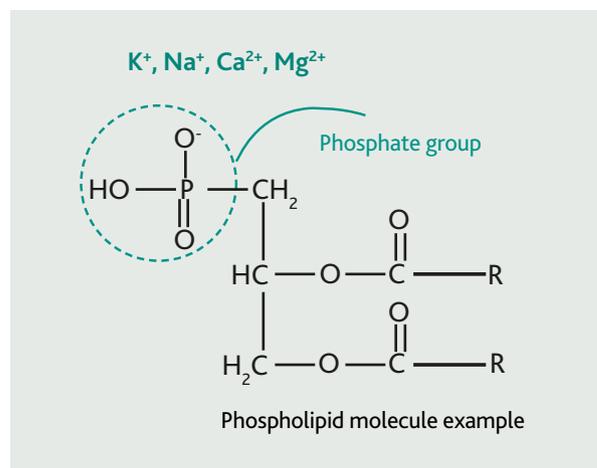


Figure 3. Effect of CO concentration on a hydrotreater's WABT.

Figure 4. Phospholipid structure.



To support refiners in their transition to renewables processing, Albemarle has introduced dedicated, more proficient guard and HDO catalysts: Ketjen Guard (KG) 56 and the ReNewFine 100 and 200 series.

Ketjen Guard (KG) 56

KG 56 is the latest introduction in Albemarle's KG portfolio. Available in a disk shape, KG 56 is an inert, macroporous guard grade with very high void fraction designed to pick up particulates, scale, and other contaminants in feedstock, including gums formed from the polymerization and condensation of unsaturates.

KG 56's trapping capacity is maximized by a combination of internal porosity and inter-disk void space. The internal pores of the disks maximize scale trapping, while the inter-disk void spaces enable trapping of the larger microporous scale and particles, thereby ensuring an undisturbed flow of oil beyond the inner porosity of the disks and preventing pressure drop onset throughout the cycle.

Consequently, KG 56 is particularly suited for units with a known history of pressure drop buildup. This includes units treating conventional feedstock derived from crudes with high salt contamination or high naphthenics, units operating in full vapor phase, and units processing renewable feedstocks.

KG 56 is available with pore densities ranging from 10 to 65 pore per inch (ppi) (see Figure 5). Stacking of KG 56 disks with increasing pore density can be used to improve trapping efficiency, which can minimize the volume of the guard bed and thus maximize the reactor volume available for loading the active catalyst.

ReNewFine catalysts

ReNewFine catalyst grades are designed to tackle the specific hydrotreater challenges that arise when processing renewables at up to 100% concentration. There are two series: the 100 series, with the main function of hydrodemetallization (HDM) and phosphorus trapping; and the 200 series designed for HDO and displaying good metals trapping capacity.

The following section discusses their application specifically for renewables co-processing. The maximum advantage of the ReNewFine grades is obtained when using the principles of the ReNewSTAX loading design technology.

ReNewFine 100 series

Alkaline metals in biofeeds are usually bonded to phospholipids. Phospholipids have the highest impact on a hydrotreater's performance because they deposit and decompose on the catalyst pore mouths, which limits feed mass transfer, restricts metals trapping, and, ultimately, may cause reactor plugging and pressure drop.

The ReNewFine 100 series consists of HDM catalysts dedicated to renewables processing applications with the main purpose of trapping phosphorus, silicon, and alkaline metals such as Mg, K, Na, and Ca; they are ideal for renewables processing. Through highly efficient phosphorus trapping, these catalysts preserve the overall capacity of the guard bed to capture metals, including Ni and V. The benefits of the ReNewFine 100 series are lower risk of pressure drop onset and lower deactivation of both the HDO and main catalyst.

As seen in Figure 6, ReNewFine 101 has significantly higher phosphorus trapping capacity compared with a conventional guard catalyst, thus setting a new standard for protection from phosphorus.

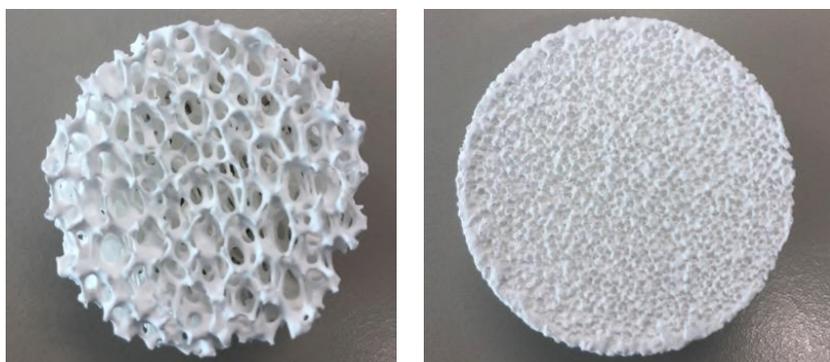
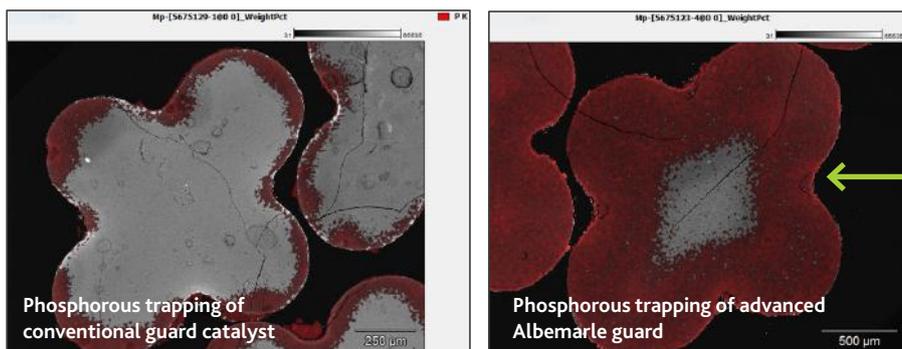


Figure 5. KG 56, Albemarle's new guard grade (left: 10 ppi; right: 50 ppi).



ReNewFine™ Phosphorous trapping

Figure 6. Comparison between the phosphorus trapping capacity of a conventional guard catalyst (left) and ReNewFine 101 (right).

TECHNICAL FOCUS

ReNewFine 200 series

The ReNewFine 200 series consists of catalyst grades developed for renewables processing with the main function of HDO. The series has very high HDO selectivity, thereby removing oxygen from the fatty acid chains in biofeed while minimizing the formation of CO and CO₂. In addition, the series displays good metals trapping capacity. Ultimately, the ReNewFine 200 series results in improved cycle length and increased product yield.

Figure 7 compares the HDO selectivity of the ReNewFine 200 series with that of conventional CoMo and NiMo catalysts.

As shown, these catalyst grades improve HDO selectivity in the reactor from 30 to up to almost 100%.

To achieve the optimal combination of metals and phosphorus trapping and HDO activity, ReNewFine catalysts are loaded in the upper section of hydrotreaters, on top of the main HDS (active) catalyst system (Figure 8). Depending on the operational targets and unit constraints, a specialized bulk metal catalyst like Nebula® or Celestia™ can be included in the main active catalyst system to maximize profitability and compensate for performance loss due to renewables treating.

ReNewSTAX loading design technology

From the guard bed to the main catalyst bed, each zone in a hydrotreater has a specific role that presents unique challenges. To tackle these challenges, Albemarle developed STAX®, a proprietary methodology for catalyst system design for hydrotreating conventional feedstock. ReNewSTAX loading design technology is an evolution of the STAX methodology for the co-processing of renewables, providing optimized stacking of catalysts for maximum activity, selectivity, and stability (see Figure 9).

Using the ReNewSTAX principles, a specialized guard system composed of KG 56 and ReNewFine grades is loaded at the top of the reactor to control pressure drop and maximize HDO activity. The remainder of the loading design consists of the main catalyst system, which is selected based on the specific conditions and targets of the operating cycle. By balancing the guard bed (with optimized HDO selectivity and phosphorus, silicon, and alkaline metals trapping capacity) and the main catalyst system, ReNewSTAX loading design technology maximizes cycle length and diesel yield.

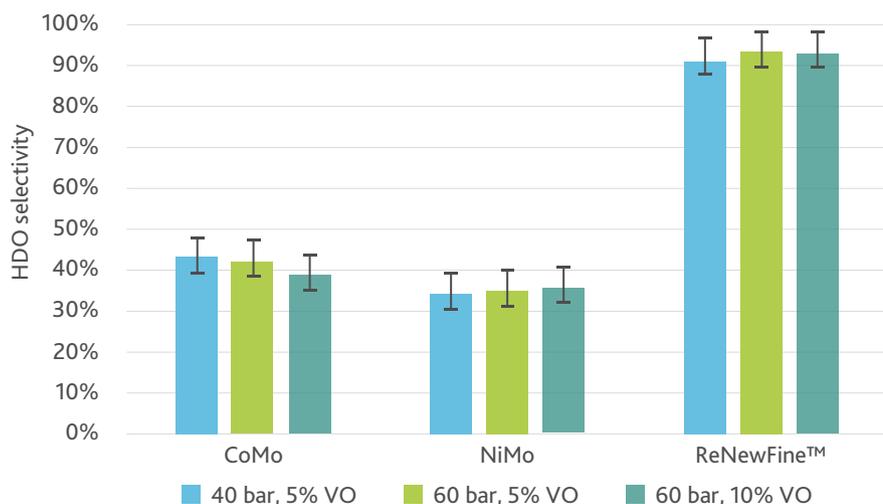


Figure 7. HDO selectivity of the ReNewFine 200 series versus conventional CoMo and NiMo hydrotreating catalysts.

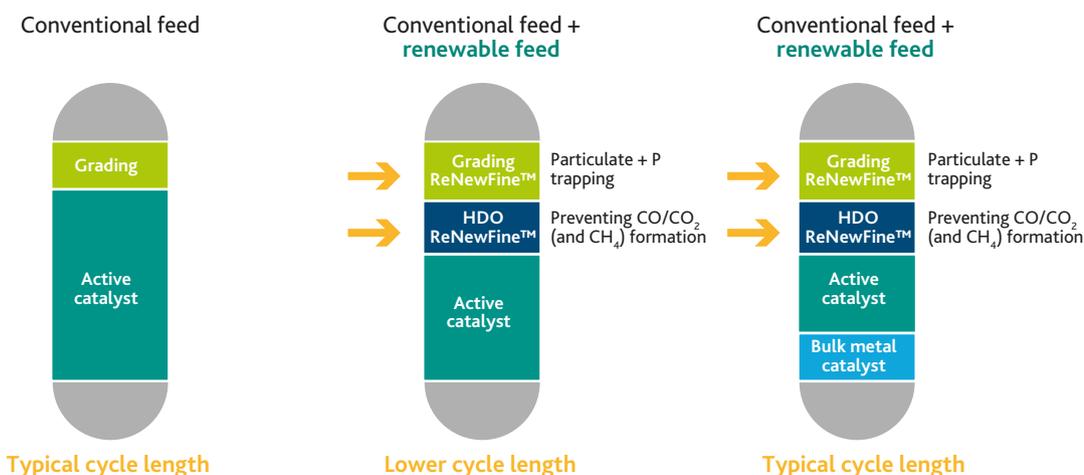


Figure 8. ReNewFine catalysts in a hydrotreater.

Conclusion

Co-processing of renewable feedstocks brings significant operational challenges, including shorter cycle length, higher hydrogen consumption, and pressure drop control issues. To support refiners in their transition to renewables processing, Albemarle has introduced dedicated, highly proficient guard and HDO catalysts: KG 56 and the ReNewFine 100 and 200 series. These grades demonstrate major advantages when applied according to the principles of the ReNewSTAX catalyst loading design technology.

Albemarle has 13 years of experience in biofeed co-processing and has led more than 50 operating cycles with renewables, including 100% vegetable oil hydrotreating. Our expertise is available to help customers power the potential of their refineries and lead the transition to processing renewables.

Contact your Albemarle representative for help with controlling pressure drop using ReNewFine grading materials; minimizing yield losses with ReNewFine HDO selective catalysts; and maximizing cycle length by balancing guard versus active catalyst requirements through ReNewSTAX loading design technology.

For further information, contact lucia.basile@albemarle.com, andrea.battiston@albemarle.com, or stefano.melis@albemarle.com

To support refiners in their transition to renewables processing, Albemarle has introduced dedicated, highly proficient guard and HDO catalysts: KG 56 and the ReNewFine 100 and 200 series.

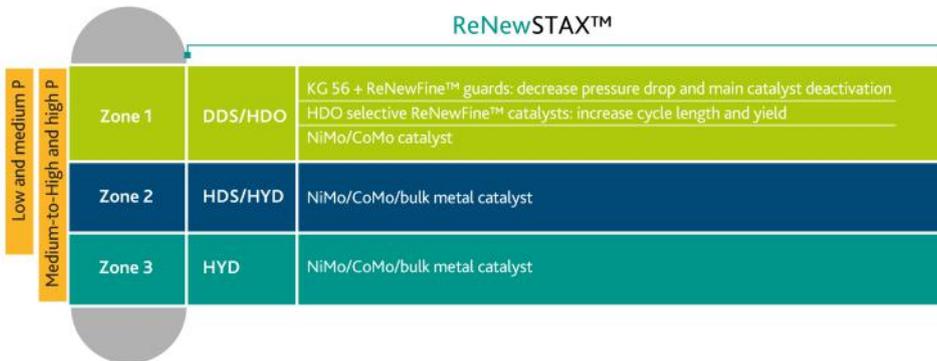
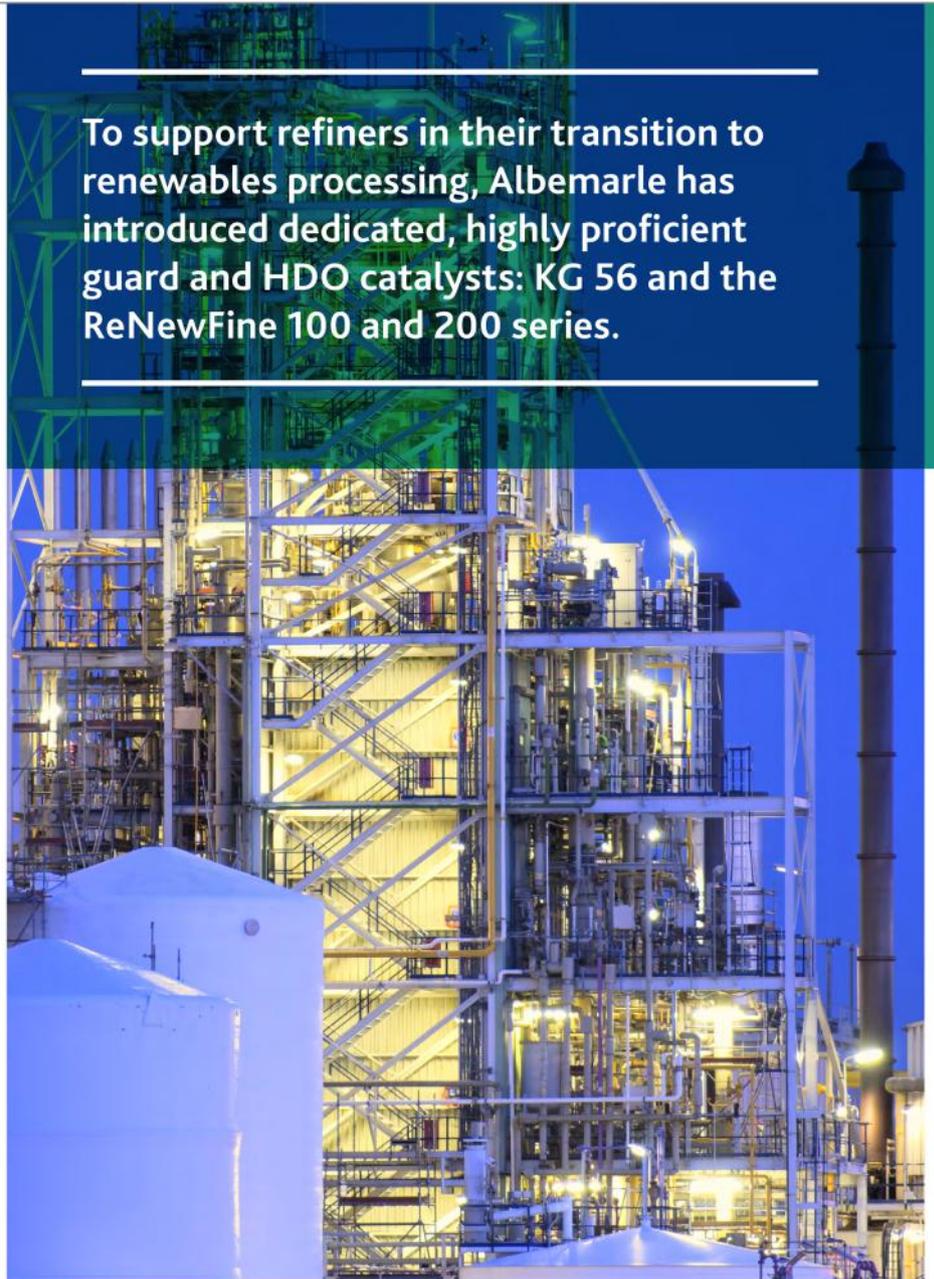


Figure 9. ReNewSTAX: Albemarle's proprietary loading technology for the co-processing of renewables.

USING CELESTIA™ CATALYST TO INCREASE PROFITABILITY IN HYDROCRACKING AND DIESEL HYDROPROCESSING

Three case studies demonstrate Celestia catalyst as a drop-in solution for unlocking energy savings and raising margins.

PIETER LUSSE, RENE SEVERENS, AND KEITH WILSON

Against a backdrop of market volatility and an energy transition that offers limited scope for new builds, refiners are hard-pressed to find creative ways to improve profitability in existing facilities. For hydroprocessing and hydrocracking, this means investigating pathways to improve operations within current units and constraints. One way is to focus on selecting the right catalyst solutions for use in existing refinery units. Albemarle's Celestia catalyst, developed jointly with ExxonMobil, is a drop-in solution demonstrated to improve unit profitability in hydrocracking and hydroprocessing applications.

Operating expenditure at a refinery has a big impact on profitability and is often determined by factors such as energy consumption, feed costs, and utilities. Older refineries frequently operate with suboptimal feed characteristics for their design specifications. As the capital projects necessary for improving the operating efficiency of these facilities are difficult to justify, hydroprocessing or hydrocracking units may be underutilized while delivering a given product slate. Overall, this combination of factors results in increased energy usage and lower margins.

Where new-build units are not possible, refiners may turn to optimizing catalyst selections as a solution to these concerns. Utilizing an Albemarle Celestia-based catalyst solution is a demonstrated solution for improving unit profitability and creating margin advantages. This novel bulk-metal catalyst was co-developed by Albemarle and ExxonMobil to enable the innovative use of existing

equipment in ExxonMobil's refineries. Following on from the development of the Nebula® bulk-metal catalyst in the 2000s, The Celestia catalyst was first introduced in a light feed hydrocracker in 2015. The catalyst has since improved margins in 15 hydroprocessing units across North America, Europe, and Asia. Celestia has facilitated creative improvements at ExxonMobil refineries by driving catalyst activity to levels unmatched by previous generations of catalyst technology.

Three case studies demonstrate how the application of Celestia technology to distillate hydrotreating and light cycle oil (LCO) and vacuum gas oil (VGO) hydrocracker pretreatment yielded exceptional margin and operating expenditure returns.

Profitability is often a multifaceted issue.

The Celestia catalyst can add value in several ways, improving margins via

- enabling greater feed flexibility: accommodating higher feed rates with less expensive feeds
- enhancing product quality and yield through improved conversion: the resultant products have lower total aromatics, sulfur and nitrogen content, and improved cetane and cloud properties
- lowering operating expenditure and increasing unit cycle length, which facilitates refinery-wide shutdown planning
- reducing energy consumption by changing the reactor temperature profile, enabling either a lower inlet temperature or a higher outlet temperature with the goal of reducing energy consumption.

Heat release management

As hydroprocessing reactions are generally exothermic, increasing the activity of the reactor has implications for the thermal management of the reactor catalyst bed. Celestia is more exothermic than other catalysts, so catalyst temperature rise is a key factor to consider when targeting optimum product quality and longest catalyst life. To manage exothermic releases and ensure the safe operation of the catalyst, ExxonMobil has developed a set of strategies for utilizing the Celestia catalyst, which includes

- dividing the catalyst load between the beds so that the temperature rise per bed is limited
- introducing larger quantities of inter-bed quench gases: cold quench gases are mixed with hot liquid and vapor between catalyst beds
- increasing the ascending temperature rise axially in the reactor by changing the reactor temperature control strategy through a combination of lowering reactor inlet temperature and/or increasing outlet temperature
- limiting early run operations to less-reactive feeds during the first 1–2 weeks of catalyst line out.

Celestia is more efficient when loaded in the mid to lower catalyst beds. This stacking design enhances the removal of refractory sulfur and nitrogen species and enhances aromatic saturation, thus improving the overall efficiency of the catalyst. The design of the facility and the unit configuration will ultimately dictate how effectively Celestia enables profitability gains.

Celestia catalyst design

The Celestia catalyst's industry-leading performance is the result of step-out hydrodesulfurization (HDS) and hydrodenitrogenation activity achieved through a unique catalyst design. The bulk-metal catalyst is synthesized almost entirely from the active metals necessary for hydroprocessing activity. Compared with leading NiMo catalysts, Celestia enables more than twice the volumetric activity and demonstrates more than two and a half times the hydrodearomatization activity. Overall, adding Celestia to a catalyst solution brings a high degree of activity improvement, even when the catalyst forms less than 10% of the reactor volume.

Implementation pathways seen to date

Thus far, the Celestia catalyst has significantly improved the economic outcomes for 15 process applications. The approaches taken in these scenarios fall broadly into two categories:

- optimizing Celestia to a predefined equipment limitation
- optimizing the Celestia catalyst load to achieve a predefined process objective. Some investment may be required to mitigate heat release, heat integration, or hydraulic impacts.

The value opportunities realized by incorporating the Celestia catalyst into a reactor load are illustrated by the following three case studies.



Utilizing an Albemarle Celestia-based catalyst is a demonstrated solution for improving unit profitability and creating margin advantages. This novel bulk-metal catalyst was co-developed by Albemarle and ExxonMobil to enable the innovative use of existing equipment in ExxonMobil refineries.



Case 1: Increased feed margin and lower energy consumption

A once-through VGO hydrocracker that converts a heavy VGO feed to clean fuels and steam cracker feed consists of a two-series reactor system containing a pretreatment reactor and a cracking reactor (see Figure 1). The unit incorporates recycle gas and hydrogen make-up gas. Heat from the cracking reactor effluent is used to preheat the reactor feed in several heat exchangers, while an exchanger bypass is available to enable full control of the cracking reactor inlet temperature. A furnace provides external preheating of the combined hydrogen gas stream as it is blended with the feed, before entering the pretreatment reactor. The reactor inlet temperature determines the extent of furnace firing required.

The catalyst system in Bed 3 of the three-bed reactor was a Nebula–NiMo mixture.

At catalyst changeover, this system was replaced with a 1:1 Celestia–Nebula system with the objective of increasing margin by raising the rate at which a heavy coker gas oil was processed in the mixed VGO feed.

The Celestia catalyst system performed well against this objective, more than doubling the heavy coker gas oil feed processed in comparison with previous cycles. Additionally, the catalyst reduced nitrogen slip to the hydrocracking catalyst beds. By improving aromatic saturation, Celestia also enhanced the product qualities, which boosted the cracking catalyst’s functionality and contributed to sustained conversion levels.

Another outcome of the overall process enhancement was a reduction in furnace firing. In loading Celestia catalyst into Bed 3, the bed exotherm was increased when processing at a similar feed rate.

Quenches were adjusted but, in the end, reactor outlet temperature rose by 4°C, which increased the hot-side heat exchanger inlet temperature. This increased the exchanger duty by 1.7 MW, therefore, with the Celestia catalyst loaded, the furnace duty fell from 16.7 to 15 MW to realize a net 10% reduction in firing and energy consumption.

The Celestia catalyst’s stability in a challenging VGO service has been demonstrated as outstanding and provided sustained energy cost savings throughout the cycle.

Case 2: Extended cycle length with improved product qualities

A VGO hydrocracker had been debottlenecked to nearly twice its original design capacity. The refinery subsequently identified an opportunity to use the Celestia catalyst to extend the

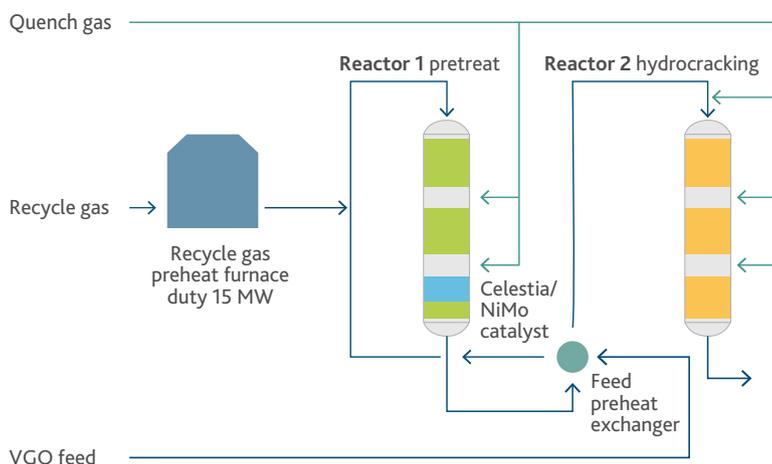


Figure 1. The configuration of the once-through hydrocracker.

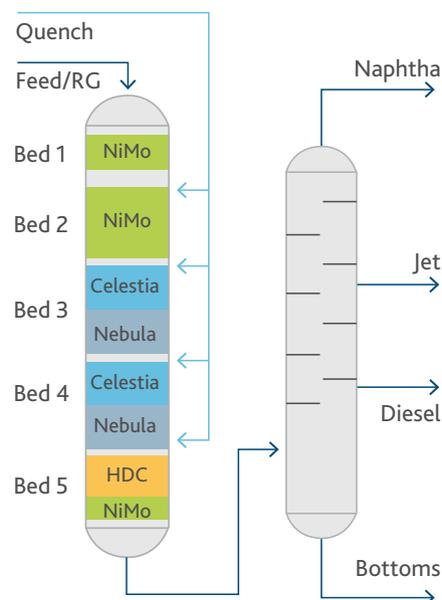


Figure 2. The split-bed configuration in the VGO hydrocracker reactor.

hydrocracker's cycle length to coincide with other unit shutdowns and thus avoid derating its capacity at end of run.

Celestia was loaded in a split configuration with Nebula across two catalyst beds in a five-bed VGO hydrocracker pretreatment reactor (Figure 2). The objective of this new catalyst system was to increase the cycle length by 60%. Achieving this would postpone a hydrocracker shutdown and catalyst replacement until the planned refinery-wide shutdown, thus leading to a 25% reduction in annualized operating expenditure.

To boost the overall pretreatment activity by 130%, a significant amount of Celestia catalyst had to be loaded according to a carefully optimized plan. To achieve enhanced product run length and the desired product quality,

the ascending temperature profile was increased.

Additional activity was obtained by balancing the Celestia and Nebula catalyst load in two separate beds, which also reduced the temperature rise per bed. The reactor inlet temperature was lowered by 12°C, while the reactor outlet temperature was maintained as per the previous cycle. The quench gas was adjusted to manage the reactor temperature profile and lower the weighted average bed temperature (WABT) by 10°C (Figure 3). Some modifications were necessary to debottleneck the reactor quench gas supply when the catalyst load was changed.

The key impacts of the combined Celestia–Nebula catalysts were to provide increased aromatic saturation

and lower product nitrogen (Figure 4) while operating at a lower reactor WABT (Figure 5). The functionality of the cracking catalyst in Bed 5 improved, which drove higher volume swell and 1 vol% yield improvement compared with the previous cycle.

The heat integration system also demonstrated improvement. The significant reduction in reactor inlet temperature, combined with maintaining a similar outlet temperature as in the previous cycle, resulted in a 5% reduction of the furnace firing energy requirement. This represents extra value delivered in this scenario.

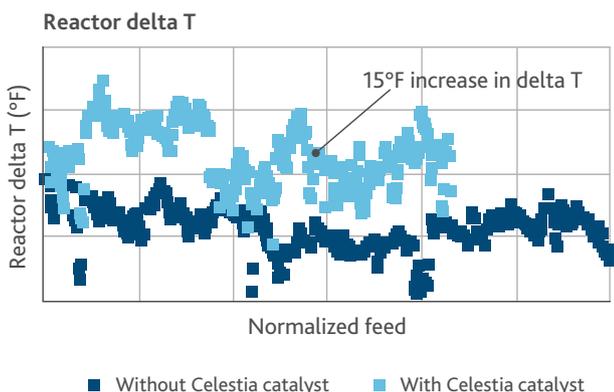


Figure 3. VGO cracker reactor exotherm.

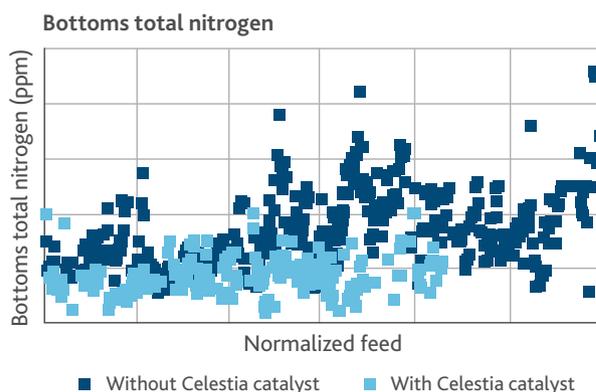


Figure 4. VGO hydrocracker product nitrogen.

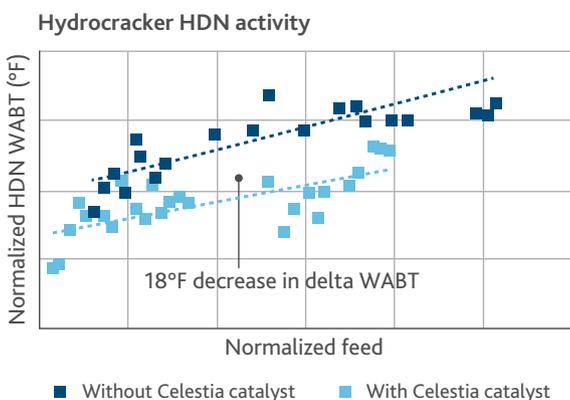


Figure 5. VGO hydrocracker normalized WABT.

Case 3: Increased distillate feed rate and improved product qualities

A high-pressure distillate unit supplies product to a 10-ppm, ultra-low-sulfur-diesel combined pool at the refinery. This hydrotreater operates as two parallel reactors processing at equal feed rates and with equal feed qualities.

Celestia catalyst was stack loaded with NiMo catalyst to replace an all-NiMo catalyst system in Bed 4 of the four-bed distillate hydrotreater (Figure 6). The load design was optimized

using process modelling to work with the unit's existing heat release management, thus avoiding investment in compression and hydraulics.

The benefits delivered by the Celestia system included a 14% increase in feed rate and, owing to the raised HDS unit activity (Figure 7), higher quality product by way of lower net sulfur content than required by the ultra-low-sulfur-diesel specification. This allowed a more challenged hydroprocessing unit to run at higher product sulfur, resulting in longer cycle length.

Although operating at higher feed rates increases the external energy input required, this was offset by the additional heat released in the Celestia catalyst bed (Figure 8), which provided an advantage for heat integration.

Overall, Celestia's stability in service has proven to be superior to the all-NiMo load. Despite the heavier feed, the Celestia catalyst has deactivated at a slower rate and maintained a favorable exotherm for longer in this application.

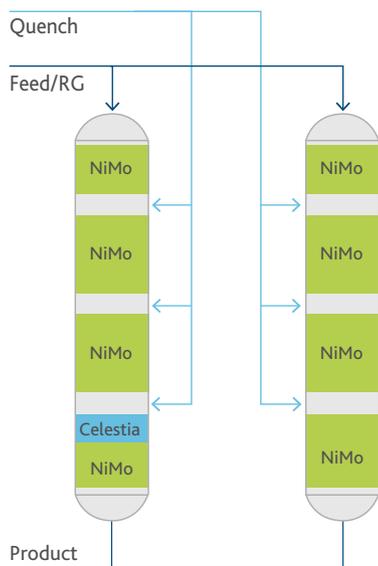


Figure 6. Celestia catalyst loaded into a distillate hydrotreater.

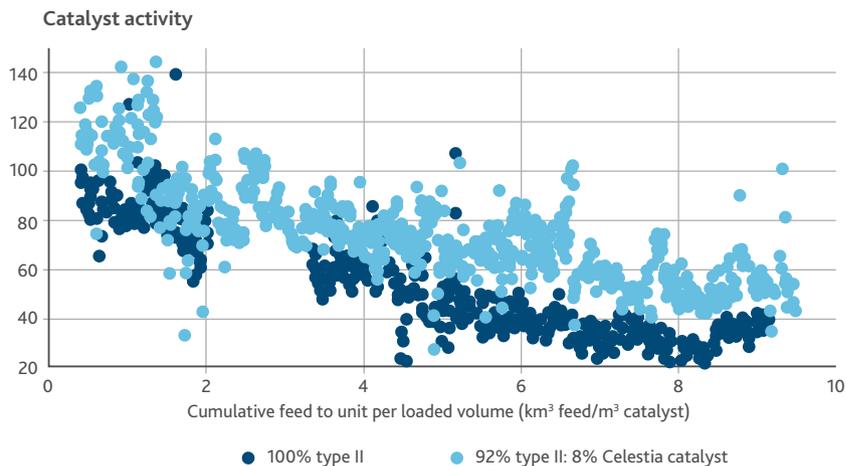


Figure 7. Distillate unit activity comparison after Celestia catalyst load.

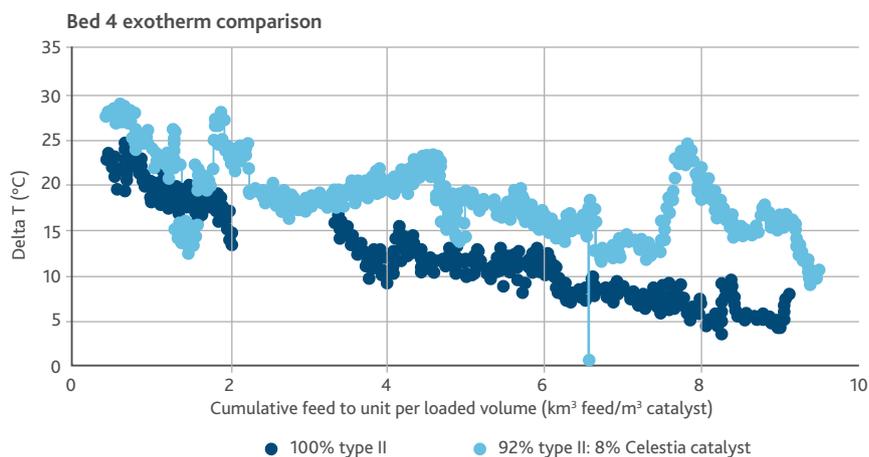


Figure 8. Distillate unit exotherm comparison after Celestia catalyst load.



Conclusions

Since the initial commercialization of the Celestia catalyst in November 2015, it has enabled refineries to capture value from their existing operations. In 15 applications to date, Celestia has been shown to be useful across several types of units, shown high catalytic activity and contributed to improved profitability.

Celestia's high activity can transform a hydroprocessing unit to enable greater profitability. However, the high activity it provides requires a different approach to catalyst deployment that entails a different way of considering value delivered. Albemarle's Celestia can

deliver multiple benefits from a single unit, so value is extended to adjacent units and blending plants.

Finally, as the Celestia catalyst increases the exothermicity of a reactor bed, the plant must be evaluated for optimum operation. Heat release and other related issues can be managed efficiently, often without extra cost, by optimizing catalyst stacking designs and utilizing different operating practices.

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FLUIDIZED CATALYTIC CRACKING UNIT PATHWAYS IN A CO-PROCESSING WORLD

Co-processing of biogenic feedstocks offers refiners more options for meeting renewable fuel standards.

CLIFFORD AVERY AND JON STROHM

Co-processing of biogenic or waste-derived oils in existing refining assets is a pathway for refiners to introduce renewable and circular carbon into finished products to meet mandates and incentives. While co-processing can be targeted for many types of units, in this article we examine Albemarle's catalyst technology in various fluidized catalytic cracking unit (FCCU) pathways.

Introduction

As a result of increased pressure to reduce life-cycle greenhouse gas emissions and decarbonize the energy industry, refiners are faced with expanding legislative incentives and mandates to increase renewable carbon content in fuels and chemicals. Consequently, many refiners either have or are considering conducting

trials for the processing of plant- or animal-based oils. Co-processing can be targeted for many units, including crude distillation towers, hydroprocessing units, and FCCUs. This article discusses FCCU co-processing and feed options and examines Albemarle's catalyst technology in laboratory testing, demonstration-scale, and FCCU operations for various biogenic feedstocks.

Refinery economics – RIN credits

Before pursuing co-processing, a refiner should consider the economics and consequences of this pathway, including the historical cost of renewable identification number (RIN) credits, the RIN credits received for co-processing, and the impact on the process unit from various co-feed options and integration strategies.

RIN credits is a system used by the US government. Other countries, regions, and states have their own systems to encourage and mandate the use of renewable fuels. The European Union uses the Renewable Energy Directive (RED), and Canada has a unique Clean Fuel Regulations that rolled out in June 2022. In the United States, some states like California, Oregon, and more recently Washington, have their own clean fuels programs, which may have added benefits above the RIN credits. However, our focus in this article will be on the United States' system (RIN) credits.

In 2005, the US government established the Renewable Fuel Standard which obligated US refiners and importers of gasoline and diesel fuels to meet target renewable fuel content. If the renewable volume content is not reached, the refiner or importer must purchase

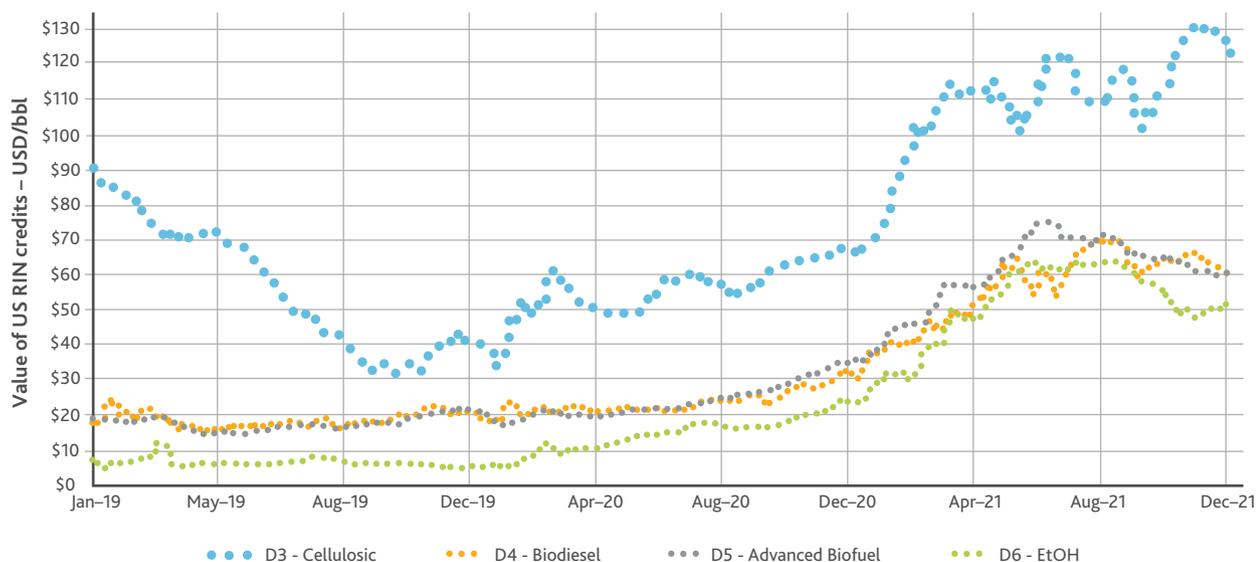


Figure 1. US Environmental Protection Agency data converted to USD/barrel on a 10-point moving average (Ref 2).

As a result of increased pressure to reduce life-cycle greenhouse gas emissions and decarbonize the energy industry, refiners are faced with expanding legislative incentives and mandates to increase renewable carbon content in fuels and chemicals.



RIN credits to ensure compliance with national and/or local regulations. This standard also established categories of biofuels and determined quotas for each category (Ref 1). The categories are:

- D3: Cellulosic biofuel. Targeted for > 60% greenhouse gas (GHG) reduction. Examples include pyrolysis oils from wood chips and other gasoline or oil with cellulosic origins.
- D4: Biomass-based diesel. Targeted for > 50% GHG reduction. Examples include converting vegetable oils (soybean, canola [rapeseed], animal fats, and waste oils including used cooking oil [UCO]) to diesel.
- D5: Advanced biofuels. Targeted for > 50% GHG reduction. Examples include non-ethanol fuels derived from corn starch, biogas, or waste digesters.
- D6: Conventional renewable fuel. Targeted for > 20% GHG reduction. Examples include ethanol or other biomass used to replace conventional transportation or heating fuels.

The value of each category is determined based on the ability to make, sell, or trade RIN credits. For example, since the D3 fuel has not met the target for volume, its credit value is high and surpasses the other categories. Figure 1 demonstrates the value trend of RIN credits (USD/barrel) starting in January 2019. Since August 2020, the value of these credits has increased significantly. D4, D5, and D6 have increased from \$5–20/bbl to \$50–70/bbl. In the same period, D3 credits increased by more than \$50/bbl. Considering this, the monetary benefit of

producing renewable fuels has increased significantly in recent years.

In some cases, there are blending caps due to product specifications or mandates based on the fuel component and RIN category. Ethanol blending in regular gasoline is limited to meet specifications required for non-flex fuel vehicles. Similarly, regulations will dictate the renewable volume obligation that can be met with the D6 category; in some countries operating within the RED II European mandates, the use of non-cellulosic ethanol or palm oil to meet renewable standards will be phased out. The starting biomass and process technologies have a significant impact on the total carbon efficiency of a fuel production pathway, hence the RIN category and value.

FCC co-processing feed options

When considering co-processing, the high diversity of feed options presents unique operational and catalytic challenges for the FCCU. Figure 2 highlights three subgroups for FCC co-processing based on the starting biomass feed category and the advantages/challenges associated.

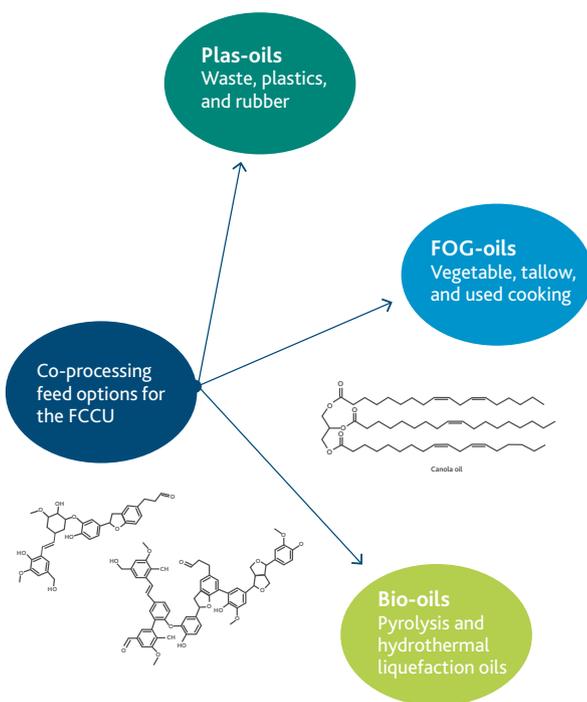
1. Plas-oils

Waste plastics and waxes from Fischer–Tropsch (FT) liquids, which are derived from synthesis gas (syngas) produced from the gasification of biomass and/or waste materials, can be readily cracked

in the FCCU due to their highly paraffinic nature, solubility in conventional vacuum gas oil (VGO)/resid feeds, and low oxygen content. Challenges with co-processing of FT-liquids are largely associated with the gasification of biomass and waste materials to generate chemical-grade syngas. They should be free from residual tars and other contaminants. The main challenges for plas-oils are residual halides from PVC/WEEE/etc., trace metals, and variable composition. The hydrocarbon composition can range from paraffinic waxes to highly aromatic and olefinic components. Other variability in the composition includes elevated oxygen

(polycarbonates and PET) and nitrogen content (nitriles, nylons, etc.) due to the diversity of plastics pyrolyzed.

Major plastics including polyethylene, polypropylene, waste tires, and polystyrene are soluble in VGO at FCC feed conditions. In theory, since they are soluble, they can be directly blended and processed in the FCCU. But collecting, sorting, transporting, and storing at the refinery may present significant logistical and economic challenges. Co-processing of plas-oils, particularly heavy residual waxes from a pyrolysis process, is also a viable co-feed for the FCCU.



ADVANTAGES

- Soluble (plastics and py-oils) in conventional FCCU feeds
- Highly variable from heavy paraffinic waxes to highly aromatic/olefin

CHALLENGES

- Variability in composition and contaminants (halides, nitriles, dienes, and metals)

ADVANTAGES

- Soluble in conventional FCCU feeds
- Paraffinic nature makes it highly crackable in the FCC
- Lower oxygen content about 10wt% than bio-oils and no free water

CHALLENGES

- Various grades and types with high variability in alkali metals and acidity
- Can begin to decompose at feed injection temperatures
- Presence of free fatty acids and decomposition lead to formation of light oxygenates

ADVANTAGES

- Lower temperature with food crops
- Demonstrated crackability within the FCC

CHALLENGES

- Insoluble in conventional feeds with water content up to 60 wt%
- Unstable at feed injection temperatures – requires retrofit of feed injectors
- High variability in alkali metals, acidity, and oxygen content (30–60 wt%)

Figure 2. Generalization of co-processing feed options for the FCCU and the advantages and challenges of each feed material.

Under the current regulatory environment, which does not provide credits for co-processing of plas-oils to fuels, the FCCU's role in the circular economy will require effective carbon tracing from waste-plastics to propylene, ethylene, and BTX.

2. FOG-oils

FOG-oils are mainly triglycerides from plant-derived oils (palm oil, soybean oil, rapeseed/canola oil, and distillers' corn oil), tallow, extracted lipids algae oils, and UCO. The paraffinic nature of triglycerides in FOG-oils make the co-feed highly crackable in the FCCU. In general, FOG-oils are soluble in conventional FCC feeds; they do not have free water and they have a relatively lower oxygen content (~10 wt%) than bio-oils. FOG-oils are produced at industrial scale with approximately 740 k/bpd production in 2020. But regional availability and direct competition with other uses, including bio/renewable diesel and food products, can lead to high pricing. In the USA, increased biodiesel and renewable diesel production has inflated the price of soybean oil: in 2020, RBD soybean oil was 2x higher than the average crude price. With palm oil, the increase in land clearing for cultivating palm trees has led to political and ecological ramifications, resulting in several EU countries removing palm oil as a renewable resource.

The use of crude FOG-oils that have not been pretreated can reduce feedstock costs but will create additional FCCU operational and catalytic issues. While UCO and inedible plants/animal fats and greases do not directly compete for food use and are generally lower cost, they often contain higher levels of metal contaminants and free fatty acids.

3. Bio-oils

Bio-oils have the distinct advantage over FOG-oils in that they do not compete as food resources. They utilize lower-valued waste streams from the agricultural (for example, corn stover, bagasse) and forestry (for example, forest residues, sawmill wastes) industries, biogenic fractions of municipal wastes (paper/cardboard, food waste), non-food crops (for example, switchgrass), and animal/livestock manure and sewage. Over the last thirty years, various conversion technologies including the thermochemical conversion of these waste streams through fast pyrolysis (FPBO), catalytic pyrolysis, hydrothermal liquefaction (HTL), hydrolysis, and gasification technologies have been developed.

FPBO has reached commercial scale, while HTL technologies demonstration and commercial plants are coming online. Currently, the total estimated capacity of thermochemical oils is under 10 k/bpd. Although this production

capacity is small, it is expected to grow significantly over the next five to ten years. In the context of this article, bio-oil co-processing in the FCC means oil produced by the fast pyrolysis of lignocellulosic wastes from agricultural and forestry industries.

Pyrolysis of lignocellulosic waste streams results in the thermochemical destruction of the hemicellulose, cellulose, and lignin content of the biomass to produce solid char, light gases, and a bio-oil comprised of a highly complex mixture of oxygenated hydrocarbons and water. The composition and properties of liquid bio-oil can vary considerably depending on the biomass feedstock, pyrolysis process technology, and any biomass pretreatment or bio-oil stabilization or processes. The relative content of cellulose, hemicellulose, and lignin fractions in the biomass vary considerably, with increasing lignin content as one moves from bagasse and corn stover to saw dust from pine wood. Higher content of lignin results in increased aromatic and phenolic content. Higher cellulose and hemicellulose results in higher pyrolytic sugars, furans, and carboxylic acids in the bio-oil. These differences result in significant variation in the bio-oil properties including acidity, stability, solubility, oxygen, and free water content, which influence FCC operational and catalytic challenges.



Operational challenges

Operational challenges in FCC co-processing vary depending on refinery equipment (Figure 3), logistics, process conditions, and type of oil. Most oils suitable for co-processing have a shelf life and are likely to experience oxidation and other reactions over time or at high temperatures. Above 100°F, oil decomposition will increase, and above 300°F, charring and spontaneous combustion may occur. In general, lower water content and further processing increase the shelf life.

FCC feed temperatures range from 300–700°F, with most FCCUs operating near 450°F. Mixing conventional gas oils

with co-processing oils may increase pre-cracking. Many co-processing oils have boiling and smoke points below process feed temperatures, but these temperatures are well above the boiling point of water, meaning vaporization will occur. With a water to steam volume expansion at 1700/1, this results in increased pressures. Most co-processing oils are up to 10 vol% oxygen, with FOG-oils sometimes reaching greater than 20%. For bio-oils, free water is another consideration. Bio-oils may reach as high as 50 vol% total (oxygen + free water) content.

Feed injection technology (FIT) nozzles utilize high pressure, steam, and a

shearing action to atomize feed. FIT nozzles are designed to utilize 2 wt% to 9+ wt% dispersion steam to atomize the feed. Co-processing oils have different viscosities, boiling points, and atomization requirements. In addition, the free water content of the co-processing oil far exceeds most design dispersion steam rates. For this reason, it is highly recommended to consult the FIT licenser when considering the type of oil and concentration of the co-processing oil to the nozzle. The FIT licenser may recommend a different dispersion steam rate, different nozzle designs, or even the addition of secondary feed nozzles for the introduction of bio-oils.

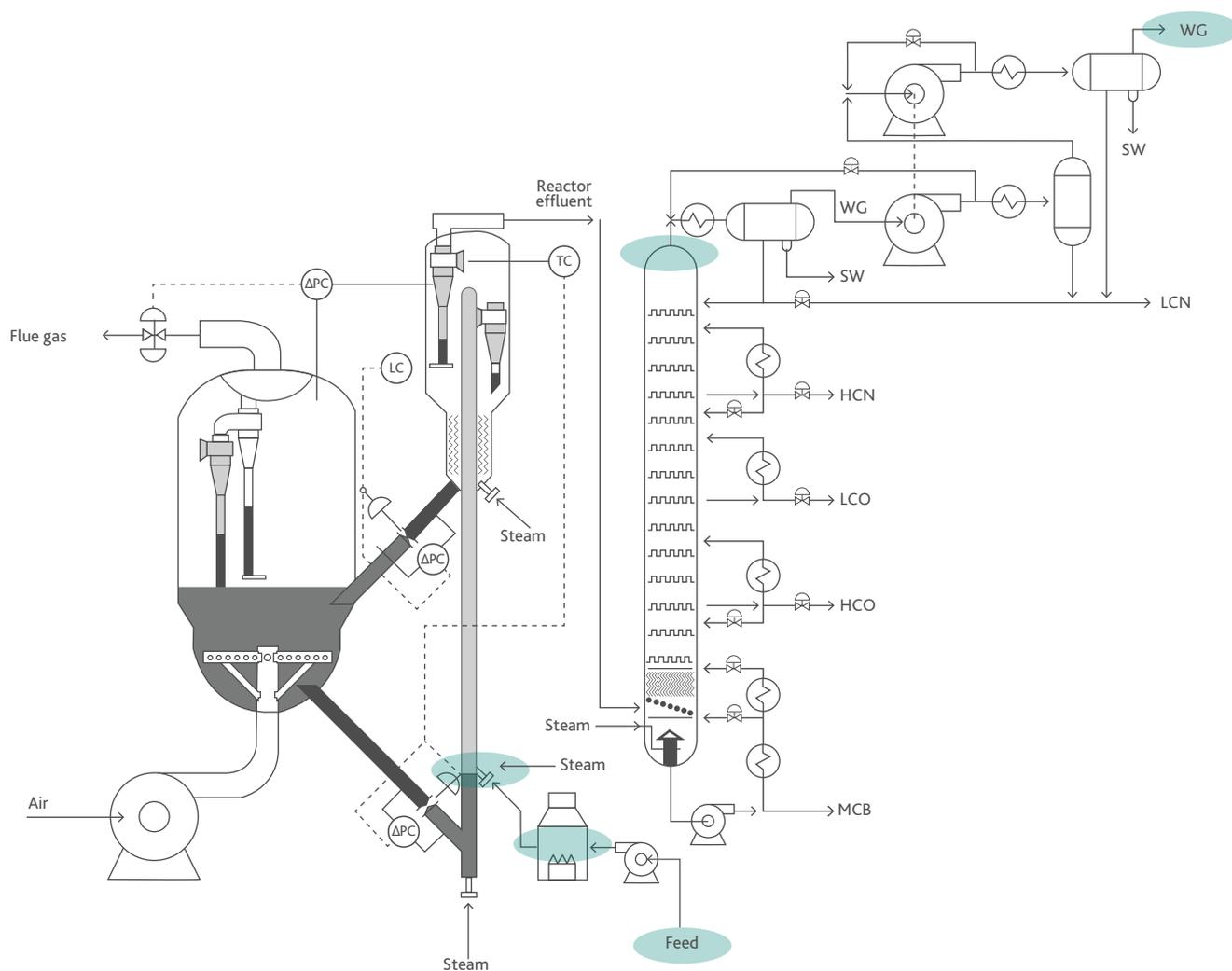


Figure 3. Representation of an FCCU and supporting operations. Circled areas represent areas of operation for consideration during co-processing.

Depending on the type and refinement of the oil, the metals content may vary drastically. Some oil metals will deposit throughout the FCC catalyst. When this happens, deactivation of the catalyst, dehydrogenation reactions, and/or pore plugging occur. For these reasons, the effects of vanadium, sodium, iron, and calcium are widely recognized within the refining industry. Vanadium and sodium deactivate the catalyst acid sites and can destroy the zeolite structure, reducing overall catalytic activity. Iron and calcium form low-melting-point eutectics, which create a vitrified outer layer on the surface of the catalyst, plugging the pores. FCC catalysts function by utilizing a high surface area and customized porosity to maximize product yields and resist the effects of Fe and Ca. When the catalyst pores plug, the Albemarle Accessibility Index (AAI) of the oils to the catalyst acid sites is reduced. This results in lower conversion and reduced yields of transportation fuels.

In co-processing oils, new contaminants are introduced while known ones may be observed at far higher levels. As seen in Table 1, for catalyst deactivation type reactions, potassium levels may reach >100 wppm in co-processing feed, which is orders of magnitude greater than levels in conventional feedstocks (about 1 wppm vanadium in gas oils and about 10 wppm in resid). Current research indicates that potassium has half the catalyst deactivation effects compared to sodium. Even so, potassium levels at 100+ wppm require as much as twice the catalyst usage rate for 10% co-processing. Thus, a stable zeolite system is key when processing these oils.

Plas-oils may have elevated nitrogen and halide levels. The nitrogen will serve as a temporary poison and neutralize acid sites while in the riser. The effects will result in reduced conversion and an increased delta coke (↑ regen temperature). The presence of halides will result in a more acidic product stream.

The consequences will result in increased main column OVHD corrosion and reduced pH in the gas con section.

Pore plugging metals like iron and calcium are frequently observed at a level of 1–10 wppm in FCC feed. In veg-oils and bio-oils, additional metals have been observed, including magnesium, phosphorous, zinc, and manganese. In current catalyst systems, magnesium is present in SOx reduction additives and on metals traps, while phosphorous is present in ZSM-5 additive. However, metals that are part of an FCC additive system do not interact with the catalyst system in the same ways as feed contaminant metals. Magnesium levels have been observed as low as zero for refined, bleached, and deodorized (RBD) FOG-oils and as high as 150+ wppm in pyrolysis and crude veg-oils. Depending on the oil type and degree of processing, phosphorous levels in co-processing feeds can reach up to 1000+ wppm. This can compound the effects of other

TEST PARAMETER	UNITS	SOYBEAN – EXAMPLES		PINE BIO-OIL – EXAMPLES			PLAS-OIL – EXAMPLES	
		CRUDE CARBONATED	REFINED	PYROLYSIS OIL A (STABILIZED)	PYROLYSIS OIL B (STABILIZED)	MILD HDO PYROLYSIS OIL	PYROLYSIS OIL A (RUBBER)	PYROLYSIS OIL B (PLASTICS)
V	wppm	1	1	<0.01	<0.01	NA	<1	<1
Na	wppm	NA	NA	5	5	NA	4	4
K	wppm	130	<1	160	9	NA	NA	NA
Fe	wppm	1	<1	31	66	NA	<2	<2
Si	wppm	NA	NA	23	10	NA	<10	<10
Ca	wppm	45	<1	400	29	NA	<3	<3
Mg	wppm	<1	<1	130	3	NA	NA	NA
P	wppm	250	<1	NA	19	NA	1	1
Cl	wppm	<1	<1	NA	55	NA	24	91
F	wppm	NA	NA	NA	NA	NA	6	2.2
Br	wppm	NA	NA	NA	NA	NA	38	333
N	wppm						7,500	11,700
wt% O, wet wt% O, dry	wt%	≈10	10.4	50.7 22.3	51.2 28.5	23.6 18.2	NA	NA
TAN	mgKOH/g	1.4	0	128	72	50	0.25	0.2
Relative cost	\$/bbl	Base	Base + \$16/bbl	Base A	Base B	Base + \$15–\$30/bbl	NA	NA

Table 1. Examples of the diversity in metals and oxygen content of a soybean oil, pine-derived bio-oil (Ref 3 and 4), and plas-oils with various feed treatments.

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contaminants, including iron. As such, the level of pore plugging metals in co-processing feed may reach as high as 500 wppm. An FCC catalyst system must possess high AAI and increased meso-porosity to process feeds with such high levels of pore plugging metals.

Thus far, damage and/or operational problems have not been documented when co-processing feeds reach the riser and reactor. The FOG-oils are highly paraffinic and will vaporize and crack easily. Some naphthenic acid (TAN) may be present. TAN has been documented to increase corrosion in distillation towers and hydrotreating units. In FCCUs, it is generally accepted that the TAN compounds will crack and pose little harm. However, to date, little has been documented on the corrosion effects of the feed section prior to the riser. As a rule of thumb, the TAN of co-processing feeds is:
bio-oils >> animal tallow > vegetable-oils

Poor thermal stability of the bio-oils can also lead to increased propensity for the formation of carbon deposits. Various injection schemes and nozzle designs can help reduce thermal coke from injection of the bio-oils to the riser. High oxygen content and elevated con carbon residue levels can lead to changes in the heating value and increased delta coke on the catalyst. The increased delta coke of bio-oils may be a concern in FCCUs with regen temperature and main air blower limit operations.

Co-processing feeds contain carboxylic acids and other oxygen-based compounds, which, when cracked, form smaller oxygen-based compounds. Most of these compounds will end up in the lighter boiling fractions (wet gas compressor [WGC] section). Elevated carbon dioxide and alcohols are commonly detected. Other compounds observed are esters, ketones, phenolics, and acids (acetic, formic, and propionic).

These acids may increase the corrosion concerns in the fractionator overhead section. Elevated methyl acrylate gas has been observed with UCO feedstocks, and tallow-based feeds in general. Elevated methyl acrylate levels are particularly common in UCO. Control of deoxygenation pathways, as discussed in the "Bio-oil feed effects and role of catalyst technologies" section, is crucial to minimizing light oxygenate formation and the impact on these supporting operations.

The light MW products from co-processing will primarily concentrate in the WGC section. The acids will react with ammonia and the pH of the systems will change. Methyl acrylate will most likely form solids. Amine units will have problems with the elevated carbon monoxide and carbon dioxide levels. In general, foaming issues will occur in the high-pressure process units and corrosion concerns are more common. While these issues have been documented, some FCCU WGC sections have recorded little difficulty. Process units that experience no problems are those that used highly refined or RBD FOG-oils (refined, bleached, and deodorized fats, oils, and grease-oils). While FCCUs have co-processed up to >15% vegetable-oil, most trials seldom exceed 10% of the total feed.

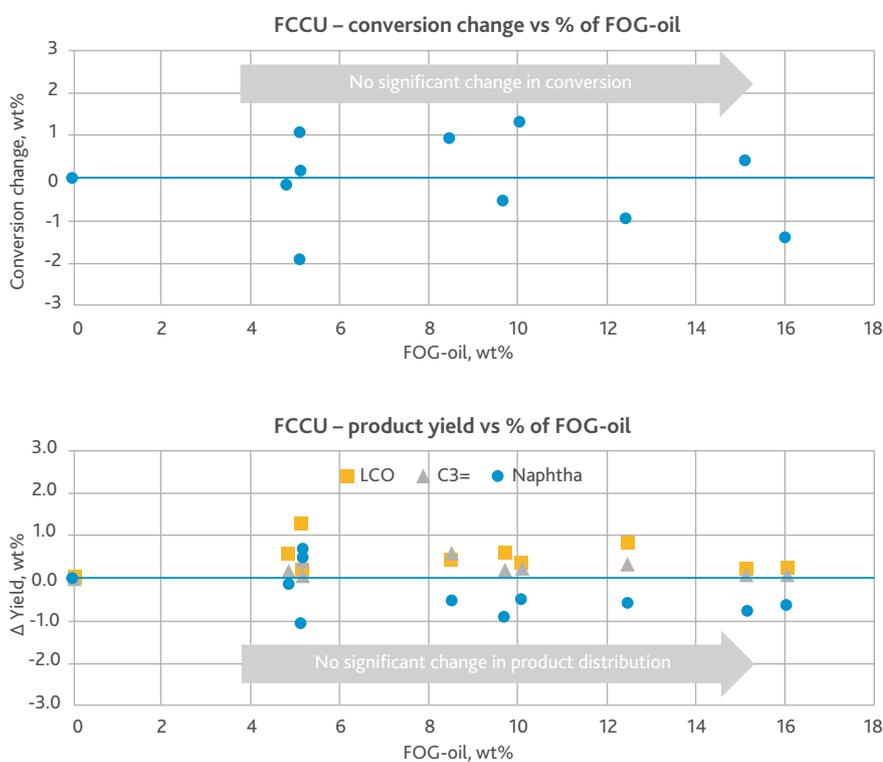


Figure 4. Conversion and major product distributions from co-processing a refined, deodorized, and bleached vegetable-oil in a commercial resid FCCU using Albemarle's high accessibility catalyst technology.

Co-processing trial using Albemarle catalyst

Co-processing with an RDB FOG-oil was performed in a commercial resid FCCU; the impact on the conversion and major products are highlighted in Figure 4. The unit typically processes a high metals, heavy resid feed using Albemarle's high accessibility catalyst for maximum metals resistance and superior resid

conversion. Since FOG-oils are soluble in the resid feed, the FOG-oil used here was blended directly. Increasing veg-oil concentration from 5 to 16 wt% had minimal impact on both conversion and major product yields (including light cycle oil [LCO], naphtha, and propylene). Delta coke remained unchanged throughout the trial. A small decrease in the catalyst addition rate throughout the trial was observed. Metals analysis of the Ecac

showed a decrease in the metal levels, likely due to the introduction of a metal-free FOG-oil into the otherwise high metal resid feed. Overall, there was minimal impact on unit performance or operations, and the trial was considered highly successful by the customer.

The high crackability of vegetable oils is further demonstrated in Figure 5. This figure highlights the results from ACE performance testing using Ecac from a high-metals unit. The Ecac is Albemarle's ACTION® catalyst technology for maximizing LPG C4-olefins.

The ACTION® catalyst technology showed increasing activity and naphtha yield as the veg-oil co-processed feed was increased up to 25wt% for this VGO operation. Evaluation of the naphtha fraction showed a small decrease in aromatic content and increased naphthene and olefin content, with no net effect on the calculated octane. LCO showed decreased yields with increasing veg-oil. There was also a decrease in bottoms and coke. Other yields including C4 and C3 olefins, LPG, and dry gas showed no significant changes.

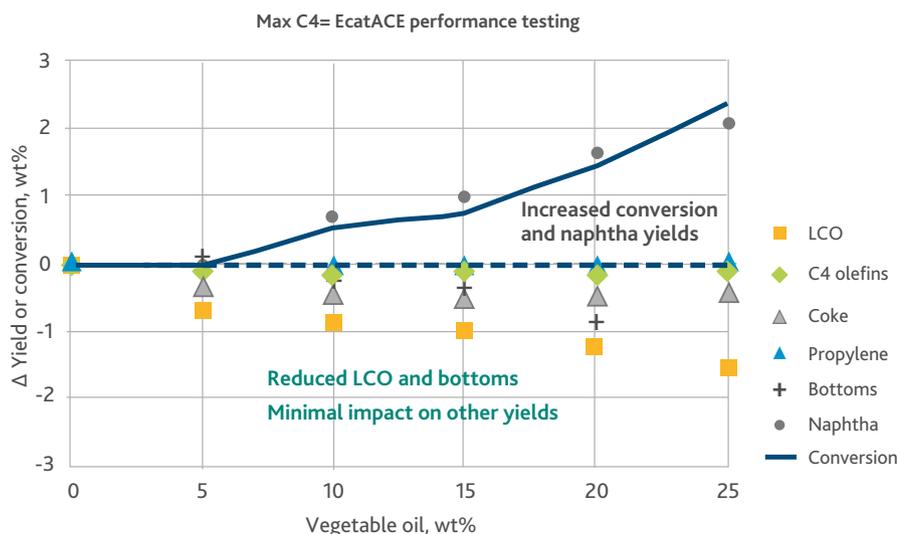


Figure 5. ACE performance testing of Albemarle's ACTION® catalyst technology for co-processing of FOG-oil.

Bio-oil feed effects and role of catalyst technologies

Unlike FOG-oils, bio-oils contain significant amounts of free water and higher oxygen content. Bio-oils are insoluble with conventional FCC VGO and resid feeds. Moreover, heating bio-oils above 150°F can result in decomposition. Poor stability of the bio-oil at feed injection temperatures can result in feed nozzle plugging and excessive delta coke, requiring further alternative feed and operational strategies for the FCCU. Alternative FIT strategies should be considered by the refiner and the licensor.

DEMONSTRATION SCALE FCCU CO-PROCESSING OF PINE DERIVED BIO-OIL			
FEED	100%VGO	95%VGO+5%BIO-OIL	90%VGO+10%BIO-OIL
Product yields, wt%, FF			
Dry gas	3.5	2.8	2.8
LPG	13.8	13.8	12.5
Gasoline	39.9	40.6	38.8
LCO	20.3	19.6	19.2
Bottoms	16.1	14.4	14.4
Coke	6.4	6	6.5
CO _x	0	1.4	2.3
H ₂ O	0	1.4	3.5
CO/CO ₂ ratio	-	1.96	2.23

Table 2. Summary of yields from co-processing pine-derived bio-oil in Petrobras's demonstration scale FCCU using Albemarle-Petrobras catalyst technology (Ref 4).

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Prior studies performed by Pinho et al, successfully demonstrated the co-processing of bio-oil in Petrobras's 150 kg/hr demonstration-scale FCCU (unit SIX) (Ref 3). A separate FIT nozzle was required to process the bio-oils. The Ecat used in the demonstration unit was supplied by FCC S.A., an Albemarle-Petrobras FCC catalyst joint venture. The impact of bio-oil concentration on the product slate data extracted from the study is shown in Table 2. Co-processing up to 5 wt% bio-oils resulted in minimal impact on the product yields for VGO operation. Lower coke, bottoms, and dry gas were observed. The gasoline yield increased slightly. However, increasing the pyrolysis oil content to 10 wt% resulted in increased coke and reduced gasoline and LCO yield. Feed oxygen was mainly converted to CO, CO₂, and water. Increasing bio-oil from

5 to 10 wt% resulted in a change in how the feed oxygen was being converted: at higher bio-oil feed amounts, the relative amount of the feed oxygen removed as water and the CO/CO₂ ratio both increased. This implies that with increasing bio-oil feed amounts, the deoxygenation pathways are changing and impacting the effect of the bio-oil on the product slate.

The four major deoxygenation pathways for oxygen removal from biogenic feeds include dehydration, decarbonylation, hydrodeoxygenation, and decarboxylation, as summarized in Figure 6. Dehydration involves oxygen and hydrogen removal as water from the bio-feed. The net effect of dehydration results in the formation of biogenic coke, resulting in higher losses of bio-carbon from useful products.

In the case of veg-oils, the thermal decomposition of the triglyceride followed by dehydration can result in the formation of light oxygenates such as aldehydes, ketones, and acrylates. These light oxygenates may undergo oligomerization reactions leading to gum and coke formation; in addition, these compounds will concentrate in the WGC section of the unit.

Decarbonylation rejects bio-carbon as CO and can increase bottoms or coke yields from both the bio-oil and conventional oil. While hydrodeoxygenation is dominant in hydroprocessing units, it also occurs in FCC operations due to hydrogen donation from the conventional feed to the bio-oil. From the perspective of FCCU operations, deoxygenation of the bio-oil through decarboxylation will

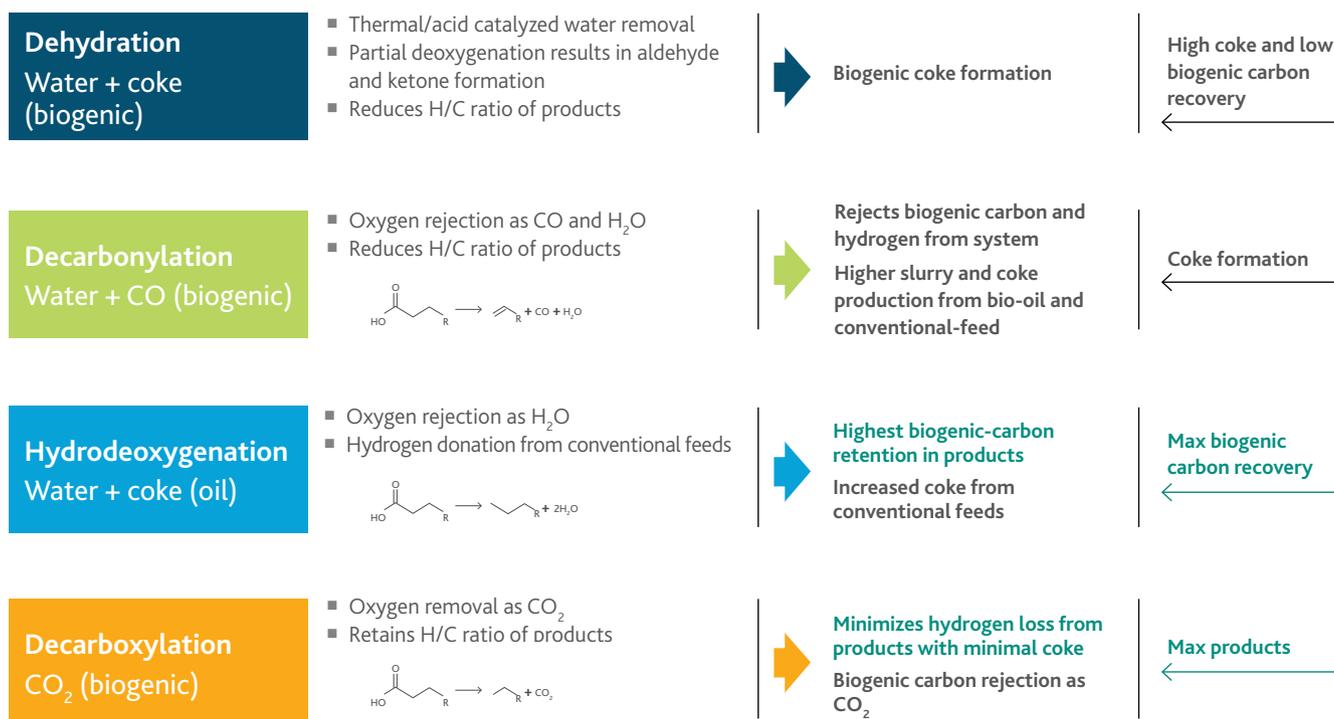


Figure 6. Major deoxygenation pathways for biogenic oxygen removal during FCC co-processing and the overall impact on product yields.

minimize the impact of the bio-oil on the FCCU product slate but will result in lower biogenic carbon incorporation into the liquid products. This presents an inherent conflict for the refiner depending on the economics of the unit, renewable fuel regulations, and associated credits – which may be contingent on the degree of biogenic carbon incorporation into the products.

The role of the catalyst in altering deoxygenation pathways to reduce the negative impact on the product slate during co-processing is presented in Figure 7. Co-processing of 20 wt% bio-oil with VGO over various lab-deactivated catalysts (DCat) was performed in Albemarle’s laboratory testing unit. Compared with the base case product slate from cracking over DCat-1 with pure VGO, the addition of bio-oil to the feed resulted in lower

gasoline and increased coke yield. By slightly modifying the catalyst, the balance between the various deoxygenation pathways can be shifted to minimize the impact of the bio-oil on the overall product slate. Compared to the base catalyst co-processing bio-oil, DCat-3 shows a reduction in coke and an increase in gasoline and LCO, thereby reducing the negative impact of the bio-oil on the product slate.

In addition to minimizing the impact of bio-oil on the product slate, the catalyst can influence how much biogenic carbon becomes incorporated into the various products. Using a mass balance approach based on yield differentials, Figure 8 shows the estimated biogenic carbon distributions when bio-oil is added to the feed for each catalyst. Approximately 80% of the biogenic

carbon ends up as non-coke or CO_x, with 42% of the carbon ending up in the naphtha or LCO fractions for the DCat-3 catalyst. This biogenic carbon in the liquid products, generated from cracking, may be eligible for meeting renewable volume obligations. This estimate is based on a mass balance approach; regional regulations may require 14C carbon tracing for validation to meet certain renewable fuel volume obligations. Additionally, to provide the needed credits to the refiner to offset higher bio-oil feedstock costs and improve refining margins, the processing route requires certification and assignment of the production route to a D-code based on lifecycle emissions of generated RINs.

Delta [(20%Bio-Oil/VGO)-VGO(DCat-1)], wt% @ iso-conversion of 65wt%

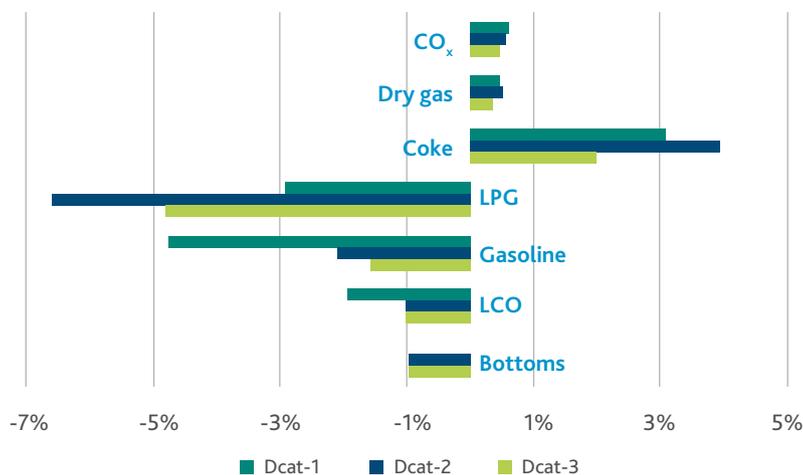


Figure 7. Example of minor modifications to the catalyst to alter the deoxygenation pathways to reduce impact on the product slate during co-processing 20 wt% bio-oil (obtained using a BTG-derived pyrolysis oil). Delta yields are calculated from the base case of pure VGO over DCat-1.

Biogenic carbon distribution, %C from bio-oil

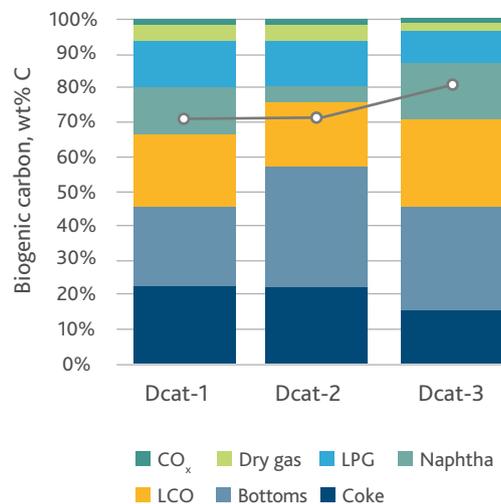


Figure 8. Estimated biogenic carbon distributions within the product slate from laboratory co-processing of 20 wt% bio-oil (obtained using a BTG-derived pyrolysis oil) and the impact of catalyst modifications.

Conclusion

Co-processing of biogenic feedstocks offers refiners options for meeting renewable fuel standards and other regulatory requirements. However, in pursuing co-processing, a refiner needs to consider various aspects, including the

- biogenic feed options and their regional availability, diversity in composition and metal content, solubility, and compatibility with the FCCU's operations.
- impact of the bio-feedstock oxygen content and form of the oxygen
- refinery configuration and conventional feed effects
- amount of biogenic feed to be co-processed
- catalyst technology required to address various levels of alkali metals and other contaminants in the bio-feed

- catalyst technologies to meet unit objectives and FCCU limitations including product slate requirements, biogenic carbon distribution within the product slate, regulatory requirements for measurement, and end-product specifications (e.g., phenolic content of fuel product).

Albemarle's current catalyst technologies have been successfully used in co-processing, including successful commercial trials processing FOG-oils that resulted in no significant impact to FCCU operation or product slate. Demonstration-scale evaluation of co-processing with <5 wt% bio-oil feeds shows a small impact on product slate. However, bio-oil co-processing at higher rates requires careful control of deoxygenation reactions to maximize biogenic carbon utilization

and enable co-processing within the objectives and limitations of the unit to

- optimize formulations within existing catalyst technologies to enable co-processing of various types of biogenic and recycled feed streams (e.g., plastic, py-oil) while working within the configuration of refinery operations and integration strategy
- identify flexible solutions to meet product targets to maximize biogenic/circular carbon in final products, including additive technologies for increasing petrochemical production.

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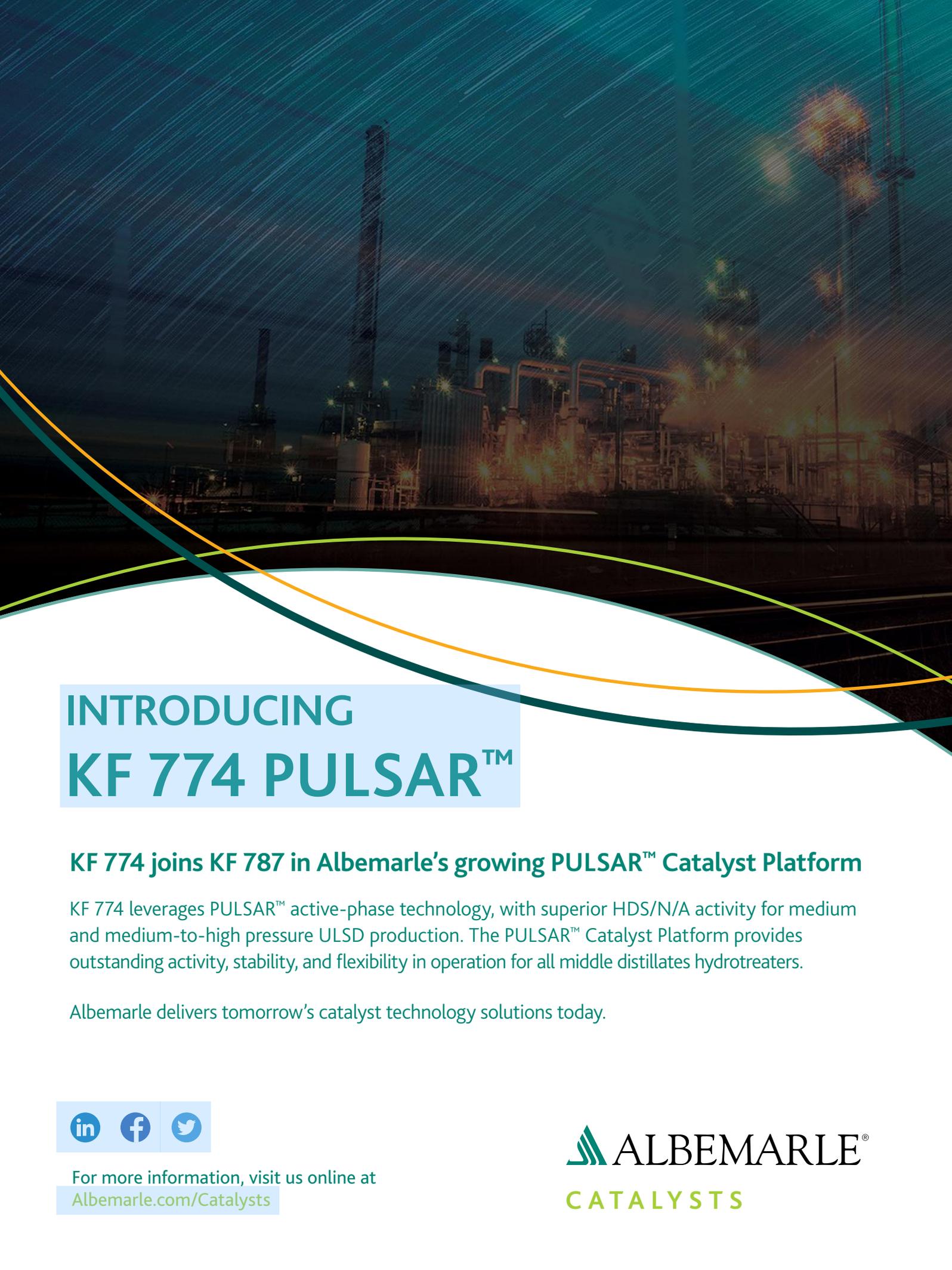
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