In those areas of the world which are experiencing low costs of natural gas, there has been a decrease in the cost of hydrogen, and this, combined with the growth in global demand for middle distillates, has prompted refiners to look to improve profitability by increasing middle distillate yields. Options under consideration have included operating an FCC (Fluid Catalytic Cracker) pretreater in a mild hydrocracking mode, switching to maximum LCO¹ (Light Cycle Oil) mode or extending the endpoint of feed to a ULSD (Ultra Low Sulfur Diesel) unit and converting the heavy fraction into diesel range material. The use of opportunity feedstocks and synthetic type feedstocks can also be considered². These approaches require specialized catalyst systems capable of providing some cracking conversion or changes to traditional unit operation, and careful attention must be given to minimizing production of excess gas and naphtha while maximizing diesel. Another seemingly simple option is to maximize the product volume swell from an existing ULSD unit through a change in catalyst and understanding the demand on operating conditions. This approach to increasing diesel yields requires a detailed understanding of feed and operating conditions such that the hydrotreater can be operated at the maximum product volume swell for the majority of the unit cycle. In this case, the benefits of increased diesel yield need to be balanced against the potential costs of increased hydrogen consumption and decreased cycle length.

A critical element in all the approaches to increasing diesel yield is the proper design and selection of a catalyst system for the hydrotreater. This paper summarizes some of these various catalytic options and the operating conditions that can be implemented to increase yields of middle distillate using existing assets with minimal investment.

As a first step, it is useful to understand the chemistry involved in hydrotreating and, in particular, the chemistry required for maximizing product volume swell. Table I lists several different classes of hydrocarbon compounds that can be found in diesel range feeds. The data shows that as hydrogen is added to a molecule, the density of the compound decreases. This indicates that even some simple reactions involved in hydrotreating result in a decrease in density of the product or put another way, result in an increase in product volume. This is especially apparent with aromatics species.
Table II lists several different aromatic and fully saturated compounds which occur in diesel range feedstock along with some selected properties. It is apparent that dramatic shifts in boiling point and density can be realized by hydrogenating aromatic compounds. The density decreases by 20-25% with boiling points shifts anywhere from 50-150°F upon saturation of the aromatic rings. This suggests that in order to achieve a high degree of product volume swell in ULSD, a detailed understanding of aromatic and polynuclear aromatic (PNA) hydrogenation is required. It is well understood that hydrogenation of aromatic compounds is a reversible reaction, and that the equilibrium conversion is less than 100% under typical conditions. The equilibrium conversion is highly dependent on temperature and hydrogen partial pressure. Figure 1 shows how the saturation of aromatics in diesel changes with H₂ partial pressure at a typical temperature for ULSD. The base pressure is around 500 psi, so the data cover the range of H₂ pressures typically encountered in ULSD. The total aromatics conversion nearly doubles with a 2.5 times increase in H₂ partial pressure.

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Figure 2 shows how the aromatics conversion changes with temperature in a typical ULSD unit. The figure compares the conversion observed for both a NiMo and a CoMo catalyst. The data clearly indicates that the NiMo catalyst has the greater aromatic saturation activity of the two catalysts shown. The product aromatics concentration is over 4% (absolute) lower for the NiMo catalyst compared to the CoMo catalyst. This difference in aromatics conversion accounts for the higher H₂ consumption typically seen for a NiMo compared to a CoMo catalyst. The chart also shows the influence of equilibrium on aromatics conversion. As the temperature increases beyond about 670-680°F the conversion actually begins to decrease as the rate of the dehydrogenation reactions has increased enough.

**TABLE I: Selected Compounds Boiling in the Diesel Range**

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>Boiling Point, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso Paraffin</td>
<td>2,3-dimethyl-octane</td>
<td>C₁₀H₂₂</td>
<td>0.738</td>
<td>60.3</td>
</tr>
<tr>
<td>Paraffin</td>
<td>n-decane</td>
<td>C₁₀H₂₂</td>
<td>0.730</td>
<td>62.3</td>
</tr>
<tr>
<td>Olefin</td>
<td>1-decene</td>
<td>C₁₀H₁₈</td>
<td>0.897</td>
<td>26.3</td>
</tr>
<tr>
<td>Naphthene</td>
<td>Decalin</td>
<td>C₁₀H₁₈</td>
<td>0.970</td>
<td>14.3</td>
</tr>
<tr>
<td>Mono Aromatic</td>
<td>Tetralin</td>
<td>C₁₀H₁₂</td>
<td>0.738</td>
<td>-7.4</td>
</tr>
<tr>
<td>Poly Aromatic</td>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>0.738</td>
<td>-7.4</td>
</tr>
</tbody>
</table>

**TABLE II: Aromatic Compounds Found in Diesel Range Feed**

<table>
<thead>
<tr>
<th>Rings</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>Boiling Point, °F</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>Boiling Point, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Naphthylene</td>
<td>C₁₀H₈</td>
<td>1.140</td>
<td>424</td>
<td>Decalin</td>
<td>C₁₀H₈</td>
<td>0.897</td>
<td>374</td>
</tr>
<tr>
<td>3</td>
<td>Fluorene</td>
<td>C₁₃H₁₀</td>
<td>1.202</td>
<td>563</td>
<td>Perhydro Fluorene</td>
<td>C₁₃H₂₂</td>
<td>0.920</td>
<td>487</td>
</tr>
<tr>
<td>3</td>
<td>Phenanthrene</td>
<td>C₁₄H₁₀</td>
<td>1.180</td>
<td>630</td>
<td>Perhydro Phenanthrene</td>
<td>C₁₄H₂₄</td>
<td>0.944</td>
<td>518</td>
</tr>
<tr>
<td>4</td>
<td>Pyrene</td>
<td>C₁₆H₁₆</td>
<td>1.271</td>
<td>759</td>
<td>Perhydro Pyrene</td>
<td>C₁₆H₂₆</td>
<td>0.962</td>
<td>604</td>
</tr>
</tbody>
</table>

**FIGURE 1: Effect of Pressure on Aromatics Hydrogenation**

**FIGURE 2: Aromatic Reduction in ULSD**
to compete with saturation reactions. At high enough temperatures both catalysts give the same conversion since they are operating in an equilibrium-controlled regime.

One significant consequence of achieving a high level of saturation of multi-ring and mono-aromatic ring compounds is higher hydrogen consumption. However, not all aromatic species are created equal when it comes to hydrogen consumption. Figure 3 shows a simple schematic of the reaction pathway for saturating a 4-ring poly aromatic compound. The hydrogenation occurs in a stepwise fashion where one aromatic ring at a time is being saturated, with each step along the pathway being subject to equilibrium constraints. The rate limiting step to the fully saturated species is hydrogenation of the last aromatic ring (the mono aromatic), and this step consumes the most hydrogen of the reactions shown in the reaction pathway. Three moles of hydrogen are required to hydrogenate the mono-ring compound compared to two moles of hydrogen to hydrogenate the rings in the poly aromatic compounds.

A number of poly aromatic species have been studied over the years leading to a good understanding of the chemistry involved in PNA saturation. In the case of naphthalene, the reaction begins with the hydrogenation of one of the aromatic rings to form tetralin, a mono-ring aromatic. The next reaction is hydrogenation of the remaining aromatic ring to produce decalin, the fully saturated species. The reactions occur sequentially with the rate of hydrogenation of the final aromatic ring an order of magnitude lower than saturation of the first aromatic ring. The reactions can be modeled as a series of first order reversible reactions. Figure 4 shows the species concentration profiles as a function of residence time for a hydrogenation reaction sequence such as that for naphthalene just discussed. The rate of the first hydrogenation reaction in the series is an order of magnitude faster than the rate of the second hydrogenation reaction. There is a rapid decrease in the concentration of the 2-ringed aromatic species at short residence times and a corresponding increase in the mono-ringed species. As contact time increases however, the mono-ring aromatic concentration begins to decrease and the fully saturated species begin to build up. This type of concentration profile suggests that there is a range of residence times in the unit corresponding to a maximum in the mono-ringed aromatic concentration.

A variety of substituted naphthalene's have also been shown to follow a similar reaction network with the rate of hydrogenation of the first aromatic ring approximately equal to that observed for naphthalene. The hydrogenation of biphenyl occurs in a stepwise fashion as well, with the rate of hydrogenation of the first aromatic ring about an order of magnitude faster than that of the mono ring compound. An interesting difference is that the rate of the first hydrogenation reaction in naphthalene is approximately an order of magnitude faster.
than the rate of hydrogenation of the first ring in biphenyl. Figure 5 compares relative reactions rates for selected aromatics species. Figure 6 summarizes pilot plant data demonstrating how the aromatic species change in ULSD product as a function of the residence time (i.e. 1/LHSV) (Liquid Hourly Space Velocity) in the reactor. Notice how the curves look very similar to the simple example discussed in Figure 4. For PNA saturation, the 2-ringed aromatic going to the mono ring aromatic, there is a fairly steep decline in concentration as a function of residence time below about 0.5 hr. Above that point, which represents space velocities of 2 hr⁻¹ or less, there is very little change due to equilibrium constraints. For monoringed aromatic saturation there is a steady increase in conversion as the residence time is increased, and eventually the mono-ringed concentration begins to decrease indicating that mono-ring saturation gets a lot more favorable as the LHSV is decreased. These data show that PNA saturation occurs fairly readily under typical hydrotreating conditions, but saturation of mono rings aromatics is much more difficult and is aided by lower LHSV.

Hydrotreaters with very short residence time (high LHSV) will have difficulty achieving higher volume swells due to the much slower rate of saturating the final aromatic ring. These units will require a higher temperature in order to drive the kinetic saturation portion of the reaction. This can have some negative effects on catalyst performance by decreasing the expected cycle time due to the higher start of run temperature and the increased fouling rate associated with it. ART (Advanced Refining Technologies) was interested in exploring aromatics saturation and the impact of product volume further, and completed some pilot plant work for a refiner. The feedstock used for this case study contained 50% cracked material, and the operating conditions included 850 psi hydrogen pressure and a H₂/Oil ratio over four times the hydrogen consumption.

Figure 7 summarizes the HDS and aromatics conversion observed for the CoMo catalyst in that test. A temperature of 665°F was required to achieve 10 ppm sulfur in this case. At that temperature about 36% aromatics hydrogenation was achieved which is less than the maximum possible aromatic saturation for these conditions.

The maximum aromatic saturation in this case is about 42% at just under 700°F as shown on the chart.

Figure 8 shows results for a NiMo catalyst on the same feed and conditions. In this case just over 640°F is required to achieve 10 ppm product sulfur and, at that temperature, about 38% aromatics conversion is achieved. Comparing with the data in Figure 7 it is apparent that the NiMo catalyst is significantly more active for HDS than the CoMo catalyst, and it achieves slightly higher aromatics saturation when running to make 10 ppm product sulfur despite running at a lower temperature.

Comparing the catalysts in maximum aromatic saturation mode reveals significantly larger differences between catalysts. Maximum aromatics conversion occurs at 685°F for the NiMo catalyst and, at that temperature, the aromatics conversion is 52%. The NiMo catalyst is achieving over 10 numbers higher aromatics conversion than the CoMo catalyst.

Figures 9 and 10 summarize the same data, but now show the impact on product volume. The yields for the CoMo catalyst system are shown in Figure 9 along with the product sulfur. In this case the difference in yields from operating in ULSD mode versus a maximum volume swell mode is very low. The difference in aromatics
conversion for ULSD and maximum aromatics is not large enough to result in any significant change in product volume. There is no economic incentive to run for maximum volume swell with this system.

The situation is different for the NiMo catalyst as shown in Figure 10. Operating in ULSD mode results in estimated distillate yields that are about 1% higher compared to the CoMo catalyst. Of course this comes at the cost of additional hydrogen consumption with the NiMo catalyst and assumes that the extra hydrogen required for stable operation is readily available at a reasonable cost. The figure also highlights the yields for running to maximum aromatic saturation. Running the unit for maximum volume swell requires an increase in temperature to around 670°F. At this temperature there is over 1.0% additional volume gain which also results in 40-60 SCFB (standard cubic feet per barrel) additional hydrogen consumption.

When estimating the benefits of operating a hydrotreater in maximum saturation mode vs. simply maintaining ULSD it is also important to realize that the entire cycle is not expected to produce the additional volume swell. Figure 11 shows the results of modeling the differences in ULSD temperature profiles during the cycle for the two operating strategies. In ULSD mode the reactor temperature is increased to maintain a constant product sulfur of 10 wppm. The end of run (EOR) is typically determined by a maximum outlet temperature and often this is the point when the product color is out of specification. In this case, EOR is reached in about 59 months. In switching to maximum saturation mode the reactor temperature is ramped up to the conditions resulting in maximum PNA/HDA aromatic conversion. The temperature is then adjusted to maintain a constant saturation level. PNA/HDA saturation activity deactivates at a slower rate relative to HDS activity, so the rate of temperature increase in PNA mode is much slower than for the HDS mode. The EOR for the PNA mode of operation is determined by the required sulfur level of 10 wppm, at which point the ULSD unit switches to maintaining the 10 wppm product sulfur until the EOR temperatures are met.

The fact that saturation activity deactivates at a slower rate than HDS activity is validated by comparing commercial operating data. API upgrade is often used as a simple measure of aromatics saturation and can be tracked through the cycle. Figure 12 summarizes commercial data for API upgrade from eight different units ranging in operating pressure from 615-1900 Psig and 0.77-3.7 LHSV. The data indicate that the API upgrade is maintained throughout the cycle in these cases.

ART next examined the value of operating in a maximum volume swell mode vs. ULSD mode. For this model it was assumed that the unit processes 50,000 barrels per day, and the data from Figure 10 is used to estimate the yields. Data, like that from Figure 12, is used to determine the cycle length expected for operating in either the HDS (ULSD mode) or maximum yield mode. Based on the understanding from Figure 11 that the expected run length will be the same for either mode, costs such as turnaround costs and operating costs will be equal and will not need to be applied in determining the financial impact of operating in ASAT mode. For this example the catalyst systems are also identical, so that cost of the catalyst would not need to be included in the financial evaluation, but when considering catalyst changes this cost would be included. Therefore, the only difference between these two modes of operation are the additional barrels of product produced by operating in ASAT mode, and
the incremental hydrogen required to do so. For this financial analysis, the cost of the feed to the ULSD unit is assumed to be $5 lower than the cost of the product being sold.

With a detailed look at only the first 50 months of the cycle where the two modes of operation have different yield structures and hydrogen usages, Figure 13 shows that the HDS mode produces nearly 79 million barrels of product, while the ASAT mode produces almost 80 million barrels of product. The barrels produced in the last 9 months of the run are not included in this total, as both operating modes will need to finish in HDS operation in order to simply meet the ULSD product targets and maximum run length.

As was stated earlier, the difference between the two modes of operation is the use of hydrogen in order to produce the additional product barrels. There is almost 80 SCFB standard cubic feet per barrel in additional hydrogen consumption to produce those barrels which, over the 50-month cycle, amounts to over 5 million cubic feet of incremental hydrogen consumed as shown in Figure 14. Using a hydrogen value of $3.00 per 1000 scf, the incremental hydrogen consumed amounts to a cost of just over $16 million dollars, or about $0.22 per barrel more than operating in HDS mode.

However, the revenue from sale of the additional product barrels produced in ASAT mode is more than sufficient to cover the cost of incremental hydrogen consumed. The net impact for this mode of operation is a $1.20 per barrel premium for operating in ASAT mode versus HDS mode for the first 50 months of the cycle.

ART has the ability to conduct detailed customer specific pilot plant testing to provide the refiner the confidence and understanding of
the various options available when considering a catalyst change. Numerous refiners have chosen to place ART catalyst into their ULSD hydrotreater in order to achieve the optimization between ULSD and maximum yield ULSD.

Both the hydrotreating catalyst system and the operating strategy for the ULSD unit are critical to providing the highest quality products. Driving the hydrotreater to remove sulfur and PNA’s improves product value, but this needs to be balanced against the increased costs of higher hydrogen consumption. Use of tailored catalyst systems can optimize the ULSD hydrotreater in order to produce higher volumes of high quality products while balancing the refiners available hydrogen.

The complex relationship between hydrotreater operation and catalyst kinetics underscores the importance of working with a catalyst technology supplier that can tailor product offerings for each refiner’s unique operating conditions. This knowledge enables ART to meet the refiner’s objectives and maximize revenue.

References


