

ISSUE 89 | SPRING 2019

Catalyst Courier

How recent catalyst developments can meet refinery challenges

KF 787 PULSAR™: a breakthrough catalyst for low - and medium-pressure middle distillates hydrotreating

Meet Celestia™: Albemarle's new bulk metal catalyst

KF 780 proves its value through market penetration

 ALBEMARLE®

INSIDE THIS ISSUE...

- 4 NEWS FROM ALBEMARLE
- 6 INNOVATIONS FOR OPTIMIZATION AND FLEXIBILITY
- 10 KF 780: SUPERIOR PERFORMANCE DELIVERED FOR MIDDLE DISTILLATE
HYDROTREATING AND FCC-PT APPLICATIONS
- 14 KF 787 PULSAR™: THE NEW BREAKTHROUGH CATALYST FOR LOW- AND
MEDIUM-PRESSURE MIDDLE DISTILLATES HYDROTREATING
- 19 CELESTIA™: A REVOLUTIONARY NEW HYDROPROCESSING CATALYST PROVIDING
ULTRA-HIGH ACTIVITY

EVENTS DIARY 2019

September

- 15–17 Abu Dhabi International Downstream Summit,
Abu Dhabi, UAE
- 19–20 RRTC 2019, Russia & CIS Refining Technology
Conference & Exhibition Moscow, Russia
- 23–24 Refining India, New Delhi, India

October

- 14–16 AFPM Operations & Process Technology Summit,
San Antonio, TX, USA

November

- 4–7 ERTC, Warsaw, Poland
- 19–21 ResidHydroTreat 2019, Kuwait City, Kuwait

December

- 3–5 14th Annual GPCA Forum, Dubai, UAE

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RAPHAEL CRAWFORD
PRESIDENT,
CATALYSTS

COLLABORATION: FROM RESEARCH AND DEVELOPMENT TO CUSTOMER SUPPORT

Modern business landscapes can change very quickly. This is particularly true in the oil and gas sector where refiners are constantly facing market shifts that demand decisions about feedstock selection, product slates, refinery reconfigurations or new technologies. At Albemarle, we anticipate customers' requirements to create innovative solutions and deliver what customers need.

Collaboration is a core value for Albemarle: we believe that two are better than one when the two act as one. This is reflected in two distinct but related ways: by collaborating in research and development and by developing closer and more dynamic relationships with our customers.

Creating new, high-performance refinery catalysts is a crucial part of what we do and a key aspect of our drive to be the technology leader in this sector. You will find details of two exciting new developments – PULSAR™ technology and Celestia™ catalyst – in this issue of *Catalyst Courier*. Collaboration played an important role in the creation of these new products. For example, the development and commercialization of Celestia, a second-generation bulk metal catalyst, is the direct result of an innovation partnership with ExxonMobil that started more than 20 years ago.

Less obvious than new products are the organizational changes we have made within Albemarle to enhance the support we offer to customers. For example, the increased technical expertise within our sales teams provides customers with input that helps with maximizing production while maintaining operational flexibility. Collaboration also encourages a more strategic view of catalyst selection and ensures that changeouts are managed to maximize value rather than merely to provide continuity.

Although our customers generally share several high-level business objectives, such as focusing on product yield and sulfur reduction, the circumstances in which they operate may be completely different. The operational priorities of a new refinery in South East Asia, for example, will be quite different from those in long-established facilities in Europe or the Americas. By working closely with customers, we can help them to identify solutions that fit their market conditions and ensure that they can respond quickly when conditions change or new opportunities arise.

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

RAPHAEL CRAWFORD
PRESIDENT, CATALYSTS

ALBEMARLE SHARES SUCCESSFUL COLLABORATION AT ARTC



Delegates at the Asian Refining Technology Conference (ARTC) in Thailand in March 2019 heard how close cooperation led to the smooth and successful startup of the new FCC unit at Nghi Son Refinery and Petrochemical's (NSRP) refinery in Vietnam. In a joint presentation with Carel Pouwels from Albemarle's FCC catalysts team, NSRP's process manager, Nguyen Kim Manh Hoang, explained why, following a lengthy and rigorous selection process, the company chose Albemarle's AFX™ catalyst for the new unit.

The industry-leading AFX catalyst employs new technology to increase propylene production and minimize secondary cracking reactions such as hydrogen transfer in FCC units.

CATALYSTS AND BROMINE SPECIALITIES BUSINESSES WELCOME NEW PRESIDENTS

Raphael Crawford, former president of Bromines Specialities, has transitioned to his new role as president of the Catalysts business. "I am delighted to be heading the Catalysts business, as it is where I started when I joined in 2012," said Crawford. "We are developing catalysts that will tackle the industry's toughest challenges while continuing to deliver value for our customers." Crawford brings a wealth of industry experience to the role as a serving member of the board of directors of the American Fuel & Petrochemical Manufacturers association.

The new president of the Bromine Specialities business is Netha Johnson. He joined Albemarle from 3M, where he was directly responsible for a global division valued at \$1.3 billion. "This is a great opportunity to lead the continued success of the Bromine Specialities global business unit while ensuring it supports the company's overall growth strategy," Johnson said. "It is also a great feeling to know that the fire safety solutions that we develop are keeping people and assets safe, every day, across the world."



Raphael Crawford



Netha Johnson

CELEBRATING THREE DECADES OF TRAINING



Specialists from the Catalysts team have recently delivered Albemarle's 30th hydroprocessing course in Amsterdam, the Netherlands, to participants from 14 different countries. The four-day course, which was tailored for refinery process and production engineers and technical managers, offered a balanced mixture of theory, exercises and outdoor activities.

Feedback from the **37 participants** rated it as "excellent", thereby cementing Albemarle's reputation as a knowledgeable solutions provider.



ALBEMARLE FOUNDATION COMMITTED TO ECONOMIC MOBILITY

Albemarle is striving to make the communities where it operates even more prosperous, healthy and vibrant, which is why it has partnered with Bank of America to invest \$20 million in nonprofit organizations across Charlotte, NC, USA, to help drive local economic mobility.

The five-year program doubles the existing investment of \$10 million and will leverage dollars to create pathways of opportunity and enhance an individual or family's ability to improve their economic status. The three key factors that affect economic mobility are early child care and education; college and career readiness; and family and child stability.

The Albemarle Foundation, a philanthropic affiliate of Albemarle Corporation, is dedicated to supporting the communities where it operates. It will be working with nonprofit partners throughout Charlotte to support initiatives ranging from improving third-grade reading proficiency, the highest indicator of future success, to supporting high-achieving, underresourced students working towards college graduation. All the

partners have research and data to demonstrate and track the success of their work in the Charlotte area.

"Our priority is to work closely with the many great resources, task forces and organizations in Charlotte that have paved the way for us to power the potential of our community," said Sandra Holub, executive director of the Albemarle Foundation. "We hope this investment sets the tone to encourage others to step up however they can, with dollars, sweat equity or social capital, to help address economic mobility in Charlotte."

“ We hope this investment sets the tone to encourage others to step up however they can, with dollars, sweat equity or social capital, to help address economic mobility in Charlotte. ”



CATALYST LEADERSHIP TEAM VOLUNTEERS AT LOCAL CHILDREN'S CHARITY



Leaders from Albemarle's Catalyst business scheduled time into a meeting agenda to volunteer at Today's Harbor for Children, a charity that provides a safe home in seaside cottages at La Porte, TX, USA for up to 64 children who have faced abuse and neglect.

Led by Raphael Crawford, then president of Bromine Specialties, the team sorted through donated clothes before bringing in dinner to share with the children. Following their experience, the team plans to incorporate volunteer projects into future meetings.

"Sitting down and eating dinner with the kids opened the door to great conversations. Seeing them talking and engaging with our team was inspiring," said Crawford.



CHRIS YANDELL
VICE PRESIDENT CLEAN FUELS TECHNOLOGIES

INNOVATIONS FOR OPTIMIZATION AND FLEXIBILITY

How recent catalyst developments can meet refinery challenges

Refineries around the world have different configurations, operate under different regulations and serve different markets. No two are same. Despite this uniqueness, there are several common and significant challenges that refiners face in relation to feedstock variability, product quality and environmental impact. For many refiners, their overall profitability will depend on how well these challenges are met and managed. Process units must run at maximum efficiency, regulatory requirements for both product quality and environmental performance must be met, and refinery systems must be able to respond and adapt to substantial changes in feedstock properties.

These complex business challenges mean that refinery operators must make very careful and informed choices about the processes and technologies that they adopt. Consider one business area: clean fuels. In this domain, the fundamental objective is to remove contamination from different fractions of crude oil and crude oil derivatives to deliver high-quality fuel products.

There are three key drivers in the clean fuels market:

- a) continuing growth in fuels demand
- b) tightening emissions regulations in all markets
- c) the need to optimize upgrading and so maximize value from heavy and dirty feedstocks.

Fueling growth

According to the International Energy Agency, global energy demand grew by 2.3% in 2018. Natural gas emerged as the fuel of choice and accounted for 45% of the rise in energy consumption. However, demand for all fuels increased and fossil

fuels met nearly 70% of this growth for the second year running.

Global demand for diesel and gasoline continue to rise year on year. For diesel, most of the demand comes from industrial end markets in sectors such as mining, logistics, railways and shipping. However, within this global picture, there are strong regional variations: growth is focused on the Middle East and Asia (particularly India, Malaysia and Indonesia) where the rates of growth are much higher than those in Europe or North America. Every refinery operator has to adjust their product slate to meet the demands of their market.

Cleaning up

In all markets, refiners are under pressure to reduce the environmental impact of their processes, to comply with more demanding regulations on air and water quality, and to deliver products that meet tighter quality specifications.

Meeting these new standards may involve cutting emissions, reducing the toxicity of



waste products or managing the amount of sulfur in fuel products. This may require significant adjustments to refining processes or even reconfigurations that require substantial capital investment.

For Albemarle, the challenge is to develop and provide products that help customers to meet these challenges and enable society in general to achieve agreed environmental objectives.

Value from the bottom of the barrel

The third driver for refiners is to increase value from the residual portion of crude oil: finding the best and most cost-effective ways to transform heavy and dirty feedstocks.

Heavy crude oil feedstocks usually contain significant amounts of aromatics. In the past, aromatic crude oils were undesirable because of their poor lubricating properties and resistance to conversion in cracking units. Also, aromatics are generally associated with contaminants

such as vanadium, nickel, nitrogen and sulfur. Today, much of the investment and operating costs for refiners are for separating the heavier aromatics and their associated contaminants from the more desirable constituents of crude oil.

The situation is complicated because, as crude oil production techniques evolve and open up new sources of hydrocarbon, crude oil blending is becoming more important. As a result, refiners must work with a wider range of raw materials and these feedstocks can may have very highly variable quality parameters. To a refinery, the element of variability in crude oil and feedstock supplies can represent a substantial cost burden.

Changing demands on catalysts

Changes in business objectives, tighter product specifications and the variable nature of feedstocks affect every aspect of refinery operation. Catalyst technology has a vital role to play in helping refiners

to overcome these challenges and maximize their profitability. Much of Albemarle's research and development efforts focus on projects and products that address these challenges.

The past six months has been an exciting time for Albemarle with two major innovations being unveiled. The first of these is Celestia™ catalyst, a unique bulk metal catalyst developed in collaboration with ExxonMobil that can deliver substantial performance benefits. The second major innovation is PULSAR™, a new technology platform for hydroprocessing catalysts designed to provide higher performance in middle distillate hydrotreating applications with limited hydrogen, difficult feedstocks and severe operating conditions.

High activity and stability without a substrate

Albemarle and ExxonMobil, through a long-standing catalyst development partnership, have co-developed the latest innovation in bulk metal hydrotreating catalysts.





Building on the success of Nebula® catalyst, which has enjoyed more than 15 years of industry-leading hydrotreating performance, the partnership has now commercialized Celestia catalyst, a new high-performance, bulk-metal catalyst that has demonstrated step-out hydrotreating activity. Celestia offers refiners substantial opportunities for increased activity and value for a fast and effective payback of a few months and a continuing and enhanced contribution to profits.

Celestia has been developed over a period of more than five years. In the beginning, the development program focused on VGO pretreatment operations, but later testing and commercial experience proved a wider application range. The first commercial application was within ExxonMobil in 2015. Results from all the pilot plants and commercial operations indicate that Celestia provides robust performance over the full cycle and is resistant to normal operating upsets. This powerful combination of characteristics means that refiners can use Celestia catalyst to transform their margins.

Its high activity and stability mean that Celestia can enable operators to

- widen the crude diet for their refinery
- coordinate multiple hydrotreating unit turnaround schedules

- meet stringent product targets without capital investment
- improve energy efficiency
- rebalance internal feeds to improve utilization
- find new opportunities for product blending.

In one example, hydrodesulfurization activity in a pretreatment reactor increased by 30% compared with a previous cycle using Nebula (Figure 1). Celestia made it possible to increase the feed rate and achieve a substantial increase in conversion activity with significant improvements in product yield and quality. For over three years of operation, Celestia maintained stable activity equivalent to that of a leading NiMo catalyst. In this case, the initial investment was paid back in less than four months.

Celestia has been successfully scaled up by Albemarle and commercialized by ExxonMobil in a variety of hydroprocessing platforms. Since its introduction, the catalyst has delivered unique levels of performance for a hydroprocessing catalyst, demonstrated robust and stable operation in a range of settings and helped to deliver substantial improvements in margins.

Premium performance and flexibility over a broad application range

PULSAR is a new technology platform for hydroprocessing catalysts that enables precise control of the morphology and dispersion of the metal active phase to deliver uniquely active, versatile and robust products.

Most of the new hydrotreating catalysts introduced to the market over the past few years have been designed to serve operations that feature high pressures and good hydrogen availability. In general, work on new catalysts for operations limited by hydrogen, such as low- and medium-pressure middle distillate hydrotreating, has been much slower and less groundbreaking. In operations of this kind, the biggest challenge for a catalyst technology is to deliver premium activity and stability when faced with limited hydrogen, difficult feedstocks and severe operating conditions.

Research into novel, alternative approaches to hydrotreating catalyst design has led Albemarle to introduce PULSAR. The first catalyst developed using this breakthrough technology is KF 787 PULSAR, which delivers superior activity without compromising stability,

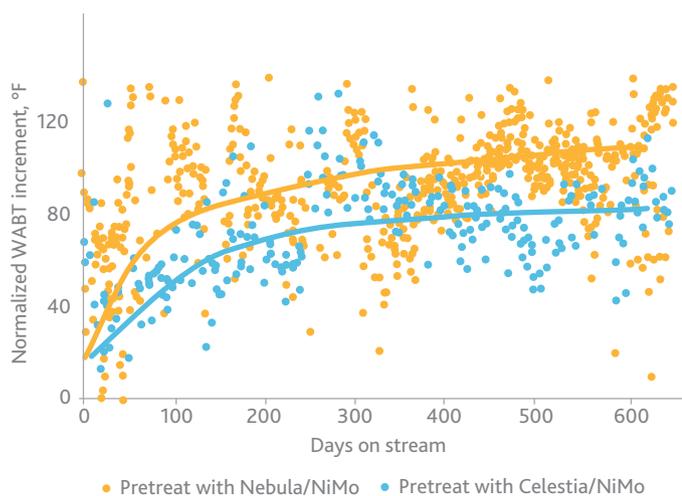


Figure 1: Hydrocracker normalized weighted average bed temperature (WABT) increment from the start of run.

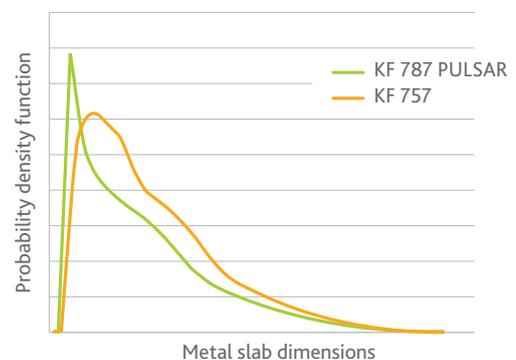


Figure 2: The size distribution of active metal slabs in KF 787 PULSAR and KF 757 after activity testing. The active metal slabs in KF 787 PULSAR are smaller and have a significantly narrower size distribution and better dispersion.

even in operations with challenging feedstocks and constrained by low hydrogen availability. A key aspect behind the catalyst's performance is the smaller average size of its active metal slabs and their improved dispersion (Figure 2).

One of the distinctive features of KF 787 PULSAR is its ability to perform consistently across the whole middle distillate application segment, from SRGO applications at well below 20 bar ppH_2 to heating oil production in the 25–35- ppH_2 range though to cracked stock upgrading to high-quality diesel at 50 bar ppH_2 . In addition, thanks to its flexibility and robustness in operation, KF 787 PULSAR can be applied in any hydrotreater section, from the reactor top to the bottom. Its robustness also means that the catalyst can cope better with operational upsets in the process unit.

This product has been developed particularly for refiners that want to maximize feed upgrading and the value of their difficult operations. Performance tests on KF 787 PULSAR to date have delivered dramatic increases in this area (Figure 3). KF 787 PULSAR is the first product from the new technology platform and Albemarle expects to release more of these products in the near future.



At Albemarle, we are committed to developing products and pursuing technical innovations that enable higher levels of performance and flexibility. For new technologies to succeed, they must promise and deliver clear business benefits. We believe the best way to do this is to focus on catalysts that enable customers to maximize value at the lowest possible cost.

The future

In a fast-changing business landscape, flexibility and reliability are top priorities for refinery operators. Flexibility, including the capability for processing low-cost crudes with demanding compositions under varied process conditions, requires robust, highly active catalyst products that deliver high levels of productivity across a wide range of process conditions.

At Albemarle, we are committed to developing products and pursuing technical innovations that enable higher levels of performance and flexibility. For new technologies to succeed, they must promise and deliver clear business

benefits. We believe the best way to do this is to focus on catalysts that enable customers to maximize value.

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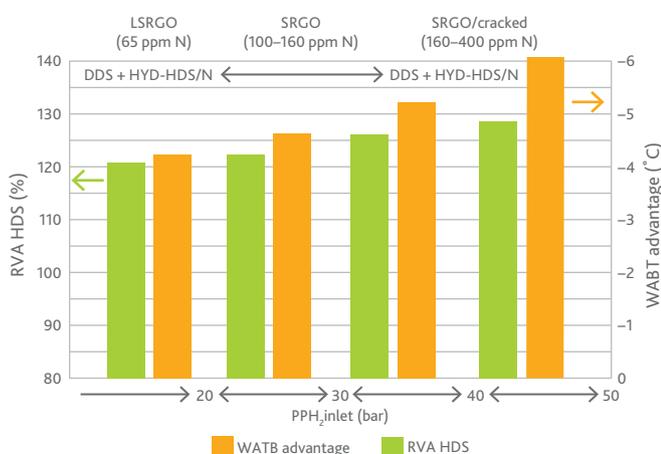


Figure 3: Relative advantage in performance of KF 787 PULSAR compared with KF 780 in various middle distillate hydrotreating ultra-low-sulfur-diesel applications at low and medium pressure.

KF 780: SUPERIOR PERFORMANCE DELIVERED FOR MIDDLE DISTILLATE HYDROTREATING AND FCC-PT APPLICATIONS

The overwhelming success of KF 780, Albemarle’s all-rounder hydrotreating catalyst

AUTHORS: ANDREA BATTISTON, HENK JAN TROMP AND JELLE VAN DE VALL

In hydrotreating, FCC pretreatment (FCC-PT) is one of the most challenging applications and the longer-term trend is to treat progressively heavier feedstocks. This requires more-efficient catalysts with enhanced coke tolerance and desulfurization activity in the top part of the reactor and improved aromatics saturation and denitrification activity for the reactor’s middle and bottom parts.

In middle distillates (MD) hydrotreating, the objective is to upgrade as much distressed feedstock to ultra-low-sulfur-diesel (ULSD) as possible. This is particularly challenging in units constrained by low hydrogen pressure and availability. For these applications, a parallel can be drawn with FCC-PT, as robust catalyst solutions are required that can deliver superior hydrodesulfurization (HDS) activity combined with high stability.

Albemarle has addressed this need by introducing KF 780 STARS®, a flexible, high-performance CoMo catalyst with very high metals efficiency and robustness that is designed to operate under the

most stringent technical and economic constraints both in VGO and distillate low- and medium-pressure operations.

KF 780 made its entrance in the market at the beginning of 2015, first for FCC-PT applications. In FCC-PT, this catalyst is mainly applied to maintain a low sulfur product level through improved HDS and to reduce nitrogen and aromatics levels for better FCC unit yields and operations. After proving itself in this demanding service, KF 780 was rolled out to the MD ULSD segment.

The acceptance of KF 780 by refiners for both applications has been extremely positive. With 12,000 tonnes delivered and 130 operations served worldwide in the four years since its introduction, KF 780 is an overwhelming success in the hydrotreating catalyst market.

An overview of the combined FCC-PT and ULSD applications worldwide is shown in Figure 1. A previous *Catalyst Courier* article¹ illustrated the use of KF 780 for FCC-PT operations. This paper focuses on the application and the advantages that the catalyst brings to refiners for MD hydrotreating.

Superior performance delivered in MD hydrotreating applications

The most profitable application of a catalyst in MD hydrotreating is to upgrade distressed feedstock to valuable ULSD product by maximizing HDS and, where applicable, hydrodearomatization (HDA) activity for higher volume swell and cetane uplift.

Operations in MD hydrotreaters below 45 bar (650 psig) hydrogen partial pressure (ppH₂) bear similarities with low- and moderate-pressure FCC-PT. The main one is that, owing to the low (effective) hydrogen pressure, hydrogenation (HYD) reactions are often inhibited, predominantly by nitrogen species. So, a parallel can also be drawn with the catalyst’s requirements for operating in such units.

KF 780 has high HDS/HYD selectivity and excellent pore mouth accessibility, which give great flexibility with respect to operating severity and to positioning in a reactor’s loading scheme. Thanks to its high HDS activity, tolerance to high nitrogen levels and excellent stability, KF 780 enables more upgrading of challenging, distressed feedstock to

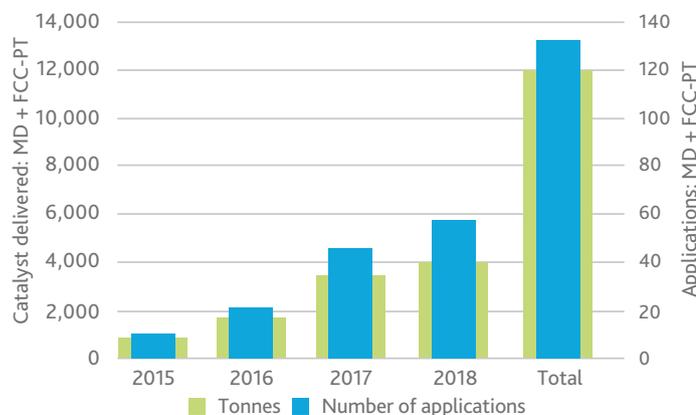


Figure 1: KF 780 catalyst sales to FCC-PT and MD hydrotreating units combined.

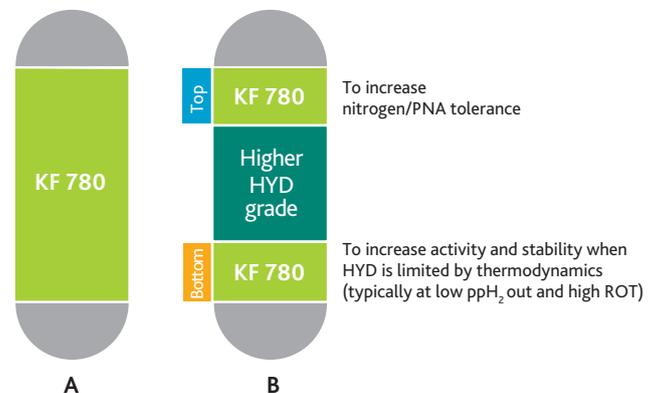


Figure 2: Typical applications of KF 780 in MD hydrotreating at low and medium pressure: (a) as a standalone solution and (b) as a STAX component in combination with catalysts with higher HYD.



KF 780 is an overwhelming success in the hydrotreating catalyst market, as proven by its market penetration: 12,000 tonnes loaded and 130 applications worldwide in four years from its introduction. ”

high-value diesel. In addition, thanks to its robustness, it helps in mitigating the risks in difficult operations where technical upsets are more likely. This makes KF 780 an extremely valuable tool for refiners to increase the operating margins of their most critical operations.

KF 780 is suitable for all positions in a hydrotreater: close to the reactor’s top and throughout the middle of the bed, where the removal of easy sulfur and nitrogen species is important; and lower in the reactor where refractory sulfur needs to be reduced to a ULSD concentration and where stability is extremely important.

As a result, KF 780 can be applied as a standalone solution throughout the entire reactor, or as a STAX® component, typically in combination with a more hydrogenating catalyst loaded in the mid-section of the reactor (Figure 2). In such a STAX configuration, KF 780 lowers nitrogen inhibition at the reactor top and increases operating stability at the reactor bottom, which are both particularly important in the presence of refractory (cracked) feedstock, low hydrogen pressure and availability, high temperature or a combination of these factors.

KF 780’s superior performance under demanding conditions is demonstrated by a pilot plant test run for a commercial ULSD operation at low-to-moderate ppH₂ (~32 bar (465 psig) outlet). In the test, the catalyst was compared with KF 758, Albemarle’s ULSD grade for low and moderate pressure before the introduction of KF 780. The test format is summarized in Table 1.

The LCO intake was increased from 8% (conditions 4–5) to 16% (conditions 6–9; feed nitrogen = 260 ppmw) while also raising the temperature substantially, to 362°C (684°F), to keep operating at a very low product sulfur level. In addition, when running at the maximum LCO intake of 16%, the hydrogen-to-oil-inlet ratio was decreased to reach a minimum hydrogen coverage of 2.5 (Condition 8).



CONDITION	PPH ₂ (BAR)	FEED TYPE	HYDROGEN COVERAGE	WABT (°C)	DAYS ON STREAM (CUMULATIVE)	
1	44	SRGO	>3.5	330	3	
2				348	6	
3				344	11	
4		SRGO + LCO (92 + 8%)		350	13	
5				352	18	
6		SRGO + LCO (84 + 16%)		362	25	25
7					3.5	30
8					2.5	36
9 = 7 (activity return point)					3.5	40

Table 1: Pilot plant test comparing KF 780 with KF 758 at high LCO content, low hydrogen coverage and high weighted average bed temperature (WABT).

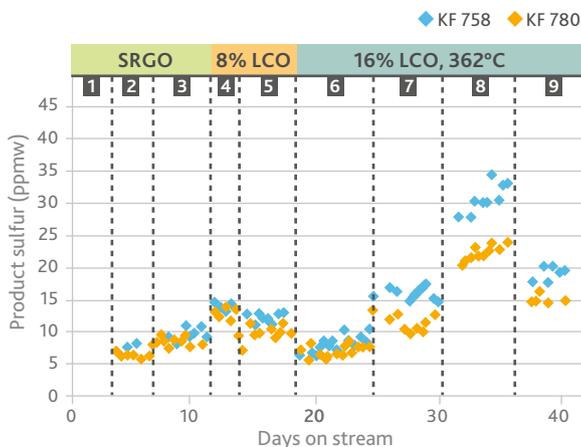


Figure 3: Product sulfur.

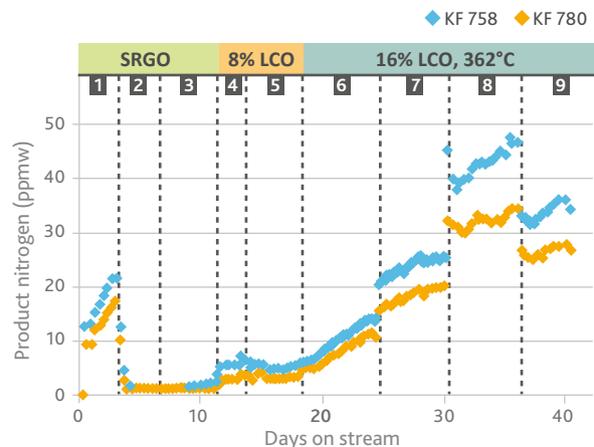


Figure 4: Product nitrogen.



Finally, an activity return point (ARP) condition was run to confirm the stability of the catalysts (Condition 9).

The sulfur and nitrogen product evolution during the test and the corresponding HDS relative volume activity (RVA) are shown in figures 3 to 5.

As can be seen in the figures, with more LCO intake and a higher operating temperature (conditions 4–9) the advantage in activity of KF 780 increases consistently, particularly with very low hydrogen coverage (Condition 8).

KF 780 provides higher HDS and HDN RVAs over the whole range of conditions, thanks to its higher HDS/HYD selectivity and better stability. This combination is the basis of its success in the market, especially in highly demanding commercial operations.

KF 780 in commercial practice

A particularly relevant MD commercial case shows how KF 780 led to an increased operating margin for a refiner when compared with the two previous cycles using KF 757 and KF 758. Note that these catalysts are among the most widely applied catalysts in the market for moderate-pressure ULSD production.

The MD hydrotreater operates at ~42 bar inlet ppH₂ and treats a blend of SRGO, HGO and LCO (8–15%). The hydrogen coverage (ratio of hydrogen input to hydrogen consumed) is very low, typically between 2.0 and 2.5.

KF 758 (Cycle 2) was preferred over KF 757 (Cycle 1) for processing more LCO. KF 780 was chosen for Cycle 3 in view of its higher activity and stability, thereby giving the opportunity to upgrade even more LCO to high-value ULSD. The overall operating objectives in Cycle 3 were to maximize the percentage of cracked feedstock

(LCO) intake and to increase the feed's final boiling point while still achieving a 12-month cycle length.

The typical operating conditions and the average feed and product properties are shown in Table 2.

In the first five months on stream, KF 780 enabled an increase in the LCO intake from 5% (Cycle 1) and 10% (Cycle 2) to 13% (Cycle 3), which is 30% more than in the best of the two previous cycles (Figure 6).

Remarkably, over the same period, the increase in LCO intake with KF 780 was obtained under significantly more difficult conditions than in the previous two cycles with the other catalysts:

- a) The makeup gas hydrogen purity was lower, which led to a drop in the hydrogen coverage to about 2.1 in Cycle 3 (Figure 7).
- b) The feed T95 distillation was similar to Cycle 1 and, on average, 8°C (14°F) higher compared with Cycle 2 (Figure 8).

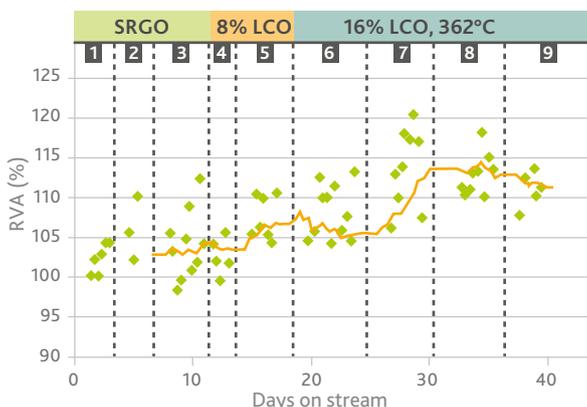


Figure 5: RVA HDS evolution for KF 780 compared with KF 758.

Typical operating conditions	
ppH ₂ (bar)	42
Hydrogen-to-oil ratio (NI/l)	70–100
Typical feed properties	
Sulfur (wt%)	0.25
Nitrogen (wt%)	200
Total aromatics (wt%)	26–34
Density (g/ml)	0.85–0.86
T95 (°C)	Up to 370
Average product properties	
Sulfur (ppmw)	10–13
Cycle length (months)	12

Table 2: KF 780 commercial case study: typical operating parameters.

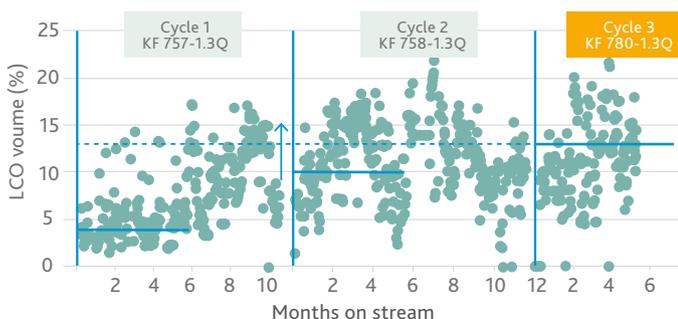


Figure 6: KF 780 commercial case study: comparison of the LCO intake.

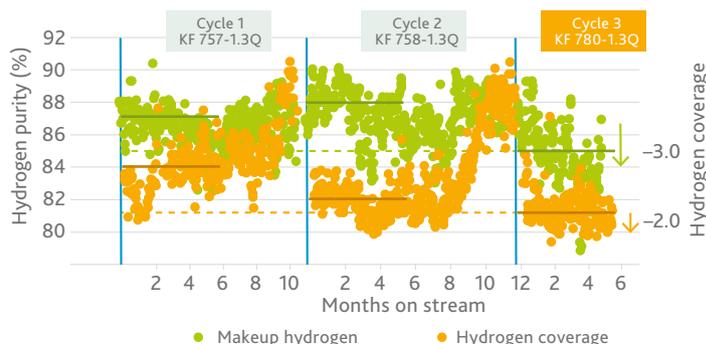


Figure 7: KF 780 commercial case study: comparison of the makeup gas hydrogen purity and the hydrogen coverage.



KF 780 has a uniquely high metals efficiency. Its innovative design combines high HDS activity, HDS/HYD selectivity and excellent pore accessibility. The result is a flexible catalyst with increased activity and superior stability whose advantage increases with difficult feedstocks and demanding conditions.



After normalizing the actual operating temperature in the unit for the additional LCO treated and the higher feed blend final boiling point, KF 780 displayed a 3–5°C (6–9°F) higher activity (lower normalized WABT, as calculated after one month on stream) compared with the two previous cycles, and even better stability (Figure 9).

Based on the excellent performance shown in its first cycle, the refinery has decided to reload KF 780 for the following run.

Conclusions

KF 780, Albemarle’s all-rounder CoMo grade for moderate pressure VGO FCC-PT and MD hydrotreating, is an overwhelming success in the refinery

catalyst market. In the first four years since its introduction, 12,000 tonnes of it have been delivered and 130 operations have been served.

KF 780 has a uniquely high metals efficiency. Its innovative design combines high HDS activity, HDS/HYD selectivity and excellent pore accessibility. The result is a flexible catalyst with superior activity and stability whose advantage increases with difficult feedstocks and demanding conditions.

KF 780’s success in the market is growing steadily thanks to the excellent performance demonstrated in commercial practice.

Reference

¹Anderson, G.: “Ketjenfine (KF) 780 STARS®: An intelligent option for FCC pretreatment (FCC-PT) applications,” *Catalyst Courier* 86, 20–23

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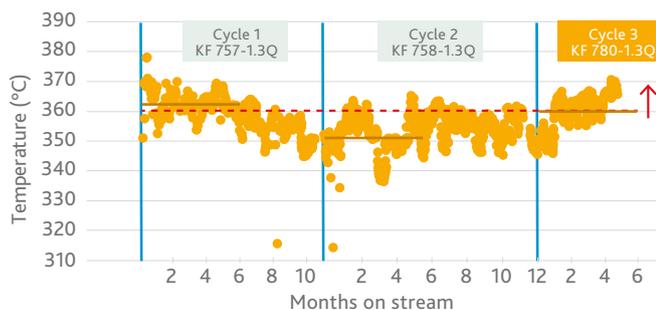


Figure 8: KF 780 commercial case study: feed blend distillation (T95).

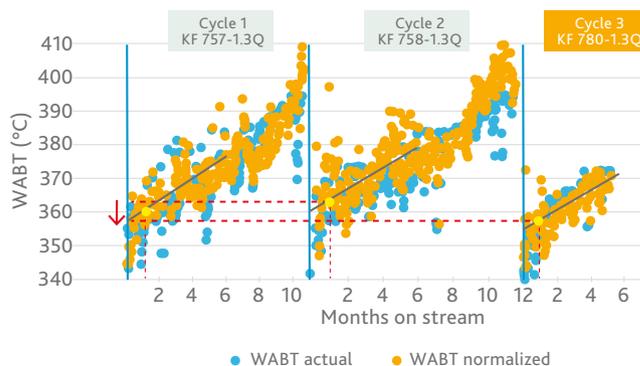


Figure 9: Commercial case study: comparison of the LCO intake.

KF 787 PULSAR™: THE NEW BREAKTHROUGH CATALYST FOR LOW- AND MEDIUM-PRESSURE MIDDLE DISTILLATES HYDROTREATING

Bringing high returns in applications with limited hydrogen, difficult feedstocks and severe operating conditions

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Over the last years, improved hydrotreating (HT) catalysts have been introduced in the market primarily to serve operations with high pressure and hydrogen availability. However, catalyst innovation for operations limited by hydrogen, such as low- and medium-pressure middle distillates HT (MD HT), has been slower and less groundbreaking. The challenge is being able to deliver both premium activity and stability in applications with limited hydrogen, difficult feedstocks and severe operating conditions.

To improve catalyst stability for hydrogen-constrained MD HT operations, suppliers followed a defensive approach and sought to develop moderately active catalyst systems with low selectivity for nitrogen removal. The drawback in adopting such catalysts is that, while benefitting from their stability in operation, refiners still cannot maximize activity and thereby extract the full operating potential and profit from their critical units.

Albemarle responded first to the need for low- and medium-pressure higher-performance catalysts by introducing KF 780 STARS®, a highly active, stable and versatile CoMo grade developed for fluidized catalytic cracking pretreatment (FCC-PT) and MD HT applications. KF 780 delivers enhanced metals efficiency for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity and higher robustness in operation. The acceptance of KF 780 by refiners for both applications has been overwhelmingly positive.

Research into novel, alternative approaches to HT catalyst design has now led Albemarle to introduce a new and superior generation of catalysts: PULSAR™. PULSAR is a breakthrough technology that effectively controls the morphology and the dispersion of the metal active phase.

The first grade of this new class is KF 787 PULSAR. This catalyst delivers superior activity without compromising stability, even in operations with challenging feedstocks and constrained by low hydrogen availability.

Challenges in low- and medium-pressure MD HT

A premium ultra-low-sulfur-diesel (ULSD) catalyst for low- and medium-pressure HT applications that process difficult feedstocks requires a perfectly balanced combination of superior activity, stability and robustness against operational upsets.

Performance in these challenging operations is constrained by both kinetics and thermodynamics.

Figure 1 shows the simplified reaction pathway for the HDS reaction and the response of its different routes to operating hydrogen pressure under thermodynamically favorable conditions. The HDS reaction consists of two routes. The direct desulfurization route (DDS) is a single-step reaction in which sulfur is converted via direct hydrogenation (HYD) to hydrogen sulfide. DDS is typically the fastest HDS pathway at very low pressure, especially for easy sulfur removal, and the one that requires the lowest hydrogen consumption. HYD-assisted HDS (HYD-HDS) occurs in parallel with DDS and is a more complex reaction requiring HYD (of at least one aromatic

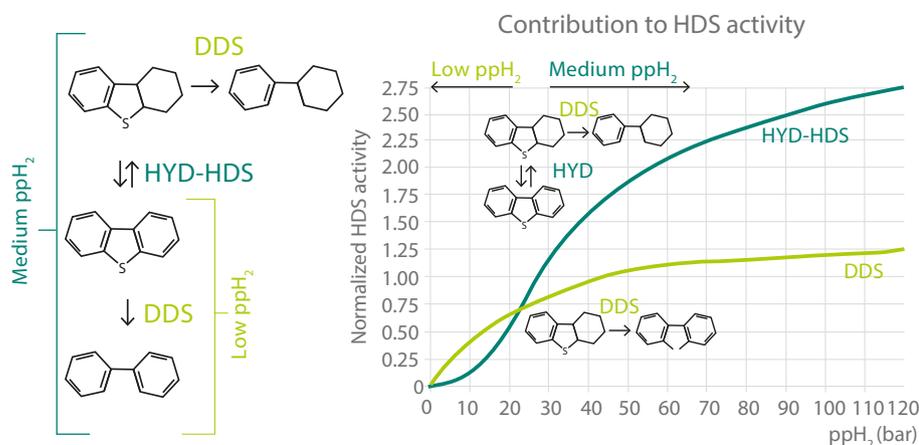


Figure 1: Response to ppH₂: DDS compared with HYD-HDS.

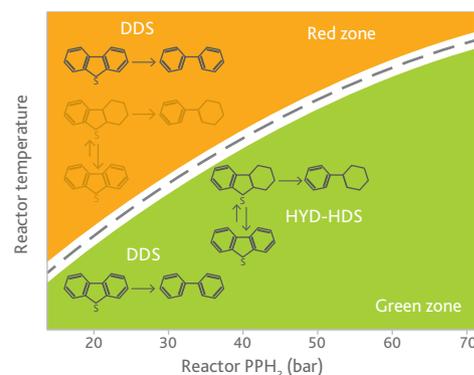


Figure 2: Operating regions in an MD HT unit.



ring) as a first step and DDS as the final one. Therefore, DDS is also necessary in the HYD-HDS route, particularly at low and medium pressure ($ppH_2 < 35\text{--}40$ bar) where HYD reactions are slow and DDS is needed to shift the equilibrium of the first HYD step. At a very low pressure, pure DDS is the dominant reaction; at low-to-medium pressure ($25\text{ bar} < ppH_2 < 40$ bar), the DDS and the HYD-HDS routes are both potentially important. The more refractory the sulfur species to be converted, the more important the contribution of the HYD-HDS route.

Note that the HDN reaction also proceeds via a HYD step. Hence, its response to hydrogen pressure and thermodynamics is similar to that of the HYD-HDS route.

For the HYD-HDS and HDN routes to be effective in an HT reactor though, additional conditions are required:

- a) a sufficiently high hydrogen coverage to preserve a high enough ppH_2 at the bottom of the reactor
- b) a sufficiently high temperature-to- ppH_2 ratio to avoid thermodynamic limitation of the HYD step
- c) limited inhibition effects by refractory feed nitrogen, especially basic nitrogen,

which adsorbs on the catalyst's HYD sites and inhibits the HYD-assisted reactions.

Based on the considerations above, it is possible to identify three typical operating regimes, or regions, for an HT reactor. These regions are illustrated in Figure 2.

The effectiveness of the different reaction routes varies by region:

- a) In the green operating region, which is characterized by a low temperature-to- ppH_2 ratio, all three reactions, DDS, HYD-HDS and HDN, are effective, with DDS being dominant for HDS at low pressure and HDN and HYD-HDS becoming increasingly more important at higher pressures.
- b) In the intermediate region (depicted in yellow), the rate of HDN, HYD-HDS and hydrodearomatization start to slow down because of limitations on the HYD steps by the thermodynamics.
- c) In the red region, the one with the highest temperature-to- ppH_2 ratio, all the HYD-assisted reaction routes are severely hindered. In this zone, the rates of removal of sulfur and nitrogen are significantly lower and HDS has to proceed almost exclusively via the DDS route.

Low- and medium-pressure HT units processing difficult feedstocks often operate totally or partially in the intermediate or in the red region already at the beginning of their cycles. This is particularly true for units with very low ppH_2 , low hydrogen coverage and/or a high space velocity, which are all conditions that lead to higher operating temperatures.

In the red operating region, not only are the HDS and HDN reaction rates slower, but other phenomena are also favored that can negatively affect the performance of a catalyst. Depending on a catalyst's properties, dehydrogenation and condensation of (nitrogen-containing) polyaromatics leading to coke formation that can block the catalyst's active sites can occur. In addition, high temperatures can cause metals migration from the active metal slabs into larger agglomerates with significantly lower activity.

When designing a premium catalyst for low and medium pressure for upgrading difficult feedstocks to high-value diesel, all these aspects must be considered. The optimal catalyst would be the one that can maximize DDS activity without compromising the potential of the HYD reactions for HDS and HDN, and that can still provide high robustness and full operating stability.

Developing such a catalyst has been the focus of Albemarle's catalyst research over the last years and has required a fundamentally new approach to catalyst design.

KF 787 PULSAR: A breakthrough innovation in MD HT catalysts

PULSAR is a new catalyst technology developed at Albemarle's catalyst research center in Amsterdam, the Netherlands.

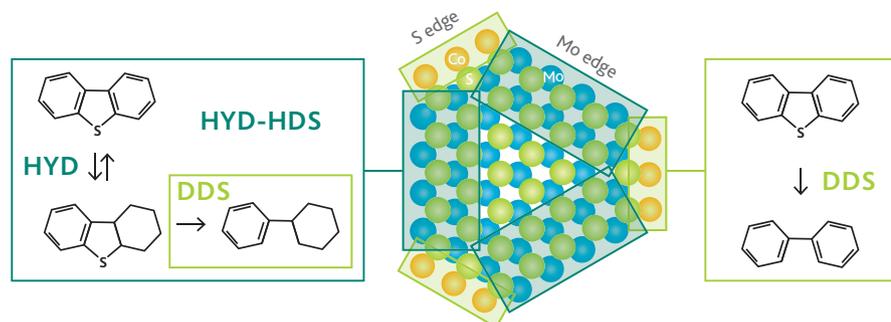


Figure 3: Model of the metal active slabs in CoMo hydrotreating catalysts and of the DDS (light-green frames) and the HYD-HDS active sites (dark-green frames).



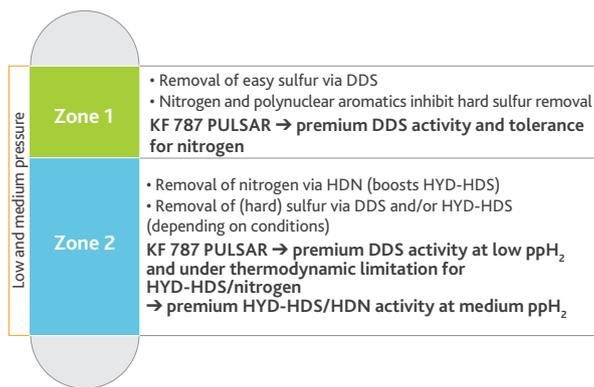


Figure 4: KF 787 PULSAR's advantages in MD HT applications.

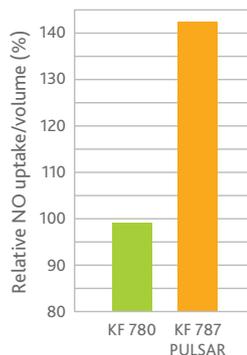


Figure 5: Comparison between the concentration of DDS sites/reactor volume of KF 787 PULSAR and KF 780.

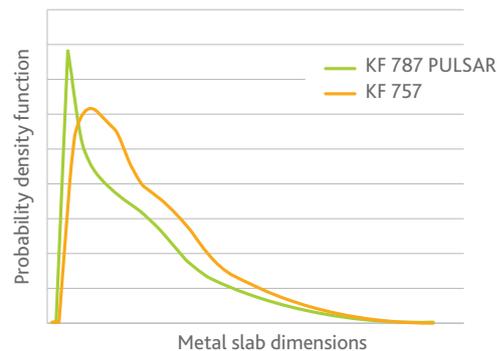


Figure 6: 3D HR-STEM analysis of the metal active slabs in spent KF 787 PULSAR and KF 757.

The first new grade with this technology is KF 787 PULSAR, a supported CoMo catalyst that is specifically designed for low- and medium-pressure MD HT. This catalyst can deliver both premium activity and stability, even in operations with challenging feedstocks and constrained by low hydrogen availability.

Thanks to its special design, KF 787 PULSAR has an extremely wide hydrogen pressure application range that stretches from very low to medium-to-high pressure (10–55 bar ppH₂).

In terms of handling and sulfidation, KF 787 PULSAR can be treated exactly like the previous STARS catalyst generation and, like STARS catalysts, PULSAR catalysts can also be rejuvenated to over 90% of their fresh relative volume activity (RVA) HDS activity through REACT™ treatment.

Specific features of the PULSAR technology are the tightly controlled morphology and size of its active metal phase. These result in very high metals dispersion, thereby boosting metal efficiency and specific activity per reactor volume.

Figure 3 depicts the most widely accepted model for the HYD CoMo metal active phase: hexagonal imperfect molybdenum disulfide (MoS₂) slabs decorated at the sulfur edges with cobalt (Co) as the promoter.

The HYD step of the HYD-HDS reaction pathway takes place on the molybdenum (Mo) edge and on the first ring of Mo

atoms adjacent to the slabs' edges (Mo atoms in the dark-green frames). In contrast, the DDS step occurs only on the Co atoms at the sulfur edge (atoms in the light-green frames).

When the metal slabs are larger, the ratio between the number of HYD-HDS and DDS sites also increases according to their geometrical constraints; hence, larger metal active slabs have a higher selectivity for HYD.

KF 787 PULSAR's advantages

Reducing the size of the metal slabs, as achieved with the PULSAR technology, increases selectivity for the DDS reaction, which brings several advantages in operation at low and medium pressures:

- HDS activity increases, even in the intermediate and red operating zones (see Figure 2).
- Nitrogen tolerance is enhanced, which enables treating of feeds with higher end points, more cracked stock intake and more basic nitrogen.
- Stability is improved thanks to the lower tendency to form coke on the catalyst's surface, particularly when operating in the intermediate and red zones.

KF 787 PULSAR's advantages in applications are summarized in Figure 4, depending on its position in an HT reactor and on its operating mode.

KF 787 PULSAR has great flexibility in application with respect to both the type of operation and the loading zone

in a reactor. Its higher nitrogen tolerance enables it to be loaded in the reactor top (or Zone 1); the higher stability makes it suited for the reactor's middle and bottom section in any (U)LSD application (Zone 2).

Equally important is that KF 787 PULSAR's metal active phase is bound to the support in a way that helps to prevent the metal agglomeration that is typical of extended use and exposure to high temperatures. This adds to the stability advantage already provided by its high metal dispersion and DDS selectivity.

The special morphology and the high presence of DDS sites in KF 787 PULSAR's active phase have been demonstrated by nitrogen monoxide (NO) chemisorption and by 3D high-resolution scanning transmission electron microscopy (3D HR-STEM) measurements.

NO adsorbs preferentially on the Co atoms at the edge of the metal slabs and can be used to measure the concentration of a catalyst's DDS sites. As shown in Figure 5, NO chemisorption tests have confirmed that KF 787 PULSAR has an exceptionally high concentration of DDS sites, i.e., almost 50% more per reactor volume than the already highly DDS selective KF 780.

In addition, 3D HR-STEM analysis has shown that the active metal slabs are significantly smaller than in KF 780 and KF 757 (Figure 6), which is in line with KF 787 PULSAR's high DDS selectivity and stability. The

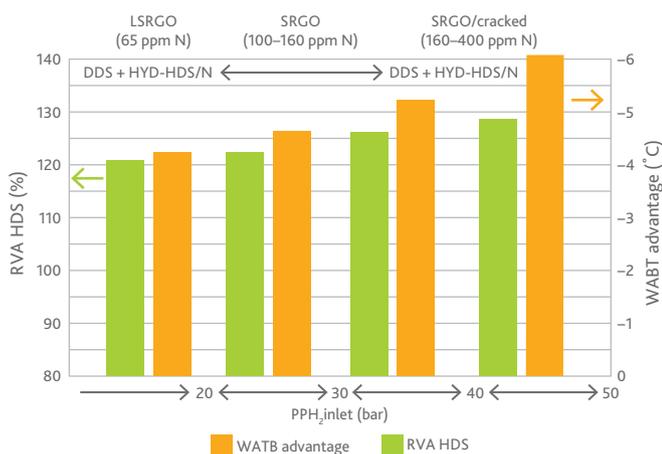


Figure 7: Relative advantage in performance of KF 787 PULSAR compared with KF 780 in various MD HT ULSD applications.

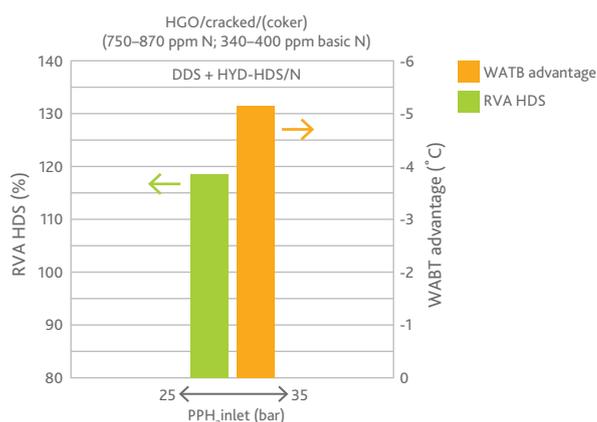


Figure 8: Relative advantage in performance of KF 787 PULSAR compared with KF 780 for heating oil production.

microscopy analysis was carried out on the spent catalysts after they had been tested side by side in a pilot plant unit for 40 d. The test was run at low hydrogen pressure (15–35 bar) with various feedstocks, including SRGO–FCC LCO blends and HGO, and included a final stress condition of 5 d with LGO (1.1 wt% sulfur; 240 ppm nitrogen; 410°C final boiling point; density = 0.861 g/ml) at 380°C at 15 bar ppH₂ outlet. The objective of this final condition was to apply additional stress to the catalysts that would simulate metal agglomeration before analyzing the active phase.

Figure 6 shows the size distribution of the active metal slabs of KF 757 and KF 787 PULSAR after the activity test. The active metal slabs in KF 787 PULSAR are smaller, with a significantly narrower size distribution, and are, thus, better dispersed. These features are the direct result of the PULSAR technology and are preserved even after use in demanding operating conditions, thanks to a reduced tendency for metal agglomeration.

These observations are remarkable when considering that the reference grade is KF 757, a catalyst very well known in the market for the stability of its active phase and its robustness in operation.

KF 787 PULSAR was tested extensively in pilot plant units with different types of feedstocks and in a large range of conditions to assess its applicability and performance advantage fully. The

results confirmed that it is a premium and fully flexible catalyst by design and suited for any ULSD MD application at low and medium pressures (Figure 7), and for heating oil (50 ppmw target product sulfur) production at low and medium pressures (Figure 8). The RVA HDS typically ranges from 120 to 130%, or up to 6°C weighted average bed temperature (WABT) advantage compared with KF 780, which is among the most active and widely applied catalyst in the low- and medium-pressure MD segments today.

Remarkably, KF 787 PULSAR's superior performance is delivered consistently across the whole MD application segment, from light SRGO applications below 20 bar ppH₂, to heating oil production in the 25–35-bar ppH₂ range, to cracked stock upgrading to high-quality diesel at 50 bar ppH₂. This flexibility is one of the advantages of the PULSAR technology and the result of the catalyst-specific design that combines high HDS activity with moderate selectivity for HYD.

The performance advantage by KF 787 PULSAR can be monetized by refiners in different ways, depending on their technical needs and the economics at play.

The most obvious utilization would be to increase upgrading of distressed feedstock to ULSD, with higher density uplift as an additional benefit. Considering KF 787 PULSAR's moderate selectivity towards HYD, the higher activity would not come

at the cost of significantly higher hydrogen consumption. The high HDS-activity-to-hydrogen-consumption ratio lowers the specific hydrogen consumption at equal sulfur removal compared with more hydrogenating catalysts. In addition, KF 787 PULSAR provides higher stability that, in combination with a lower start-of-run WABT, leads to longer cycles and thus lower changeout and downtime costs.

Another tangible economic advantage is KF 787 PULSAR's flexibility in operation: by fitting all the reactor zones in the most diverse applications, it can be utilized in any low- and medium-pressure MD HT unit with significant advantages for refiners' catalyst pool management and logistics.

Other important economic advantages are the catalyst's high robustness in case of operational upsets, the energy savings in view of the potentially lowered WABT and delayed capital investments for revamping units that are potentially constrained by catalyst activity.

The main key features and advantages in application of KF 787 PULSAR are summarized in Figure 9.

Although KF 787 PULSAR has just been launched in the market and is already operating in its first commercial reference, research at Albemarle on the new PULSAR technology is continuing at full speed.





As new applications are being explored, future PULSAR grades are being perfected and will be introduced shortly to accompany KF 787 PULSAR.

Conclusions

In recent years, Albemarle has made significant progress in developing catalysts for low- and medium-pressure MD HT.

Research into alternative approaches to HT catalyst design and production has now led to the introduction of a new and superior generation of catalysts: PULSAR. This is a breakthrough technology that, among other things, enables precise control of the morphology of the metal active phase and its dispersion. The active metals slabs in PULSAR catalysts are smaller and better dispersed, and have an extremely narrow size distribution.

The first grade of this new generation is KF 787 PULSAR. This catalyst was developed to bring high returns primarily for refiners that process high nitrogen and cracked feedstock, including operations

constrained by low operating pressure and limited hydrogen availability.

KF 787 PULSAR is a fully flexible MD HT catalyst by design. The typical activity advantage with difficult feedstocks is 6°C WABT compared with KF 780 STARS. Remarkably, KF 787 PULSAR performs consistently across the whole MD application segment, from light SRGO applications at well below 20 bar ppH₂, to heating oil production in the 25–35-bar ppH₂ range, to cracked stock upgrading to high-quality diesel at 50 bar ppH₂.

The performance advantage of KF 787 PULSAR can be monetized by refiners in different ways, depending on their technical needs and the economics at play, starting from increased upgrading of distressed feedstock to ULSD, with higher density uplift as an additional benefit, to longer operating cycles leading to lower changeout and downtime costs.

Another tangible economic advantage derives from the catalyst's full flexibility

in operation. KF 787 PULSAR fits all low- and medium-pressure MD HT operations and all reactor zones, from the top to the bottom, which greatly simplifies refiners' catalyst pool management and logistics. It also offers high robustness in case of operational upsets.

Although KF 787 PULSAR is already operating in its first commercial reference, future PULSAR grades are being perfected and will shortly be introduced in the market.

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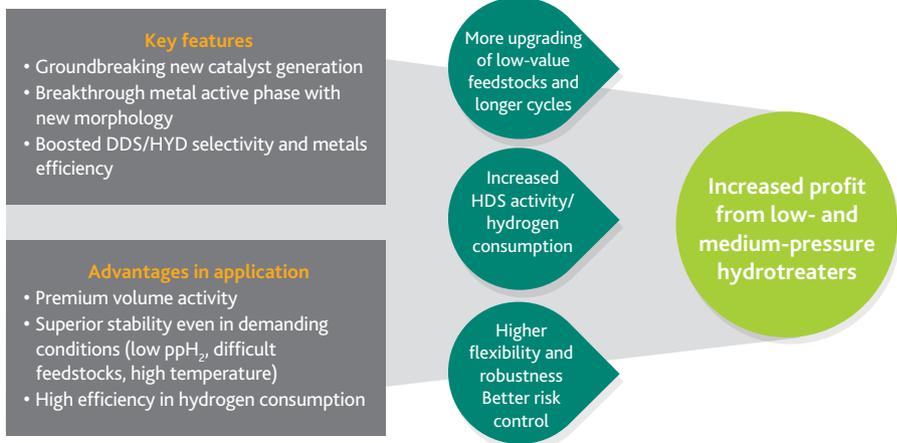


Figure 9: Key features and advantages in application.

CELESTIA™: A REVOLUTIONARY NEW HYDROPROCESSING CATALYST PROVIDING ULTRA-HIGH ACTIVITY

The new member of Albemarle’s bulk metal catalyst family

AUTHORS: BOB LELIVELD AND BARBARA SLETTENHAAR

Albemarle and ExxonMobil have co-developed and commercialized a breakthrough in hydrotreating catalysts. Built on the success of Nebula®, Celestia, a new bulk metal catalyst, offers a step change in hydrotreating activity.

The success of Nebula inspired the joint Albemarle–ExxonMobil research team to take bulk metal catalysts to the next level. That inspiration led to the discovery of the Celestia catalyst formulation and to the scale up to an industrial product. Celestia catalyst was first deployed within ExxonMobil in 2015. Since then, Albemarle and ExxonMobil have deployed Celestia alongside Nebula and conventional catalysts at ExxonMobil sites worldwide. The experiences are very positive and can be summarized as:

- In every commercial application, Celestia catalyst shows an activity advantage up to three times that of conventional supported catalysts.
- Both in distillate hydrotreaters and in LCO/VGO hydrocrackers, Celestia catalyst yields exceptional returns with payback times being as short as four months.

Bulk metal catalysts

Celestia is the new member of Albemarle’s bulk metal catalyst family. Bulk metal catalysts have advantages compared with conventional (supported) hydrotreating catalysts for several process and functional reasons:

- Supported catalysts (based on an alumina support) have activity limitations owing to the amount of active metal that can be deposited on the pore walls of the carrier material. Bulk metal catalysts such as Nebula and Celestia contain predominantly metal sulfides in forms that incorporate porosity and, thus, avoid the activity-

limiting issues that affect supported catalysts.

- The activity of supported catalysts is inhibited by the strong interaction between the active metal and the carrier material. This interaction results in their being classified as having Type II functionality because they contain a mixture of Type II active sites and the lower-activity Type I active sites. Bulk metal catalysts are not limited by a base interaction and contain a much greater proportion of the advantaged Type II active sites.
- Bulk metal catalysts contain more active metal per given volume and the active metal has a greater concentration of high-activity Type II sites.

Commercial hydrotreaters are not loaded with 100% bulk metal catalysts. Typically, bulk metal catalysts are loaded toward the bottom of a reactor in a sandwich configuration with conventional catalysts. Tuning the position and the amount of the bulk metal catalyst enables different targets to be met.

Splitting the Celestia and Nebula loads over different beds enables exotherm

control and optimization of the quenching strategy. When designing the final reactor load, it is important to consider the unit’s hydrogen availability and makeup hydrogen compressor capacity. Design work should evaluate the increased mechanical load on reactor internals such as the catalyst support grid, the associated beams and the outlet collector arising from Celestia’s higher loading density before deployment.

After loading, start-up is similar to that for activating supported catalysts. The sulfur level required to activate Celestia and Nebula is about double that for a conventional catalyst, so a longer hold time is necessary to sulfide the catalyst fully. The Celestia catalyst activation procedure has been successfully commercialized in units utilizing stacks of Nebula and NiMo catalysts.

Versatile solutions

From a kinetics perspective, Celestia is most effective when used in high-pressure applications. Consequently, the initial commercialization focused on hydrocracking pretreatment and distillate hydroprocessing applications that benefit from operating at high hydrogen partial pressures.

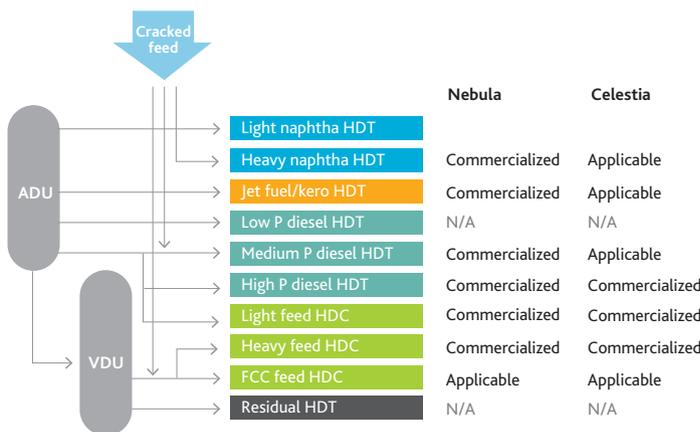


Figure 1: Applications of Nebula and Celestia.



Celestia has demonstrated significant economic improvements arising from upgrading more-severe feedstocks, increased feed rates and conversion, improved product quality and/or enabling new processing opportunities in both fuels and lubricant base stock service. Value has also come from how Celestia's high activity can affect adjacent units. Further applications of the technology in stack configurations are planned for other hydroprocessing platforms, including distillate hydrotreaters and hydrocrackers.

In conclusion, Celestia and Nebula are versatile catalyst solutions applicable to many hydroprocessing platforms, from naphtha to VGO. As mentioned earlier, ExxonMobil and Albemarle have successfully commercialized Celestia in distillate hydrotreating and light- and heavy-feed hydrocracking pretreatment (see Figure 1). Each deployment has been based on carefully designed, stacked-load catalyst configurations with supported

catalysts and/or Nebula at ExxonMobil operating refineries in Europe, Asia Pacific and the Americas. The key to successful deployment is to combine detailed process chemistry, kinetic and engineering knowledge with a thorough understanding of the economic needs of the refinery when designing a loading scheme.

Unit A: Celestia in LCO hydrocracking pretreatment service

Celestia was deployed in a North American ExxonMobil LCO hydrocracker in 2015 following a successful 18-year and 5-cycle operation using Nebula to provide superior hydrocracking pretreatment performance. Both Celestia and Nebula were loaded in the LCO hydrocracker; the Celestia load accounted for 26% of the pretreatment reactor's catalyst load. Celestia was stack loaded in two of the pretreatment reactor's four catalyst beds (Figure 2) with a leading NiMo catalyst.

Although classed as a light-feed hydrocracker, the unit processes a challenging feed blend typically containing 70% of a deep-cut medium cycle oil and 30% straight-run HGO distillate feed to maximize on-specification diesel production. The feed has high sulfur, nitrogen and aromatics contents, and a typical API value of 10–12 (Table 1). The business objective for using Celestia was to increase the unit feed rate and improve feed flexibility and distillate yield and quality. Accurately assessing the performance of Celestia in commercial operation was a secondary goal. Consequently, the Celestia load was similar to the Nebula stack load used in the previous cycle to provide a consistent basis for evaluating Celestia's performance against Nebula and leading NiMo catalysts.

A performance test on the hydrocracker's operation about three months after start-

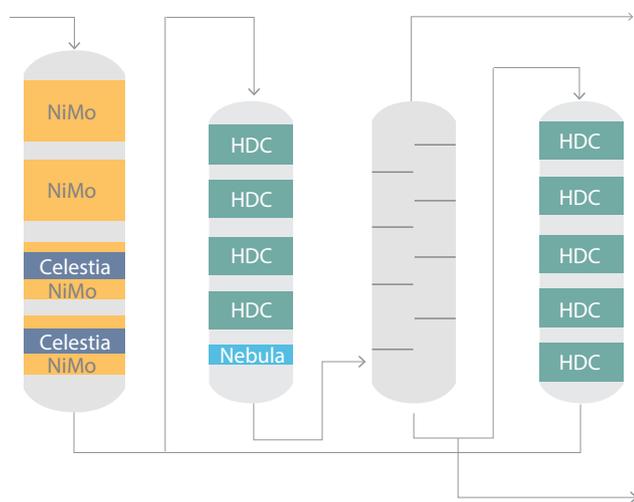


Figure 2: Loading diagram for Unit A.

	MEDIUM CYCLE OIL BASE – HEAVY	HEATING OIL
Pressure, psi	1400 (97 bar)	
Liquid hourly space velocity, h ⁻¹	1.3–1.4	
Feed split, vol%	70–85	15–30
(API) gravity	10–12 (0.986–1.000 kg/l)	28 (0.887 kg/l)
Sulfur, wt%	3.9–4.1	1.7
Nitrogen, ppm	1400–1700	270
Aromatics, wt%	85–90	37
Feed initial boiling point, °F	292 (144°C)	257 (125°C)
10%	461 (238°C)	528 (276°C)
50%	586 (308°C)	649 (343°C)
90%	692–704 (367–373°C)	713 (378°C)
95%	715–728 (379–387°C)	730 (388°C)
Final boiling point, °F	776–795 (413–424°C)	793 (423°C)

Table 1: Feed and operating conditions Unit A.

	AROMATIC SATURATION	HYDRODESULFURIZATION	HYDRODENITROGENATION
Relative volume activity	>200	>160	>170

Table 2: Activity overview of Celestia versus Nebula in Unit A.

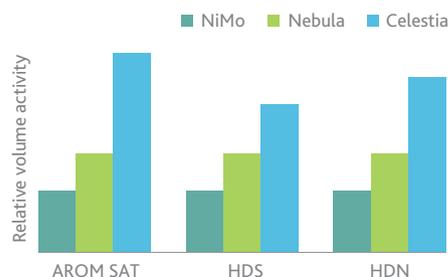


Figure 3: Activity overview of the different catalysts loaded in Unit A.

up confirmed the initial research findings: that Celestia has a significant activity advantage compared with Nebula and a step-out performance compared with leading NiMo catalysts (Figure 3).

The test showed that Celestia’s activity advantage ranged from 1.7 times to more than twice Nebula’s activity for cycle oil hydrocracking service. Table 2 shows a breakdown of Celestia’s aromatic saturation, hydrodesulfurization (HDS) and hydrodenitrogenation activity.

Celestia has enabled the hydrocracking unit to process more distillate-cut cycle oil from the fluidized catalytic cracking unit by increasing the LCO cut point to improve the yield while decreasing the fluidized catalytic cracking bottoms yield. This advantage has been achieved in combination with processing a significant feed volume.

Commercially, Celestia has significantly and sustainably improved the hydrocracker’s catalyst system for better unit performance and value capture. The benefits arise from multiple sources simultaneously and exceed in scope and magnitude all the expectations for Celestia. The benefits and process advantages from applying Celestia include

- more than 30% higher total HDS activity in the pretreatment reactor over the previous cycle (Figure 4)
- an increased feed margin by processing at a higher feed rate and an increased rate of medium cycle oil achieved by raising the cycle oil end point



- significantly higher conversion and fuels product yields through its step-out aromatic saturation ability
- improved HDS performance and increased diesel yield enabled by turning down the cracking activity while still meeting product sulfur targets
- improved distillate and gasoline product qualities and overall volume swell through its exceptional saturation ability
- a stability matching that of the conventional supported catalysts in the same reactor beds. Celestia has proven to be robust to operating upsets and has maintained its activity for more than three years in operation.
- The economic benefits derived from the Celestia application in this service are significant. In this example, the payback period for investing in Celestia was less than four months and profitable operations have continued for more than three years.

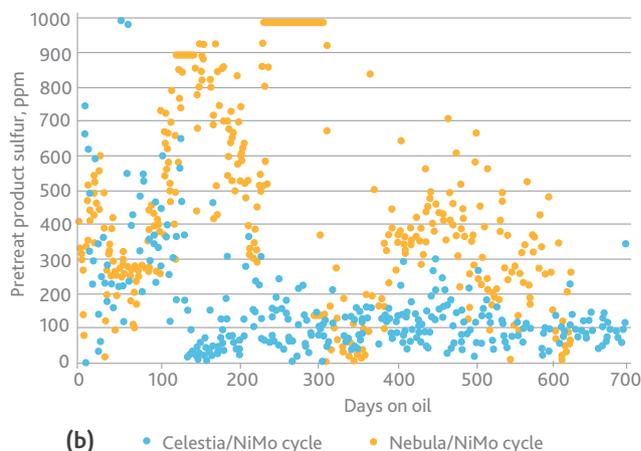
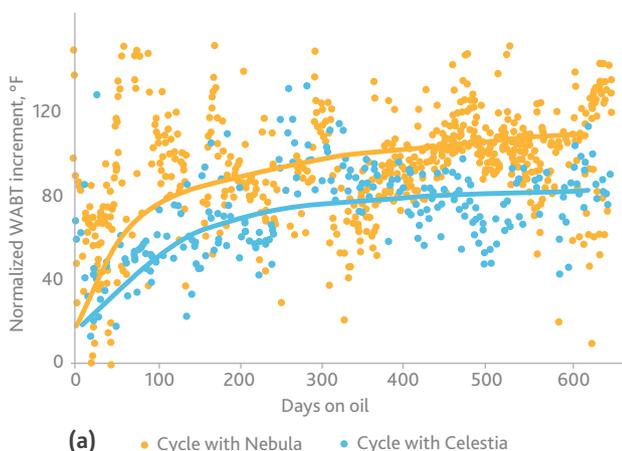


Figure 4: (a) Weighted average bed temperature and (b) product sulfur overview of two different cycles of Unit A.



Unit B: Celestia in VGO hydrocracking pretreatment service

Celestia provides similar benefits for heavier feed compositions. A stacked load of Celestia and Nebula (Figure 5) was loaded into the pretreatment section of a once-through heavy-feed hydrocracker processing a challenging blend of high-end-point virgin and coker VGO to produce fuels and a bottoms hydrocrackate that is exported to an ExxonMobil affiliate as steam cracker feed. The feed includes a heavy coker gas oil stream with a high end point and contains heavy, highly refractory sulfur and nitrogen (Table 3).

The volume load of Celestia and Nebula was designed to stay within the unit's process and engineering constraints while ensuring an attractive return. The hydrocracker performance and economics were evaluated using advanced hydroprocessing kinetic modeling technology to optimize the Celestia, Nebula and supported NiMo catalyst load splits and locations. The unit's pretreatment reactor was loaded with about 30% Celestia and Nebula. The Celestia deployment was a first application; Nebula had been part of previous reactor loads.

The addition of Celestia produced outstanding performance benefits for the unit:

- The feed rate of a highly challenging coker VGO was maximized during most of the cycle (Figure 6).
- The nitrogen slip from the pretreatment to the cracking reactor fell from 50–70 to 10–20 ppm.
- The unit conversion increased: the diesel and jet yields were higher (Figure 7).
- The product qualities improved, including the diesel cetane and the jet smoke point.
- The Celestia and Nebula bed temperature rise increased, which improved heat recovery and led to energy savings.
- The hydrocrackate quality was also significantly better and resulted in improved product yields and qualities when processed in the affiliate steam cracker.
- The stability of both Celestia and Nebula matched those of the supported catalysts. Consequently, the cycle length met the planned duration while maintaining high performance levels.

Conclusions

There are many ways for refineries to capture value by applying Celestia catalyst, see Figure 8.

Widen the crude diet envelope: Using Celestia catalyst provides the option to process more-challenging feeds in hydrocracking pretreatment without sacrificing unit run length through increased catalyst deactivation. This is also true for cracked stocks such as LCO or coker-derived feeds. Upgrading cracked stocks presents the opportunity for higher margins.

Making new products and blending opportunities: Applying Celestia can improve product quality and yields. It can provide additional feed saturation that leads to volume swell and increased yield, as hydrogen is converted into liquid products. Improvements in diesel cetane and related lower product aromatics are also possible, though the extent depends on the feed quality and the process conditions. Profitability arises from selling a higher-value product as a premium stock to a fuel blending plant or by a reduction in cetane improvement additives. In hydrocracking pretreatment, Celestia catalyst improves the conversion performance of the hydrocracking stage by

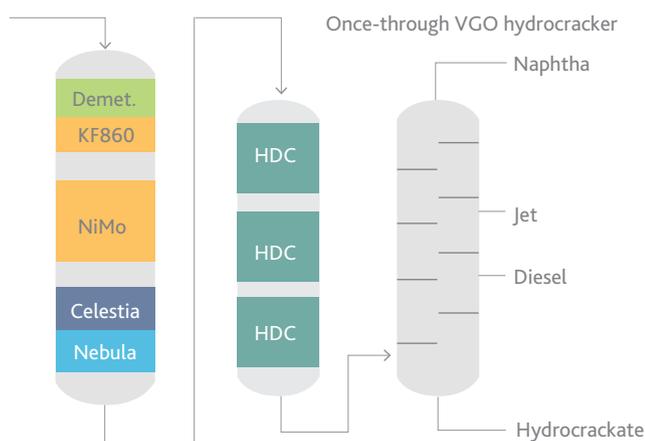


Figure 5: Loading diagram for Unit B.

	VGO BLEND FEED
Pressure, psi	2000 (138 bar)
Liquid hourly space velocity, h ⁻¹	1.8–1.95
(API) gravity	19–21 (0.928–0.940 kg/l)
Sulfur, wt%	1.8
Nitrogen, ppm	1600
Aromatics, wt%	52
Feed initial boiling point, °F	505 (263°C)
10%	676 (358°C)
50%	849 (454°C)
90%	995 (535°C)
95%	1050 (566°C)
Final boiling point, °F	1270 (688°C)

Table 3: Feed and operating conditions for Unit B.

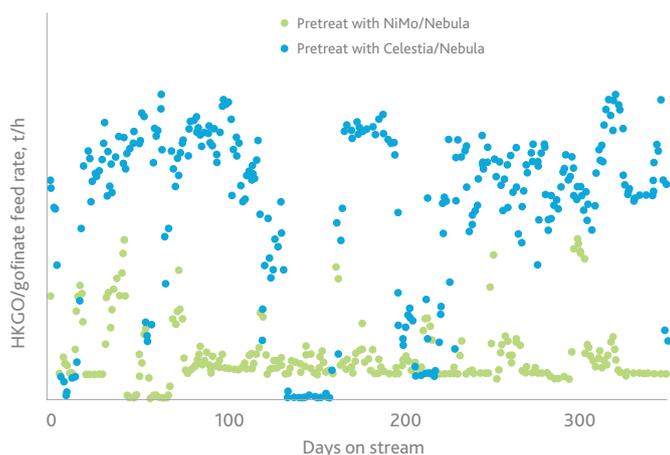


Figure 6: Comparing the feed rate of coker VGO in Unit B.

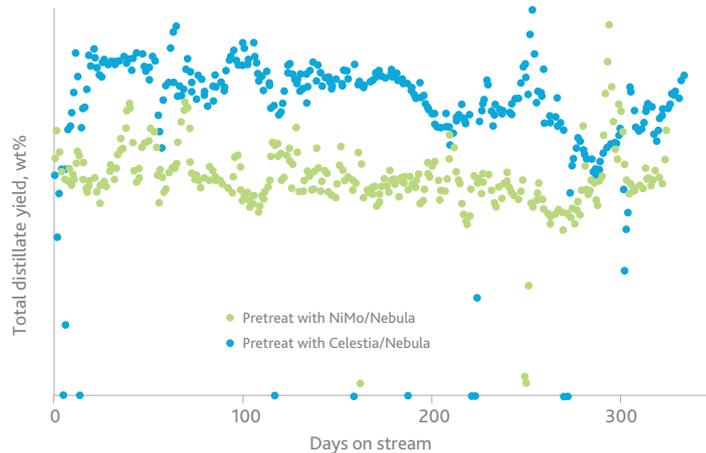


Figure 7: Comparing the yields of two different cycles in Unit B.

lowering the amount of organic nitrogen slip and the aromatic content in the feed to the hydrocracking catalysts. Added value is possible by tuning the hydrocracker operation to higher volume yields and more valuable products while simultaneously meeting cycle length targets.

Alignment of turnaround schedules:

The additional activity Celestia catalyst provides helps in managing the unit's run length to coordinate with the shutdowns in the overall refinery schedule. For improved efficiency, its cycles can be matched with wider refinery shutdowns to avoid units sitting idle. Typically, buying additional activity to increase a single unit's run length is not economically justified. However, the justification can change when non-optimum cycle timing affects other refinery units.

Energy efficiency: Celestia provides a higher exotherm compared with conventional catalysts because of its higher aromatic saturation ability and overall higher hydroprocessing activity. This resulted in a lower start-of-run temperature for the overall reactor and improved heat capture in the feed-effluent heat exchange system, both of which result in significantly less furnace firing.

In the 15 years since it was commercialized, Nebula technology has developed a reputation as an outstanding hydrocracking catalyst solution. With the introduction

of Celestia to the catalyst portfolio from Albemarle and ExxonMobil, the opportunities have become wider, more penetrative and more productive to enable new horizons in hydroprocessing capability and margin achievement. Whether what is required involves upgrading more-difficult and profitable feeds, producing products to meet increasingly stringent environmental standards or enabling higher product quality levels, Celestia's activity advantage makes it possible to transform a hydroprocessing unit and enable greater business profitability.

Bibliography

With permission, this article is based on three earlier publications:

- Wilson, K., Burns, L., Lingaraju, P. et al.: "Increased flexibility and profitability from new hydroprocessing catalyst," *PTQ* (Q1 2019)
- Leliveld, B., Slettenhaar, B., Burns, L. et al.: "Growing earnings in time of change: A case study in unlocking refinery-wide value through high-performance catalysts," paper AM-19-ISSUES presented at the Annual Meeting of the American Fuel & Petrochemical Manufacturers, San Antonio, TX, USA (March 17–19, 2019)
- Parker, D., Burns, L., Wilson, K. et al.: "Ultra-high activity for process gains," *PTQ Catalyst Supplement* (2019)

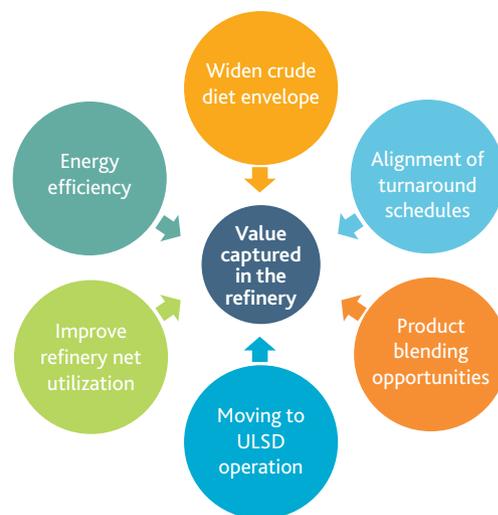


Figure 8: The potential benefits of applying Celestia catalyst.



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A pulsar is shown in space, emitting two powerful beams of light that sweep across the sky. The pulsar itself is a bright, glowing core surrounded by a swirling, blue and white accretion disk. The background is a dark, starry space.

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