Criterion Catalysts & Technologies (Criterion) offers a broad range of zeolite catalysts to satisfy a variety of refinery hydrocracking objectives. We also provide the feed pretreatment catalysts that are vital to preserving the function of the main cracking catalysts.

Hydrocracking is replacing fluidised catalytic cracking as the refinery conversion process of choice. The reasons are simple: the shift from gasoline to diesel in many parts of the world; the flexibility of the hydrocracking process, which makes it relatively easy to alter the product slate to meet changing market demands; the ability of the process to make high-quality transport fuels, particularly ultralow-sulphur diesel, directly from difficult-to-process feeds; and, finally, the ease with which hydrocrackers can be integrated with ethylene crackers in the petrochemicals sector.

The performance of hydrocracking units is fundamentally dependent on the zeolite catalyst used to break down the heavier oil molecules. However, as feed quality generally declines, it is becoming increasingly common to find units whose performance, notably run length, is limited by the decline in activity of the feed pretreatment catalyst, the role of which is to protect the zeolite from harmful sulphur and nitrogen compounds and trace metals.

**Catalyst Selection**

We work closely with refiners to select the most appropriate hydrocracking and pretreatment catalysts to meet their individual process needs. This involves a detailed analysis in which reference will be made to feedstock quality; the desired product slate; the design of the hydrocracker and its normal operating regime; the amount of hydrogen available; and the target cycle length. Process modelling and pilot plant trials are part of the toolbox used to pinpoint the best catalysts for individual hydrocrackers and also to develop the most effective unit operating strategy.

**Technical Service**

Criterion customers benefit from the support of knowledgeable and experienced technical service engineers at every stage of the process cycle.

The technical support available to customers goes beyond advising on the selection of suitable catalysts. We routinely provide consultation during catalyst activation and, thereafter, we help customers with information as they seek to optimise the performance of their hydrocrackers. Using our Cat-Check knowledge management system, we can help them to build a clear picture of the way the unit is performing as the process cycle develops. This helps to customers to optimise operating conditions to best effect, understand process anomalies and troubleshoot any process problems quickly and efficiently. We are always looking for ways to provide information that will help to increase a unit’s profit margin.
HYDROCRACKER PRETREATMENT

Criterion is a global leader in hydrotreating catalysts and has a track record that stretches back for more than 50 years. Criterion catalysts can be currently found in about 850 hydrotreating units around the world used for product quality upgrading and hydrocracker pretreatment.

Over the past 10 years, we have continually pushed the boundaries of hydrotreating catalyst technology and raised hydrodenitrogenation (HDN) and hydrodesulphurisation (HDS) activity to ever higher levels (Figure 1). Our current hydrotreating offer is based mainly on two technology platforms: ASCENT (now in its second generation) and CENTERA. Both of these platforms can be used to formulate CoMo–alumina and NiMo–alumina catalysts; the former are best suited to low-severity feed operations and the latter come into their own with more challenging feeds, for example, with higher end points, more cracked fractions and higher metal and nitrogen levels.

ASCENT catalysts have a mixture of Type I and II active sites. They appeal to refiners seeking to strike the best balance between activity and hydrogen consumption; they are physically strong, which makes handling straightforward; and they are easily regenerated (>90% fresh catalyst activity) using conventional means.

CENTERA catalysts possess 100% Type II active sites and hence offer the highest possible level of activity. They are made using advanced techniques that result in excellent retention of activity (the active sites are locked into place), which provides refiners with outstanding operational flexibility.

Our most popular catalysts on each of these platforms are ASCENT DN-3551 and CENTERA DN-3620.

**ASCENT DN-3551**

A NiMo–alumina catalyst with a good balance of HDN and HDS activity and a relatively low hydrogen demand. Noted for its stable high-temperature performance, physical resilience and ease of conventional regeneration, DN-3551 provides an extremely tolerant, cost-effective pretreatment solution in many hydrocracking applications.

**CENTERA DN-3620**

Criterion’s flagship hydrocracker pretreatment catalyst; it has the highest activity and stability of any of our hydrotreating catalysts. It is also a NiMo–alumina catalyst but with 100% Type II active sites. It is the preferred choice in high-severity units running feeds with elevated nitrogen levels or high percentages of cracked or high-end-point stocks. The catalyst has class-leading performance and remarkable retention of activity. Refiners can exploit this last point in different ways to suit their individual operational objectives: to extend cycle lengths; to reduce the nitrogen slip to the cracking catalyst; to process tougher feeds; or, as less reactor volume is taken up by a more active and stable catalyst, to include additional catalysts in the pretreatment section with extra functionality.

**PROOF POINT: REFINERY IN THE USA**

The challenge posed by a refinery operator in the USA was to provide a pretreatment catalyst that would enable feeds containing up to 10% deasphalted oil to be cracked without reducing its three-year planned cycle length. We achieved this by using CENTERA DN-3620 to increase the HDN activity significantly in the lower part of the reactor so that the upper level could be loaded with a larger volume of the less active but more robust and highly tolerant ASCENT DN-3551, which essentially created an activity gradient within the reactor and maintained the same HDN activity as before. This system is enabling the refinery to process 8–10% deasphalted oil for the entire three-year cycle.
ZEOLITE HYDROCRACKING CATALYSTS

Criterion’s hydrocracking catalysts are made by Zeolyst International (Zeolyst), a joint venture formed in 1988 with silica and zeolite specialist PQ Corporation (Figure 2).

Research conducted by Criterion and Zeolyst has produced a series of hydrocracking catalysts recognised for their stability and good balance of activity and selectivity, which result in long run lengths and slow yield declines. Zeolyst catalysts are currently installed in more than 70 hydrocracking units around the world.

**High diesel (HD) series**

Designed for maximum diesel yield, our classic 500 series includes Z-503, which has been used widely in combination with HDN catalysts in hydrocracker pretreatment units to convert the most difficult nitrogen compounds more easily. Our step-out HD catalyst range is specifically designed to maximise the production of heavier distillates from more difficult feedstocks. This includes Z-HD10, which is designed for even higher diesel yield in second-stage reactors, and Z-HD11, which improves the properties of the unconverted oil products. State-of-the-art catalyst Z-2513 provides the same high diesel yield with even higher activity and, at the same time, improves the cold flow properties of the diesel.

**Middle distillate (MD) series**

Intended for use in maximum middle distillate (kerosene and diesel) applications, our classic 600 series includes Z-623 and Z-673, which combine intermediate activity with high selectivity to middle distillates. These catalysts are specifically designed to provide a constant high yield of kerosene and diesel with excellent product properties. They are also tolerant of the relatively unreactive molecules in recycled unconverted oil streams, as they require only low bleed rates to prevent longer-term deactivation and polyaromatic deposition. Z-MD10 is a stepout catalyst being developed to further increase middle distillate yield. State-of-the-art catalyst Z-2623 provides higher selectivity than Z-623 with even higher activity and, at the same time, improves the cold flow properties of the middle distillates.

**Flexible (FX) series**

For a flexible portfolio of naphtha and middle distillates, our state-of-the-art catalysts Z-3723 and Z-3733 supersede the classic 700 series and are specifically designed to convert heavy oil feedstocks into high yields of high-quality middle distillates with lower levels of gaseous by-products. Z-2723 provides the same high activity as Z-3723 with even higher middle distillate selectivity while improving cold flow properties. Step-out catalyst Z-FX10 maintains the high middle distillate yield of Z-2723 while improving the quality of the hydrowax normally sent to an ethylene cracker. Its advanced formulation enhances aromatics saturation and thus improves middle distillate yield, product quality and catalyst stability. This combination of properties makes the catalyst especially suitable for converting high-boiling-range feedstocks into high-quality diesel and jet fuel products in either recycle or once-through operations.

**Naphtha (NP) series**

Designed for maximum naphtha yield, our classic 800 series catalyst range includes Z-853, which is specifically designed to hydrocrack heavy oil feedstocks to produce high yields of high-quality naphtha and middle distillates in either recycle or once-through operations. Step-out catalyst Z-NP10 provides even more heavy naphtha product with reduced liquefied petroleum gas yield.

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**Figure 2:** Middle distillate selectivity (150–370°C) as function of activity at equal conversion in a series-flow application.
PROOF POINT: SHELL DEER PARK REFINING
Shell Deer Park Refining increased its profits by tens of millions of dollars after collaborating with Criterion, Zeolyst and Shell Global Solutions on a hydrocracker revamp. A new catalyst system, new reactor internals and a revised operating strategy improved the flexibility of the hydrocracker, thereby enabling it to swing between gasoline and distillate modes to take advantage of seasonal product demand shifts.

PROOF POINT: NORTH AMERICAN REFINER
A North American refiner replaced Z-853 with Z-NP10 in a series-flow hydrocracker. This was on the basis of the new catalyst’s relatively low production of C4- light ends. The refiner’s usual feedstock is 100% fluidised catalytic cracker cycle oil. In naphtha mode, the unit achieves up to 95% conversion based on a 204°C cut point. In kerosene/diesel mode, it achieves up to 70 vol% production of middle distillates based on a 177°C cut point.

PROOF POINT: A REFINERY OPERATOR IN THE NETHERLANDS
A refinery operator in the Netherlands was finding it very difficult to make its 19-month hydrocracker cycle target owing to loss of pretreatment catalyst activity, which was the result of deteriorating feed quality. At Criterion’s suggestion, the operator switched to CENTERA DN-3620. Once the unit had stabilised, the weighted average bed temperature data indicated that a 19-month cycle length would be easily achieved. On this basis, the operator decided to use the activity advantage to feed the unit with an increased proportion of heavier vacuum gas oil from the vacuum distillation unit.

PROOF POINT: CANADIAN HYDROCRACKER USED TO PROCESS SYNTHETIC FEED
The run length of a Canadian hydrocracker used to process synthetic feed was limited by the performance of the pretreatment catalyst. Pilot plant trials indicated that CENTERA DN-3620 would provide a 5°C increase in activity under the conditions in the unit. This was subsequently confirmed in the refinery hydrocracker, which is no longer limited by the performance of the pretreatment catalyst. The operator is using the improved activity to achieve a lower nitrogen slip to the cracking reactor to preserve the activity of the cracking catalyst and so extend the cycle length.

TECHNOLOGY LEADERSHIP
Criterion Catalysts & Technologies is an integral part of the Shell Global Solutions network of companies. This gives us a deep insight into industry needs and trends, and a strong feel for the business from the viewpoint of a major refinery owner and operator.

We also gain access to process modelling and optimisation technology targeted at refining applications, which is particularly valuable when it comes to more fundamental catalyst studies.

Most importantly, our strong links with Shell Global Solutions, a leading refinery technology licensor, facilitate genuinely integrated and customised hydrocracking solutions encompassing process design, reactor internals and catalysts, all three elements being of the same high standard.

• Shell Global Solutions provides technical support to over 50 refinery sites worldwide.
• It has signed 12 hydrocracking licences in the last five years.
• It has more than 60% of the hydroprocessing reactor internals market.
• Shell is one of the largest hydrocracker operators in the world, with its capacity of 512,000 bbl/d.

CONTACT US
For more information about how we can help you to enhance operational performance, meet increasingly stringent environmental regulations and increase revenues, visit us at www.criterioncatalysts.com.