Hydroprocessing Catalysts from The Chevron and Grace Joint Venture
Editor’s Note:

Although this is only the second special issue of the Catalagram® dedicated solely to hydroprocessing, we at Advanced Refining Technologies salute our sister publication, the Grace Davison Catalagram on the fiftieth anniversary of its publication.

Advanced Refining Technologies has reaped the benefits of Grace Davison's long-standing technical leadership in refining catalyst manufacture and technical service and strengthened it with the technology power of Chevron R&D and process expertise.

As a result, ART has leapt to a leadership position in hydroprocessing catalysis since it was formed eight years ago. We offer a full range of HPC catalysts for distillate and fixed bed resid hydrotreating and ebullating bed resid hydrocracking and are recognized as the industry leader in resid hydroprocessing technology. Our technical service group, backed by both Chevron and Grace R&D, is able to solve your most difficult processing issues.

We hope you find the information provided here helpful in your operations. Like the Grace Davison Catalagram, we look forward to celebrating the 50th anniversary of Advanced Refining Technologies leadership.

Sincerely,

Scott K. Purnell
General Manager and Managing Director
Advanced Refining Technologies
In this Special Issue of the CATALAGRAM®

The SmART Catalyst System™: Meeting the Challenges of Ultra Low Sulfur Diesel
By Charles Olsen, Ph.D.
In this reprint from Catalagram® 97 from 2005, we update commercial usage of the SmART Catalyst system, which utilizes both CoMo and NiMo catalysts, 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. The article features an update on current ULSD operations with the SmART Catalyst System Series.

Continued Improvements in Advanced Pretreating by ART With Our Newest FCC Pretreat Catalyst, AT795
By Brian Watkins
As challenges in meeting clean fuels regulations continue to become more daunting, Advanced Refining Technologies continues to improve its line of ultra high activity FCC pretreat catalysts for our ApART™ Catalyst Systems. This article is an overview of the performance of the newest member of our FCC pretreat family, AT795, which is capable of significantly reducing required SOR temperatures for both HDS and HDN.

Cetane Improvement In Diesel Hydrotreating
by Greg Rosinski and Charles Olsen, Ph.D.
This article discusses the importance of cetane in ULSD. The SmART Catalyst System, which utilizes both the CoMo and NiMo catalyst, results in a cetane uplift which is nearly two numbers higher than an all-CoMo system with only a small increase in hydrogen consumption. For H2 constrained refiners this is an ideal solution for improving the product cetane.

Hydrocracker Pretreat Catalyst Development
By Dave Krenzke, Ph.D., Jifei Jia, Ph.D., Charles Olsen, Ph.D, Brian Watkins and Woody Shiflett, Ph.D.
ART introduces the second generation DX™ catalyst for hydrocracker pretreat, 590DX, our new high performance technology aimed at helping refiners meet the challenges presented by clean fuels.

ART’s Latest Catalyst Technology for EB Resid Hydrocracking
By Balbir Lakanpal, Darryl Klein, Pak Leung, Nan Chen, Pietro Greco and Ashok Monteiro
The ebullating bed resid hydrocracking process has an advantage in that a wide variety of crudes can be processed, allowing the upgrading of resid to almost saleable distillates, very good quality FCC/HC feed VGO, and low sulfur fuel oil. However, processing such opportunity crudes has its challenges, and ART has developed and commercialized its latest EB resid hydrocracking catalyst technology, HSLS™, to help achieve that goal successfully and economically.

Advanced Refining Technologies’ Answers to 2009 NPRA Q&A Questions on Hydrotreating
By Charles Olsen, Ph.D., Brian Watkins, Gordon Chu, Woody Shiflett, Ph.D., Dave Krenzke, Ph.D., and Geri D’Angelo

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The SmART Catalyst System®: Meeting the Challenges of Ultra Low Sulfur Diesel

In 2001, ART introduced the SmART Catalyst System® Series to help refiners deal with the severe demands of ultra low sulfur diesel (ULSD). The SmART 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; ART CDX, a high activity CoMo catalyst, efficiently removes the unhindered, easy sulfur via the direct abstraction route and ART CDY, a high activity NiMo catalyst, then attacks the remaining sterically hindered, hard sulfur. Pilot plant work has proven that the properly configured SmART System provides higher activity than either the CoMo or NiMo catalyst alone.

ART CDX and ART CDY, individually or as part of a SmART Catalyst System, were selected for 14 diesel units in 2004, and most of these applications aim to evaluate ULSD capability and/or produce ultra low sulfur fuels in advance of the regulations for economic benefit.

Optimizing the SmART Catalyst System

An important aspect of the SmART Catalyst System is determination of 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 refiners’ requirements, and selected feed properties and operating conditions as discussed in detail previously in Catalagram No. 95 (March 2004).
One clearly important parameter which must be considered is the boiling range of the feedstock. Sulfur speciation on a wide variety of feedstocks has shown that there is a strong correlation between the fraction of multi-substituted dibenzothiophenes (hard sulfur) and the feed endpoint. Once the D86 endpoint increases beyond about 625°F there is a rapid increase in the fraction of hard sulfur contained in the feed. This has a large impact on catalyst activity as shown in Figure 1. The figure shows pilot plant data comparing results from treating two feeds with different endpoints over the same catalyst under identical conditions. At ultra low sulfur levels there is about 30°F difference in reactivity of the two feeds with the lower endpoint feed more reactive. Clearly, feed endpoint and the amount of hard sulfur are critical parameters that influence the optimum SmART configuration.

Another critical feed property that must be accounted for is the nitrogen content. It is generally accepted that nitrogen inhibits aromatic saturation reactions through poisoning of acidic sites on the catalyst. Recall that the primary reaction pathway for removal of hard sulfur is via hydrogenation of an aromatic ring, and it is not surprising that feed nitrogen content has a serious, negative impact on HDS activity.

The magnitude of the impact can be seen in Figure 2 which summarizes data for a NiMo and a CoMo catalyst activity on an SR feed before and after selectively removing the nitrogen via an adsorption process. The difference in activity on the two feeds is quite large. Increasing the nitrogen content from 25 to 160 ppm results in a loss in HDS activity of 40-50°F for both catalysts. Comparing the catalysts on the low nitrogen feed shows that the NiMo catalyst has about 15°F higher activity relative to the CoMo catalyst, and that decreases to an advantage of about 5°F or less on the higher nitrogen feed. This suggests the impact of nitrogen is different for NiMo and CoMo catalysts with the CoMo catalyst more tolerant of nitrogen. This is another important consideration when designing the optimum SmART System.

Hydrogen availability, in terms of hydrogen pressure and hydrogen circulation, also takes on greater importance in ULSD. Figure 3 is a chart showing how the relative HDS rate constant changes as a function of the excess hydrogen (H₂/Oil ratio divided by the hydrogen consumption) for both high and low pressure operation. Note the range in operating pressure from low to high represents the conditions typically encountered in diesel hydrotreating. At high pressure, increasing the H₂/Oil is beneficial for both SR and 20% LCO feeds up to a point, after which further increases in H₂ rate provide little additional benefit. At low pressure, the effect of H₂/Oil ratio is quite different. In that case, the relative rate constant for both feeds shows a steady increase with increasing hydrogen rate. The benefit of increasing H₂/Oil never reaches a plateau as observed in the high pressure case indicating that more hydrogen is always better at low pressure. The effect of pressure is also readily apparent in the figure. Comparing the relative rate constant for high and low pressure at a typical H₂/Oil ratio reveals that the activity at low pressure is only...
10-20% of that at high pressure for 20% LCO and SR feed respectively.

**Controlling Hydrogen Consumption**

One of the key advantages of the *SmART System* is the efficient use of Hydrogen. Figure 4 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 large 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 varies with feed and operating conditions such as those discussed above. 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 result of the different kinetics for sulfur and aromatics removal and is a critical consideration when customizing a *SmART System*.

To help understand the differences in kinetics it is useful to compare the performance of CoMo and NiMo catalysts alone. Figure 5 shows a comparison of the hydrogen consumption over a NiMo and CoMo catalyst for a straight run feed at ULSD conditions. The amount of hydrogen consumed by sulfur, nitrogen and olefins removal is essentially the same for each catalyst and is not shown. What separates the two catalysts is the amount of aromatics saturation which occurs, and in particular, the amount of mono ringed aromatics which are hydrogenated. In this case, an additional 70 SCFB of hydrogen is consumed with the NiMo catalyst due to mono ringed aromatics saturation. This represents excess hydrogen consumption.
above that required for the removal of sulfur.

Figure 6 is a similar chart for LCGO feed. In this example, the NiMo catalyst hydrogenates more PNA (2 rings and greater) and mono ringed aromatics compared to the CoMo catalyst accounting for an additional 110 SCFB of hydrogen consumption above that required for sulfur, nitrogen and olefins removal. Clearly, in cases where hydrogen consumption needs to be minimized, a NiMo catalyst for ULSD is the wrong choice. Unfortunately, in many of these cases a CoMo catalyst does not provide the best activity for ULSD, and it is precisely these units where the SmART System is ideal as it offers the highest activity and is more efficient with hydrogen compared to an all NiMo system.

It perhaps appears contradictory that a NiMo catalyst is included in the SmART System due to its high hydrogenation activity making it preferred for hard sulfur removal, and yet, under some conditions the hydrogenation activity is too high and excess aromatics saturation occurs. This highlights one of the keys to designing the proper system. The design involves increasing the hydrogenation selectivity of the system to provide highest HDS activity, while at the same time minimizing hydrogen consumption (i.e. minimizing excess aromatics saturation).

Figure 6 shows a schematic of the reaction pathway for poly aromatics saturation. Naphthalene, a two ringed aromatic molecule, is featured at the top of the figure. The reaction begins with the hydrogenation of one of the aromatic rings to form tetralin, a mono ring aromatic. The next reaction in the sequence is hydrogenation of the remaining aromatic ring to produce decalin, a fully saturated molecule. Each step is reversible and subject to equilibrium constraints. The slowest reaction in the sequence is the saturation of the mono ring aromatic. The reaction sequence for a substituted biphenyl is also shown at the bottom of the figure. The sequence is essentially the same. In both examples the hydrogenation of the mono aromatic is the slowest step and also consumes more hydrogen compared to the other hydrogenation reactions shown; three moles of hydrogen per mole of aromatic are consumed by the saturation of the mono ring aromatic compared with two moles of hydrogen/mole for the multi ringed aromatics.

The reaction sequences shown in Figure 7 can be treated as a series of first order reversible reactions where the intermediate (the mono ring aromatic) is the desired product. For these sorts of reaction systems the intermediate often tends to be favored at shorter contact times (see Chemical Reaction Engineering by Octave Levenspiel [Wiley, 1998], for example), and it is this tendency which is exploited when customizing a SmART System. The effective residence time in both the CoMo and NiMo beds of a system is short compared to the overall reactor residence time, and this helps minimize the hydrogenation of the mono ring aromatic (i.e. minimize hydrogen consumption).
Figure 8
Limiting Aromatics Saturation

Table I
Commercial Experience with ART CDX, CDY and the SmART Catalyst System

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<th>Refiner</th>
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<td>4Q04</td>
<td>2Q05</td>
<td>2Q04</td>
<td>3Q04</td>
<td>1Q05</td>
<td>2006</td>
<td>2006</td>
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<tr>
<td>Catalysts</td>
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<td>CDX</td>
<td>CDX</td>
<td>CDX</td>
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<td>750</td>
<td>650</td>
<td>1290</td>
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Figure 8 shows the effect of residence time, as indicated by 1/LHSV, on aromatics saturation. For PNA saturation, the two ringed aromatic going to the mono ring aromatic, there is a fairly steep curve for conversion as a function of residence time below about 1 hr. Above that point, which represents space velocities of 1 hr⁻¹ or less there is very little change due to equilibrium constraints. For mono ring aromatic saturation there is a steady increase in conversion as the residence time is increased indicating more and more saturation as the residence time is increased (i.e., LHSV is decreased). Both sets of curves suggest aromatic saturation can be limited by appropriate choice of LHSV, or in the case of a SmART System, by adjusting the relative quantities of CoMo and NiMo catalyst.

SmART System Experience

The SmART System is the culmination of an extensive effort put towards understanding the chemistry and process conditions required for ultra low sulfur fuels. In addition, properly designed high activity catalysts must be used in order to take full advantage of the SmART System concept. ART has devoted significant resources to designing the best ULSD catalysts for use in the SmART System, and this effort has lead to the commercialization in 2004 of a new CoMo catalyst CDX, and a new NiMo catalyst CDY. These new technologies benefit from the optimization of the alumina chemistry to give the right surface area and pore size distribution, as well as providing the right surface chemistry (i.e., acidity).

ULSD production with the CDX/CDY SmART System began early in 2004, in a North American refinery processing a feed containing 20-40% of a high endpoint LCO. Since that time, CDX and CDY have been selected for 14 different diesel applications either as components in SmART Systems or as a complete charge. A list of commercial applications of CDX, CDY and SmART Systems is shown in Table I. It is apparent from the table that the SmART catalyst technology has been successfully applied to a wide range of feeds and conditions. In most cases it has been selected based on the high activity demonstrated in pilot plant testing.

As these and other recent successes demonstrate, Advanced Refining Technologies has developed state-of-the-art technologies aimed at helping refiners meet the challenges of clean fuels. These successes are the result of harnessing the unique heritage of ART which includes a collective expertise in material science, catalyst formulation, and manufacturing know-how. The science of designing specific catalyst components to operate in an optimum system is a fundamental part of ART’s catalyst technology. With the advent of clean fuels, ART seized the opportunity to extrapolate their catalyst system expertise from resid to lighter feedstocks. As a result, ART has been able to deliver high performance technologies ranging from StART™ Systems for Si tolerance in coker naphtha applications, SmART Systems for ULSD, and ApART™ Catalyst Systems for cat feed hydrotreating.

ART strives to continuously improve the performance of its catalysts, and the current focus of that effort is on maximizing the effectiveness of the catalytic metals. As described in Catalagram No. 96 (October 2004), ART’s new CoMo catalyst, CDX, benefits from improved metals utilization through the application of novel metals chemistry and a unique impregnation technique. These same techniques have been successfully applied to a new NiMo catalyst called an NDXi. As shown in Figure 6, this catalyst has significantly higher activity for ULSD than ART CDY and the conventional reference NiMo catalyst.

NDXi, commercialized in early 2005, has become the NiMo catalyst component of the SmART System.

**Figure 9**

![ART NDXi Has “Step Out” Activity](image)

**Figure 9**

ART NDXi Has “Step Out” Activity
Editor's Note:

A lot has changed since ART first introduced the SmART Catalyst System® series for ULSD in 2001. Many ULSD units have been built or retrofitted and are now into their second or third cycles. Most countries in the world are either mandating ULSD from their refineries, or in the process of doing so.

ART has made many improvements in its offerings for making ULSD as a result of extensive investment in the research and development of new and improved catalysts for expanding performance and flexibility. Since the introduction of CDY and CDX, ART is already on its third generation of catalysts. The premier catalysts used in today’s SmART system are 420DX and NDXi.

The table below shows the commercial experience of the SmART System. There are many repeat users among the more than 70 unit start-ups that have occurred using the SmART catalyst system. A wide variety of feedstocks and operating conditions are represented from units all over the world.

### SmART Catalyst System Users List

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Start-up Date</th>
<th>% Cracked Stock</th>
<th>Product Sulfur (ppm)</th>
<th>Pressure (psig)</th>
<th>% NiMo Catalyst</th>
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<td>700</td>
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<tr>
<td>Mid Continent, USA</td>
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<td>750</td>
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<tr>
<td>Japan</td>
<td>2005</td>
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<td>7</td>
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<td>Korea</td>
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<td>0</td>
<td>10</td>
<td>825</td>
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<tr>
<td>Russia</td>
<td>2005</td>
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<tr>
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<td>Pressure (psig)</td>
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Continued Improvements in Advanced Pretreating by ART with Our Newest FCC Pretreat Catalyst, AT795

ART’s AT575, AT775 and AT792 catalysts have long proven their performance advantage of outstanding stability and exceptional ability to provide consistent, high quality feed for their FCC units. In keeping with this tradition, ART is introducing its newest ultra high activity VGO catalyst, AT795. Figure 1 compares the activity of several FCC pretreat catalysts supplied by ART including the newest catalyst, AT795. The results from side-by-side testing of AT575 and AT795 clearly show that AT795 outperforms AT575 by almost 150% for HDS while maintaining similar activity for HDN.

Advanced Refining Technologies® (ART) first introduced the ApART™ catalyst system for superior FCC feed pretreating in 2002. The ApART technology was designed to provide maximum HDS activity while also providing significant upgrading of FCC feeds. This technology has been widely accepted with over 50 units in commercial service since its inception. As challenges in meeting clean fuels regulations continue to become more daunting, Advanced Refining Technologies continues to improve its line of ultra high activity FCC Pretreat catalysts, and strives to provide refiners with superior technology and first-class performance.

Advancing Refining Technologies
Chicago, IL USA

Brian Watkins
Technical Service Engineer
This newest member to the FCC pretreat family is capable of significantly reducing required SOR temperatures for both HDS and HDN. AT795 offers refiners a significant boost in its ability to generate low sulfur FCC products as well as deliver the benefits of nitrogen removal and poly aromatic saturation. Taking advantage of the synergistic effects in ApART by combining AT795 with AT575 provides unlimited opportunities for FCC feed upgrading.

An additional benefit of AT795 is improved aromatic saturation activity. Comparing an ApART system with AT795 to a system with AT792 clearly shows increased conversion of aromatics in FCC pretreat applications. This increase in aromatics saturation translates to improved FCC feed quality and increased yields from the FCC operation. The pilot plant work shown in Figure 2 used a feedstock with 1.5 wt.% Sulfur and 4700 ppm nitrogen.

AT795 is a NiCoMo catalyst that has outstanding HDS activity coupled with high HDN activity. This catalyst provides superior HDS performance in order to meet stringent gasoline sulfur regulations while also allowing refiners to benefit from improved FCC feed upgrading typically only found in pure NiMo applications. Refiners looking to add more hydrogen to their FCC feeds for additional conversion are going to reap the benefits of combining AT795 with AT575 in a new and improved ApART system.
Demand for higher performance in diesel engines has resulted in an increase in minimum cetane numbers for diesel fuel. It is expected that the desire for higher cetane will continue as indicated by the recommendations of the World Wide Fuels Charter. Thus, it is important for refiners to understand the effects of both feedstock and processing parameters on the cetane of diesel fuel to enable them to more effectively manage their distillate hydrotreating units to meet ever more stringent fuels specifications.

While some diesel is produced in hydrocrackers, the vast majority of diesel is processed in diesel hydrotreaters (DHT’s) which usually co-process streams such as FCC LCO, LCGO, SR diesel, and Kerosene. The units processing significant amounts of cracked stocks need special attention in order to meet product cetane requirements. To understand why this is so it is necessary to know what cetane is, and how the different molecular species influence it.

The cetane number is a measure of the ignition quality of diesel fuel and is based upon the compound cetane or hexadecane which is assigned a cetane number of 100. It is analogous to the octane number in gasoline. Gasoline octane increases with olefin, aromatic, and iso-paraffin contents, whereas cetane number increases with paraffin and naphthene contents.
Thus, a fuel with a high cetane value has low octane and vice versa.

Table 1 lists some pure compounds and their corresponding cetane number. As can be seen, paraffins, particularly normal paraffins, have very high cetane numbers while aromatics, especially naphthalene type aromatics, have very low cetane numbers. Certain distillate range materials like FCC LCO are high in naphthalenes which explains the low cetane number of LCO feedstocks.

The actual cetane number is rarely analyzed in refineries since it requires a specialized motor for its determination. Most refiners’ use cetane index, typically, ASTM D-976 and ASTM D-4737. D976 uses the API gravity and the 50% distillation point, whereas D4737 uses the gravity with the 10%, 50% and 90% distillation points. The two equations are shown below:

**ASTM D-976**

\[
\text{cetane index} = -420.34 + 0.016*\text{API}^2 + 0.192*\text{API}^2*\log(\text{T50}) + 65.01*\log(\text{T50}) - 0.0001809*\text{T50}^2
\]

Where T50 is the D86 50% point in degrees °F

**ASTM D-4737**

\[
\begin{align*}
\text{Cetane index} &= \frac{45.2 + 0.0892*(T10-215) + [0.131 + 0.901*B][T50-260] + [0.0523 - (0.420B)^2][T90-310] + [0.00049][T10-215]^2 - (T90-310)]^2 + (107B) + (60B^2)}{\text{T10-215}} \\
\end{align*}
\]

Where: \(B = \text{Exp}(-3.5*(\text{sp. gr.} - 0.85))\) – 1 and the D86 temperatures are in °C

Figure 1 compares the cetane index (D976) for a number of different distillate feed sources. It is readily apparent that FCC LCO’s have the lowest cetane while straight run (SR) materials have the highest cetane. Distillate feeds derived from coking operations tend to have a cetane similar to SR material, while kerosene tends to have somewhat lower cetane owing to the lower boiling point. For the diesel range materials, the feeds with lower API gravity (LCO) have lower cetane index demonstrating that within a given boiling range the API is a reasonable tool for estimating the cetane index.

Figure 2 shows the cetane index as a function of poly aromatics content for a variety of distillate feeds. The LCO’s clearly have the highest concentration of poly aromatics and correspondingly lower cetane index. The SR, LCGO and vacuum bottom gas oil (VBOG) all have considerably lower PNA content with higher cetane index values compared to the LCO’s. Kerosenes have very low polynuclear aromatics (PNA) content, but because of the lower molecular weight (kerosene generally has compounds containing less than 16 carbon atoms) the cetane index is slightly lower than for SR diesel material. The figures make it clear that when it comes to cetane, LCO is a problem due to the high PNA content.
Treating feedstocks that contain LCO will become more challenging as LCO yields increase and cetane requirements become more stringent. With this in mind, it is useful to survey the level of performance currently being achieved in commercial diesel hydrotreating units today. This will help to define what the reasonable level of cetane uplift that can be expected is, and if there is a practical maximum uplift that can be achieved via hydrotreating. It is also useful to ascertain whether current operations indicate if cetane changes (decreases) during the cycle. All of these are important questions for refiners interested in increasing diesel yields from lower quality feedstocks.

There are a number of parameters which influence cetane improvement in the diesel hydrotreater. Hydrogen partial pressure and LHSV are key operating conditions which effect the product cetane. Catalyst selection also plays an important role since at higher pressures NiMo catalysts have a higher PNA saturation activity compared to CoMo catalysts.

Figures 3 shows the level of cetane increase (measured by delta cetane index) that has been achieved commercially as a function of unit LHSV. Generally speaking, as LHSV decreases the potential cetane improvement increases. At a LHSV around 1 hr⁻¹ or less, cetane index increases of 10 or more numbers are achievable (provided the H₂ pressure is high enough), while at a LHSV greater than about 1.7 hr⁻¹ the cetane improvement is about 4 numbers or less.

Figure 4 summarizes the cetane increase as a function of unit pressure. Not surprisingly, higher pressure units tend to achieve much larger cetane increases. In these examples, the cetane uplift is typically less than 6 numbers when the unit pressure is less than 1000 Psig. Cetane uplift increases to 8-10 numbers as pressure increases beyond 1000 psig. The data in Figures 3
and 4 also suggest there might be a practical limit to cetane improvement achieved from typical hydrotreating. Comparing the cetane uplift achieve by Refiners A and C shows about 8-10 number improvement for both units despite the difference in operating pressure at similar LHSV.

Figure 5 summarizes the commercial data in another way. It shows how the cetane increase correlates with the API gravity of the feed. In general, the cetane uplift increases as the feed API decreases. Figure 6 shows how the observed API increase correlates with the cetane index increase. This data shows that the API uplift is a reasonable predictor for the cetane increase.

The hydrogen consumption is another important consideration when discussing cetane improvement. There is a general rule of thumb that says the hydrogen consumption is roughly equal to (100* API Uplift) or (100* Cetane uplift). Averaging the H₂ consumption required for the observed cetane increase with the units discussed here indicates that the H₂ consumption varies from about (80*Cetane uplift) at low pressure (Refiner D) to (150-175* Cetane uplift) for the high pressure units (Refiners A & C). The data suggests the rule of thumb is a reasonable estimate for H₂ consumption for units operating below about 1000 psig.

These data demonstrate that as the unit conditions (LHSV and pressure) get more favorable for PNA saturation, the cetane uplift increases. However, is cetane uplift constant during an entire cycle?

Figure 7 summarizes the observed cetane from three ULSD units currently using SmART systems. Refiner A is a high pressure unit with a LHSV around 1. The feed to this unit contains 40-50 vol.% LCO. This unit has not experienced a significant decline in cetane uplift during the cycle. Refiner B is a higher LHSV unit, with a lower pressure...
than Refiner A, but the feed is relatively light with about 35-40 vol.% LCO and LCGO. Despite the lower pressure and higher LHSV, this refiner also did not see an appreciable decline in cetane uplift during the cycle. Refiner C is a higher pressure unit with a lower LHSV compared to Refiner B. The feed is high in sulfur with large (>80 vol.%) amounts of cracked stock, especially LCO. This unit does show a slow, steady decline in cetane uplift; the cetane uplift is 2-3 numbers lower after more than two years on stream. This suggests that units with difficult feeds containing high fractions of LCO and other cracked stocks, or units without sufficient hydrogen, will experience decreasing cetane uplift during the cycle.

As mentioned previously, the catalyst system will also have an impact on the degree of cetane uplift achieved in a hydrotreater. It is common knowledge that NiMo catalysts have a higher saturation activity than CoMo catalysts, and therefore a NiMo catalyst is expected to deliver greater cetane uplift. Figure 8 summarizes pilot plant data which demonstrates this. These data were generated using a 50% LCO containing feed, and shows that the NiMo catalyst results in almost twice the cetane uplift compared to the CoMo catalyst. The SmART Catalyst System, which utilizes both the CoMo and NiMo catalyst, results in a cetane uplift which is nearly 2 numbers higher than the all CoMo system with only a small increase in hydrogen consumption. For H₂ constrained refineries this is an ideal solution for improving the product cetane.
he stringent legislation that has been enacted in many parts of the world for clean fuels has demanded that refiners produce fuels with very low levels of sulfur. In order to meet refiners increasing needs, significant improvements in hydrotreating catalysts are needed. In order to synthesize and develop highly efficient hydrotreating catalysts for this service, an in-depth understanding of the relationship between catalyst structure and catalytic activity is needed. In 2001, Grace and Chevron formed Advanced Refining Technologies® to provide world class hydrotreating catalyst technology for the refining industry. Since its inception, ART has concentrated on developing high performance technologies aimed at helping refiners meet the new challenges presented by cleaner fuels. This has lead to the introduction of several new technologies including the SmART system for ULS D , the ApART™ catalyst system for FCC pretreating, and high activity catalysts for hydrocracker pretreat applications. Continuing this effort, ART is introducing its second generation DX™ catalyst for hydrocracker pretreat, 590DX, in 2009.

Hydrocracker Pretreat Catalyst Development

Good hydrodenitrogenation (HDN) activity is the primary function of a hydrocracker pretreater as organic nitrogen compounds are detrimental to the performance of the downstream hydrocracking (HCR) catalyst. The rate limiting step in the HDN reaction pathway is aromatic ring saturation. This is because the most refractory nitrogen compounds are pyridine structures where the nitrogen atom is incorporated into the aromatic ring. The development of an improved HDN catalyst therefore needs to focus on the properties that enhance ring saturation. Two key considerations in the endeavor are active metals utilization and optimization of catalyst support properties.
The current generation of hydrotreating catalysts relies on the formation of Type II active sites during catalyst activation. Type II sites are known to provide significantly higher activity at the same metals loading as catalysts containing Type I active sites. An effective way to maximize the concentration of Type II active sites is through the use of chelate technology during the metals impregnation step of catalyst manufacture. ART has been steadily improving the application of chelates as detailed in Catalagram #96, 2004. To further improve the effectiveness of these new chelated catalysts, the support must be designed to enhance the chelate chemistry as well as tailored for the optimum surface area and pore structure for the targeted application.

Figure 1 summarizes the progression of hydrocracker pretreat catalyst technology through the years. As can be seen, there has been significant innovation since the formation of the ART joint venture in 2001. NDXi is an ultra high activity catalyst for hydrocracker pretreat and ULSD applications. This catalyst has been selected for more than 50 units for ULSD and hydrocracker pretreat since its commercialization in 2005. NDXi was selected for many of these applications through competitive pilot plant testing where the performance advantages were easily demonstrated. NDXi has shown significant HDN activity advantages over the previous generation catalyst, AT580. Since the level of active metal is similar for both catalysts, it is a good demonstration that chelate technology offers incredible potential for producing highly active sites compared to conventional (non chelated) catalysts.

Figure 2 compares the VGO HDN activity of AT580, NDXi and the newest catalyst, 590DX. This pilot plant comparison was completed on a VGO with a final boiling point above 1100°F, and it contained 1150 ppm nitrogen and 2.7 wt.% sulfur. The conditions represent an accelerated aging condition and the data are normalized to 1 ppm product nitrogen. It is clear from the figure that 590DX has more than 10°F higher HDN activity than NDXi under these severe conditions.

Figure 3 summarizes more pilot plant data which compares 590DX with NDXi on a variety of VGO feeds. The nitrogen content of the feeds ranges from 600 to 1200 ppm, and the sulfur content varies from about 1.5 wt.% to just under 3 wt.%. 590DX consistently shows 10-20°F HDN activity advantage over NDXi over a wide range of feeds and conditions. Furthermore, the test work has shown that the stability of 590DX is comparable to NDXi consistent with the similarity in pore size distributions for the two catalysts.
As 590DX and other recent successes demonstrate, Advanced Refining Technologies has developed high performance technologies aimed at helping refiners meet the challenges presented by clean fuels. This has been accomplished in a few short years by capitalizing on the extensive material science and catalyst knowledge encompassed by combining Grace Davison and Chevron. 590DX is merely the latest catalyst resulting from the dedicated effort to offer the best technology for refining today.

References

1. Krenzke, Dave; Vislocky, Jim. Hydrocarbon Engineering (2007), 12(11), 57-58
ART’s Latest Catalyst Technology for EB Resid Hydrocracking

The refining industry is once again going through the cyclical challenge of maximizing margins, and with that, efficient bottom of the barrel upgrading using a wide range of opportunity crudes continues to be the focus. The Resid hydrocracking (RHC) refiner, an ebulliating bed resid hydrocracking process, has an advantage where such a wide variety of crudes can be processed allowing upgrading the resid to almost saleable distillates, very good quality FCC/HC feed VGO, and low sulfur fuel oil. However, processing such opportunity crudes has its challenges, and ART has developed and commercialized its latest EB Resid hydrocracking catalyst technology to help in achieving that goal successfully and economically.

ART’s catalyst development efforts were directed after the following needs from the RHC operator’s:

- Same or higher resid conversion at reduced organic sedimentation to allow higher on-stream factor with opportunity crudes.
- Improve quality (sulfur) of upgraded products and stability of HT resid product.
- Higher HDCCR conversion (for bottoms going to Coker feed).
- Higher API on total converted products(synthetic crude production).
- Improve catalyst usage economics ($ cat/bbl feed) on the RHC.
Organic sediment formation in the RHC is a key factor of operability and on-stream factor for the RHC refiner, and is very dependent on the characteristics of the resid, which is a function of the crude source. ART, in close co-operation with its joint venture partner Chevron, has done considerable work in defining the characteristics of the resid and its impact on the sediment formation in the RHC, which has allowed the development of the its new RHC catalysts.

Three different resid feeds, A, B and C were identified and proprietary techniques were used to characterize beyond the conventional SARA (Saturates, Aromatics, Resins and Asphaltenes) analysis. The asphaltenes were further broken down to “good” and “bad” asphaltenes from Sediment formation standpoint in the RHC process. As shown in Figure 1, even though the asphaltenes content of these feeds was not too different, further characterization showed large differences in the ratio of good to bad asphaltenes, with Feed A being having the lowest ratio of good/bad asphaltenes. The feed reactivity using from pilot plant tests, Figure 2, confirmed that Feed A with the lowest good/bad asphaltenes ratio, or highest feed difficulty factor, had the highest organic sediment formation per unit resid Conversion (Sediment (ppm)/Resid Conversion (%)) ratio, with all other parameters being constant.

Research efforts were then directed, keeping in mind the above listed goals, to develop RHC catalysts that would allow the lowest Sediment/Resid Conversion ratio.

After the very successful and wide acceptance commercially of the LS (Low Sediment) technology platform in 2004, ART’s latest development for RHC catalysts is the HLSLS™ (High Stability Low Sediment) technology platform.
The HSLS™ technology incorporates a novel base, along with an advanced and special process technology for efficient metals impregnation (Figure 3). The proprietary alumina, with very specific pore size distribution (Figure 4), and the process technology allows efficient use of the active metals.

Extensive pilot plant data, using ART’s standard feed, for the HSLS™ technology showed higher stability, as measured by the resid conversion coefficient, and higher resid conversion as compared to a range of previous catalyst technologies (Figure 5). For the three feeds tested, namely A, B, and C, the HSLS™ technology exhibited higher HDM (Figure 6), higher MCR removal (Figure 7), and slightly higher sulfur removal (Figure 8).

The sediment suppression ability of the HSLS™ technology, in Figure 9, for the three different feeds, showed the degree of benefits that can be achieved for the broad range of these feed stocks. The pilot tests, and the advanced feed characterization, confirms the huge benefit (~40% reduction) in the application of the HSLS™ technology for Feed A (having a low good/bad asphaltenes ratio), very good sediment suppression (15-20%) for Feed B (medium good/bad asphaltenes ratio), and small benefit for Feed C (high good/bad asphaltenes ratio). Sediment/Resid Conversion ratio reduction of 50%, 20% and 9% was obtained using the HSLS™ catalyst technology, Figure 10, for Feed A, B and C respectively.

The HSLS™ catalyst technology has been use commercially very successfully in several RHC units since 2008, with the undermentioned multiple benefits:

- Lower Sediment formation (7-20%), allowing reduced frequency of clean out of downstream equipment – higher on-stream factor and lower maintenance costs. In
Figure 7
Higher Con Carbon Removal with HSLS™

PP Data - HDMCR (Con Carbon)

2 - 4% Higher MCR removal with HSLS™

Figure 8
HSLS™ has slightly higher HDS Activity

PP Data HDS

1 - 3% Higher HDS with HSLS™

Figure 9
HSLS™ Technology Platform - Sediment Suppression

Sediment vs. Resid Conversion - Pilot Plant Data (Commercial Points)

~40% Lower Sediment

2 - 3% Higher Conversion
some cases this has allowed higher Resid Conversion and/or flexibility of more opportunity crude processing.

- Higher MCR removal – better Coker feed quality
- Improved HDS of the distillate and unconverted resid.
- Significant reduction (5-15%) in fresh catalyst usage (specific) rates
- Higher HDM – more value for metals recovery on spent catalyst

Additional test work with other Resid feedstock’s and commercial trials are also planned.

The HSLSTM technology platform offers new opportunities to the RHC refiner as an effective and efficient catalyst for the bottom of the barrel upgrading in Ebullating Bed Resid Hydrocracking.

Figure 10
Feed Type vs. Catalyst Technology - Maximum Resid Conversion Pilot Plant Data

Sediment Suppression per unit Resid Conversion with HSLSTM Catalyst Technology

References
What are the challenges and concerns with hydroprocessing biodiesel such as palm oil, vegetable oil or animal fats? HT Question #1

Brian Watkins
Advanced Refining Technologies

Taking a detailed look at the compounds found in typical renewable oils shows that these oils could be treated as classic petroleum based compounds. ART analyzed different renewable sources of fuels in order to better understand the possible chemistry that would occur if they were processed in a conventional hydrotreater. Bio-based sources of oils can be of significant value when incorporated into the ULS diesel pool due to the low contaminant concentrations and high cetane number of the resulting products.

The major saturated and unsaturated fatty acids found in these oils can consist of materials such as palmitic acid (C16:0), linolenic acid (C18:3), linoleic acid (C18:2), oleic acid (C18:1), eicosenoic (C20:1) and erucic acids (C22:1) in varying percentages. In the unbroken, unprocessed form, the triglyceride molecules are significantly outside the diesel pool range as they have molecular weights of 700 or greater, while the typical diesel pool has a molecular weight of less than 400 and these triglyceride molecules cannot be blended into the diesel pool at the levels required to meet renewable fuel standards. This requires conversion of the triglyceride in the hydrotreater in order for it to be used. Since these renewable feeds are derived from a biological source, they also contain a high concentration of oxygen that is entirely dependent on the length and degree of saturation of the fatty acid chains. This quantity of oxygen is important, as under normal hydrotreating conditions the oxygen will react with the hydrogen to form water. This water, if generated in a significant enough quantity due to high percentages of oxygen in the hydrotreating feedstock, may cause problems such as weakening the catalyst support or redistribution of the active metals and loss of surface area. Another concern is that these renewable feed sources can include various contaminants. An analysis of several different biofeed sources has indicated the presence of contaminants such as sodium, calcium and phosphorus. Use of GRACE’s adsorbents and other specialty catalysts these contaminants are able to be controlled.

Through the once hydrotreated however, these n-paraffins can be of significant value for ULSD as they have typical cetane numbers ranging from 95 to 110 which can provide a significant boost for those refiners processing feeds with lower cetane (i.e. FCC LCO’s) as the typical diesel hydrotreater has only a small effect on cetane with cetane upgrade of about 2-4 numbers. The downside is that as the percentage of renewable feeds are placed into the hydrotreater, the resulting n-paraffins will increase the cloud point of the diesel which in various areas of the world can be problematic.
Using one of Advanced Refining Technologies’ high performance distillate hydrotreating catalysts, we have been able to capitalize on renewable sources of fuel by bypassing the purchase of renewable products for blending at the pump and instead processing the raw materials through conventional hydrotreating equipment to produce a higher quality ULSD product. Additional information regarding the co-processing of these materials can be found in the 2008 NPRA paper (AM-08-80) "New Opportunities for Co-Processing Renewable Feeds in Refinery Processes."

What are the experiences and plusses/minuses (cost / fouling / flexibility/ H₂ partial pressure) with dual processing of coker naphtha with straight run diesel / kero streams in a single hydrotreater with downstream fractionation? HT Question #11

Dave Krenzke
Advanced Refining Technologies

The driving force for co-processing coker naphtha and straight run diesel/kero is to simultaneously produce reformer feed and ULSD/ULSK. In order to accomplish this, a number of issues need to be addressed:

- Expanded guard beds to prevent catalyst bed fouling and pressure drop increase
  - Coker naphtha is highly olefinic and requires a bed of activity grading to prevent bed plugging from polymerization.
  - Coker naphtha may also contain coke fines so additional particulate grading is required.
  - Coker naphtha usually contains Si from the antifoam agent used in the coker and depending on the crude source may contain arsenic so a contaminant guard bed is required to protect the downstream hydrotreating catalysts.
  - The expanded guard beds reduce the volume of active catalyst and consequently reduce cycle length.
- Decrease in hydrogen partial pressure and higher heat release
  - The addition of coker naphtha results in greater feed vaporization and higher hydrogen consumption resulting in a lower hydrogen partial pressure and increased catalyst deactivation.
  - The saturation of olefins releases significantly more heat than other hydrogenation reactions leading to large exotherms. Since the EOR is usually determined by a maximum outlet temperature, this could result in a shorter cycle length.

Quality of reformer naphtha

- The downstream stripping/distillation will have an impact on the quality of the naphtha streams as any remaining H₂S from the stripper bottoms will concentrate in the light naphtha.
- The sulfur content of the heavy naphtha may increase near the End Of Run (EOR) due to recombination. To protect the reformer, the EOR temperature may need to be lowered or a sulfur trap installed.

In conclusion, co-processing coker naphtha and straight run diesel/kero is feasible but may result in a cycle length penalty and/or require additional equipment such as a sulfur sorber.

Does anyone bottom dump and water wash the reactor walls during catalyst change-out where nitrogen-blanketing would otherwise be required? When using the water flood approach, we have experienced extended delays when dumping and reloading ULSD reactor vessels. What can be done to expedite this without compromising safety? HT Question # 12

Woodrow Shiflett
Advanced Refining Technologies

At least one international major refiner typically wet dumps most all hydrotreater and hydrocracker reactors for safety reasons. Owing to the long history of the practice with this refiner, the appropriate balance between expedited change-out timelines and safety was achieved some time ago.
What techniques are being used to shutdown and startup units without flaring?
What equipment modifications have been made to eliminate flaring during shutdown/startup?
HT Question #13

Geri D’Angelo
Advanced Refining Technologies

Flaring can be greatly reduced or totally eliminated by using the fuel gas system and purging via an amine scrubber in most applications. Another option is routing the overhead stripper and/or hydrogen purge from the separator gas to the refinery's wet gas system. The wet gas systems normally run at a lower pressure so the volume left in the equipment is minimized and can then be routed to the flare.

Lines from high pressure separators and stripper tower overhead piping systems to fuel gas systems via an amine contactors can be used to remove H₂S.

The industry practice is to maintain H₂S (hydrogen sulfide) presence when circulating H₂ (hydrogen) at operating temperature during a start-up. What experience do you have where activity was not significantly impacted as a result of high temperature operation without H₂S presence? Please indicate amount of time in this condition. Is there any difference or concerns with heating up with N₂ (nitrogen) instead of H₂ in terms of reduction? HT Question #15

Geri D’Angelo
Advanced Refining Technologies

The catalyst is in danger of being reduced during sulfiding when the atmosphere changes into H₂ only instead of H₂/H₂S at temperatures above 500˚F. If H₂S is lost during the sulfiding it is imperative to reduce the temperatures back down to below 400˚F until H₂S can be re-established into the system and the sulfiding can be resumed. Keeping the temperature high in a H₂ rich atmosphere is a favorable condition for metals reduction. The reduced metals cannot be reactivated in situ so the result is lower than expected activity.

I’m aware of at least one sulfiding where a purge valve was left open. The purge valve was not "board operated" and was forgotten about. The catalyst reached 550-600˚F in a H₂ rich environment for an extended time, and was never able to achieve the 500 ppm sulfur spec. The refiner had to quickly dump and reload another batch of catalyst before they could resume low sulfur diesel production.

Heating up in nitrogen poses no risk of catalyst metals reduction. There may be issues with gas circulation because of the higher molecular weight. Note, however, the hydrogen is necessary during a sulfiding.

After a catalyst loading, is it standard practice to flush the unit to cutter stock or slop until product is clear as opposed to re-circulating back to a feed tank or directly back to the unit charge? What are the concerns and risks? HT Question #16

Gordon Chu
Advanced Refining Technologies

Sulfiding Chemistry

<table>
<thead>
<tr>
<th>As Loaded</th>
<th>Reduced and Sintered</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>NiS</td>
</tr>
<tr>
<td>MoO₃</td>
<td>MoS₂</td>
</tr>
<tr>
<td>H₂, H₂S, 430 - 450˚F (fast)</td>
<td>H₂, no H₂S</td>
</tr>
<tr>
<td>H₂ ~500˚F</td>
<td>Ni, MoO₂</td>
</tr>
</tbody>
</table>

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Gordon Chu
Advanced Refining Technologies
It is ART’s standard practice to flush the unit to cutter stock or slop until the product is clear before re-circulating it back to the unit charge. This step is to ensure to remove the catalyst fines from the catalyst. Otherwise, catalyst fines could get back into the catalyst beds causing excess pressure drops.

What are the preferred response options to different sizes of hydrotreater furnace tube leaks? Discuss different response options for large ruptures versus very small leaks. HT Question # 17

Geri D’Angelo
Advanced Refining Technologies

Slowly de-pressuring to downstream lower pressure H₂ manifold or refinery fuel gas system for small controlled leaks. Most newer hydrotreaters are equipped with emergency pressure reduction systems that can rapidly dump a unit to flare system for evacuation during a major leak/rupture.

Typically silica has been associated with naphtha streams. More recently silica is being seen in heavy oil feeds. What are refiners experiences with this issue? How does this impact catalyst life and what are the solutions? HT Question # 18

Woodrow Shiflett
Advanced Refining Technologies

Silica, or silicon-containing compounds, in heavy oil feeds can arise from two general sources. Bitumen-derived syncrudes, in addition to potentially containing some decomposition products from delayed coker sourced silicon antifoam, can in some cases contain exceptionally small particulate silica from the tar sand source. The second general source is comprised of upstream or pipeline additives that are used for various wellhead applications or pipeline applications.

How do you deal with catalyst deactivation issues when both silica and arsenic are present in hydrotreater feed? HT Question #19

Charles Olsen
Advanced Refining Technologies

Feeds containing both silica and arsenic present a unique challenge to refiners because the contaminants poison hydrotreating catalyst via different mechanisms. Silicon fragments in the feed are known to distribute uniformly throughout the catalyst particle. They react with the alumina O-H groups forming a strong chemical bond with the alumina. Experience has shown that an effective catalyst for Si pick up has very high alumina surface area and pore volume which provide space to store the Si. ART offers AT724G for applications requiring a silica guard, and it has been used with a variety of feeds from naphtha to VGO.

Arsenic, on the other hand, poisons the catalyst active metal sites. Arsenic in the feed reacts with nickel on the catalyst to form nickel arsenide, NiAs. Based on this stoichiometry, a nickel based arsenic trap can theoretically pick-up about 1.28 wt.% As for each 1 wt.% Ni on the catalyst. The actual capacity will depend on process conditions (in particular temperature) and the concentration of arsenic in the feed. ART offers several different catalysts for arsenic protection including AT535, AT575 and AT580. The choice of catalyst depends on the feed and conditions of the particular application.

In units with both Si and As, two catalysts are typically offered to handle the contaminants, one for silica and one for arsenic (i.e. AT724G and AT575). The amount of each is determined by the amount of Si and As in the feed, the LHSV and the desired cycle length. This approach has proven effective at protecting the main catalyst from Si and As poisoning, but it can also decrease the volume of active catalyst since most of the guard catalysts are lower in activity than the main catalyst. To alleviate this, Advanced Refining Technologies will be commercializing a new catalyst called AT734G. This catalyst has been specifically designed to provide a high capacity for both Si and As thus eliminating the need for two separate guard catalysts.
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