Beyond ULSD

The economic incentive to produce diesel is substantial in today’s refining environment. While ultra low-sulphur diesel (ULSD) margins over heating oil and fuel oil have fallen off from their record highs, they are still encouraging refiners to maximise their diesel yield. Although the distillate hydrotreater (DHT) has traditionally not been a significant source of profitability within a refinery, the recent situation has changed due to a series of new business drivers, including the distillate supply/demand balance, cost of crude and clean fuels legislation. The global distillate market is expected to remain tight over the next few years, which will continue to encourage refiners to favour diesel production over gasoline. Thus, incentives to increase distillate volume will remain high, with additional volume coming from feeds that are traditionally destined for gasoline, heating oil or fuel oil product pools. Although redirecting heavy naphtha is a way to generate additional diesel barrels, a greater incentive exists to increase the endpoint of diesel streams or upgrade more FCC light cycle oil (LCO) from the heating or fuel oil pool into on-road diesel.

Since 2005, when Euro 4 ULSD specifications became effective, the value of diesel over lower quality dispositions has increased by a factor of 3–5 times (see Figure 1). Thus, there is considerable economic incentive to upgrade heavy diesel molecules or convert LCO into ULSD product now and for the foreseeable future.

The technical challenge, however, will be to maximise this volume while simultaneously meeting the increased fuel quality requirements, particularly the specifications for sulphur, boiling point, density, cetane and cold flow properties. The good news, and the subject of this article, is that ULSD can act as an enabler for further upgrading.

ULSD chemistry: good match with diesel upgrading

There are two key elements of ULSD that make diesel upgrading easier when compared with the older low-sulphur diesel (LSD) operation: a richer hydrogenation environment and a cleaner product that is devoid of most sulphur and nitrogen species. Both of these factors promote aromatic saturation, ring opening, isomerisation and cracking reactions.
This improved operating environment can then be leveraged in a number of different ways to capture a range of upgrading opportunities (see Figure 2). There are two key enablers for implementing these upgrading opportunities: high-activity ULSD catalysts and reactor process technology, both of which are required to implement the additional chemistries.

First key enabler: ULSD catalyst portfolio
A strong ULSD catalyst portfolio is a key enabler for upgrading diesel quality beyond the sulphur specifications. A robust, flexible and high-performance ULSD catalyst portfolio provides four key elements that enable upgrading reactions:

- Maximises activity to reduce the volume of catalyst necessary to achieve ULSD targets, freeing up reactor volume for other upgrading catalyst system options
- Provides a range of CoMo and NiMo catalysts to control hydrosulphurisation (HDS), hydrodenitrogenation (HDN) and ASAT in feed preparation for upgrading catalyst systems
- Offers the flexibility to modify hydrogen consumption to offset hydrogen requirements associated with additional upgrading requirements

![Figure 2 ULSD enables upgrading chemistries](image_url)

![Figure 3 Criterion DHT/ULSD catalyst portfolio performance history](image_url)
- Provides a flexible set of products that can be presulphurised, activated and regenerated to meet unit process requirements, as well providing attractive multi-cycle economics.

Criterion’s ULSD portfolio added a third generation of catalysts in 2008–2009, representing advances in Ascent and Centera technologies. These two developments, Ascent Plus and Centera, provide a sizable increase in ULSD performance in both CoMo and NiMo catalysts compared with the first- and second-generation catalyst technologies (see Figure 3).

These catalysts enable the production of ULSD in a reactor volume that is only 60–75% (~10–15°C more activity) of that required for the first-generation ULSD products. The Centera products in particular provide an opportunity to reduce ULSD catalyst requirements into a smaller volume, freeing up space to utilise other upgrading catalysts in the same reactor system. Both the CoMo DC-2618 at a lower operating pressure and NiMo DN-3630 at a higher operating pressure offer a gain in activity (see Figure 4).

Refiners who designed their ULSD units with first-generation products can take advantage of the additional activity to increase run length or upgrade more diesel, by processing tougher feeds or just more barrels. This additional upgrading can be accomplished by reducing the ULSD catalyst volume in a multi-bed reactor, thus freeing up space for upgrading catalysts in the latter beds (see Figure 5). This article will discuss the latter subject of generating more diesel, upgrading poor-quality feeds or producing a higher-value diesel product.

**Second key enabler: reactor process technology**

Implementing additional chemistries requires proper control over the reaction environment, which in many cases requires much finer control over gas and liquid flows, as well as reaction temperatures, given that they may be different from normal ULSD operations. In fact, if proper mixing and redistribution do not occur, there can be a detrimental impact on the catalytic environment, which can reduce product quality or degrade yields.

The performance of such reactors is not only determined by the loaded catalyst but also to a large extent by the design of its internals. In the last 15 years, there has been considerable attention on the issue of
distribution in a two-phase flow environment: insufficient distribution of gas and liquid inside the reactor leads to under-utilisation of the catalyst and local hot spot formation. This has detrimental effects on catalyst cycle length, product quality, unit reliability and process safety.

There are a number of reactor internals designed by Shell Global Solutions that contribute to the distribution and utilisation of the catalyst bed (see Figure 6). These include the liquid distributor (HD tray) and quench assembly (Ultra Flat Quench or UFQ), both of which address maximum contacting of liquid and gas with the catalyst, with uniform temperature control of both phases.

Shell Global Solutions’ HD trays have been able to improve the performance of units by effectively distributing gas and liquid over the catalyst bed. Besides the HD tray, the UFQ has been used for higher severity applications such as ULSD and hydrocracking units, which have a large heat release and require large temperature changes from bed to bed.

Typically, the temperature increase per bed is limited to 30–40°C and the bed length to 3–6m for hydrocrackers and 10–12m for hydrotreating units. Quench zones are positioned between beds, facilitating the addition of quench gas and/or liquid to the reaction medium. Traditionally, cold quench hydrogen is introduced to drop the reaction temperature, improve product quality and reduce catalyst deactivation. Increasingly, cold liquid quenches are applied that have a higher heat capacity and thus more easily lower the reactor temperature while not increasing the (gas) compression cost. However, this is at the expense of an added quench oil pump. The choice between gas and liquid quench is mainly dictated by the availability of a quench stream, the overall economics of the process, and the specific product quality and production requirements. In a few cases, a combination of both a gas quench and a liquid quench is applied.

In all cases, quench internals such as the UFQ are required in the interbed in order to:

- Thoroughly mix a hot process stream with a cold quench stream
- Remove any radial temperature and concentration maldistribution in the liquid and gas entering from above
- Distribute the gas and liquid streams evenly over the subsequent catalyst bed below.

The UFQ concept is based on separate mixing of the gas and liquid phases before contacting of the two phases is executed. It is a patented design, where gas-gas and liquid-liquid interactions are first effected separately to provide equilibrated gas and liquid phases that are homogeneous.

UFQ combines the advantage of impingement technology for liquid mixing with the
efficiency of vortex technology for gas mixing. The benefits can best be demonstrated by looking at a more extreme example of managing heat release. A Shell-licensed hydrocracker commissioned in April 2009 operates in once-through mode at 85%. The reactor has six catalyst beds and, since start-up, the unit has experienced stable radial temperature gradients. Radial delta T values in the top of each bed are generally 3°C or lower, indicating good functioning of the UFQ and HD trays.

Figure 7 shows daily average radial ∆Ts measured over a period of two months for all the individual beds for the hydrocracker reactor. As seen in the figure, Radial ∆Ts for all individual beds is below 3°C, indicating good functioning of the UFQ system.

Upgrading options
Aromatic saturation
There are two (catalyst plus process) options for aromatic saturation (ASAT), and the choice of which one is better for a given situation depends on the degree of ASAT required (see Figure 8).

Single stage options
Base metal catalysts

<table>
<thead>
<tr>
<th>PNA conv., %</th>
<th>20-30</th>
<th>60-90</th>
<th>80-95</th>
<th>&gt;90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ASAT, %</td>
<td>0</td>
<td>0-30</td>
<td>20-80</td>
<td>40-90</td>
</tr>
</tbody>
</table>

Two stage ASAT
Base + noble metal catalysts

<table>
<thead>
<tr>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>80% SRGO/ 20% LCO</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>20% LCO</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>886</td>
</tr>
<tr>
<td>Sulphur, wppm</td>
<td>14 520</td>
</tr>
<tr>
<td>D-86 T-90, °C</td>
<td>347</td>
</tr>
<tr>
<td>PNA, wt%</td>
<td>19.0</td>
</tr>
<tr>
<td>Total aromatics, wt%</td>
<td>36.5</td>
</tr>
<tr>
<td>Cetane number, CN</td>
<td>44.0</td>
</tr>
<tr>
<td>Delta CN</td>
<td>4.5</td>
</tr>
<tr>
<td>H₂ consumption, Nm³/m³</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1
The first option is relatively new in practice, in part because ULSD pretreatment chemistry and catalyst improvements have enabled ASAT to progress much further than in the earlier LSD (300–500 wppm sulphur) era. As the hydrogenation environment improved for ULSD, PNA conversion increased to 60–90%, depending on the unit pressure and catalyst system employed. The difficulty in LSD operations, however, was that there was no appreciable conversion of mono-aromatics. Now, with a base-metal hydrogenation catalyst such as Centinel Gold DN-3330 combined with new process hardware provided by Shell Global Solutions, improved ASAT can drive total aromatics conversion above 50% in the single-stage process configuration (see Figure 5).

Enhanced aromatics saturation (EAS) involves utilising a bed or two of a multi-bed ULSD unit for ASAT. In this scenario, all or most of the HDS and HDN reactions occur in the lead beds of the reactor. The low levels of organic sulphur and organic nitrogen in the latter beds of the reactor create an environment that is favourable for ASAT to occur. The ULSD is then processed in the latter beds to meet targets for cetane, density and aromatics content. This allows a portion of the reactor to be operated in a temperature range that is favourable for ASAT, which maximises ASAT and the product property improvements associated with it throughout the catalyst cycle. This is illustrated as the ASAT sweet spot in Figure 9.

The EAS concept can be demonstrated on the pilot scale by examining some SOR pilot plant data. When a second-generation ULSD catalyst such as DN-3330 is applied at the same SOR conditions as a first-generation product such as DN-3110, a significant improvement in ASAT and associated product properties is observed (see Table 1).

There are several units operating in North America with Centinel Gold DN-3330 in this multi-bed configuration, using the EAS mode of operation to maximise the LCO content to the ULSD pool.

In the commercial example shown in Table 2, the refinery’s challenge was to process all of its LCO over the course of the entire cycle. In a typical ULSD operation, the unit will begin to lose hydrogenation activity throughout the cycle, particularly during the second half of the cycle. Noticeable developments include a drop in hydrogen consumption, \( \Delta T \) and subsequent degradation of key product properties such as density, boiling point, aromatics and cetane as the cycle progresses past the midpoint.

<table>
<thead>
<tr>
<th>Property</th>
<th>Feed origin</th>
<th>Product (LCO/hydrotreated - 55/45 (vol basis))</th>
<th>Feed-prod or % Delta or conv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m³</td>
<td>922.9</td>
<td>872.6</td>
<td>50.3</td>
</tr>
<tr>
<td>Cetane index</td>
<td>28.0</td>
<td>37.9</td>
<td>9.9</td>
</tr>
<tr>
<td>ASTM D-4737A</td>
<td>24.31</td>
<td>0.92</td>
<td>96%</td>
</tr>
<tr>
<td>UV aromatics (wt% arom C)</td>
<td>36.16</td>
<td>15.37</td>
<td>57%</td>
</tr>
<tr>
<td>PNA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillation D-2887 (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 wt%</td>
<td>209</td>
<td>196</td>
<td>13</td>
</tr>
<tr>
<td>50 wt%</td>
<td>275</td>
<td>257</td>
<td>18</td>
</tr>
<tr>
<td>90 wt%</td>
<td>344</td>
<td>330</td>
<td>14</td>
</tr>
<tr>
<td>95 wt%</td>
<td>358</td>
<td>351</td>
<td>8</td>
</tr>
</tbody>
</table>

*Max reactor temperatures of 375°C
Since the unit was designed around a high-activity HDS/HDN system using DN-3330 catalyst and also incorporated a gas/liquid quench capability using UFQs in the latter beds, it has been able to operate in EAS mode at the point in the run where hydrogenation activity would normally drop off. The unit is able to maintain a high level of product upgrading even when some reactor temperatures are high enough to normally suppress aromatic saturation, hydrogen consumption and subsequent product quality improvement (see Table 2).

The ultimate benefit for this EAS mode of operation is to keep all the LCO in the refinery ULSD pool, thus generating €3M/yr in upgrade of ~10 m³/hr of LCO. This unit has been successfully achieving ULSD while processing all of the LCO produced in the refinery for five years.

Two-stage deep aromatic saturation

Two-stage ASAT technology, indicated as DAS for deep aromatic saturation, has been in commercial practice for diesel upgrading for at least 20 years. The most common applications to date have been for the production of Swedish diesel (5–10 wt% aromatics) and California CARB diesel (10–20 wt% aromatics).

Typical requirements for the first-stage operation are to prepare a ULSD feedstock for the second-stage noble metal catalyst system. Since the noble metal catalyst can be poisoned by H₂S and NH₃, these by-products are removed in an inter-stage stripper, and the stripped liquid is recombined with clean treat gas to complete the aromatic saturation reactions (see Figure 5).

Noble metal systems result in a high level of ASAT, even for mono-aromatics. The amount of LCO upgrading via this type of operation is limited only by the aromatic precursors in the feed and the H₂ supply of the unit. An extreme example using 100% LCO feed is shown in Table 3. Special consideration would need to be given to this operation because of the high hydrogen consumption and subsequent heat release/∆T for this high aromatics conversion operation.

Table 3

<table>
<thead>
<tr>
<th>Operating mode</th>
<th>2 stage</th>
<th>100% LCO</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure</td>
<td>Medium</td>
<td>960</td>
<td>859</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>7300</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Sulphur, wppm</td>
<td>79.1</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Total aromatics (FIA), vol%</td>
<td>24.1</td>
<td>40.2</td>
<td></td>
</tr>
<tr>
<td>Cetane index, D-976</td>
<td>&lt;20</td>
<td>44.9</td>
<td></td>
</tr>
<tr>
<td>Delta CN</td>
<td>25+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid yield, vol%</td>
<td>115.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ consumption, Nm³/m³</td>
<td>475</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An advantage of two-stage ASAT units is that they can be designed for low- to moderate-pressure operation. The major disadvantages are that they are more complex than single-stage operations and are hydrogen intensive.

Selective ring opening

A means of upgrading diesel product quality that is more hydrogen efficient than ASAT is via selective ring opening (SRO), which not only can provide improved diesel product quality (density, aromatics, cetane) but also a distillate-selective reaction pathway. By delivering on all three of these benefits — H₂ consumption, product quality, and operational simplicity — SRO technology has emerged as a leading technology for diesel upgrading.

Figure 10

Figure 10 Effect of selective ring opening on aromatics conversion
efficiency, improved quality and diesel selectivity — SRO provides a very economically attractive upgrading route.

The SRO chemistry is enhanced by the clean nature of the ULSD product. Catalyst acidity is carefully controlled to avoid full hydrocracking, which would result in an excessive distillate yield shift to naphtha. Utilising SRO for cetane enhancement results in some shift of distillate to naphtha. The naphtha yield (or distillate yield loss) in SRO applications depends on the catalyst system employed (the amount of SRO catalyst required), feed properties, process conditions, unit quench capabilities and so on. Like EAS, SRO catalysis can occur in a single-stage reactor system, since base metal reaction promoters are typically used. The multifunctional catalysts used in the SRO system permit some naphthenic molecules to exit the reversible aromatic saturation loop via conversion (see Figure 10), increasing the overall conversion, particularly in operating regimes that can be limited by thermodynamic equilibrium, such as EOR conditions.

Thus, the SRO catalyst systems can deliver comparable cetane at reduced hydrogen consumption (see Figure 11) and are less sensitive to EOR conditions where hydrogenation conditions deteriorate.

SRO catalyst systems can deliver the required density, aromatics and cetane at ~10% lower overall H₂ consumption (see Figure 11) and are less sensitive to EOR conditions where hydrogenation conditions deteriorate.

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putting 25–30% LCO into the overall pool, maximising upgrading for density and cetane improvement in their moderate- to high-pressure ULSD units, which have been adapted with SRO catalyst systems. In the commercial operation shown in Table 4, the refinery is able to put all the LCO it produces into one of its ULSD units, and meet the overall cetane and density requirements, while minimising overall H₂ consumption.

SRO will also be very useful for applications in Europe and Asia, helping to incorporate more LCO in a constrained hydrogen environment. SRO catalyst systems are a drop-in solution for distillate cetane and density improvement in H₂-constrained units. However, the product separation capabilities of any unit where SRO catalyst application is being considered must be evaluated to ensure the additional naphtha and light ends production can be managed.

**Mild hydrocracking**

With sufficient operating pressure and hydrogen availability, mild hydrocracking (MHC) of diesel feed components to gasoline can provide an opportunity to upgrade the quality of the diesel product, as well as an operating flexibility to capture any shifts in diesel and gasoline margins. MHC is different from full hydrocracking in that conversion objectives are much lower.

The first benefit of MHC is to selectively convert the poly-aromatics to gasoline boiling-range product, demonstrated by the reaction chemistry shown in Figure 12. These primarily di-aromatic molecules are partially saturated in the ULSD portion of the reactor, and are then cracked to mono-aromatic naphtha boiling-range molecules.

From the product diesel perspective, this is a selective way to remove the worst molecules and generate a much higher quality product. This can be seen in Table 5, where significant incremental improvement in aromatics, density and cetane can be achieved with ~10% naphtha production. This table compares the upgrading possible with a conventional ULSD solution (NiMo catalyst) and a MHC ULSD solution when processing a feedstock that contains LCO. This MHC option is designed to be different to SRO in that naphtha production is desired and diesel/naphtha yield is controlled.

Ultimately, while this catalyst system could be considered a drop-in solution, the product separation equipment must be evaluated to ensure the additional naphtha and light gases (C₇-C₁₀) produced can be accommodated. Other considerations should be given to make-up and treat gas requirements, and quench capabilities to best manage the additional heat release associated with the conversion reactions. Several of these units have been built or revamped to meet both the regional sulphur requirements for ULSD as well as to maximise the LCO upgrade to clean fuels production.

**Cold flow improvement via catalytic dewaxing**

At low temperatures, products with waxy components start to crystallise and affect the flow characteristics of the product. To avoid problems of fuel supply to an engine or lubricating problems under low-temperature conditions, diesel fuels and lube oils often have stringent specifications on flow properties at low temperature. To ensure the various products meet low-temperature flow properties, three main cold flow property specifications are used. Pour point (PP) is mainly used for base oils specifications. Cloud point (CP) and cold filter plugging point (CFPP) are usually used for diesel fuels.

PP is measured by ASTM D-97 and is the temperature at
which a sample can just be poured (just pumpable) when it is cooled down under standardised conditions. This point is 3°C above the temperature at which sufficient wax has crystallised to prevent normal flow of the sample.

CP is measured using ASTM D-2500 and is the temperature at which the first crystals of wax (usually linear alkanes) appear when a sample is cooled under standard conditions.

CFPP is measured by IP309 and is the temperature at which sufficient wax has crystallised to block a specified filter when a sample is cooled down under standard conditions in specific equipment.

The so-called waxy components responsible for the cold flow properties of diesel for transportation and heating oil for domestic and industrial applications be maximised, while yield losses are minimised during the summer season when cold flow improvement is less important or not required. Small amounts of cold flow improvement additives can reduce CFPP and PP significantly. However, CP cannot be significantly improved using additives. CP improvement with additives is typically a maximum of 5–7°C. Kerosene can be blended with diesel fuels to improve CP without additives. Typically, a CP improvement (reduction) of ~1°C is achieved for every 10 vol% kerosene blended. PP improvements of ~3°C are achieved for every 10 vol% kerosene blended. If CP is the defining cold flow specification, dewaxing is often necessary. In general, if a CP improvement >5–7°C is desired, catalytic dewaxing is a more economic solution than additives/kerosene blending.

The main drivers for implementing catalytic dewaxing are:

- Achieve cold flow property specifications
- Avoid expensive cold flow improvement additives
- Reduce kerosene blending
- Process heavier (higher CP/PP/CFPP) feedstocks
- Process waxy crudes
- Co-process biodiesel feedstocks to produce renewable diesel.

In catalytic dewaxing processes, the normal and slightly branched alkanes are removed either by selective cracking to lighter products (selective cracking dewaxing) or by selectively isomerising n-alkanes and further isomerising slightly branched alkanes to lower melting point isomers (isomerisation dewaxing). Shape-selective catalysts are used in these processes. These catalysts have physical properties that allow straight-chain and slightly branched paraffins to enter their pores...
and be converted while excluding other molecules. The isomerisation-dewaxing process has the intrinsic advantage of minimal yield loss of distillate boiling-range material into light products (naphtha and C_7-C_4 gases) compared with selective cracking dewaxing.

Shell Global Solutions and Criterion have developed selective cracking (SDD-800) and isomerisation (SDD-821) dewaxing catalysts. Both of these catalysts have extensive commercial experience. SDD-800 is a shape-selective catalyst developed for single-stage dewaxing applications and is tolerant of H_2S and NH_3. This makes catalyst loads utilising SDD-800 a drop-in option for ULSD units. A typical single-stage dewaxing operation is shown in Figure 13. The hydrotreating (HT) catalyst selection is based on catalyst cycle length, HDS requirements, HDN requirements, H_2 consumption limitations and other unit performance requirements/limitations. SDD-800 has a mild cracking function to selectively convert waxy molecules.

The cracking function results in a slight decrease in distillate yields. SDD-800 is formulated to minimise naphtha and light gas production in selective cracking dewaxing. Diesel yield/selectivity is a critical performance parameter for selective cracking dewaxing catalysts. During summer periods, when no dewaxing is required, the dewaxing bed can simply be switched off by quenching the dewaxing bed. In Figure 14, the distillate yield as a function of CP improvement is shown for SDD-800 and a conventional selective cracking dewaxing catalyst.

In the typical CP improvement range, the diesel yield achieved with SDD-800 is 5–10 wt% higher than conventional selective cracking catalysts at constant CP improvement (ΔCP). In an economic environment that favours diesel over gasoline, this is a substantial benefit.

SDD-821 is a second-stage ultra-selective noble metal
isomerisation dewaxing catalyst designed/formulated to maximise distillate yields. SDD-821 is a noble metal catalyst and must be used in the second stage of a two-stage operation to ensure a low-sulphur and low-nitrogen environment. The primary advantage of two-stage isomerisation dewaxing over single-stage selective cracking deactivation is a higher diesel yield. An example of a two-stage isomerisation dewaxing unit is shown in Figure 15.

A comparison of the yields from single-stage operation with SDD-800 and two-stage operation using SDD-821 is shown in Table 6. This comparison was made using the same feedstock and target CP improvement (20°C).

There are substantial distillate yield and cetane advantages with the two-stage operation. While these advantages are significant, they come at the cost of greater unit complexity, higher H₂ consumption and higher catalyst costs. The two-stage approach is usually impractical in a single reactor unit. This makes single-stage dewaxing more practical as a drop-in solution for existing units. Note that the results for an individual unit depend strongly on feed properties, operating conditions and catalyst system.

### Commercial example combining multiple upgrading options

One refiner faced a challenge in which several low-quality streams required upgrading to meet a series of “beyond ULSD” product qualities across two different operating modes.

In sulphur-only ULSD mode, the unit processed mostly LCO with some LVGO (see Table 7). In upgrading mode, additional straight-run streams were added. The challenge of the upgrading mode was to also satisfy jet fuel smoke point specifications, as well as diesel cetane and cold flow properties.

The solution was to build a system that had a robust ULSD base catalyst system to reduce sulphur and prepare feed for further upgrading, adding catalysts to accomplish the kero/jet smoke point improvement, cetane upgrade and cold flow improvement. Pilot plant testing was conducted to validate catalyst system capabilities. In addition, a process configuration was selected to permit the right control of properties for the two modes of operation. The result was a single-stage operating configuration (see Figure 16).

This configuration allows most of the work in the ULSD mode to be accomplished by the first two beds in the first reactor, while the latter catalysts are turned off by managing both temperatures and product qualities coming out of the lead beds. This operation is very diesel selective and the resultant hydrogen consumption is low given the primary upgrading is for desulphurisation (see Table 8).

In upgrading mode, the lag beds are turned on, and the temperatures for dewaxing and MHC are independently adjusted to meet the three critical product quality parameters: jet smoke point, diesel cetane number and diesel cold flow properties (solidification point).

### Table 8

<table>
<thead>
<tr>
<th>Product properties for multi-upgrading example</th>
<th>ULSD mode</th>
<th>Upgrading mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yields, wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Naphtha</td>
<td>1.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Jet fuel</td>
<td>98.3</td>
<td>72.0</td>
</tr>
<tr>
<td>Diesel</td>
<td>101.5</td>
<td>102.2</td>
</tr>
<tr>
<td>Total (100+H₂ cons)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kero properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>816.3</td>
<td>816.8</td>
</tr>
<tr>
<td>Smoke point, mm</td>
<td>12.4</td>
<td>21.3</td>
</tr>
<tr>
<td>Diesel properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>844.4</td>
<td>832.1</td>
</tr>
<tr>
<td>Sulphur, wppm</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Solidification point, °C</td>
<td>0</td>
<td>-9</td>
</tr>
<tr>
<td>Cetane number</td>
<td>35.6</td>
<td>47.8</td>
</tr>
</tbody>
</table>

Figure 16 Single-stage ULSD/ dewaxing/MHC unit
As anticipated, the hydrogen consumption for this mode of operation is measurably higher than that of the ULSD mode, while the volume of clean products remains high during a period when much of the feed components would normally be downgraded because they could not meet product quality requirements.

This unit started up in 2002 and continues to operate with the original catalyst system to meet evolving upgrading needs. Of particular value has been the ability to deliver upgrading with a very efficient H₂ footprint using the MHC chemistries, measurably smaller than if ASAT was used to satisfy the jet smoke point and diesel cetane requirements, thus saving the refinery an estimated €1.6 million per year in H₂ costs alone.

This example illustrates how a ULSD unit design and operation can be expanded to include multiple added chemistries and provide improved flexibility to capture upgrading opportunities, making the return on this investment much more attractive.

Conclusions
In the past, LSD and higher sulphur-content distillates were not suitable for further upgrading without extensive additional treating to reduce organic sulphur and nitrogen levels. The clean nature of ULSD makes it an ideal platform for additional upgrading. Cetane, density, cold flow property and aromatics quality improvements are possible with drop-in catalyst solutions for existing ULSD units, capital project revamps and for the design of new units.

In addition to catalyst as an enabler for going “beyond ULSD”, reactor hardware and process technology improvements enable one or multiple upgrading chemistries to occur in a single-stage, moderate-pressure system, making this a cost-effective unit for producing clean distillate products. These combined catalyst and process options provide opportunities to improve refinery economics by capturing the margins for high-quality ULSD over lower-value fuels. Possible choices include, but are not limited to, the processing of heavier feeds, handling additional LCO and providing crude slate flexibility. For example, the economic incentive for upgrading LCO to ULSD is high, ranging from $3–5/b over gasoline to $20/b over low-sulphur fuel oil (LSFO). Raising the LCO rate by an incremental ~10 m³/hr can generate €3M/yr, thus easily justifying a change to capture these benefits.

The opportunities described in this article ranged from simple catalyst changes to capital project upgrades, and all of these options are currently being practised. These commercial examples clearly demonstrate how refiners have implemented solutions to build flexibility into this ULSD asset, making it an engine driving opportunities to improve profitability in any economic climate.

ASCENT and CENTERA are marks of Criterion Catalysts & Technologies.

References
5 Torrisi S, Manna U, De Boks O, Technology Enhancements to Increase Diesel Quantity and Quality while Maximizing LCO Processing, Petrotech 2009 Conference, New Delhi, India, Jan 2009.

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