

# Increased flexibility and profitability from new hydroprocessing catalyst

A new bulk metal catalyst enables upgrading more difficult feeds and delivering products to meet environmental standards and higher quality levels

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Refiners have faced, and will continue to face, numerous external challenges to maintain profitable operation. Four key focus areas for refiners to remain competitive include: maximising high value products, reducing feed costs, optimising capacity, and meeting more stringent regulations. Balancing these key factors is critical to achieving profitability. Employing leading edge hydroprocessing catalyst technology can improve profitability in all of these focus areas.

ExxonMobil and Albemarle, through a long-standing catalyst development partnership, have co-developed a breakthrough in hydrotreating catalysts. Built upon the success of Nebula catalyst, the partnership has commercialised Celestia, a new bulk metal catalyst that has demonstrated another step change in hydrotreating activity. Celestia's activity boost allows profitable processing of difficult feeds with higher end point, nitrogen and sulphur content, enables an increase in capacity, and results in volume gain via aromatic saturation activity. An added advantage of the new catalyst is creation of value beyond the hydrotreating unit. For example, the increased activity allows processing of heavier straight run feed that upgrades vacuum gasoil (VGO) into diesel, allowing resid imports to the FCC.

Over the last three years, ExxonMobil and Albemarle have deployed Celestia alongside Nebula and conventional catalysts at ExxonMobil sites around the world. Carefully designed combinations of Celestia, which has activity two to three times that of the conventional catalysts, were deployed in stacked configurations with Nebula. The combination lead to significant increase in the total activity in the reactor. Application of these technologies in distillate hydrotreaters, as well as light cycle oil (LCO) and VGO hydrocracker pretreaters, has yielded exceptional returns with some paybacks as low as four months. However, the key to extracting value from higher activity is to understand how the catalyst can be applied to unlock value through

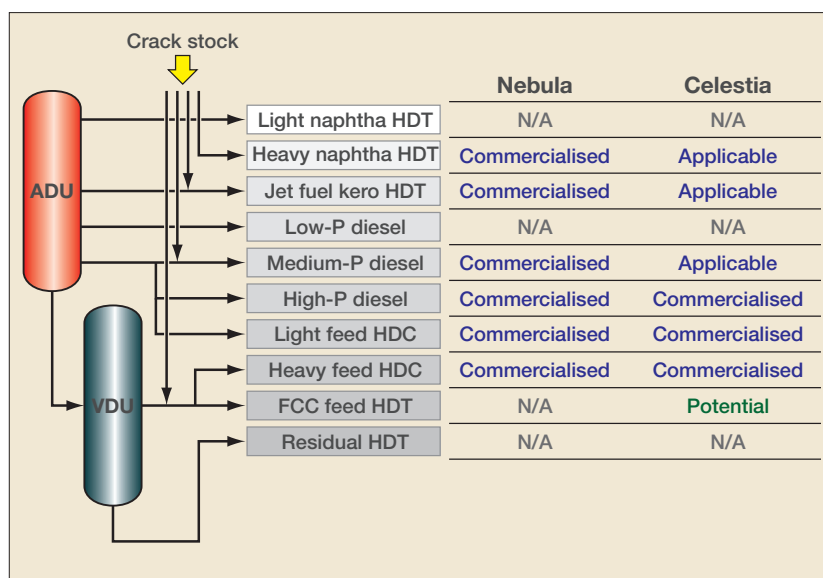


Figure 1 Applications of Nebula and Celestia

## Feed to LCO hydrocracker

| Cycle oil<br>(30-80% of feed) | VGO (balance<br>of feed) |
|-------------------------------|--------------------------|
| 2.5-4 wt% S                   | 1.2-1.7 wt% S            |
| 1000-1700 wppm N              | 160-325 wppm N           |
| 9-14 API                      | 26-30 API                |
| 695-715°F T95                 | 700-750°F T95            |

**Table 1**

integration. This article will present case studies to illustrate the properties and performance of Celestia, as well as show how ExxonMobil maximised margin improvement in a challenging environment in an LCO hydrocracking unit.

### Versatile solutions

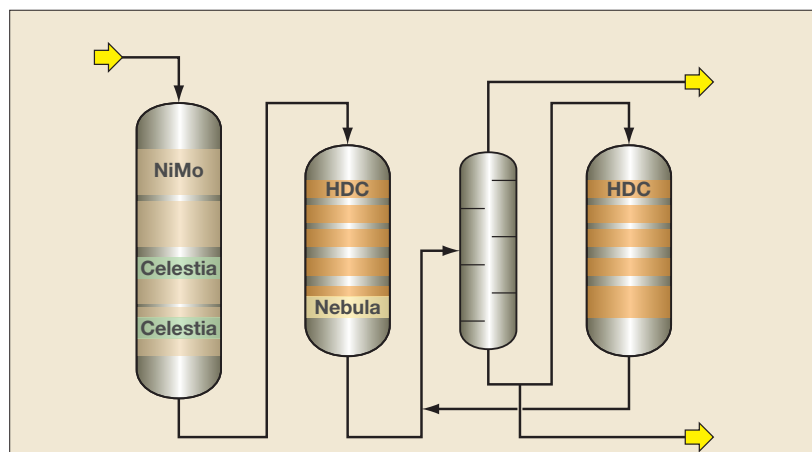
Celestia and Nebula are versatile catalyst solutions applicable to many hydroprocessing platforms, from naphtha to VGO. ExxonMobil and Albemarle have successfully commercialised Celestia in distillate hydrotreating, light feed hydrocracking pretreat, and heavy feed hydrocracking pretreat (see **Figure 1**). Each of its deployments to date have been based on carefully designed stacked catalyst load configurations with supported catalysts and/or Nebula at ExxonMobil operating refineries located in Europe, Asia-Pacific, and the Americas. The key to successful deployment is to combine detailed process chemistry, kinetic, and engineering knowledge with a detailed understanding of the economic needs of the refinery.

For process chemistry and kinetic understand-

ing, Albemarle's Stax technology for kinetic modelling relies on detailed understanding of the science behind hydroprocessing. Stax applies this knowledge to match catalyst functionality to the location in the hydroprocessing loading system. This technology enables detailed and optimised catalyst loads to be developed on a functional zonal basis, tailored to meet the refiner's objectives and feed types, and is applicable to flexible hydroprocessing platforms.

From a kinetic perspective, Celestia is most effective when used in high pressure applications. As such, initial commercialisation priorities have focused on hydrocracking pretreat and distillate hydroprocessing applications that benefit from operating at high hydrogen partial pressure. Given the very high volumetric activity, Celestia has been subject to extensive pilot plant testing to support expanding the technology's applications. Testing has confirmed that its improved performance also extends into the medium pressure range of hydrotreating applications.

Celestia has demonstrated significant base economic improvement, arising from upgrading more severe feedstocks, increased feed rate, increased conversion, improved product quality, and/or allowing new processing opportunities in both fuels and lube base stock service. The value has also come from how the high activity can impact adjacent units. More detailed discussions are listed in the following commercial applications. Further applications of the technology in stack configuration are planned for additional hydroprocessing platforms, including distillate hydrotreaters and hydrocrackers.



**Figure 2** Schematic with combination of hydrotreating (HDT) and hydrocracking (HDC)

### Case study: light cycle oil hydrocracking

Celestia has been commercialised in a North American LCO hydrocracker to provide an efficient, alternative way to upgrade LCO to on-spec transportation fuel. The key processing objective for using Celestia was to increase/debottleneck the unit feed rate, improve feed flexibility, and improve distillate yield and quality.

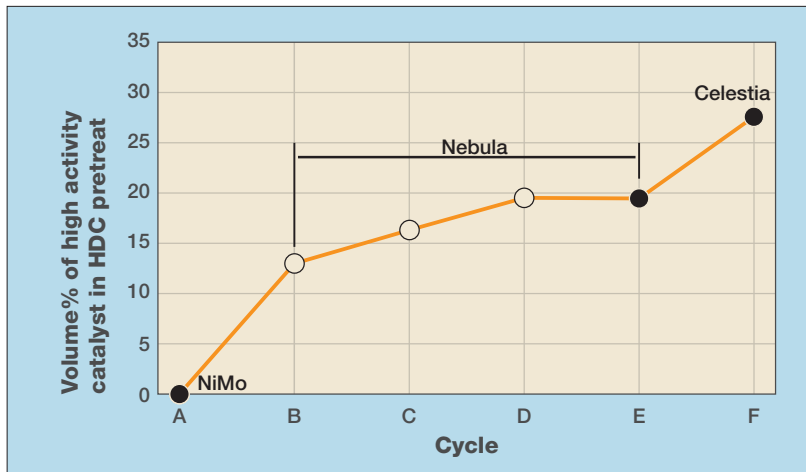
Both Celestia and Nebula were loaded in the unit, with

Celestia loading accounting for approximately 26% of the pretreat reactor catalyst load. The unit processes a blend of cycle oil and heating oil, with feed properties shown in **Table 1**.

**Figures 2 and 3** illustrate the Celestia and Nebula stack loading plan, and the progressive increase in using high activity bulk metal catalysts for hydrocracking pretreat over subsequent cycles. The success of bulk metal catalyst technology in this service has justified a steady increase in vol% of load from 13% Nebula to almost 30% Celestia/Nebula over five successive cycles and 18 years' profitable operation. Initially, this was done to mitigate the risk of adding a bulk metal catalyst given that Nebula was new to the market. However, ExxonMobil and Albemarle now have over 15 years of commercial experience on deploying and operating bulk metal catalysts. This led to ExxonMobil deploying the optimal amount of bulk metal catalyst in the unit.

The relative activity advantage of Celestia versus Nebula catalysts in LCO hydrocracking service is illustrated in **Figure 4**, showing breakdown of aromatic saturation (arosat), hydrodesulphurisation (HDS), and hydrodenitrogenation (HDN). This activity advantage is also apparent in the commercial performance, where the catalyst has delivered outstanding results in terms of challenged feed penetration, product yields, and product quality.

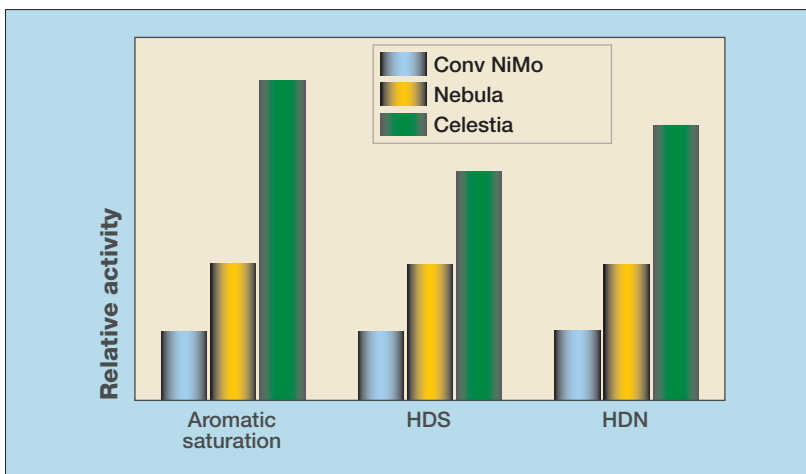
The step-out activity of the Celestia catalyst delivers value in a number of ways. Chief among them is processing greater quantities of more difficult feeds. The hydrocracking unit now processes heavier cycle oil from the FCC, achieved by increased LCO cut point to increase yield while decreasing FCC bottoms yield. The hydrocracker is able to produce on-spec ultra low sulphur diesel (ULSD) while



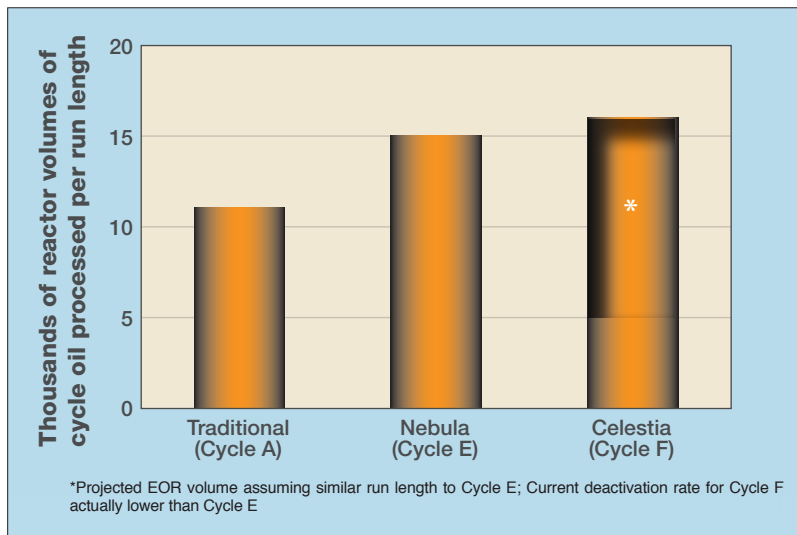
**Figure 3** Vol% of high activity catalyst in HDC pretreat vs cycle

processing a greater volume of deeper cut LCO from the FCC. In this particular case, the hydrocracker also processed more straight run VGO along with the LCO. **Figure 5** shows thousands of reactor volumes of cycle oil processed per run length. **Figure 6** shows the increase in the amount of reactor volumes of processed LCO per day. **Figure 7** shows that the total feed rate (LCO and VGO) is also increased in the current cycle.

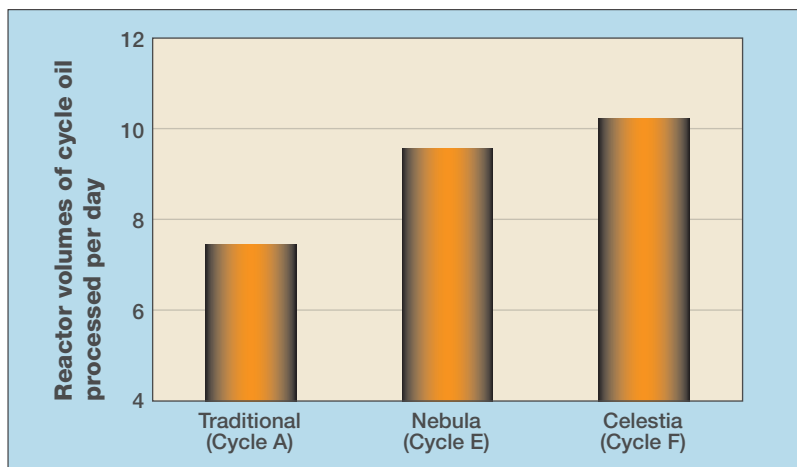
The concept of Nitrogen-BBL is the vol% concentration of nitrogen containing molecules in the feed multiplied by the volume of the feed. **Figure 8** uses this basis to compare the performance in the various runs and indicated that Celestia enabled the processing of more of the nitrogen containing molecules per day to enhance the hydrocracking functionality of the process unit.



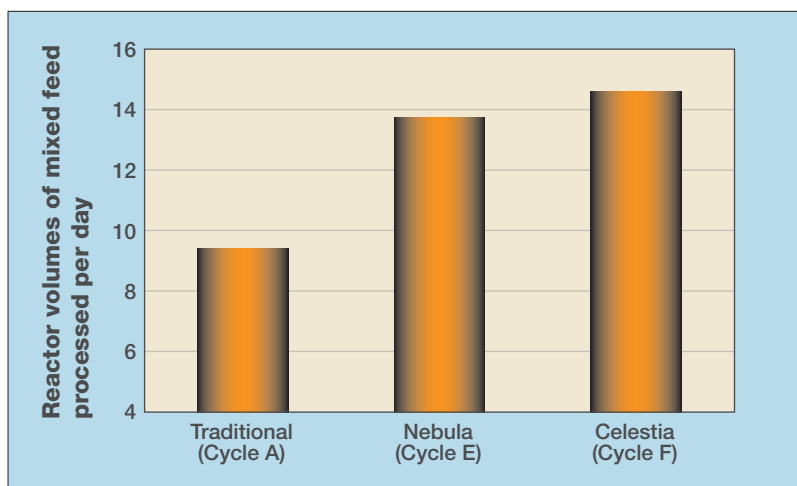
**Figure 4** Celestia activity advantage vs Nebula and conventional NiMo catalysts



**Figure 5** In a given cycle length Celestia enables the reactor to process more total feed



**Figure 6** Celestia enables processing an increased amount of LCO



**Figure 7** More mixed feed processed in Cycle F compared to other catalyst systems

**Celestia enables running difficult price-advantaged feeds**

| Feed Property | Delta (Cycle E F) |
|---------------|-------------------|
| API           | -1.8°             |
| Feed N        | +67 wppm          |
| T95           | +11°F             |
| T98           | +14°F             |

**Table 2**

**Figures 5 to 8 and Table 2** show that even when processing more difficult feeds with an increased endpoint of LCO, increased feed density, and an increased feed nitrogen content, Celestia's activity could go even further and increase the total feed rate at a constant nitrogen slip. The measured product sulphur in the diesel cut after the pretreat reactor was below the results of the previous cycle (see **Figure 9**).

Despite an increase in feed rate and feed severity, the normalised weighted average bed temperature (WABT) for Celestia is lower compared to two previous loads with Nebula (Cycles D and E). **Figure 10** shows the normalised WABT increment from the baseline, indicating that the deactivation observed for Celestia to be no different to previous cycles.

The economic drivers to process difficult feeds are highlighted in **Table 3**. It is notable that Celestia enabled a significant volume swell in addition to being able to process higher EP LCO. In this example, the payback from investment in this catalyst was less than four months with a sustained profitable operation for over four years.

Adding Celestia to the cata-

**Celestia pays for itself with a ~ four-month payback period**

|   |                     |
|---|---------------------|
| + | Cycle oil rate      |
| + | Straight run rate   |
| + | HDN                 |
| + | Opportunity feeds   |
| + | Arosat/volume swell |
| ~ | Four month payback  |

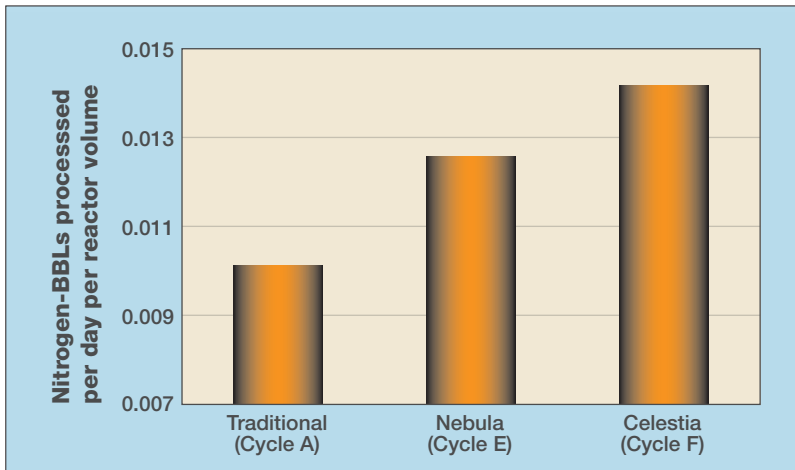
**Table 3**

lyst system led to a significant increase in aromatic saturation activity, with increases in heteroatom (sulphur and nitrogen) removal. Its deployment has been successful, with significant economic benefit, as described in the case study above, notably by the following metrics:

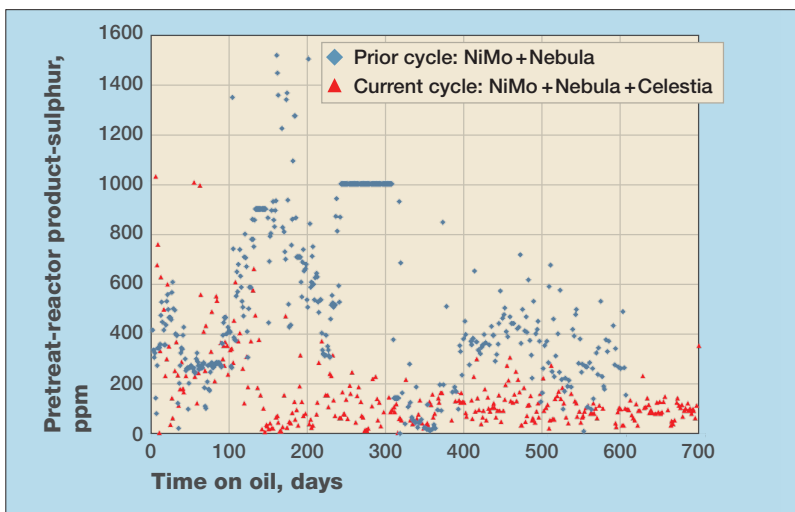
- Enabled processing of both greater feed rates and more challenging mixed feed
- Celestia increased total HDS activity in the pretreat reactor by over 30% versus prior cycle
- Celestia enabled a different unit operating strategy, with high HDS and HDN in pretreat allowing conversion severity in downstream reactors to be reduced, with increases in distillate yield
- Distillate product qualities were improved and significant volume swell achieved (a density uplift of close to 2°API)
- The Celestia stability has matched that of conversional supported catalysts located in the same reactor beds. Its activity stability has been maintained for over three years of operation.

**Case study: heavy feed hydrocracking**

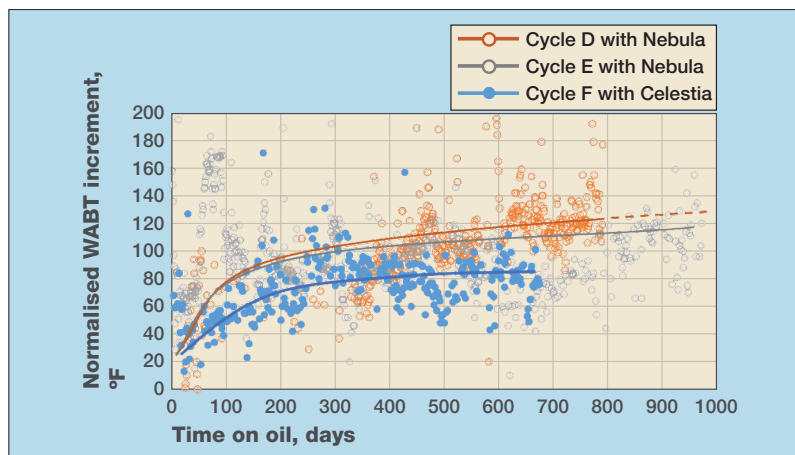
Celestia provides similar benefits as in the previous case on heavier feed compositions. A stacked load of Celestia



**Figure 8** Significantly higher amount of feed N processed with Celestia



**Figure 9** Sulphur slip in the output stream from the pre-treat section is significantly lower in Cycle F (current cycle) with Celestia compared to Cycle E (previous cycle) despite higher feed N



**Figure 10** Overall pre-treat WABT is lowest for Celestia operation

and Nebula was loaded into the pretreat section of a once-through heavy feed hydrocracker, processing a challenging blend of high endpoint virgin and coker VGOs to produce fuels and steam cracker feed. The volume load of Celestia and Nebula was evaluated to balance staying within the unit process and engineering constraints, while simultaneously ensuring the deployment generates an attractive return. The hydrocracker performance and economics were evaluated using advanced hydroprocessing kinetic modeling technology to optimise the Celestia, Nebula, and supported NiMo catalyst load splits and locations. The unit pretreat reactor was loaded with approximately 30% Celestia/Nebula. The Celestia deployment was a first application; Nebula had been part of prior reactor loads. The addition of Celestia produced high performance benefits for the unit.

- The feed rate of a highly challenging coker VGO was maximised during most of the cycle
- Nitrogen slip reduced from 50-70 ppm to 10-20 ppm
- Unit conversion increased with higher naphtha, diesel and jet yields
- Product qualities increased, higher diesel cetane and jet smoke point
- Higher heat recovery led to a reduction in furnace firing and significant energy savings
- The catalyst stability of both Celestia and Nebula matched supported catalysts, with cycle length meeting the planned duration while maintaining high performance levels.

### Considerations for implementing Celestia

High activity catalysts will result in higher bed heat release. Increased temperature rise can be mitigated by controlling the amount of Celestia loaded per bed and increasing quench gas flows above the Celestia bed to lower inlet temperature, or below the bed to lower the outlet temperature. Bed temperature rise can be trimmed by combining Nebula and Celestia in single beds. A combined load can be an optimum catalyst solution to maximise margin opportunity while meeting operating constraints. Alternatively, splitting the Celestia load between adjacent beds allows additional quench capability to manage the reactor heat balance.

Celestia delivers outstanding saturation functionality and, in particular, outstanding aromatic saturation activity. With increased saturation

activity comes increased hydrogen consumption. Assuring sufficient hydrogen availability and adequate make-up hydrogen compressor capacity is key to realising the performance improvements.

Celestia is heavier and therefore loads to a higher bulk density than conventional supported catalysts. Including it will increase the mechanical load on reactor internals such as catalyst support grid, associated beams, and outlet collector. Increased mechanical stresses should be evaluated prior to deployment.

Celestia is supplied as a 1.5mm diameter quadrilobe extrudate, with options for a 2mm diameter quadrilobe to be available shortly. The process pressure drop in a Celestia bed will be comparable to other supported catalysts of similar size and shape.

### Start-up and line-out comparable to support catalyst procedures

Despite Celestia's significant difference in activity to traditional catalysts, start-up and activation procedure is similar to supported metal oxide catalysts, with the objective of converting the oxides to the most active form, metal sulphides. The procedural steps required to activate the catalyst are similar to those commonly practised to activate supported catalysts. One notable difference is that the stoichiometric sulphur uptake required to adequately sulphide it is approximately double that for most supported catalysts. The increased catalyst sulphur uptake requires additional time to fully sulphide the catalyst. The Celestia catalyst activation procedure has been successfully commercialised in units utilising catalyst stacks comprising Nebula and NiMo.

The start-up procedure also conforms to industry standard practice to process virgin-only feeds and avoid high temperatures for the first three days on stream after activation has been completed. It is advisable to transition to processing highly reactive or high end point feeds in stages. Feed staging helps control early cycle heat release during the early line out phase. For VGO or other heavy feed blends, it may be advisable to stage the feed introduction, prioritising lower end-point feeds and finishing with highest end-point feeds. Feed staging VGOs is a means of protecting Celestia's highly active sites from excessive deactivation by de-edging the catalyst in a planned and measured process.



## Conclusion

Celestia catalyst in a carefully designed catalyst load offers multiple opportunities to maximise processing advantage. To fully exploit it, one must consider how to monetise the activity, not just in the unit but beyond the battery limits and even beyond the refinery boundary. Evaluating the catalyst should include meeting the needs of the individual unit, such as cycle length, product quality targets, feed rate, and so on. External advantage can often be more significant for operating economics, for example deconstraining crude selection, enabling improved fuels blending opportunities, and improved feed quality to export units often have significant advantages. Several key examples are:

- Celestia offers an ultra-high HDS/HDN/HDA catalyst activity that can enable a light feed hydrocracker to meet multiple performance targets. Increased HDS/HDN performance in the pretreat reactor can allow the process to operate in de-conversion mode by reducing the cracking reactor severity, leading to increased diesel/jet yield and improved product cetane. Improved cetane will change how the refinery can blend low cetane molecules into the diesel pool and could enable a higher diesel volume output from the refinery.
- Adding Celestia to a reactor can enable other catalysts such as de-met, arsenic trap or other margin improving components to be co-loaded without losing HDS and HDN functionality. Celestia offers the same benefit as having an extra reactor, or saving on the capital cost of adding an extra reactor.
- Hydroprocessing units that operate with seasonal diesel cloud point constraints can benefit by loading Celestia. Its high HDS and HDN activity can help to free up reactor space and allow a dewaxing process (like ExxonMobil's MIDW) to be incorporated into the same reactor.

A Celestia load can enable significant cycle length improvements when processing a given feed. A hydroprocessing unit turnaround for catalyst change is a complex and expensive planning process. Most units operate to a planned cycle length that coordinates with other plant shut-

down planning. Celestia processing capability can significantly extend a hydroprocessing unit run-time, and even eliminate a unit shutdown by allowing the unit to bridge to the next planning cycle.

Over the 15 years since it was first commercialised, Nebula technology has developed a reputation as an outstanding hydrocracking catalyst solution. With the introduction of Celestia to the catalyst portfolio from ExxonMobil and Albemarle, the opportunities have become wider, more penetrative, and more productive, enabling new horizons in hydroprocessing capability and margin achievement. Whether that involves upgrading more difficult and profitable feeds, producing products to meet the increasingly stringent environmental standards, or enabling higher product quality levels, with Celestia's activity advantage it becomes possible to transform a hydroprocessing unit and enable greater business profitability.

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