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

The new member of Albemarle's bulk metal catalyst family

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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.

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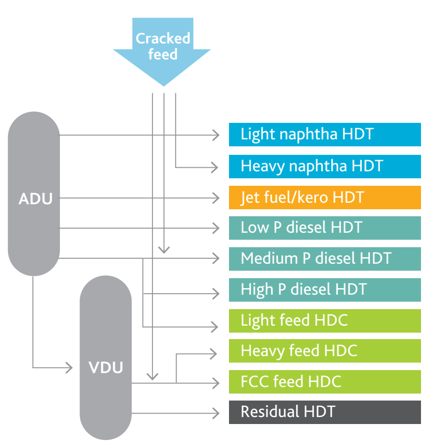

	Nebula	Celestia
Light naphtha HDT		
Heavy naphtha HDT	Commercialized	Applicable
Jet fuel/kero HDT	Commercialized	Applicable
Low P diesel HDT	N/A	N/A
Medium P diesel HDT	Commercialized	Applicable
High P diesel HDT	Commercialized	Commercialized
Light feed HDC	Commercialized	Commercialized
Heavy feed HDC	Commercialized	Commercialized
FCC feed HDC	Applicable	Applicable
Residual HDT	N/A	N/A

Figure 1: Applications of Nebula and Celestia.

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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-

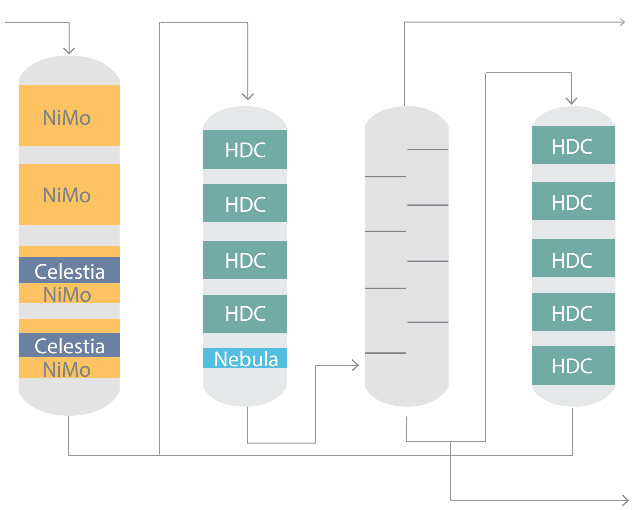

Figure 2: Loading diagram for Unit A.

	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.

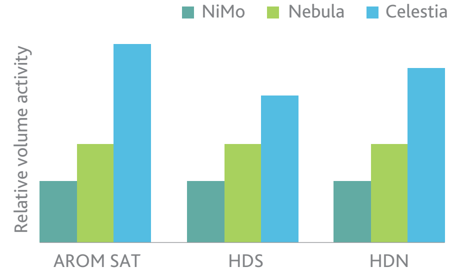

Figure 3: Activity overview of the different catalysts loaded in Unit A.

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 conversional 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.

"In every commercial application, Celestia catalyst shows an activity advantage up to three times that of conventional supported catalysts."

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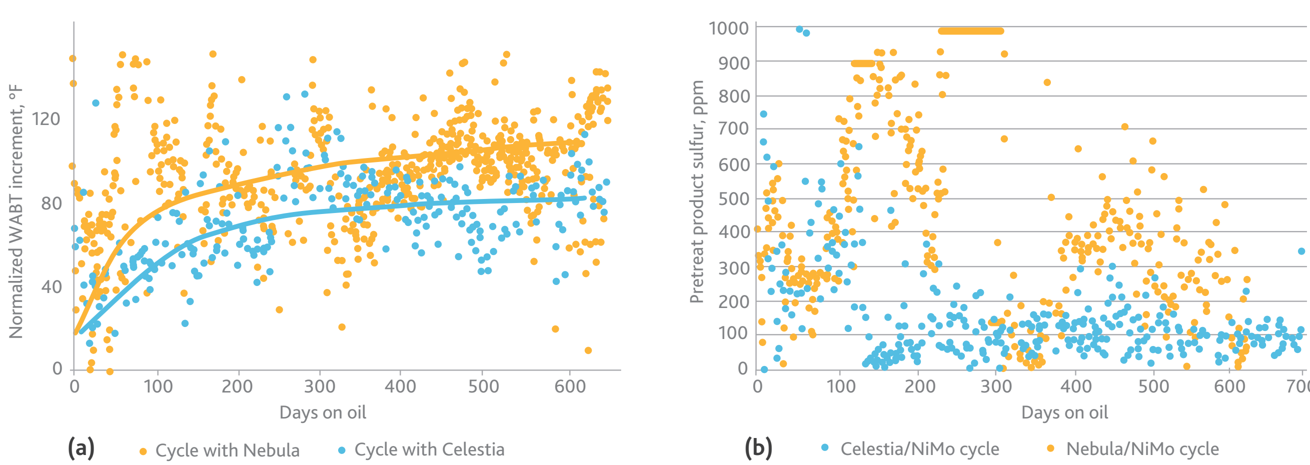

Figure 4: (a) Weighted average bed temperature and (b) product sulfur overview of two different cycles of Unit A.

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

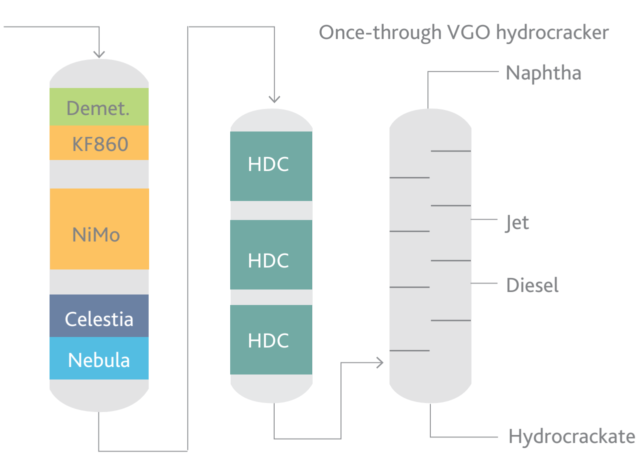

Figure 5: Loading diagram for Unit B.

	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.

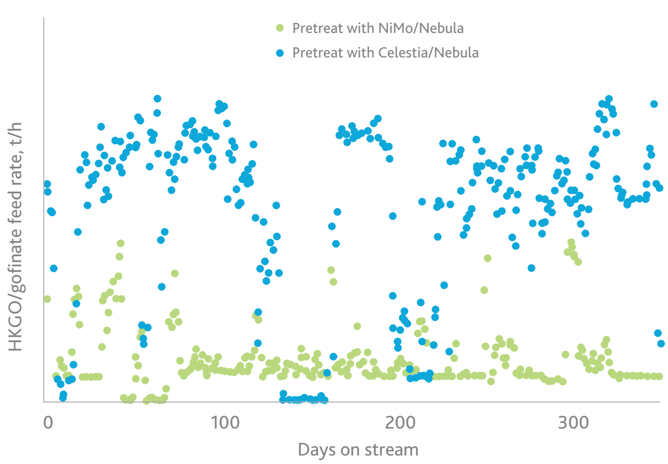

Figure 6: Comparing the feed rate of coker VGO in Unit B.

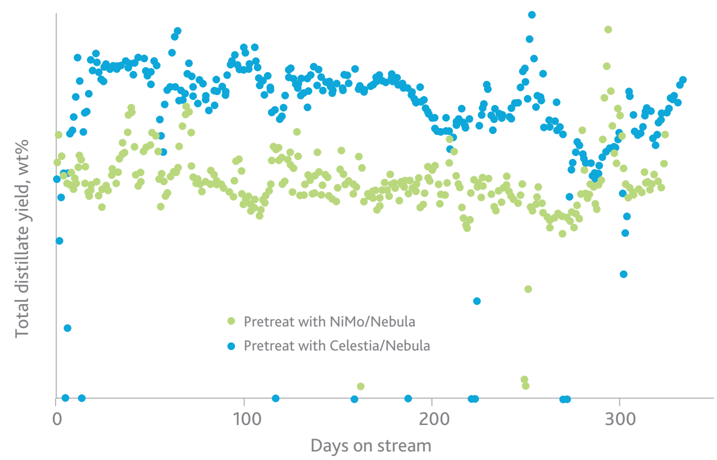

Figure 7: Comparing the yields of two different cycles in Unit B.

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:

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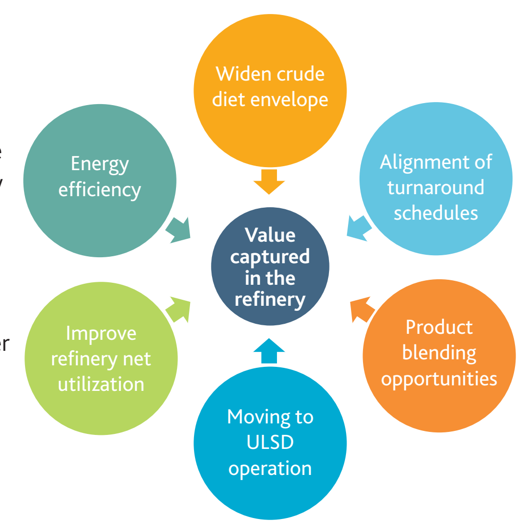

Figure 8: The potential benefits of applying Celestia catalyst.

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