DOING WONDERS FOR DIESEL PRODUCTION

Gary Podrebarac, Rajesh Samarth and Kerry Rock, CDTECH, USA, **look at increasing diesel production from the refinery FCC.**

Although gasoline was once the primary driver in refinery design and operation, that has begun to change in recent years. In Europe, taxation and fuel economy have made diesel the preferred fuel and gasoline is being exported. In the US, gasoline is being squeezed by substitution with ethanol and diesel margins are more attractive than gasoline. CDTECH's FCC naphtha desulfurisation technology gives refiners the flexibility to produce low sulfur heavy cat naphtha as a separate product for blending into the diesel pool, maximising diesel production and optimising refinery operation.

Sulfur concentration in the gasoline pool is being reduced in many parts of the world. In Europe, Euro V regulations, implemented in 2009, require less than 10 ppm sulfur in gasoline. Since 2008, the gasoline sulfur specification in the US and Canada has been less than 30 ppm average, and a further reduction to 10 ppm is under consideration by the US. In Europe and North America, diesel with sulfur content in this low range is referred to as ultra low sulfur diesel (ULSD). In Russia, gasoline sulfur content will be reduced to 10 ppm by 2015. It is likely that sulfur specification throughout the rest of the world will also become more stringent over time.

Gasoline is a complex product with many important quality parameters aside from sulfur concentration, including vapour pressure, benzene concentration, boiling range, and octane rating. In some regions, such as the EU and India, demand for diesel is higher than for gasoline. In others, including the US, the demand for diesel is projected to grow while gasoline demand declines (Figure 1).

To reduce gasoline product and increase diesel product, some refiners produce lower end point gasoline, routing the heavier cut of the full range gasoline to the diesel pool.

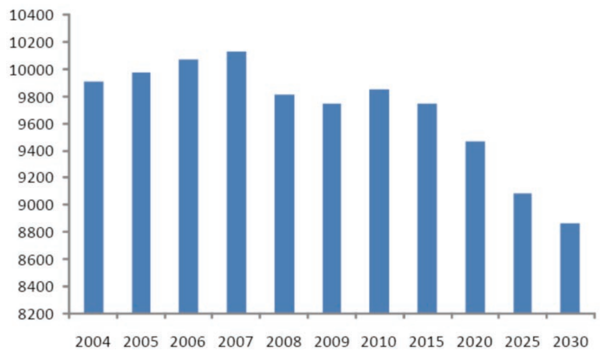

Figure 1. Projected change in North American gasoline demand. Source: Hart Energy Consulting.

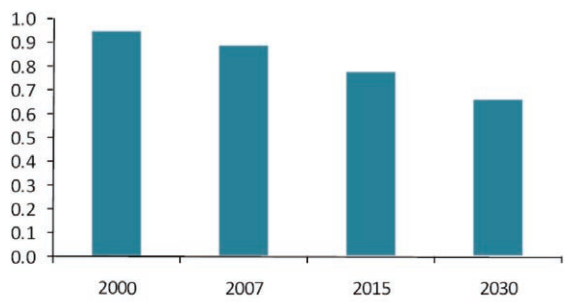

Figure 2. Projected change in global gasoline:distillate ratio. Source: Hart Energy Consulting.

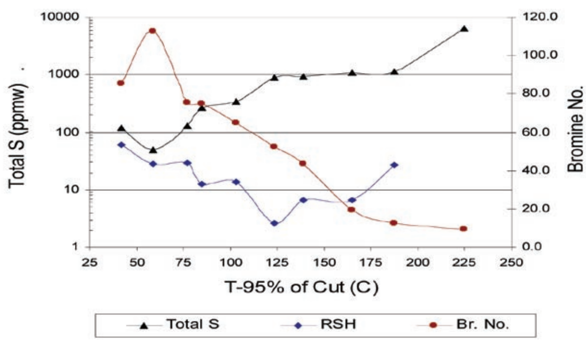

Figure 3. Concentration profiles of total S, RSH, and olefins (as bromine number) in FCC gasoline.

This results in higher capacity requirements for the diesel hydrotreaters, which are often already fully utilised.

To remove sulfur from FCC gasoline, CDTECH offers light cat naphtha (LCN) CD*Hydro* and CD*HDS* processes. These processes, which employ the principle of catalytic distillation, conduct selective hydrodesulfurisation in a distillation environment. The full range gasoline is split into three different cuts, giving the refiner considerable blending flexibility. It is possible to use the CD*HDS* process to tailor the sulfur content of the distillate and bottom product, making it feasible to produce 30 ppm low end point gasoline and a heavier cut that meets the less than 10 ppm sulfur specification for blending into the diesel pool. This flexibility can provide significant value by debottlenecking the diesel hydrotreater.

Properties of FCC gasoline

Figure 3 is a plot of the concentrations of total sulfur, mercaptan sulfur (RSH), and olefins (measured via bromine number) as a function of the boiling point of the FCC gasoline. In the light end of the gasoline, the olefin concentration is high and the total sulfur concentration is relatively low. Nearly all the total sulfur is in the form of RSH. As the boiling point increases, the sulfur concentration begins to increase quite significantly while the RSH concentration actually declines. In the heaviest end, most of the sulfur is contained in compounds such as thiophene, methyl thiophene, etc. Conversely, the olefin concentration profile follows the opposite trend: the lighter end of gasoline is olefin rich while the heavier end contains very little olefin.

The data illustrate the challenge involved in treating the light end of the gasoline through to the heavy end. To meet a 30 ppm sulfur spec, the light cut requires only 70% sulfur conversion, the middle cut (near 135 ˚C) requires 96.8% conversion, while the heaviest cut requires 99.5% sulfur conversion.

The preservation of olefins is vital to reducing hydrogen consumption and minimising octane loss. Olefin saturation, although inevitable in a hydrodesulfurisation process, is minimised when the sulfur conversion is minimised. With this mind, an ideal desulfurisation process would provide an environment where the highest severity is applied only to the heavy fraction of the gasoline, which has high sulfur and low olefin concentrations. The olefins in the heavy fraction also have lower octane than the olefins in the light fraction. The reaction severity would be decreased for the lighter fractions, which have lower sulfur and higher olefin concentrations. Treating the lighter fraction at lower severity limits the saturation of valuable olefins in this olefin rich region.

Process overview

CDTECH has developed a selective treatment method for the full range FCC gasoline that optimises the severity for treating different cuts of gasoline to maximise sulfur removal while minimising olefin loss. As shown in Figure 4, the first step is to treat the lightest fraction of the gasoline in a LCN CD*Hydro* unit where the RSH is nondestructively removed. The LCN CD*Hydro* unit is not a hydrodesulfurisation step. It operates at very mild conditions, resulting in no measurable olefin loss.

Part of the rectification section of the LCN CD*Hydro* column contains catalyst packed in a distillation structure. The rest of the column contains conventional

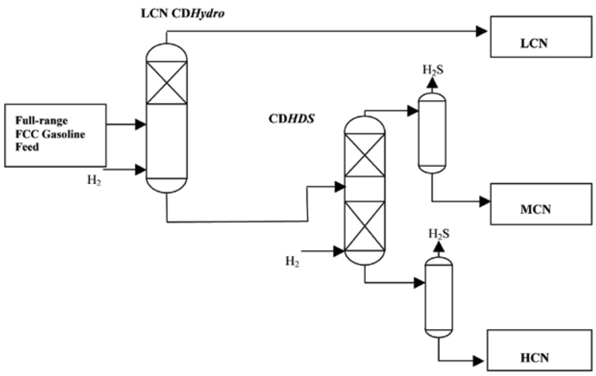

Figure 4. A proposed flow scheme to maximise blend flexibility.

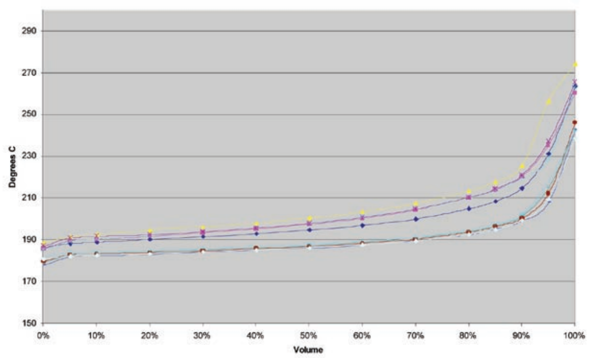

Figure 5. Boiling range of HCN product.

distillation trays. The LCN CD*Hydro* unit works by performing an addition reaction between the RSH and the contained diolefins over the catalyst to form a heavier sulfide (RSR). The heavy sulfide distills to the bottom of the LCN CDHydro column and exits with the bottom product.

The light product from the LCN CD*Hydro* column has very low RSH, very high olefin concentration, a high octane rating, and a relatively high RVP. Some refiners choose to isolate this fraction in order to increase the number of degrees of freedom in the blending operation.

The LCN CD*Hydro* column bottoms go to the CD*HDS* column. This is the hydrodesulfurisation step that converts the sulfur in the gasoline to H_2S. The CD*HDS* column also contains a hydrodesulfurisation catalyst packed in a distillation structure. Since the process is based on distillation, the catalyst structure below the feed point operates at much higher temperatures than the catalyst structure above the feed point. This has the effect of increasing the reaction severity on the heavy portion of the gasoline, where the sulfur conversion requirement is the highest and the olefin content is the lowest. Simultaneously, the medium cat naphtha (MCN), which contains higher olefin levels and less refractory sulfur compounds, goes up the column where the conditions are less severe than at the bottom. Thus, the reaction conditions in the CD*HDS* unit are ideally suited to the stated goals of preserving olefins and minimising octane loss.

Since the CD*HDS* unit performs distillation, there is an opportunity to isolate two additional FCC gasoline fractions to increase blending flexibility and control the end point of the product. The CD*HDS* column distillate product (MCN) makes an ideal low end point blend stock for the gasoline pool.

End point flexibility

The CD*HDS* column bottom product (HCN) can also be isolated and is a high end point product; however, it is important to realise that this product has a very low sulfur concentration. The HCN can be desulfurised to sulfur concentrations that are lower than that required for the gasoline pool without sacrificing olefins and octane in the MCN bound for the gasoline pool. This increases the number of its potential uses while maintaining good economics on the treatment of the MCN. The HCN can be blended into the gasoline pool if desired. If low end point requirements become constraining, the HCN can be sent into a low sulfur or an ultra low sulfur diesel pool without requiring any further sulfur removal, making it ideal for blending into the diesel pool. Thus, the HCN will not occupy capacity in the refinery's diesel hydrotreater (DHT), which otherwise could potentially cause a DHT bottleneck.

The ability of the CD*HDS* column to produce a higher sulfur distillate and lower sulfur bottom product is unique and cannot be replicated by installing a gasoline splitter downstream of a fixed bed HDS unit. The product from a fixed bed HDS unit contains heavy sulfur components such as recombinant mercaptans and sulfides. When the gasoline produced from a fixed bed unit is distilled, the bottom product will contain more sulfur than the distillate product. To meet the sulfur specifications required to send this bottom product into the diesel pool, two options exist:

- Send it for further treatment in the DHT, which may restrict diesel production in the refinery.
- Treat the entire gasoline stream to reach a sulfur level well below the desired diesel specification, which will result in a very large octane loss in the gasoline pool, but will not restrict diesel production.

The refiner may opt to undercut the gasoline and send only a low end point feed through the gasoline HDS unit, but this still requires running the heavy gasoline range material through the DHT. The CDTECH flow scheme does not take up capacity in the DHT and therefore gives refiners an opportunity to debottleneck diesel production. However, some licencees operate their units in this manner on a seasonal basis to satisfy changing market conditions. By taking advantage of the HCN as a separate product, the refiner avoids having to treat this material in a separate hydrotreater. This mode of operation commercially demonstrates the flexibility of the technology to operate on feedstocks of variable boiling range.

Long catalyst life

Treating cracked streams in fixed bed HDS units can result in catalyst coking and fouling, which in turn can cause high pressure drop. These problems are addressed by periodically shutting down the units to vacuum out the upper layers of catalyst. To help reduce fouling, these units require a selective hydrogenation unit (SHU) upstream to significantly reduce reactive dienes from the feed.

An added benefit of conducting the HDS reaction in a catalytic distillation environment is the significantly longer catalyst life. The reflux in the CD column provides a sink for the heat of reaction, so catalyst hot spots are virtually eliminated. The reflux also provides a washing action where coke precursors are removed from the surface of the catalyst before they have an opportunity to develop into larger formations that deactivate the catalyst or plug the catalyst bed. Inspections of many CD units over the past 15 years have confirmed the validity of this mechanism. CD*HDS* units, which do not require an upstream SHU, have been in operation for more than six years with no apparent loss of catalyst activity.

The CD*HDS* technology is unique in that the desulfurisation step does not limit the run length of the FCC unit, even as refiners press for FCC cycles of up to six years and eventually more. For refiners employing shorter FCC turnaround cycles, the catalyst in the CD column can last for multiple cycles.

Hydrogen usage

The CD*HDS* process is very selective in minimising olefin saturation and maximising octane retention. As a result, hydrogen consumption is moderate.

In addition, the CD*HDS* column is designed to run at modest hydrogen recirculation rates, which results in a smaller recycle compressor with less power consumption. Since the hydrogen recirculation rates are low, the CD*HDS* process can run with lower purity hydrogen than a typical fixed bed unit. Given the tight supply of hydrogen in most refineries, these can be significant operational factors.

Another consideration is the refiner's fallback position in the event that the hydrogen recycle compressor goes down unexpectedly. Given the modest hydrogen requirements of the CD*HDS* unit, it is possible to run it on once through hydrogen until the repair is completed. In a typical fixed bed unit, it is impractical to attempt to match the recirculation rates on a once through basis due to the much higher required hydrogen rates. Therefore, it will be necessary to shut down the FCC naphtha treater and the FCC unit until the compressor repair is completed. The ability of the CD*HDS* process to operate on once through hydrogen means it does not have to shut down for a recycle compressor outage.

Case study

One refinery using CD*Hydro*/CD*HDS* will soon be ready to produce HCN as a separate ULSD blendstock. The stream, already containing less than 10 ppm sulfur, is currently being sent to the gasoline pool until piping modifications are completed. The stream will then be sent to an existing DHT product stripper where H_2S will be removed to meet the final blending specifications for ULSD. As a result, approximately 10% of the total FCC gasoline will then be diverted to the diesel pool. Figure 5 shows the typical distillation range of the HCN over several days of operation. The 180 - 190 ˚C IBP and 240 - 275 ˚C end point will fit well within the normal diesel boiling range of 175 - 325 ˚C.

Conclusion

The LCN CD*Hydro* and CD*HDS* processes, which employ catalytic distillation for hydrodesulfurisation of gasoline, offer significant advantages over fixed bed hydrodesulfurisation processes. The selective treatment of the full range gasoline fractions ensures maximum octane retention with low hydrogen consumption. In addition to lower utility consumption, these processes offer extremely long catalyst life. They provide the refiner with operating reliability, blending flexibility, and the potential to debottleneck the DHT capacity and thus maximise diesel production.