Selected Answers to the 2010 NPRA Q&A Hydroprocessing Questions

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Question # 10

Brian Watkins
Advanced Refining Technologies

What are refiners' experience with respect to unit availability, catalyst performance and product quality when co-processing "renewable" feedstocks in a ULSD unit? Is there a big variation in operability with different sources of renewable feedstocks?

ART has conducted testing on various petroleum blends containing between 10-80% renewable sources of feedstock. The catalysts most active for this type of processing are AT580 and NDXi, both premium high activity NiMo catalysts used widely in ULSD and hydrocracking pretreat service. The data show that simple bio-based oils such as soybean, rapeseed & palm oils, when co-processed in a diesel feedstock require essentially the same temperature for 10 ppm product sulfur as the diesel feed alone. Comparing the feeds at ultra low sulfur levels suggests that the co-processing of the renewable oils has a small effect on the performance of the hydrotreater with the variability being about 10°F for <10 ppm product sulfur.

Due to the nature of the renewable sources, a boost in the product cetane index is also observed due to the increase in n-paraffin content in the diesel product. These n-paraffin's, however, raise concerns about the diesel product cloud point. Normal paraffin’s have a significantly higher cloud point than other hydrocarbons of similar carbon number. Since hydrotreating converts the fatty acid chains into long chained n-paraffin’s, the cloud point of the hydrotreated product will increase compared to the product using a SR base feed only. At lower blending concentrations the effect is minimal, but it needs to be considered depending on the target market for the product.

Based on these results, the use of ART’s high activity hydrotreating catalysts can enable refiners to co-process renewable oils through conventional refining equipment. Co-processing can be incorporated into a refiner’s operating strategy with minimal detriment to catalyst stability or yields, but the effect on an individual operation will depend on the base feed and conditions requiring ART to evaluate the options for refiners who wish to consider incorporating co-processing biofeeds into their operation, but want to understand the optimum configuration to maximize their profitability.
Question #12

Charles Olsen
Advanced Refining Technologies

Now that ULSD production has seen several cycles what are the SOR and EOR operating conditions? What catalyst formulations are being used (NiMo, CoMo, regen, and various blends)?

The types of catalysts being used in ULSD are typically current generation, high activity Type II catalysts, and the catalyst loadings cover the range from 100% CoMo catalysts for lower pressure units to 100% NiMo catalysts for higher pressure units with no H₂ constraints. A large percentage of units have been using a combination of NiMo and CoMo catalysts as in the SmART Catalyst System® from Advanced Refining Technologies. The SmART Catalyst System is based on a staged catalyst approach utilizing a high activity CoMo catalyst like 420DX for efficient removal of sulfur via the direct abstraction route and a high activity NiMo catalyst like NDXi which effectively removes the multsubsti- tuted dibenzothiophenes via the hydrogenation route.

One of the big advantages of using a staged catalyst approach like this is illustrated in the figure labeled Question 12. The figure shows that as NiMo catalyst is added to the catalyst system there is a large increase in HDS activity relative to the all CoMo reference, and eventually, a maximum in HDS activity is reached.

The position and magnitude of this optimum varies with feed and operating conditions, especially H₂ partial pressure. The figure also includes the relative H₂ consumption, and again, as the percentage of the NiMo component increases, the H₂ consumption relative to the base CoMo system increases. Notice, however, that in this case the relationship between H₂ con-

sumption and the fraction of NiMo catalyst is nonlinear. In the region where the system shows the highest activity the hydrogen consumption is only slightly greater than that for the all CoMo system, and well below that for the all NiMo catalyst. It is this ability to balance HDS activity and H₂ consumption to meet individual refiner requirements that sets the SmART Catalyst System apart.

Exact start of run conditions will of course vary with feed and operating conditions, but a typical SOR WABT is around 640-660°F. The typical ULSD unit has a LHSV of around 1 hr⁻¹ with an inlet pressure of around 850 Psig, although ULSD unit pressures vary from a low of around 500 Psig to a high around 2000 Psig. Observed deactivation rates have been in the range of 1-3°F/mo depending upon the feed and operating conditions.

End of run conditions have been determined by a unit constraint such as a reactor inlet temperature limitation or some product attribute, most commonly product color. We’ve observed, as an average, an EOR WABT around 730-740°F. It's important to note that for diesel product color it is the reactor outlet that is important. We’ve observed reactor outlets as high as 760°F in some cases with no detrimental impact on product color.

There are also a number of ULSD units which suffer from Silicon and Arsenic poisoning. These units tend to have shorter run lengths and will include a sizeable bed of guard catalyst to protect the active catalyst below.

Perhaps somewhat surprising is the number of ULSD units which have exceeded expectations in terms of cycle length. Many grassroots and revamped units were designed for two year cycles and actually ran 3-4 years. For the units which have changed out we’ve seen catalyst...
loadings which include adjustments to the relative amounts of NiMo and CoMo catalysts, the addition of new, higher activity catalysts which weren’t available when the unit started up, and in some cases a portion of catalyst load is made up of reactivated catalysts. These reactivated catalysts are regenerat-ed and further processed to redisperse the active metals using proprietary processes such as PHOENIX which was developed by ART and is now currently offered by TRICAT. In most of the latter cases reactivated catalyst makes up only part of the reactor fill with the remaining volume new catalyst.

**Question #13**

Robert Wade  
Advanced Refining Technologies

Severe fouling of diesel and gas oil hydrotreating preheat exchangers has been a growing problem. What are the causes and how can these be prevented? Has anyone tried antifoulant injection in this service?

We have not had success reducing fouling effects by adding antifoulants. It is our experience that adding antifoulants at best treats the symptom of the problem, and at worst further contributes to localized and downstream fouling. We recommend that the source of the fouling contaminant be identified through analysis and addressed at the source. If this is not possible then we revisit the basic design of the heat exchanger in question and ensure that it is operating in a shear controlled flow regime so that fouling effects are minimized.

**Question #16**

Meredith Lansdown  
Advanced Refining Technologies

ULSD reactor feed/effluent heat exchanger leaks can be a big problem meeting product specifications. What are practices for detecting and preventing leaks? Are there new technologies or mechanical specifications to prevent cross contamination?

Even small leaks in the feed/effluent heat exchanger in ULSD units can cause problems with meeting product specifications and can shorten cycle lengths. Seal welding the exchanger tubes to the tube sheet in the design phase can help prevent leaks from developing in the first place. When the unit is online, several different methods exist for detecting leaks. Often times, the challenge lies not only in figuring out whether or not there is a leak, but actually locating it.

Sulfur speciation of feed and product is one of the more common methods for determining whether or not there is a leak. When carefully implemented, this method can be used to detect extremely small leaks in ULSD units. Since the easily converted sulfur species are expected to be removed in the hydrotreater, their presence in the product stream indicates that a leak in the feed line is allowing them to pass into the effluent. Sulfur speciation does not require sampling the reactor effluent or other samples points from which samples are not routinely taken, however, it also does not allow the refiner to pinpoint which exchanger is actually leaking.

Radioisotope tracers with external detectors mounted on the external lines of the exchangers can be used for feed leaks greater than 0.05-vol.%. In this method, the isotope is injected upstream of the exchanger on the feed side, and the detectors measure the response time downstream. Having detectors on the effluent side of each exchanger is helpful in identifying which exchanger is leaking. Sometimes a pickup of the tracer on the feed side of the exchanger can show up as a leak, so with this method secondary leak detectors are often used as well. When using radioisotope tracers, it is important to ensure that the residence time is sufficient to notice the delay in picking up the signal. It is also important to sample the exchanger effluent lines in order to determine whether the leak is tracer pickup or an actual leak.

Feed leaks as low as 100 ppmv in the product can be detected using radioisotope tracers with effluent sampling instead of mounting external detectors. The tracer is injected into the feed inlet of one exchanger at a time and samples are obtained and analyzed onsite from the effluent side. The radiation counts from the exchanger effluents will indicate which exchanger is leaking.

Gas tracers, such as helium, are useful in determining whether or not there is a leak, but it may be difficult to quantify the leak size under 0.1-vol.% because it may be difficult to obtain a representative sample.

TRACERCO has developed a group of chemical tracers that have even better limits than radioisotope tracers to find very small leaks, which do pose a threat to catalyst run length and product quality. These chemicals are selected to closely match process fluids. Since they are very stable, they flash in the presence of high temperatures in a hydrotreating reactor but then condense with the effluent without actually reacting themselves. They can be detected in the product at levels as low as 1 ppm, so theoretically, a leak as low as 1 ppm can be detected using this method. In using these chemicals as tracers, though, the samples must be sent to a laboratory for analysis. Also, this method does not indicate which exchanger is leaking.
**Question # 17**

**David Krenzke**  
Advanced Refining Technologies

Are there documented cases of organic chlorides coming in with certain crudes? If so, what is their impact on hydrotreating units?

From our experience crudes do not naturally contain organic chloride compounds. However, in some cases they become contaminated with organic chlorides from production additives or some in-refinery sources. Small amounts of chloride do not have a negative effect on hydrotreating catalyst performance. Initially the chloride will react with the alumina support to form aluminum chloride. This will then interact with trace amounts of water vapor in the gas phase to form hydrogen chloride which in turn reacts with the alumina support further downstream eventually reaching an equilibrium which will limit the concentration of chloride on the catalyst. The presence of HCl in off gas may, however, present corrosion problems for downstream equipment.

**Question # 19**

**Brian Watkins**  
Advanced Refining Technologies

What are the key strategies to maximize the heavy diesel barrels in the diesel pool without cracking? Consider blending and dewaxing etc. to meet product specifications.

Increasing the quantity of heavier boiling fractions (LCO, coker, light gas oils) to the diesel hydrotreater has a number of impacts both on the performance of the hydrotreater and on the resulting ULSD product properties. Higher boiling fractions typically increase the amount of hard sulfur compounds, as well as increasing the amount of nitrogen and complex aromatic species. This has the combined effect of lowering the product cetane and limiting end of run (EOR) by making it difficult to maintain diesel ASTM color. Since general hydrotreating reactions do little to shift distillation, only a small quantity of higher boiling materials can be placed into the pool to maintain the product distillation specifications.

With the use of a selective ring opening (SRO) catalyst as part of the catalyst charge ART is able to improve diesel product cetane numbers by reducing total aromatic and PNA levels. The significant improvement in saturation activity is shown in the labeled 19-1. The SRO systems provides lower total aromatics and PNAs over a wide range of temperatures which translates to higher product cetane. The addition of SRO catalyst also helps provide additional EOR life in terms of product color. A catalyst system utilizing a high activity NiMo (NDXi) coupled with a selective ring opening catalyst will provide the same HDS and HDN activity, while having the ability to process additional LCO and other higher boiling fractions as well as achieving higher aromatic saturation conversion compared to the hydrotreating catalyst alone.

The SmART Catalyst System with SRO catalyst capability is very effective for reducing aromatic rings found in heavier feedstocks providing improved cetane and color performance. The majority of the increase in cetane from conventional hydrotreating is due to the saturation of poly aromatic compounds with some moderate amount of mono aromatic saturation. Saturating aromatic rings is an effective way to improve cetane, but there is a practical limit to the amount of cetane uplift that can be achieved. The reaction becomes thermodynamically limited near the end of the cycle resulting in a much lower level of cetane uplift and possible color problems. A better approach is aromatic saturation followed by selective ring opening.
The reaction schemes shown under Question 19-2 show the significant increases in cetane that can be achieved through selective ring opening.

The resulting product has a higher cetane, lower aromatics and boiling point, and avoids the issue of thermodynamic control at the end of the run. Additional information on this process can be found in the NPRA paper AM10-166.

Advanced Refining Technologies is well positioned to provide assistance on how best to maximize unit performance and to take advantage of opportunities to successfully process more complex feeds into the ULSD pool. ART has developed catalysts specifically designed to handle more difficult feeds exemplified by the SmART Catalyst System Series technology for ULSD. The technology has been widely accepted and the addition of an SRO catalyst to the ULSD catalyst portfolio provides refiners with greater flexibility in the operation of their diesel hydrotreating units.

**Question # 20**

**Greg Rosinski**  
Advanced Refining Technologies

How do refiners quantify the impact of sodium on hydroprocessing units, specifically those processing either residuum or VGO feeds?

Sodium (Na) is a severe catalyst poison that can cause significant activity loss even at low levels. It works by promoting the sintering of catalytic metals and neutralizing acid sites. Typical sources of sodium include a malfunctioning de-salter, sea water contamination or caustic contamination. Depending on the source of sodium, the signs of poisoning include rapid activity loss and an increase in pressure drop. The figure labeled Question 20 shows the impact of sodium poisoning on catalyst activity.
The figure indicates that for a sodium content of 0.5 wt.% the activity is at most 60% of fresh catalyst activity. This translates to roughly 30°F loss in activity for 1 wt.% sodium on the catalyst.

Question #21

Geri D’Angelo
Advanced Refining Technologies

Silica uptake on gas oil and diesel hydrotreating units is an increasing problem. What is the source of silica in these feeds? Are there effective ways to manage this silica?

Silicon is typically found coming from two locations in the refinery. Refiners having a coking process which requires antifoam usage generally see high concentrations of silicon in the naphtha and other light cuts from these units. Recently, refiners have been observing an increase in silicon levels coming from the crude tower and have begun to trace this to synthetic and other crudes new to the refinery. The process of making synthetic crude often involves a coking process, and many different crude suppliers use additives containing silicon added during the crude drilling process, and pipeline companies are using silicon containing additives injected into the crudes for both flow enhancing performance and foaming issues. The silicon tends to concentrate into most of the lighter cuts in the refinery including naphtha, kerosene, diesel and some gas oils. We’ve seen many of these types of units processing a feed directly from the crude unit which used to run for years between catalyst change outs, and now they shut down every one to two years due to silicon poisoning. The units did not have any guard catalyst installed as the refiners were not expecting silicon in a feed from the crude tower.

Some of the crude suppliers and pipelines have agreed to look into using different chemicals and technologies to decrease the amount of silicon ending up in the synthetic and other crude types. Progress in reducing the silicon values has been made by some of the suppliers which has been confirmed by several refiners. The reductions of the silicon values have been as high as 400%.

The most effective way to manage the silicon, assuming it can’t be removed from the feed slate, is to use a silicon guard catalyst near the top of the reactor to protect the main bed catalyst from poisoning for as long as possible. ART offers two catalysts which are effective at trapping silicon. AT724G catalyst is a high surface area silicon guard which has silicon pick up of capacity 20 wt.% Si. Even higher levels of pick up have been observed in units which operated at higher temperatures. ART also offers AT734G catalyst which is a combined silicon and arsenic guard. It has a silicon capacity similar to AT724G catalyst with 4 times the arsenic capacity. Both AT724G catalyst and AT734 G catalyst also have moderate activity and are used for activity and size grading at the top of the catalyst bed.

Question #22

David Krenzke
Advanced Refining Technologies

How are ULSD units maximizing catalyst life/cycle length? Is feedstock or catalyst analysis used to locate sources of contaminants, especially arsenic?

ULSD units are maximizing cycle by controlling several critical operating parameters including:

• Hydrogen partial pressure: Hydrogen purity and recycle gas rate need to be maintained at target levels to minimize coke formation. The figure labeled Question 22-1 summarizes pilot plant data demonstrating the impact H₂ availability has on activity in ULSD. For ULSD operations, ratios of hydrogen consumption to hydrogen to oil in excess of 5 to 6 provide greater stability and optimum performance of the catalyst.

**Question 22-1**

<table>
<thead>
<tr>
<th>H₂/Oil/H₂ Consumption</th>
<th>Relative HDS Rate Constant</th>
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</thead>
<tbody>
<tr>
<td>300 Psi H₂</td>
<td>0</td>
</tr>
<tr>
<td>750 Psi H₂</td>
<td>120</td>
</tr>
</tbody>
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<tr>
<th>20% LCO</th>
<th>SR</th>
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• **Feed distillation:** The feed end point has a significant impact on the required temperature to meet a product sulfur target. Increases in feed boiling point quickly increase the concentration of hard sulfur as well as increasing nitrogen and PNA levels. The figure labeled Question 22-2 shows how the fraction of hard sulfur in the feed increases with increasing end point of the feed. A high end point tail on the feed distillation will reduce the temperature span between SOR and EOR by requiring a higher WABT to produce the same product specifications, which in turn increases the deactivation rate as well as increasing hydrogen consumption.

• **Sulfur conversion:** Over-conversion even by even a small amount can significantly increase the catalyst deactivation rate. Higher temperatures to produce a lower product sulfur than needed increase coke deposition causing a higher rate of deactivation. Some refiners are using closed loop control with an on-line product sulfur analyzer to maintain on-spec product to prevent over-conversion.

• **Feed composition:** Higher concentrations of cracked stocks (coker & LCO) increase the concentration of hard sulfur which requires higher temperatures to remove. Cracked stocks also increase the olefin and PNA concentrations in the feed resulting in an increase in hydrogen consumption, higher exotherms and lower outlet hydrogen partial pressure. The net effect is a shorter cycle length due to higher operating temperatures and an increase in deactivation rate.

• **Consistent feedstock analysis is important to determine the presence of contaminants which can significantly impact catalyst life. Some of the more common ULSD catalyst poisons are silicon and arsenic. These can be difficult to detect in the feed at low concentrations and may also occur intermittently depending on the feed source.

• **Spent catalyst analysis:** A post mortem on spent catalyst is a useful way to detect the presence of unexpected contaminants and helps to optimize subsequent catalyst loadings in the unit. A good way to determine the average concentration of poisons like arsenic and silicon is from an analysis of spent catalyst from various locations in the reactor. Once the concentration is estimated an appropriate catalyst loading with guard materials can be utilized.