Celebrating 100 years of operations at our Curtis Bay Works
Advanced Refining Technologies (ART®), is the joint venture of Chevron Products Company and W. R. Grace & Co.’s Grace Davison catalysts business unit, created to develop, market and sell a comprehensive line of state-of-the-art hydroprocessing catalysts. Since our formation in March 2001, we have firmly established ourselves as a leading supplier of premium hydroprocessing catalysts and technical service to the petroleum refining industry worldwide.

ART brings new standards of product innovation and customer service to the global refining industry by harnessing the technical expertise of both Chevron and Grace Davison in catalyst development and their broad experience in supporting refiners. With the combination of Grace Davison’s material science, manufacturing, marketing and sales strength, and Chevron’s extensive experience from operating its own refineries and leadership in design and process licensing, ART offers refiners one-stop access to hydroprocessing knowledge and technical service unparalleled in the industry.

ART brings refiners the unique synergies derived from our parent joint venture partners being leaders in hydroprocessing catalyst technologies. Chevron, and now Chevron Lummus Global (CLG) represent over 35 years of experience designing and licensing RDS and VRDS units, as well as operating resid hydroprocessing and distillate hydrotreating units at Chevron refineries. Grace Davison has over 50 years of experience in manufacturing hydroprocessing catalysts. Leveraging the refining and hydroprocessing experience of Chevron with Grace Davison's expertise in specialty materials and catalyst technologies makes ART uniquely equipped to quickly commercialize and deliver innovative products to the dynamic hydroprocessing marketplace.

To keep pace with the high demand for ART catalysts driven by heavy resid hydroprocessing applications and more stringent clean fuels standards, ART has expanded manufacturing capacity at its existing North American plants. ART acquired Orient Catalyst Company’s (OCC) hydroprocessing catalyst technologies, and the HOP® catalyst product line in 2002; and obtained an ownership position in Kuwait Catalyst Company (KCC) which has manufactured HOP resid hydroprocessing catalysts under license since 2001.

ART’s comprehensive line of hydroprocessing catalysts deliver maximum sulfur removal and upgrading for a wide range of feedstocks. ART offers hydroprocessing catalysts for the resid segment of the hydroprocessing market, including the fixed-bed Onstream Catalyst Replacement (OCR) resid process and ebullating bed applications, as well as a complete product line of premium catalysts for distillate hydrotreating of heavy VGO/DAO, diesel, kerosene and light naphtha applications.
Dear Hydroprocessor:

As Advanced Refining Technologies, LLC approaches the tenth anniversary of the joint venture, we are not only reflecting on our success, but on our plans for the future. In these past ten years, ART has emerged as a leader in hydroprocessing catalysts, with the leading share of resid hydrotreating catalysts and a significant and growing share of the distillate hydrotreating business. We recently completed our strategic business review with our parents, Chevron and Grace, and they are pleased with our business performance and excited about our future growth opportunities.

In this, our third ART Catalagram®, we introduce two new catalysts, AT734G catalyst, a combined silicon and arsenic guard catalyst for our StART™ Catalyst System, and AT795 catalyst for the commercially proven ApART™ catalyst system for superior FCC feed pretreating. Finally, we preview PHOENIX™ technology, a regeneration and reactivation process for ART’s Type II catalysts built on our DX® platform, that was developed by ART and scaled up to commercial scale with the help of TRICAT.

ART’s primary and central foundation is a customer commitment to proven industry-leading catalysts and technical service backed by the research and development power of both the Chevron and Grace organizations. To this end, we at ART look forward to providing you with innovative solutions to your hydroprocessing challenges for many years to come.

Scott K. Purnell
General Manager and Managing Director
Advanced Refining Technologies, LLC
Hydroprocessing Catalysts from Chevron and Grace

ART delivers innovative and economic hydroprocessing catalyst solutions worldwide, helping refiners on their never-ending quest to upgrade difficult petroleum feedstocks into clean fuels and other valuable products.

Supported by cutting edge research and development and world class technical service, the joint venture between Chevron and Grace combines over 60 years of material science expertise and catalyst formulation experience with over 3,300 unit-years operating experience. In addition, our partner affiliate licenses exceed 260 units across the globe.

Let ART be part of your solution. For more information on our products, contact us.

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04 Impact of Processing More LCO
By Charles Olsen, Greg Rosinski and Brian Watkins
Processing LCO as part of the feed to a ULSD unit can be challeng- ing since the quality, quantity and endpoint of LCO affect catalyst activity and product properties. These challenges can be overcome with proper choice of catalyst system and an understanding of the impact LCO has on both unit performance and ULSD product quality. ART is well positioned to provide assistance on how best to maximize unit performance and to take advantage of opportunities to successfully process more LCO into ULSD.

09 AT734G: A Combined Silicon and Arsenic Guard Catalyst
By Charles Olsen
Refiners are often looking for opportunities to purchase lower cost crudes and other feedstocks, and while these opportunity feeds may help improve profitability there can be some consequences. Many of these new feeds coming into the refinery contain unknown levels of catalyst poisons such as arsenic and silicon. To help deal with these uncertainties, ART has successfully commercialized a combined silicon and arsenic guard catalyst, AT734G.

14 AT795: The Latest Advance in FCC Feed Upgrading from ART
By Greg Rosinski and Brian Watkins
Advanced Refining Technologies has developed catalysts specifically designed to handle the more difficult feeds encountered in FCC pretreating. These catalysts are typically utilized in the ApART™ Catalyst System which is a staged catalysts approach that has been widely accepted with over 50 commercial units since its inception in 2002. ART continues to improve its line of high activity FCC pretreat catalysts with the commercialization of AT795 catalyst.

18 PHOENIX: A Regeneration and Reactivation Process for Type II Catalysts
By Charles Olsen and Brian Watkins, ART and David Jones and Gordon Frampton, TRICAT
Type II catalysts have found wide application in a variety of hydrotreating applications especially ultra low sulfur diesel and hydrocracking pretreat units. One of the problems with these types of catalysts is a high loss of activity following a conventional regeneration. To address this issue ART developed PHOENIX, a process to restore members of ART’s DX® family and other catalysts with Type II functionality to near fresh catalyst activity. TRICAT has been approved for use of the PHOENIX™ process, and it has been proven commercially at TRICAT facilities.

22 Selected Answers to the 2010 NPRA Q&A Hydroprocessing Questions
By Geri D’Angelo, Brian Watkins, Dave Krenzke, Greg Rosinski, Meredith Lansdown, Robert Wade and Charles Olsen
Impact of Processing More LCO

FCC LCO has long been a common component of feed to diesel hydrotreaters. More recently, there has been greater interest in processing higher quantities of LCO due to economic considerations and to meet the market demand for ULSD products. LCO has a number of impacts both on the performance of the hydrotreater and on the resulting ULSD product properties. The extent of the impact depends upon a number of factors including the amount of LCO in the feed, and the catalyst used in the ULSD unit.¹

It is generally accepted that the addition of LCO to the diesel unit increases feed severity and requires an increase in reactor temperature in order to meet the
Figure 1
Impact of LCO Content on Hydrotreater Performance

Figure 2
LCO Endpoint Effects Activity

In addition to the amount of LCO, the endpoint also has a significant influence on the reactivity of the feed. Figure 2 compares the performance of two 30% LCO blends relative to the straight run feed. The higher EP LCO has an endpoint of 780°F by D2887 compared to 749°F endpoint for the lower EP LCO. This difference corresponds to an additional 800 ppm of hard sulfur in the feed for the higher end point LCO in addition to a 15% increase in PNA's. The LCO endpoint effects are apparent even when blended into the straight run feed. The higher endpoint feed requires about 20°F higher temperature relative to the lower endpoint feed at low severity, and nearly 30°F higher temperature for ULSD sulfur levels.

Processing LCO also has an impact on the product quality of the hydrotreated diesel. A significant problem relates to the aro-
matics content as LCO’s tend to have very high concentrations of naphthalene type aromatic species which have very low cetane numbers causing the LCO to have relatively low cetane. The high PNA content also has an impact on diesel product color. This becomes important as end of run (EOR) is approached since ULSD units processing LCO blends will have product go off color at a lower temperature relative to an SR feed.

A survey of commercial operating units shows there are a number of operating parameters which influence cetane improvement in a diesel hydrotreater, most notably hydrogen partial pressure, LHSV and feed API gravity (i.e. amount of LCO). Generally speaking, as LHSV decreases the potential cetane improvement increases.

Commercial ULSD experience has shown that for LHSV’s around 1 hr\(^{-1}\) or less, cetane increases (as measured by cetane index, ASTM D-976) of about 10 numbers are achievable provided the H\(_2\) pressure is high enough when processing LCO blends. At higher LHSV’s (greater than about 1.7 hr\(^{-1}\)) the potential cetane improvement decreases to about 4 numbers or less.

Not surprisingly, higher pressure units tend to achieve much larger cetane increases. It has been observed that the cetane uplift is typically less than 6 numbers when the unit pressure is less than 1000 Psig while the cetane uplift increases to 8-10 numbers as pressure increases beyond 1000 Psig. A more detailed discussion can be found in reference 2.

As might be expected, there is a significant cost in hydrogen to achieving very high cetane increases from feeds containing LCO. Figure 4 shows how the H\(_2\) consumption increases with increasing cetane uplift from the same commercial ULSD unit.
For cetane number increases of 5-8 numbers the H₂ consumption is consistent with the rule of thumb that H₂ consumption equals 100*Δcetane. Notice, however, that getting increases beyond the 8 numbers in this case come at a very large increase in H₂ consumption; at 9-9.5 numbers of cetane improvement the H₂ consumption is over 1200 SCFB, a 30% increase in H₂ consumption per incremental cetane number. This suggests there is a practical limit to the cetane improvement achievable for a given set of feed and operating conditions, and in this commercial example it looks to be about 8 numbers.

Another potential product quality issue when processing LCO containing feeds is the diesel color. It is generally accepted that the species responsible for color formation in distillates are polynuclear aromatic (PNA) molecules. Some of these PNAs are green/blue and fluorescent in color which is apparent even at very low concentrations. Certain nitrogen (and other polar) compounds have also been implicated as problems for distillate product color and product instability. Work conducted by Ma et.al.³ concluded that the specific species responsible for color degradation in diesel are anthracene, fluoranthene and their alkylated derivatives. Other work completed by Takatsuka et.al.⁴ showed that the color bodies responsible for diesel product color degradation were concentrated in the higher boiling points in the diesel (>480°F) suggesting that color can be improved by adjusting the diesel endpoint. 

PNA's such as these are readily saturated to one and two ringed aromatics under typical diesel hydrotreating conditions at start of run (SOR), but as the temperature of the reactor increases towards EOR, an equilibrium constraint is reached whereby the reverse dehydrogenation reaction becomes more and more favorable. At some combination of ‘low’ hydrogen partial pressure and ‘high’ temperature, PNA's actually begin to form (or reform) resulting in a degradation of the diesel product color.

Figure 5 summarizes data from a commercial ULSD unit using ART catalysts. The data show that the product color exceeded 2.5 ASTM, the pipeline color specification for diesel, at reactor outlet temperatures above 730°F. The feed to this unit contained 30-50% LCO and it was
operated at 1.0 LHSV and 850 Psig inlet pressure.

Figure 6 summarizes some pilot plant data which was generated as part of a larger color study on a sample of used CDXi, a premium CoMo catalyst for ULSD. The figure shows a comparison of the diesel product color achieved from a SR feed and a 30% LCO blend at 2100 SCFB \( \text{H}_2/\text{Oil} \) ratio and two pressures. The SR feed results in acceptable color over a wide range of temperatures for both pressures shown. The product from the LCO blend, on the other hand, goes off color (>2.5 ASTM) between 730-740°F at 800 Psig while at 1200 Psig the temperature can exceed 760°F before going off color. This clearly demonstrates the significant impact that \( \text{H}_2 \) partial pressure has on diesel product color when processing LCO containing feeds.

Processing LCO as part of the feed to a ULSD unit can be challenging since the quality, quantity and endpoint of LCO affect catalyst activity and product properties. These challenges can be overcome with proper choice of catalyst system and an understanding of the impact LCO has on both unit performance and ULSD product quality. 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 LCO into ULSD.

References
2. G. Rosinski and C. Olsen, *Catalagram* 106, Fall 2009
3. X. Ma, et. al., Energy and Fuels, 10, pp 91-96 (1996)
AT734G: A Combined Silicon and Arsenic Guard Catalyst

Refiners are often looking for opportunities to purchase lower cost crudes and other feedstocks, and while these opportunity feeds may help improve profitability there can be some consequences. Many of these new feeds coming into the refinery contain unknown levels of catalyst poisons such as arsenic and silicon and, in fact, ART has seen an increase in the number of units experiencing poisoning from these contaminants in recent years as more of these opportunity feeds are processed.

Arsenic (As) is found in many crudes including some from West Africa, Russia, Venezuela and many synthetic crudes. Unlike the silicon from antifoams, evidence suggests that arsenic is distributed throughout the whole boiling range. Table I shows examples of the arsenic content for several crudes and the distribution through various cuts.

Arsenic is a permanent catalyst poison which means once it is on the catalyst it cannot be removed via regeneration or other means. It is a severe poison since a small amount results in significant activity loss. The arsenic is believed to bind with the metal sulfide sites, and in particular the active nickel on the catalyst forming nickel arsenide.

To demonstrate the impact of arsenic on catalyst activity, ART obtained a series of spent catalyst samples from a refiner. The catalyst samples had different levels of arsenic because of their location in the reactor. These samples were carefully regenerated in the laboratory and then activity tested using a diesel.
feed containing 50% FCC LCO under conditions producing <500 ppm sulfur. Figure 7 summarizes the results of that work. The catalyst had lost 15°F of activity after only 1000 ppm of arsenic poisoning, and the activity loss quickly increases to about 60°F at 1 wt.% arsenic on the catalyst.

The ultimate arsenic capacity of a catalyst is strongly dependent on temperature, similar to silicon pick up. Figure 8 shows how the arsenic pick up varies as a function of catalyst temperature for an ART NiMo catalyst. These results were obtained by analyzing spent samples retrieved from a three reactor unit processing 100% cracked naphtha from a synthetic crude source. The first reactor was operated at very low temperature (~275°F) in order to saturate diolefins, the second

<table>
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<th>Oil Type</th>
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<tr>
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<tr>
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<tr>
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<tr>
<td>Libya</td>
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<tr>
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<tr>
<td>Venezuela</td>
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</tr>
<tr>
<td>Wyoming</td>
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<table>
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<th>Distillation Cut</th>
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</tr>
<tr>
<td>HVO</td>
<td>25</td>
<td>Residuum</td>
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</table>

reactor was designed to saturate mono-olefins and operated at about 430°F. The last reactor had an inlet of 570°F and an outlet temperature of approximately 650°F. The arsenic content on the catalyst correlated with the temperature of the reactor as depicted in the figure. The data demonstrates the temperature dependence of arsenic pick up, and further indicates that a high nickel catalyst can pick up very high arsenic levels if the operating temperature and feed concentration are high enough.

A number of catalyst basket tests and spent catalyst data have provided additional evidence that catalysts containing nickel are much more effective for trapping arsenic, and Figure 9 summarizes some of this data. The figure shows that the relative arsenic pick up observed on a variety of catalysts correlates well with the catalyst nickel content.

These data, combined with the increasing incidence of catalyst poisoning from arsenic, prompted ART to develop a high surface area arsenic guard catalyst utilizing the highly successful AT724G catalyst technology platform. The goal of the development was to provide a single catalyst for applications suffering from both silicon and arsenic poisoning. In those types of units catalyst suppliers have typically recommended two guard catalysts, one each for silicon and arsenic. With the commercialization of AT734G catalyst, one guard layer is sufficient for both contaminants leaving more reactor volume available for the active catalyst.
Figure 10 summarizes some results from a catalyst basket where several ART catalysts were evaluated along with AT734G. AT734G picks up about four times more arsenic compared to AT724G, and even picks up more than some high Ni catalysts like NDXi and AT580.

Data from another catalyst basket is shown in Figure 11. This basket was installed in a unit processing cracked naphtha from a synthetic crude. Again, AT734G significantly outperforms AT724G and AT535 in terms of arsenic capacity.

Catalyst basket data confirms the superior arsenic pick up of AT734G, but what about silicon pick up? Figure 12 compares the Si pick up of AT734G and AT724G observed in a number of different catalyst baskets.
These baskets were installed in coker naphtha units as well as diesel units which suffer from Si poisoning. The data show that the Si pickup of AT734G is on average the same as the Si pick up of AT724G. Notice a few basket samples show extremely high Si pick up, in excess of 25 wt.% Si. These were installed in diesel units and experienced much higher temperatures than some of the baskets showing lower Si values.

The data demonstrates that ART has successfully commercialized a combined silicon and arsenic guard catalyst, AT734G. Like AT724G, it has moderate activity making it suitable for activity grading in applications processing cracked stocks. Several refiners have already selected AT734G because of its high capacity for both silicon and arsenic; it has 4 times the arsenic capacity of ART's highly successful AT724G silicon guard, but with the same silicon capacity making it an excellent new addition to the StART™ Catalyst System.

### Figure 12
Comparison of Silicon Pick Up

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<th>Basket</th>
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<td>Basket B</td>
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<tr>
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<tr>
<td>Basket H</td>
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![Comparison of Silicon Pick Up](image-url)
AT795: The Latest Advance in FCC Feed Upgrading from ART

Advanced Refining Technologies 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, ART continues to improve its line of high activity FCC Pretreat catalysts, and strives to provide refiners with superior technology and first-class performance.

ART’s AT575, AT775 and AT792 have long proven their performance advantages of outstanding stability and exceptional ability to provide consistent, high quality feed for FCC units. In keeping with this tradition, ART is introducing its newest high activity VGO HDS catalyst, AT795. AT795 benefits from using ART’s expertise in alumina synthesis which enables an increase in the surface support acidity promoting higher HDN activity and saturation activity at severe conditions.

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conditions. This enhanced ability for HDS and HDN allow for use of this product in a wide range of operations.

Figure 13 compares the activity of AT795 to its predecessor AT792. The results from side-by-side testing clearly show that AT795 outperforms AT792 by greater than 20% for HDS, HDN and aromatic saturation. This indicates that AT795 offers refiners a significant increase in their ability to produce lower sulfur FCC products as well as improve FCC yields from higher nitrogen and poly aromatics removal from the FCC feed.

Coupling the improved HDS activity of AT795 with the activity of AT575 allows refiners to produce low sulfur and nitrogen FCC feeds at significantly lower SOR temperatures. This gives
refiners the choice between increasing cycle life or processing more difficult feeds. Figure 14 shows the advantage of using the new system over previous ApART systems with AT575.

Not only is the improvement seen for HDS, but significant boosts above an all NiMo system for HDN and aromatic conversion are observed as well. This pilot plant work was completed at high pressure using a West Coast feed containing 40-45% coker gas oil. This confirms that not only is this system capable of delivering the low sulfur FCC products, but is also capable of improving FCC yields due to the increased PNA saturation ability of the AT795 catalyst system.

Figure 15 compares two ApART systems containing 25% each of AT792 or AT795. A consistent 5 number advantage in aromatics conversion can be observed for the AT795 ApART system. This work was conducted using a feed with 1.5 wt.% sulfur and over 4700 ppm nitrogen.

Refiners operating low pressure units typically designed primarily for sulfur removal will also benefit from using AT795. Figure 16 illustrates pilot plant work showing the advantage is still in excess of 10% as compared to AT792 for HDN while still having an advantage in HDS performance.

The proper choice of an FCC pretreat catalyst system must, in addition to other potentially important considerations such as feed metals removal, represent an optimization of sulfur removal capability as well as HDN and saturation activity. The flexibility of the ApART system offers the potential to provide maximum HDS activity, and thus lowest FCC gasoline sulfur content, while also providing a maximum in FCC unit conversion at constant coke operation. In a more general view, optimum ApART catalyst systems will exist with respect to gasoline sulfur and gasoline yield for specific FCC pretreater/FCC combinations.

ART’s understanding of its ApART catalyst systems capabilities and their influence on the operation and performance of the FCC unit permit these optimum solutions to be identified for the specific refiner’s situation.
AT795 is a VGO HDS catalyst that has shown outstanding HDS activity coupled with extremely high HDN and HDA activity. This catalyst will augment refiners need for better FCC feed conversion as well as providing support in producing lower sulfur clean fuels. Refiners looking to drive more hydrogen into their FCC feeds to gain additional conversion are going to see the benefits of the ApART system using AT795 with its high HDN and HDA activity. Combining this with the demonstrated stability of AT575 and other ApART system components indicates that AT795 will be able to provide this ultra high activity with excellent stability.
PHOENIX: A Regeneration and Reactivation Process for Type II Catalysts

**Gordon Frampton**
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Type II catalysts have found wide application in a variety of hydrotreating applications especially ultra low sulfur diesel and hydrocracking pretreat units. ART offers a range of Type II catalysts built on the DX® technology platform which includes CDXi, 420DX CoMo catalysts; and NDXi, 590DX NiMo catalysts. The high activity of these catalysts is due in part to the unique chelate technology employed in their manufacture, a description of which can be found in Davison Catalagram® No. 96, 2004.

One of the issues with these types of catalysts is a high loss of activity after a conventional regeneration. To address this, TRICAT has developed the PHOENIX: A Regeneration and Reactivation Process for Type II Catalysts.

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**Charles Olsen**
Worldwide Technical Services Manager
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Type II catalysts typically recover only 70-80% of fresh catalyst activity following a conventional regeneration. At that activity level the catalysts are suitable for cascading to less demanding applications, but are not active enough to reuse in ULSD or hydrocracking pretreat units.

Figure 17 compares the activity of a series of DX catalysts which have been carefully regenerated to different carbon levels using conventional techniques.

Regeneration to low carbon levels still only results in a catalyst which has 10-15°F lower activity compared to fresh DX catalyst. This indicates over-regeneration in an effort to remove nearly all of the carbon results in no gains in catalyst performance with an increase in regeneration expense.

To address the issue of catalyst reuse, ART developed the PHOENIX™ process, a proprietary technology to restore DX and other catalysts with Type II functionality to near fresh activity. It involves a controlled regeneration followed by a proprietary re-activation which results in 90-95% of fresh catalyst activity recovery. Figure 18 compares the activity of Fresh and PHOENIX DX catalyst. In this case the catalyst was restored to within 95%+ of fresh catalyst activity.

ART has worked with TRICAT to scale up this technology to commercial scale. The PHOENIX process overview includes screening and segregating the spent catalyst to remove support media and oversize/undersize material prior to regeneration.
Lot retails are collected and analyzed for a variety of contaminants, and the particle size distribution and physical properties are also determined to make sure the catalyst is suitable for reuse. Once the catalyst is approved for regeneration, it is processed in TRICAT’s patented ebullated bed regeneration process. With this process the target carbon and sulfur levels can be achieved in a single pass with 15-18% lower attrition relative to other processes.

Once regenerated, the catalyst goes through the reactivation process which involves the application of nanoscale dispersents and a carefully controlled drying step. It is critical that the correct amount of dispersing agent is used for optimum activity, and further, it is important that the catalyst is dried properly. A catalyst which has excess dispersing agent after drying will perform poorly as will one with too little. This is demonstrated in Figure 19 which shows how sensitive catalyst activity is to the amount of dispersing agent.

Commercial scale reactivation via PHOENIX has been demonstrated for the DX™ catalyst platform in TRICAT facilities. Figure 20 compares the activity of fresh CDXi, a lab prepared PHOENIX CDXi and a commercial PHOENIX CDXi. The activity recovery of the PHOENIX samples are within 95% of the fresh catalyst activity. This process has been repeated in several commercial runs of the PHOENIX process using CDXi.
The PHOENIX process has also been applied to other Type II catalysts. Figure 21 compares the activity of a fresh Type II catalyst with the PHOENIX catalyst. The activity of the PHOENIX catalyst again exceeds 95% of fresh activity providing a viable option for catalyst restoration.

TRICAT has been approved for use of the PHOENIX process, and it has been proven commercially for both DX and several other Type II catalysts at TRICAT facilities. Activity recovery has easily met the 90-95% of fresh activity target in all cases so far. For details on how this process may apply to your spent Type II catalyst, please contact either TRICAT or ART to discuss how the PHOENIX process can bring back life to your regenerated catalyst inventory.
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 feed stocks?

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 coprocess 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 multisubstituted 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 consumption 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

![SmART Systems vs All CoMo Reference](image-url)
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 regenerated 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 treat 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.

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**Question 19-1**

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<tr>
<td>740</td>
<td>45</td>
</tr>
<tr>
<td>750</td>
<td>50</td>
</tr>
</tbody>
</table>

**Total Aromatics**

**PNA’s**
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 desalter, 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.

<table>
<thead>
<tr>
<th>H₂/Oil/H₂ Consumption</th>
<th>750 Psi H₂</th>
<th>300 Psi H₂</th>
</tr>
</thead>
<tbody>
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<td>Relative HDS Rate Constant</td>
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<td>100</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

**Question 22-1**
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.
Because traditional distillation techniques fall short of drying ethanol to an acceptable level, water removal with molecular sieve adsorbents (zeolites) is the method of choice. In our pursuit of helping customers obtain high ethanol contents we have developed EnSieve® molecular sieve.

Designed for ethanol dehydration, EnSieve® molecular sieve offers outstanding benefits. Its unique structure provides a superior rate of adsorption and higher ethanol recovery due to the low co-adsorption of ethanol. Its minimal attrition means longer service life. Product composition minimizes side reactions such as the formation of aldehydes and ketones.

The Renewable Technologies product line draws on Grace Davison’s expertise in catalysis and separations to develop and provide technologies for purification, drying and biomass conversion.

The Renewable Technologies product portfolio includes:

- EnSieve® molecular sieve for ethanol dehydration
- TriSyl® silica and EnPure® adsorbents for feedstock and biodiesel purification
- EnRich™ catalysts for renewable fuels and chemicals

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