Growth in refined products is strongly driven by the demand for clean diesel and new regulations on gasoils between now and 2020. Notably, cumulative annualised global growth in diesel/gas oil demand is predicted to be about 2%, outpacing gasoline at 1.3% with the estimated gasoline/diesel gas oil ratio dropping from 0.85 in 2012 to 0.81 in 2020. In addition to continued growth in Asia and continuing recovery elsewhere, motor vehicle mileage standards and ethanol mandates in North America and emerging regulatory restrictions on marine fuels add further momentum to this trend. Bunker fuel regulations becoming effective in 2015 requiring 0.1 wt% sulfur limits in Emission Control Areas (ECAs) in North America and northern Europe will underlie a demand shift to diesel/gas oil products with an expected concurrent boost in diesel price primarily due to quality requirements. Meanwhile, refining capacity additions outstripping global demand in the 2015 – 2020 period will continue to pressure refining margins. In short, it will be a period of opportunity for those refiners that have the flexibility of having hydrocracking capabilities, especially those coupled with a robust ultra low sulfur diesel (ULSD) hydrotreater, who can marry their catalyst system needs and operational responses to changing economic scenarios.

This article addresses catalyst technology approaches and processing tactics to optimise hydrocracking and diesel hydrotreating applications.

**Molecular management**

Of all diesel boiling range materials, fluid catalytic cracking (FCC) light cycle oil (LCO) stands out as one of the lowest value feedstock materials. It is usually the most difficult to manage operationally in the unit largely due to the combination of olefins and the refractory nature of the feed. It has the highest demand for hydrogen to produce a clean diesel or even 0.1 wt% sulfur marine gas oil, and offers heat release management challenges when processed at higher fractions in a unit feed. Provided there is adequate hydrogen supply,
Hydroconversion targets for removal of heavy components. Hydrodemetalisation (HDM) needs driven by heavy vacuum HDN needs for the hydrocracking function lower in the Isomerisation (for lube needs). Aromatics removal (lube or FCC applications). HDS needs for products such as ULSD, marine gas oil, and as ‘diluent’ components to aid in managing hydrogen consumption limitations and heat release issues in hydrocrackers designed for more paraffinic and naphthenic feeds.

Processing tactics are balanced between these feedstock molecular management considerations and the designs, limitations and strategic intent of the unit in the refining scheme. Hydrocrackers have traditionally been designed with intent to pump hydrogen into the feedstock to convert heavier, higher boiling materials into more valuable products while capitalising upon aromatics saturation to increase volume swell as well as product value parameters (density, cetane, smoke point, etc.). Until recently, ULSD has been a secondary priority and generally not even a consideration in the original design of the bulk of hydrocracking units operating today. With a robust ULSD unit in the refinery, this prioritisation need not be overriding, but can be augmented by the utilisation of the latest catalyst systems for hydrocracking that have been designed for maximum hydrodesulphurisation (HDS) activity as well as the fundamental hydrodenitrogenation (HDN), hydrocracking, and saturation needs.

The versatile hydrocracker

While several hydrocracker configurations are in current usage, two dominate the landscape, especially when addressing clean fuels production: single stage, once through (SSOT) configurations and two stage, recycle (TSREC) configurations.

The SSOT configuration is both simple and versatile and represents the simplest configuration when unconverted oil (UCO) has high value as either a lube plant feed or FCC feed. This configuration dominates the market for conversion below 70%.

Catalyst system optimisation for the SSOT is often influenced strongly by the desired outlet for the UCO it produces: lube plant feed will favor higher viscosity index (VI), aromatics saturation and desulphurisation (HDS) while FCC feed will favour nitrogen removal (HDN), poly nuclear aromatics removal and desulphurisation (HDS). Balanced with these needs are the light product drivers: ULSD or the less demanding 5% sulfur marine fuel. If ULSD production is a target and cannot be produced within the SSOT unit constraints, it is critical to factor in and model the effect of this preprocessed component as feed to the ULSD unit. It will clearly include more difficult, sterically hindered sulfur compounds for HDS in the ULSD unit.

Catalyst system selection and optimisation is controlled by a number of constraints that must be accommodated in a single stage:

- Hydrodemetalisation (HDM) needs driven by heavy vacuum gas oil (HVGO) and/or deasphalted oil (DAO) components as well as by crude source (arsenic and other contaminants) and coker products in the feed (silicon contaminations).
- HDN needs for the hydrocracking function lower in the catalyst system.
- Hydroconversion targets for removal of heavy components.
- HDS needs for products such as ULSD, marine gas oil, and UCO.
- Aromatics removal (lube or FCC applications).
- Isomerisation (for lube needs).

SSOT catalyst system optimisation is further challenging when the application involves a unit converted from former service such as FCC pretreatment or, in less common cases, diesel LCO is sometimes best processed in the hydrocracker along with other feeds such as atmospheric gas oils (AGOs) or vacuum gas oils (VGOs). Adding to the equation is that all LCOs are not created equal. Depending upon the refinery configuration and the FCC, the LCO may be produced from an FCC with a feed pretreater and consequently contain fairly modest levels of sulfur and nitrogen. Although they appear to be ‘easier’ feeds due to their lower levels of contaminants, the remaining impurities are also the toughest to treat.

Coker gasoils can be processed in either the hydrocracker or ULSD unit subject to individual unit capacities and infrastructure limitations such as hydrogen availability, pressure, end point, and impurities. Heavy coker gas oils (boiling well above the diesel range) are best sent to the hydrocracker although they can present challenges for catalyst life cycles depending upon design and limitations. A hydrocracker originally designed or revamped for VGO service is the most suitable outlet. This offers higher potential to maximise diesel yields, especially in recycle flow configurations and higher pressures. Light coker gasoils, on the other hand, are readily processed to ULSD in a diesel hydrotreater provided there is adequate hydrogen partial pressure and the unit has the appropriately tailored catalyst system to remove contaminants and provide sulfur conversion.

Straight run (SR) gas oils present the least challenging processing constraints, and can be fed to either the hydrocracker or ULSD unit although the ULSD unit is typically the preferred outlet. Exceptions include cases where the SR feeds are needed as ‘diluent’ components to aid in managing hydrogen...
treating. In such cases, heat release and hydrogen consumption come into play as these units typically contain only a few, deep beds. Semantics can sometimes obscure the proper application of catalyst technology. A ‘mild hydrocracker’ is merely a low conversion SSOT (<40%) and is most effectively evaluated as a part of the SSOT catalyst system continuum.

SSOT systems typically demand the highest activity catalyst components for hydrotreating needs for HDN and HDS. ART and CLG have met this challenge over time as can be noted from the rapid innovation and delivery of hydrocracking pretreatment catalysts (Figure 1). ART’s latest pretreat catalyst ICR 512, has successfully met the feed severity challenges to enable obtaining the most from the downstream hydrocracking catalysts. In addition, it has allowed product properties, such as ULSD, to be maintained and even improved with more difficult feedstock.

Lacking the flexibility of recycle and adjustment of the recycle cut point (RCP), product selectivity in the SSOT is controlled by the choice of the catalyst system, and largely the choice of the hydrocracking catalyst component(s), and the operating temperature regime and span. Hydrocracking catalyst product families typically exhibit a trade off between selectivity to distillates and activity (temperature required for a target conversion level). Premier catalyst performance is defined by innovations that increase both selectivity and activity. Figure 2 shows the progression of such performance for the hydrocracking catalysts provided by ART.

Catalyst system design in an SSOT can involve more than a single solution. While a single hydrocracking catalyst from the ‘B’ range might seem an obvious solution for a refiner desiring ‘A’ selectivity but lacking the infrastructure to compensate for the lesser activity, synergies in multicatalyst combinations might instead point to a system of ‘A’ and ‘C’ catalyst and can actually achieve a better result than pure ‘B’ alone.

TSREC configurations offer a high level of flexibility in addition to providing the more favorable means to achieve conversion levels of 90% plus. TSREC configurations also are the preferred means to achieve full naphtha/gasoline selectivity.

TSREC units offer the refiner the ability to operate the two stages differently in order to simultaneously meet separate goals for each stage. This configuration also offers the flexibility to ‘balance’ the stages to optimise the desired product selectivity and qualities. Note that although this unit is shown with two reactors, they are often built with multiple reactors, generally as part of the first stage providing even greater ability to process poorer value stocks. As an example, the first stage could be targeted to both provide a diesel draw suitable for marine fuel blending as well as pretreatment for the second stage which could be targeted to produce ULSD. Contrasted to the SSOT, the TSREC has added operational flexibility provided by the ability to adjust RCP and per pass conversion in each stage plus a second catalyst system that allows optimisation of an additional catalytic component. In addition, TSREC will enable production of other very high quality products such as JET-A which can be recovered as a single product or recovered with the ULSD, depending upon economics of the day. In addition, feedstocks can be shifted with the ULSD unit to further add operating space. This integration and flexibility permits the refinery to take full advantage of seasonal or frequent economics.

Catalyst system selection and optimisation in the first stage is often influenced by feed quality and contaminants; nitrogen, sulfur, metals, silicon, and arsenic being the typical suspects. This is especially challenging for older, existing units but equally even for new units. A comparison from the early days of hydrocracking to the present is shown in Table 1.

Following removal of feed contaminants, the remaining catalyst volume can be used to achieve the conversion and selectivity goals. Often the first stage is required to achieve 50 - 60% conversion after removing feed contaminants for both...
stages. Depending upon unit objectives, first stage cracking catalyst can be chosen from any of the 'A', 'B', or 'C' groups and will include catalysts such as ICR 183, ICR 180, or ICR 162. These catalysts have exhibited very stable and robust performance to achieve these levels of conversion to the desired products and with a long operating cycle.

Second stage catalyst selection will largely be driven by performance of the first stage to achieve the desired overall unit goals. Second stage catalyst will contribute significantly to product quality improvement and to the ability to achieve very high levels of conversion to the desired product, typically diesel or total distillate. ICR 240 and ICR 250 have provided many two stage recycle units with a very robust operation and very high product quality such as jet smoke point and diesel cetane.

Combined with a robust first stage pretreat and hydrocracking operation described earlier the second stage can provide unmatched selectivity and product qualities while processing even the most difficult feeds.

**Catalyst system optimisation**

Catalyst system selection and optimisation is also a critical aspect for ULSD production in a diesel hydrotreater. As discussed above for hydrocrackers, catalyst selection for ULSD is dependent upon feed quality and contaminants. In addition, operating constraints such as $H_2$ availability exert significant influence on the catalyst system selection. ART introduced the SmART Catalyst System® in 2001 to help refiners deal with these complex interactions between feed and operating constraints while at the same time meeting the unit operational goals. The system utilises the latest catalyst technology, which is layered in the proper proportions to provide the best performance while at the same time meeting individual refiner requirements. The catalyst staging is designed to take advantage of the different reaction mechanisms for sulfur removal; a high activity CoMo catalyst such as 420DX or 425DX efficiently removes the unhindered, easy sulfur via the direct abstraction route, and a high activity NiMo catalyst like NDXi or 545DX then attacks the remaining sterically hindered, hard sulfur. Experience has proven that the properly configured SmART Catalyst System provides better performance than either the CoMo or NiMo catalyst alone.

One of the key advantages of the SmART Catalyst System is the efficient use of hydrogen. Figure 3 illustrates how the system can be tailored to provide the best balance of high HDS activity while minimising $H_2$ consumption. The figure shows that as NiMo catalyst is added to the system there is a significant increase in HDS activity relative to the all CoMo reference, and eventually, a minimum in the product sulfur curve is reached (i.e. maximum HDS activity). The position and magnitude of this minimum varies with feed properties and operating conditions.

The figure also shows the relative $H_2$ consumption, and again, as the percentage of the NiMo component increases, the $H_2$ consumption relative to the base CoMo system increases. In the region where the system shows the best activity the hydrogen consumption is only slightly greater than that for the all CoMo system, and well below that for the all NiMo catalyst. This is a direct result of the different kinetics for sulfur and aromatics removal and is a critical consideration when customising a SmART Catalyst System. For units that have hydrogen constraints the key to designing the proper catalyst system is increasing the hydrogenation selectivity to provide highest HDS activity while at the same time minimising hydrogen consumption (i.e. minimising excess aromatics saturation). How this is accomplished is shown in Figure 4 which compares the concentration profiles for poly and mono ringed aromatics as a function of residence time for a CoMo and NiMo catalyst under typical ULSD unit conditions.

The figure shows a rapid decrease in poly aromatics concentration and a corresponding increase in mono ringed aromatics for both catalysts as the residence time is increased. Clearly, however, the NiMo catalyst is much more efficient at hydrogenating the final aromatic ring as evidenced by the lower mono ringed aromatic concentration with increasing residence time compared to the CoMo catalyst. At the longest residence time (lowest LHSV) on the chart, the NiMo catalyst has about 15 numbers (absolute) lower mono ringed aromatics concentration than the CoMo catalyst, and that corresponds to about 50 Nm$^3$/m$^3$ higher hydrogen consumption for the NiMo catalyst.

These data demonstrate that the hydrogenation activity of the system can be tuned by adjusting the relative volumes (i.e. residence times) of the CoMo and NiMo beds in the reactor. Of course, not all units have a $H_2$ constraint, and in those cases the incremental increase in aromatics saturation and the correspondingly higher hydrogen consumption obtained by the NiMo catalyst like 545DX offers benefits such as cetane improvement and the ability to process more cracked stocks. Commercial experience with the SmART catalyst system has demonstrated that a properly designed ULSD unit combined with the right catalyst system can process up to 100% cracked stocks to produce <10 ppm sulfur and providing significant cetane uplift and volume swell.

A hallmark of the SmART system is flexibility. In applications where there is sufficient $H_2$ availability and partial pressure, a catalyst like 545DX is likely the most active system for HDS. However, it will consume significantly more hydrogen due to its efficiency at catalysing hydrogenation reactions. If the incremental hydrogen consumption cannot be tolerated, a SmART system can be designed which will deliver high HDS activity and minimise hydrogen consumption. In cases where the hydrogen pressure is lower, the SmART system is often more active than either component alone without increasing the $H_2$ consumption significantly over the all CoMo system. For low pressure diesel units the best option is a catalyst like 425DX which has been specifically designed for superior performance at low pressure.

**Conclusion**

State of the art technical support is required to get the most from today's advanced catalysts and catalyst systems. Assessing and recognising unit limits is key to achieving the refiner's operating goals, especially before a hard limit is reached that will result in a shortened cycle, reduced throughput, or both.

**References**