A critical element with all approaches to increasing diesel yield is the proper design and selection of a catalyst system for the hydrotreater. Part I discusses strategies for taking advantage of the properties of a premium diesel catalyst formulation with appropriate operating conditions.

High middle distillate demand provides opportunities for considering custom catalysts for higher diesel yields. Even more so, relatively low cost hydrogen production in certain markets provides further incentive to invest in premium catalyst. Options under consideration have included operating FCC pretreaters in mild hydrocracking mode, switching to maximum LCO mode or extending feed endpoint to a ULSD unit and converting the heavy fraction into diesel range material. The use of opportunity feedstocks and synthetic type feedstocks can also be considered.

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 product volume swell from a current ULSD unit through a change in catalyst and understanding 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, increased diesel yield benefits need to be balanced against the potential costs of higher hydrogen consumption and decreased cycle length.

Maximizing Product Volume Swell

It is useful to understand hydrotreating chemistry, particularly with regard to maximizing product volume swell. Table 1 lists several different classes of hydrocarbon compounds found in diesel range feeds, showing that compound density decreases as hydrogen is added to the molecule. This indicates that even some simple reactions involved in hydrotreating result in product density reduction and a resulting product volume increase. This is especially apparent with aromatic species.

Table 2 lists several different aromatic compounds occurring in diesel range feedstock along with some selected properties and the corresponding fully saturated compound. It is apparent that dramatic shifts in boiling point and density can be realized by hydrogenating aromatic compounds. The density decreases by 20-25%

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Formula</th>
<th>Density, g/cc</th>
<th>°API</th>
<th>H/C Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso Paraffin</td>
<td>2,3-dimethyl-octane</td>
<td>C₁₀H₂₀</td>
<td>0.738</td>
<td>60.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Paraffin</td>
<td>n-decane</td>
<td>C₁₀H₂₀</td>
<td>0.730</td>
<td>62.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Olefin</td>
<td>t-decane</td>
<td>C₁₀H₂₀</td>
<td>0.741</td>
<td>59.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Naphthene</td>
<td>Decalin</td>
<td>C₁₀H₁₈</td>
<td>0.897</td>
<td>26.3</td>
<td>1.8</td>
</tr>
<tr>
<td>MonoAromatic</td>
<td>Tetratin</td>
<td>C₁₀H₁₄</td>
<td>0.970</td>
<td>14.3</td>
<td>1.2</td>
</tr>
<tr>
<td>PolyAromatic</td>
<td>Naphthalene</td>
<td>C₁₂H₈</td>
<td>1.140</td>
<td>-7.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 1. Hydrocarbon compounds found in diesel range feeds.
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. At a “typical” ULSD hydrotreating temperature and base pressure around 500 psi, ULSD conversion can be shown to increase with increasing hydrogen pressures, such that total aromatics conversion nearly doubles when H₂ partial pressure increases by a factor of 2.5.

**Figure 1** 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 4.0% (absolute) lower for the NiMo catalyst compared to the CoMo catalyst. This difference in aromatics conversion accounts for the higher hydrogen 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 to compete with saturation reactions. At high enough temperatures, both catalysts give the same conversion since they are operating in an equilibrium-controlled regime.

### Hydrogen Consumption

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 2** 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-ringed 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.³ In the case of the 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 3** shows the species concentration profiles as a function of residence time for

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**Table 2.** Dramatic shifts in boiling point and density are observed when hydrogenating PNAS.

<table>
<thead>
<tr>
<th>Rings</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>Naphthalene</td>
<td>C₁₀H₈</td>
<td>1.240</td>
<td>424</td>
</tr>
<tr>
<td>3</td>
<td>Fluorene</td>
<td>C₁₄H₁₀</td>
<td>1.202</td>
<td>563</td>
</tr>
<tr>
<td>3</td>
<td>Phenanthrene</td>
<td>C₁₄H₁₀</td>
<td>1.180</td>
<td>630</td>
</tr>
<tr>
<td>4</td>
<td>Pyrene</td>
<td>C₁₄H₁₀</td>
<td>1.271</td>
<td>759</td>
</tr>
</tbody>
</table>

---

**Figure 1.** Comparison of aromatic saturation capacity of NiMo vs CoMo catalyst shows NiMo has higher conversion capability. However, both catalysts exhibit similar conversion in equilibrium controlled regime.
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 napththalene is approximately an order of magnitude faster than the rate of hydrogenation of the first ring in biphenyl.4

**Figure 4** summarizes pilot plant data demonstrating how the aromatic species change in ULSD product as a function of the residence time (i.e. 1/LHSV) in the reactor (where LHSV is liquid hourly space velocity). Notice how the curves look very similar to the simple example previously discussed in Figure 3. 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 0.5 hr⁻¹ or more there is very little change due to equilibrium constraints. For mono-ringed aromatic saturation, there is a steady increase in concentration 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-ring 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 (SOR) temperature and the increased fouling rate associated with it.

ART® (Advanced Refining Technologies, LLC) 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 4 times (4X) the hydrogen consumption. The results of which will be discussed in detail as Part II of Custom Catalyst Systems for Higher Diesel Yields.

To this end, conducting detailed unit-specific pilot plant testing delivers 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 refiner’s 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 to be discussed in Custom Catalyst Systems for Higher Diesel Yields: Part II.

Editor’s Note:
This article was prepared from a more detailed article prepared by Brian Watkins and Charles Olsen at the March 17-19, 2013, AFPM Annual Meeting in San Antonio, Texas (AFPM paper #AM-13-10: “Custom Catalyst Systems for Higher Yields of Diesel”).

Literature Cited


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EIA Updates Refinery Statistics: Run Rates, Inventories, etc

Crude oil refinery inputs in the U.S. averaged about 15.4 million bpd during the week ending November 8, 2013, 343,000 bpd higher than the previous week’s average. Refineries operated at 88.7% of their operable capacity last week (i.e., “last week” referring to business week ending Friday, Nov. 8). Gasoline production rose from the previous week, averaging 9.4 million bpd. Distillate fuel production increased last week to 4.9 million bpd.

U.S. crude oil imports averaged about 7.8 million bpd last week, up by 620,000 bpd from the previous week. Over the last four weeks, crude oil imports averaged 7.5 million bpd, 7.5% below the same four-week
period last year. Total motor gasoline imports (including both finished gasoline and gasoline blending components) last week averaged 446,000 bpd. Distillate fuel imports averaged 130,000 bpd last week.

U.S. commercial crude oil inventories (excluding those in the Strategic Petroleum Reserve) increased by 2.6 million barrels from the previous week. At 388.1 million barrels, U.S. crude oil inventories are above the upper range for this time of year. Total motor gasoline inventories decreased by 0.8 million barrels last week, but are near the top of the average range. Finished gasoline inventories increased while gasoline blending component inventories decreased. Distillate fuel inventories decreased by 0.5 million barrels last week and remain near the lower limit of the average range for this time of year. Propane/propylene inventories fell 1.3 million barrels last week and are in the lower portion of the average range. Total commercial petroleum inventories decreased by 5.9 million barrels last week.

Total products supplied over the last four-week period averaged 19.7 million bpd, up by 5.0% from the same period last year. Over the last four weeks, motor gasoline product supplied averaged about 9.0 million bpd, up by 4.7% from the same period last year. Distillate fuel product supplied averaged 3.9 million bpd over the last four weeks, up by 6.9% from the same period last year. Jet fuel product supplied is up 0.1% compared to the same four-week period last year.

U.S. Refiners Triple Fuel Exports over Last Decade

According to a November 14 Bloomberg report, the U.S. has become the world’s fueling station, sending more gasoline, diesel, and other refined petroleum products abroad than ever before. Exports of these fuels have almost tripled in 10 years. In 2011, the U.S. became a net exporter of refined oil products for the first time since World War II. Exports are forecast to keep rising as European refiners close, domestic crude production rises, and demand swells in emerging markets.

Gazprom Neft helps PetroVietnam meet Euro-5 Standards

Gazprom Neft announced November 12 that they and Vietnam Oil and Gas Group (PetroVietnam) have signed a framework agreement setting out the terms of Gazprom Neft’s proposed acquisition of a stake in the Dung Quat oil refinery and the refinery’s planned modernization program. Gazprom Neft will acquire a 49% share in Binh Son Refining and Petrochemical, which controls and manages the refinery. The two parties are currently in negotiations over the price of the stake.

As part of the modernization program, the capacity at Dung Quat will be increased from the current 6.5 million tonnes to 10-12 million tonnes within one year and the plant will improve the technical efficiency of its motor fuel production to meet the Euro-5 standard. Gazprom Neft’s financial contribution to the modernization project will be proportional to its stake.

Alexander Dyukov, Chairman of the Management Board of Gazprom Neft, said; “Our Company’s long-term strategy calls for a major increase in refining volumes outside Russia. Access to the capacity at Dung Quat will allow Gazprom Neft to enter the Asian market for refined products, which is one of the fastest growing and most promising markets globally. For this refinery upgrade project in Vietnam Gazprom Neft will draw extensively on the Company’s experience in modernizing our refining capacities in Russia and Europe, where all plants now produce fuel meeting the Euro-5 standard. By working with PetroVietnam we will ensure that the Vietnamese market enjoys a stable supply of refined products that meet world standards.”

U.S. NGL Output Competing with OPEC and Refinery Markets

The growth in NGL plant output means end-use consumption depends less on receiving supply from refinery operations. It could also further limit demand for OPEC crude oil. At a minimum, U.S. natural gas liquids (NGL) plant production will add about 525,000 bpd to global oil supply, and the rest of the world will add another 350,000 bpd between now and the end of 2015, according to the recently-released Global Crude Oil Outlook from consultancy EIA Energy.

The primary implication of growing NGLs is that they further limit the call on OPEC crude, the group says. At the same time, the growth in NGL plant output means end-use consumption depends less on...
receiving supply from refinery operations. The production of ethane, LPG and plant condensates (pentanes plus) from gas processing can replace the demand for LPG or naphtha from refineries. For example, new ethylene cracker capacity around the world may either be geared to run ethane or have the flexibility to switch between ethane, plant LPG and naphtha.

Likewise, pentanes plus can replace naphtha as a crude oil diluent. And of course, plant LPGs may compete with refinery LPGs. The contribution of gas processing to “oil” supply is somewhat akin to the growth in alternative fuels, which have replaced refinery-derived transport fuels. As a result, global refinery throughput growth will increasingly not track global “oil” demand growth, making refining profitability even more elusive, according to the ESAI Energy outlook.

U.S. Refiners Rejoice as EPA Unveils Plan to Reduce Renewable Fuels Mandate

The U.S. Environmental Protection Agency (EPA) said it would wait until spring to issue a specific renewable fuels quota, though they did say in the draft rule that it would be in a range of 15 billion to 15.52 billion gallons for renewable fuels such as corn ethanol and biodiesel from soybeans. That compares with 18.15 billion gallons set in the legislation, according to a November 15 Bloomberg report.

The Obama administration proposed November 15 a reduced quota for the amount of renewable fuel that refiners must use next year, bowing to industry complaints that the targets contained in 2007 legislation were too high. The range is in line with an August draft that was leaked and prompted intense lobbying from industry officials.

Overall, the proposal, which is set to be finalized in the first quarter of 2014, would reduce demand for corn-based ethanol and lower compliance costs for refiners such as Valero Energy Corp. and Tesoro Corp. “While the agency took a step in the right direction, more must be done,” said Jack Gerard, the chief executive of the American Petroleum Institute. “They are getting close to making sure they don’t breach us through the blend wall,” he said.

The agency also proposed a range for the mandate for biodiesel and cellulosic products, such as those made from corn stalks or woody waste, which would be somewhere from 2.0 billion gallons to 2.5 billion gallons. That’s below the 3.75 billion gallon target spelled out in the legislation, and compares to 2.21 billion gallons from the leaked draft. This “could significantly chill investments in advanced biofuels projects,” Brent Erickson, executive vice president of Biotechnology Industry Organization, said in a statement. “We will focus over the immediate comment period on convincing the administration to right the course on this policy.”

EPA officials say they are listening to those concerns and have pledged to preserve a market for what are dubbed “next generation fuels.” In presenting a range, the agency would allow outside groups to weigh in over the next two months prior to a final EPA decision.

Refiners, fast-food restaurants, motorboat makers and chicken farmers have all pushed the EPA to scale back the ethanol mandate, saying it risks ruining engines by forcing more ethanol to be blended into gasoline and is acting to push up demand for corn. Gasoline demand is falling, and so rising requirements for renewable fuels are ramping up the percentage of those fuels in the overall mix.

Refiners, which have waged a battle against the corn ethanol mandate, haven’t fought so hard against biodiesel, as it doesn’t present the same constraints as ethanol. Escalating the required amount of ethanol could force refiners to sell blends with more than 10% of the corn-based fuel, a phenomenon known as “hitting the blend wall,” according to the American Petroleum Institute.

Fuel with more than 10% ethanol can cause engine materials to break down and damage emission-control systems, according to research from the oil-industry group. Supporters of ethanol say newer cars can run on fuels with 15% ethanol, and many flex-fuel vehicles can use 85% ethanol.
Refiners Finding Processing Shale Crudes is No Easy Task

Unusual contaminants resulting from upstream and midstream shale production and treating operations has caught many refiners by surprise

Prepare for high variability when processing “tight” light oil is the general consensus of those refiners processing paraffinic shale crudes since at least 2012. High variability can include oscillating variations in plant run rates, particularly affecting equipment efficiencies, including compressors, pumps, blowers, heat exchangers, etc.

Paraffinic crudes destabilize asphaltic crudes, such as the heavier crudes from Canada. Increased crude distillation unit (CDU) furnace fouling and fouling in the cold train and hot train of the CDU and other units is also a problem with the unusual contaminants in crudes coming out of the Bakken, Eagle Ford and other oil-laden shale plays. Further downstream, these waxy crudes have initiated hydrotreater preheat train fouling.

While shale crudes may not have the same contaminant problems as with heavy crudes from Venezuela and other regions, such as nickel, vanadium, sulphur, etc., they are contaminated with production and hydraulic fracturing chemicals, such as barium and lead. Moreover, even though shale crudes are very low in sulfur bearing compounds, they do contain H2S. Sulfur and H2S is not the same thing! The tramp amines left over from the drilling fluids and treatment programs that upstream and midstream producers use to control H2S at the wellhead and in the pipeline, and controlling shale crude oil odor in transport (particularly by truck or rail) lead to increased overhead corrosion, beginning in the refinery’s desalter and CDU (i.e., amine hydrochloride salt induced corrosion).

More importantly, processing these light-to-superlight shale tight oils in the 40-70 °API range limit the refiner’s flexibility to absorb more naphtha, making it important to carefully choose the right technologies and tools to modify the naphtha train, particularly when it involves naphtha hydro treating. Problems such as hydrotreating catalyst deactivation, not only concerns North American refiners, but refiners in other regions that are on the verge of introducing more shale crudes into their refinery operations.

Nonetheless, it takes more than just a steep learning curve to curtail profit opportunities with these types of crudes. Many other operational challenges and related process economics can deter profitability. For example, before declaring insolvency in January 2012, Petroplus was making good progress toward reducing operating costs in their refineries. The goal was to achieve operating cost savings of $80 million per year within three years. In 2011 alone, $50 million savings were achieved through staffing level reductions (both employees and contractors), pension plan adjustments, and maintenance cost efficiencies.

But the benefits of that hard work were wiped out by two big surprises going back to 2011. They were negative foreign exchange impacts ($35 million), and unexpected catalyst cost increases ($20 million). These unexpected cost increases were big factors in the Petroplus insolvency and the ensuing shutdown of five European refineries in January 2012.

For several years prior to insolvency, Petroplus employees knew they had big opportunities in the area of catalyst selection and procurement. But efforts to achieve these savings were thwarted by resistance to change across the Petroplus group, especially in how catalyst decisions were reached and contracts awarded, according to former BP FCC and hydro treating expert, George Hoekstra, who reviewed the company’s publicly available data. Hoekstra concluded that historical relationships and old ways of working proved impossible to break. As a result, Petroplus suffered intolerable catalyst cost. Taking this instance as an example and going forward with new challenges, such as blending shale based crudes with asphaltic heavy Canadian crudes, refiners will have to consider new ways of dealing with so much operational variability, especially at the desalter and CDU, when processing unconventional tight oils from shale.
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