Abstract

The dynamics of global gasoil and ultra low sulfur diesel (ULSD) demand are driven by regulatory demands for transport diesel and evolving needs for vastly improved marine bunker quality in specific emission control areas (ECA's), as well as by economic growth. It is expected that this will drive regional variability in ULSD/0.1% sulfur gas oil differential over time and consequently provide incentives for refiners to maximize flexibility in both hydrotreater distillate yields and ULSD unit performance. Adding in an expectation of gasoline supply becoming long in the Middle East over the next several years, the refiner is further motivated to evaluate and select premier catalyst systems for the production of diesel products from both their hydrotreating and diesel treating units. This article describes how best to address this challenge.

As it has been noted widely, the growth in refined products is strongly driven by the demand for clean diesel and new regulations on gasolines between now and 2020. Notably, cumulative annualized 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 2020.1 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% sulfur limits in emission control areas (ECA's) 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 hydrotreating capabilities, especially those coupled with a robust ULSD hydrotreater, who can marry their catalyst system needs and operational responses to changing economic scenarios.

In early 2013, Advanced Refining Technologies (ART) and Chevron Lummus Global (CLG) announced an agreement in which ART has the exclusive right to sell CLG’s hydrotreating and lubes hydroprocessing catalysts to petroleum refiners worldwide for unit refills. The result dramatically streamlines hydrotreating catalyst supply and improves technical service focus for refining customers by establishing ART as the single point of contact for all their hydrotreating catalyst needs. In this context, this article addresses cata-
Molecular Management and Hydroprocessing Units

Of all diesel boiling range materials, FCC LCO stands out as one of the lowest value feedstock materials. It is usually the most difficult to manage operationally in a hydroprocessing unit largely due to the combination of olefins and the refractory nature of the LCO. It has the highest demand for hydrogen to produce a clean diesel or even 0.1 wt.% sulfur marine fuel, and offers heat release management challenges when processed at higher fractions in a hydroprocessing unit feed. Provided there is adequate hydrogen supply, LCO is sometimes best processed in the hydrocracker along with other feeds such as AGO’s or VGO’s. Adding to the equation is that all LCO’s are not created equal. Depending upon the refinery configuration, 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 gas oils can be processed either in the hydrocracker or ULSD unit subject to individual unit capacities and infrastructure limitations such as hydrogen availability, pressure, endpoint, and impurities. Heavy coker gasoils (boiling well above the diesel range, >975 ºF) are best sent to a hydrocracker although they can present significant challenges to processing in significant quantities even in modern, robustly designed hydrocrackers. A hydrocracker originally designed or revamped for VGO service is a most suitable outlet. This offers more potential to maximize 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 the required sulfur conversion.

Straight run (SR) gasoils 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 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 capitalizing 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 prioritization need not be overridden, but can be augmented by the utilization of the latest catalyst systems for hydrocracking that have been designed for maximum HDS activity as well as the fundamental HDN, hydrocracking, and saturation needs.

The Versatile Hydrocracker and Catalyst System Flexibility

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. A perspective over a decade of application is provided in Figure 1.

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 low conversion market (>70% of that market). The SSOT process configuration is shown in Figure 2.

Catalyst system optimization 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 desulfurization (HDS), while FCC feed will favor nitrogen removal (HDN), poly-nuclear aromatics removal and desulfurization (HDS). Balanced with these needs are the light product drivers: ULSD or the less-demanding 0.1 wt.% 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 pre-processed com-
ponent 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 optimization is controlled by a number of constraints that must be accommodated in a single stage:

- Hydrodemetalization (HDM) needs driven by 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 requirements for the hydrocracking function of the catalyst systems that follow
- 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)
- Isomerization (for lube needs)

SSOT catalyst system optimization is further challenged when the application involves a unit converted from former service such as FCC pretreatment or, in less common cases, diesel 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 hydrotreater” 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 to meet HDN and HDS needs. Chevron Lummus Global, teaming with Advanced Refining Technologies, have met this challenge over time as noted from the rapid commercialization of hydrocracking pretreatment catalysts, as shown in Figure 3.

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 4 shows the progression of such performance for the hydrotreating catalysts provided by ART.

Catalyst system design in an SSOT can involve more than a single solution. While a single hydrotreating 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 multi-catalyst 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. The configuration is shown in Figure 5.

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 optimize 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 optimization 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 flexi-
Catalyst system selection and optimization 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 can be equally challenging even for new units.

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.

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 these days.

ULSD units also face challenges in molecular management that a properly designed catalyst system and optimized processing scheme can help the refiner maximize his profit goals. To help refiners deal with the severe demands of ULSD, ART developed a staged catalyst system in 2001. This commercially successful system utilizes state-of-the-art catalyst technology which is staged 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 efficiently removes the unhindered, easy sulfur via the direct abstraction route, and a high activity NiMo catalyst 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 catalysts alone.

An important aspect of the staged catalyst system is designing the optimum proportions of the CoMo and NiMo catalysts that will deliver the best performance. This is dependent upon a number of factors including the unit objectives, feed and operating constraints. A more detailed discussion of these factors and how they impact system design can be found in references 3 and 4.

One of the key advantages of the system is the efficient use of hydrogen. Figure 6 illustrates how the system can be tailored to provide the best balance of high HDS activity while minimizing H₂ 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, shown in Figure 6, varies with feed properties and operating conditions.

The figure also shows the relative H₂ consumption, and again, as the percentage of the NiMo component increases, the H₂ 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 customizing the staged catalyst system.

For units that have a hydrogen constraint, the key to designing the proper catalyst system is increasing the hydrogenation selectivity to provide highest HDS activity while at the same time minimizing hydrogen consumption (i.e. minimizing excess aromatics saturation). How this is accomplished is shown in Figure 7 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.
Figure 7 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 300 SCFB 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) in the CoMo and NiMo beds in the reactor. Of course, not all units have a H₂ constraint, and in those cases the incremental increase in aromatics saturation and the correspondingly higher hydrogen consumption obtained by the NiMo catalyst 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 provide significant cetane uplift and volume swell.

In applications where there is sufficient H₂ availability and partial pressure, a NiMo catalyst is likely the most active system for HDS. However, it will consume significantly more hydrogen due to its efficiency at catalyzing hydrogenation reactions. If the incremental hydrogen consumption cannot be tolerated, a SmART system can be designed which will deliver high HDS activity and minimize hydrogen consumption. In cases where the hydrogen pressure is lower, the staged catalyst system is often more active than either component alone without increasing the H₂ consumption significantly over the all CoMo system.

**Service**

State of the art technical support is required to get the most from today’s advanced catalysts and catalyst systems. Assessing and recognizing unit limits is key to achieve the refiner’s operating cycle goals, especially before a hard limit is reached that will result in a shortened cycle, reduced throughput, or both. ART’s experienced technical support and operations staff understand these issues.

The journey together begins with specification of the appropriately tailored catalyst system for the processing and economic needs, and continues with how catalysts are loaded and how the unit is started up to achieve the most from the catalyst. A major multi-national, vertically integrated energy company, working with the licensor and catalyst supplier, can provide a powerful depth of knowledge on how to optimize catalyst and unit operations.

**References**

2. Torchia, Dan; Arora, Arun; and Vo, Luyen. “Clean, green, hydrocracking machine,” Hydrocarbon Engineering, June 2012.