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ART’s complete line of hydroprocessing catalysts

- Distillate hydrotreating
- Hydrocracking
- Lubes processing
- Fixed bed resid processing
- Ebullating bed hydrocracking
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Optimizing Hydroprocessing Catalyst Systems for Hydrocracking and Diesel Hydrotreating Applications: Flexibility Through Catalysis
By W.K. Shiflett, Ph.D. Dan Torchia, and Charles Olsen, Ph.D.
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By Brian Watkins
Advanced Refining Technologies
Editorial

When Chevron and Grace joined together in 2001 to form Advanced Refining Technologies (ART), we set our goals based on the values of our parents: technology expertise, world-class research and development, global manufacturing footprint, and a complete portfolio of hydroprocessing catalysts designed to meet the challenges of today’s refiners.

Starting from a strong base of resid hydrotreating catalysts for Chevron Lummus Global (CLG)-designed units, ART’s portfolio also initially included ebulliating bed resid hydrocracking and distillate hydrotreating catalysts. Early in 2013 we fulfilled our vision of offering a complete portfolio of hydroprocessing catalysts when we signed an agreement with CLG giving ART the exclusive right to sell CLG’s hydrocracking and lubes hydroprocessing catalysts to CLG’s licensees and other petroleum refiners for unit refills. The agreement streamlines hydrotreating catalyst supply and improves technical service for refining customers by establishing ART as the single point of contact for all their hydrotreating catalyst needs.

This issue of Catalagram® 113SE is the first publication that covers our growing list of products. There are articles featuring our hydrocracking, ebulliating bed resid, fixed bed resid, and distillate hydrotreating catalysts, all written by our team of industry-leading technical experts in these fields.

Take a look below for an overview of our full portfolio. Then, we invite you to read about our catalysts in commercial operations. If you have questions about our catalysts and want to know how these catalysts, backed by our strong technical service, can improve the performance and operation of your unit, please call us at +1.410.531.4000 or e-mail us at catalysts@grace.com.

Thank you for your support of Advanced Refining Technologies,

Scott K. Purnell
Managing Director
Abstract

The dynamics of global gasoil and ultra low sulfur diesel (ULSD) demand are driven by regulatory demands for transport diesel and evolving needs for vastly improved marine bunker quality in specific emission control areas (ECA's), as well as by economic growth. It is expected that this will drive regional variability in ULSD/0.1% sulfur gas oil differential over time and consequently provide incentives for refiners to maximize flexibility in both hydrocracker distillate yields and ULSD unit performance. Adding in an expectation of gasoline supply becoming long in the Middle East over the next several years, the refiner is further motivated to evaluate and select premier catalyst systems for the production of diesel products from both their hydrocracking and diesel treating units. This article describes how best to address this challenge.

As it has been noted widely, the growth in refined products is strongly driven by the demand for clean diesel and new regulations on gasoils between now and 2020. Notably, cumulative annualized global growth in diesel/gasoil oil demand is predicted to be about 2%, outpacing gasoline at 1.3%, with the estimated gaso-line/diesel-gasoil oil ratio dropping from 0.85 in 2012 to 0.81 in 2020.1 In addition to continued growth in Asia and continuing recovery elsewhere, motor vehicle mileage standards and ethanol mandates in North America and emerging regulatory restrictions on marine fuels add further momentum to this trend. Bunker fuel regulations becoming effective in 2015 requiring 0.1% sulfur limits in emission control areas (ECA's) in North America, and northern Europe will underlie a demand shift to diesel/gasoil oil products with an expected concurrent boost in diesel price primarily due to quality requirements. Meanwhile, refining capacity additions outstripping global demand in the 2015-2020 period will continue to pressure refining margins. In short, it will be a period of opportunity for those refiners that have the flexibility of having hydrocracking capabilities, especially those coupled with a robust ULSD hydrotreater, who can marry their catalyst system needs and operational responses to changing economic scenarios.

In early 2013, Advanced Refining Technologies (ART) and Chevron Lummus Global (CLG) announced an agreement in which ART has the exclusive right to sell CLG’s hydrocracking and lubes hydrotreating catalysts to petroleum refiners worldwide for unit refills. The result dramatically streamlines hydrotreating catalyst supply and improves technical service focus for refining customers by establishing ART as the single point of contact for all their hydrotreating catalyst needs. In this context, this article addresses cata-
Molecular Management and Hydroprocessing Units

Of all diesel boiling range materials, FCC LCO stands out as one of the lowest value feedstock materials. It is usually the most difficult to manage operationally in a hydroprocessing unit largely due to the combination of olefins and the refractory nature of the LCO. It has the highest demand for hydrogen to produce a clean diesel or even 0.1 wt.% sulfur marine fuel, and offers heat release management challenges when processed at higher fractions in a hydroprocessing unit feed. Provided there is adequate hydrogen supply, LCO is sometimes best processed in the hydrocracker along with other feeds such as AGO’s or VGO’s. Adding to the equation is that all LCO’s are not created equal. Depending upon the refinery configuration, the LCO may be produced from an FCC with a feed pretreater and consequently contain fairly modest levels of sulfur and nitrogen. Although they appear to be “easier” feeds due to their lower levels of contaminants, the remaining impurities are also the toughest to treat.

Coker gas oils can be processed either in the hydrocracker or ULSD unit subject to individual unit capacities and infrastructure limitations such as hydrogen availability, pressure, endpoint, and impurities. Heavy coker gasoils (boiling well above the diesel range, >975 °F) are best sent to a hydrocracker although they can present significant challenges to processing in significant quantities even in modern, robustly designed hydrocrackers. A hydrocracker originally designed or revamped for VGO service is a most suitable outlet. This offers more potential to maximize diesel yields, especially in recycle flows configurations and higher pressures. Light coker gasoils, on the other hand, are readily processed to ULSD in a diesel hydrotreater provided there is adequate hydrogen partial pressure and the unit has the appropriately tailored catalyst system to remove contaminants and provide the required sulfur conversion.

Straight run (SR) gas oils present the least challenging processing constraints, and can be fed to either the hydrocracker or ULSD unit, although the ULSD unit is typically the preferred outlet. Exceptions include cases where the SR feeds are needed as “diluent” components to aid in managing hydrogen consumption limitations, and heat release issues in hydrocrackers designed for more paraffinic and naphthenic feeds.

Processing tactics are balanced between these feedstock molecular management considerations and the designs, limitations and strategic intent of the unit in the refining scheme. Hydrocrackers have traditionally been designed with intent to pump hydrogen into the feedstock to convert heavier, higher-boiling materials into more valuable products, while capitalizing upon aromatics saturation to increase volume swell as well as product value parameters (density, cetane, smoke point, etc.). Until recently, ULSD has been a secondary priority and generally not even a consideration in the original design of the bulk of hydrocracking units operating today. With a robust ULSD unit in the refinery, this prioritization need not be over-ridden, but can be augmented by the utilization of the latest catalyst systems for hydrocracking that have been designed for maximum HDS activity as well as the fundamental HDN, hydrocracking, and saturation needs.

The Versatile Hydrocracker and Catalyst System Flexibility

While several hydrocracker configurations are in current usage, two dominate the landscape, especially when addressing clean fuels production: single-stage, once-through (SSOT) configurations and two-stage, recycle (TSREC) configurations. A perspective over a decade of application is provided in Figure 1.

The SSOT configuration is both simple and versatile, and represents the simplest configuration when unconverted oil (UCO) has high value as either a lube plant feed or FCC feed. This configuration dominates the low conversion market (>70% of that market). The SSOT process configuration is shown in Figure 2.

Catalyst system optimization for the SSOT is often influenced strongly by the desired outlet for the UCO it produces: lube plant feed will favor higher viscosity index (VI), aromatics saturation and desulfurization (HDS), while FCC feed will favor nitrogen removal (HDN), poly-nuclear aromatics removal and desulfurization (HDS). Balanced with these needs are the light product drivers: ULSD or the less-demanding 0.1 wt.% sulfur marine fuel. If ULSD production is a target, and cannot be produced within the SSOT unit constraints, it is critical to factor in and model the effect of this pre-processed com-
ponent as feed to the ULSD unit. It will clearly include more difficult, sterically-hindered sulfur compounds for HDS in the ULSD unit.

Catalyst system selection and optimization is controlled by a number of constraints that must be accommodated in a single stage:

- Hydrodemetalization (HDM) needs driven by HVGO and/or deasphalted oil (DAO) components as well as by crude source (arsenic and other contaminants), and coker products in the feed (silicon contaminations).
- HDN requirements for the hydrocracking function of the catalyst systems that follow
- Hydroconversion targets for removal of heavy components
- HDS needs for products such as ULSD, marine gas oil, and UCO
- Aromatics removal (lube or FCC applications)
- Isomerization (for lube needs)

SSOT catalyst system optimization is further challenged when the application involves a unit converted from former service such as FCC pretreatment or, in less common cases, diesel treating. In such cases, heat release and hydrogen consumption come into play as these units typically contain only a few, deep beds. Semantics can sometimes obscure the proper application of catalyst technology. A “mild hydrocracker” is merely a low-conversion SSOT (<40%) and is most effectively evaluated as a part of the SSOT catalyst system continuum.

SSOT systems typically demand the highest activity catalyst components to meet HDN and HDS needs. Chevron Lummus Global, teaming with Advanced Refining Technologies, have met this challenge over time as noted from the rapid commercialization of hydrocracking pretreatment catalysts, as shown in Figure 3.

Lacking the flexibility of recycle and adjustment of the recycle cut point (RCP), product selectivity in the SSOT is controlled by the choice of the catalyst system, and largely the choice of the hydrocracking catalyst component(s), and the operating temperature regime and span. Hydrocracking catalyst product families typically exhibit a trade-off between selectivity to distillates and activity (temperature required for a target conversion level). Premier catalyst performance is defined by innovations that increase both selectivity and activity. Figure 4 shows the progression of such performance for the hydrocracking catalysts provided by ART.

Catalyst system design in an SSOT can involve more than a single solution. While a single hydrocracking catalyst from the “B” range might seem an obvious solution for a refiner desiring “A” selectivity, but lacking the infrastructure to compensate for the lesser activity, synergies in multi-catalyst combinations might instead point to a system of “A” and “C” catalyst and can actually achieve a better result than pure “B” alone.

TSREC configurations offer a high level of flexibility in addition to providing the more favorable means to achieve conversion levels of 90% plus. TSREC configurations also are the preferred means to achieve full naphtha/gasoline selectivity. The configuration is shown in Figure 5.

TSREC units offer the refiner the ability to operate the two stages differently in order to simultaneously meet separate goals for each stage. This configuration also offers the flexibility to “balance” the stages to optimize the desired product selectivity and qualities. Note that although this unit is shown with two reactors, they are often built with multiple reactors, generally as part of the first stage providing even greater ability to process poorer value stocks. As an example, the first stage could be targeted to both provide a diesel draw suitable for marine fuel blending as well as pretreatment for the second stage which could be targeted to produce ULSD. Contrasted to the SSOT, the TSREC has added operational flexibility provided by the ability to adjust RCP and per-pass conversion in each stage, plus a second catalyst system that allows optimization of an additional catalytic component. In addition, TSREC will enable production of other very high quality products such as JET-A which can be recovered as a single product or recovered with the ULSD, depending upon economics of the day. In addition, feedstocks can be shifted with the ULSD unit to further add operating space. This integration and flexi-

FIGURE 2: SSOT Process Configuration

FIGURE 3: Commercial Development Timeline for High Activity SSOT Hydrocracking
Catalyst system selection and optimization in the first stage is often influenced by feed quality and contaminants - nitrogen, sulfur, metals, silicon, and arsenic being the typical suspects. This is especially challenging for older, existing units but can be equally challenging even for new units.

Following removal of feed contaminants, the remaining catalyst volume can be used to achieve the conversion and selectivity goals. Often the first stage is required to achieve 50-60% conversion after removing feed contaminants for both stages. Depending upon unit objectives, first stage cracking catalyst can be chosen from any of the “A”, “B”, or “C” groups.

Second stage catalyst selection will largely be driven by performance of the first stage to achieve the desired overall unit goals. Second stage catalyst will contribute significantly to product quality improvement and to the ability to achieve very high levels of conversion to the desired product, typically diesel or total distillate these days.

ULSD Unit and Catalyst System Optimization

ULSD units also face challenges in molecular management that a properly designed catalyst system and optimized processing scheme can help the refiner maximize his profit goals. To help refiners deal with the severe demands of ULSD, ART developed a staged catalyst system in 2001. This commercially successful 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; a high activity CoMo catalyst efficiently removes the unhindered, easy sulfur via the direct abstraction route, and a high activity NiMo catalyst then attacks the remaining sterically hindered, hard sulfur. Experience has proven that the properly configured SmART Catalyst System provides better performance than either the CoMo or NiMo catalysts alone.

An important aspect of the staged catalyst system is designing 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 unit objectives, feed and operating constraints. A more detailed discussion of these factors and how they impact system design can be found in references 3 and 4.

One of the key advantages of the system is the efficient use of hydrogen. Figure 6 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 significant 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, shown in Figure 6, varies with feed properties and operating conditions.

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 direct result of the different kinetics for sulfur and aromatics removal and is a critical consideration when customizing the staged catalyst system.

For units that have a hydrogen constraint, the key to designing the proper catalyst system is increasing the hydrogenation selectivity to provide highest HDS activity while at the same time minimizing hydrogen consumption (i.e. minimizing excess aromatics saturation). How this is accomplished is shown in Figure 7 which compares the concentration profiles for poly and mono ringed aromatics as a function of residence time for a CoMo and NiMo catalyst under typical ULSD unit conditions.
Figure 7 shows a rapid decrease in poly aromatics concentration and a corresponding increase in mono ringed aromatics for both catalysts as the residence time is increased. Clearly, however, the NiMo catalyst is much more efficient at hydrogenating the final aromatic ring as evidenced by the lower mono ringed aromatic concentration with increasing residence time compared to the CoMo catalyst. At the longest residence time (lowest LHSV) on the chart, the NiMo catalyst has about 15 numbers (absolute) lower mono ringed aromatics concentration than the CoMo catalyst, and that corresponds to about 300 SCFB higher hydrogen consumption for the NiMo catalyst.

These data demonstrate that the hydrogenation activity of the system can be tuned by adjusting the relative volumes (i.e. residence times) in the CoMo and NiMo beds in the reactor. Of course, not all units have a H₂ constraint, and in those cases the incremental increase in aromatics saturation and the correspondingly higher hydrogen consumption obtained by the NiMo catalyst offers benefits such as cetane improvement and the ability to process more cracked stocks. Commercial experience with the SmART catalyst system has demonstrated that a properly designed ULSD unit, combined with the right catalyst system, can process up to 100% cracked stocks to produce <10 ppm sulfur and provide significant cetane uplift and volume swell.

In applications where there is sufficient H₂ availability and partial pressure, a NiMo catalyst is likely the most active system for HDS. However, it will consume significantly more hydrogen due to its efficiency at catalyzing hydrogenation reactions. If the incremental hydrogen consumption cannot be tolerated, a SmART system can be designed which will deliver high HDS activity and minimize hydrogen consumption. In cases where the hydrogen pressure is lower, the staged catalyst system is often more active than either component alone without increasing the H₂ consumption significantly over the all CoMo system.

**Service**

State of the art technical support is required to get the most from today’s advanced catalysts and catalyst systems. Assessing and recognizing unit limits is key to achieve the refiner’s operating cycle goals, especially before a hard limit is reached that will result in a shortened cycle, reduced throughput, or both. ART’s experienced technical support and operations staff understand these issues.

The journey together begins with specification of the appropriately tailored catalyst system for the processing and economic needs, and continues with how catalysts are loaded and how the unit is started up to achieve the most from the catalyst. A major multi-national, vertically integrated energy company, working with the licensor and catalyst supplier, can provide a powerful depth of knowledge on how to optimize catalyst and unit operations.

**References**

2. Torchia, Dan; Arora, Arun; and Vo, Luyen. “Clean, green, hydrocracking machine,” Hydrocarbon Engineering, June 2012.
Advanced Refining Technologies (ART) first introduced the SmART Catalyst System® for ultra low sulfur diesel in 2001. Since that time, the technology has been widely accepted by the refining industry as top tier. The first SmART System began operation early in 2004 at a North American refinery processing a feed containing 40% of a high endpoint LCO. Since then, DX catalysts have been selected for numerous applications as either stand-alone catalysts or as components in a SmART system. One of the keys to the success of the technology has been the application of high activity catalysts such as CDXi, 420DX, NDXi, 590DX and 591DX into the system. ART has continued to devote significant resources to the development of higher activity catalysts, and this effort has resulted in the recent commercialization of 425DX (CoMo) and 545DX (NiMo). These catalysts represent the third generation of DX catalysts and offer refiners unparalleled performance for production of ULSD. Figure 1 summarizes the generations of catalysts offered by ART for diesel service.

ART has sold over 41 million pounds of catalyst into diesel applications with the vast majority of that being catalysts from the DX platform. The latest additions to the SmART portfolio build upon this highly successful technology platform.

545DX is a new NiMo catalyst first announced in 4Q 2012. The catalyst utilizes a new alumina support developed by ART researchers which optimizes the surface acidity and pore size distribution and that, combined with the optimized metals composition, significantly enhances reactions that are limited by ring saturation such as nitrogen and refractory sulfur removal.

The improved activity of 545DX over NDXi is readily apparent in Figure 2. The figure summarizes pilot plant testing that was completed for a refiner who is currently using NDXi in their ULSD unit. They have had two extremely successful cycles with NDXi and are interested in seeing what the new catalyst can do for them.

545DX has over 10 °F (6 °C) higher HDS activity compared to NDXi on this difficult feed containing over 30% FCC LCO. That corresponds to a significant extension to cycle length or, alternatively, this refiner...
Increasing Performance
CDXi
NDXi
590DX
591DX
545DX
420DX
425DX
ART Formation
SmART Catalyst System
NiMo and CoMo performance determined at different conditions

FIGURE 1: Generations of ART Diesel Catalysts

FIGURE 2: 545DX has Significantly Higher HDS Activity

FIGURE 3: 545DX Offers Higher Product Volume Swell

could process a more difficult feed and maintain the current cycle length. In addition to much higher HDS activity, 545DX also has substantially higher aromatics’ saturation activity. Figure 3 summarizes the API increase observed during this run. 545DX approaches nearly one number higher API increase compared to NDXi. The significantly higher hydrogen uptake with 545DX represents a capability for additional volume swell and improved product quality compared to NDXi.

ART has conducted many pilot plant evaluations for a variety of refiners aimed at demonstrating the superior performance of 545DX. Feedstocks from straight run to 100% FCC LCO have been evaluated, and 545DX consistently shows 12 °F (7 °C) higher HDS activity at 10 ppm product sulfur compared to NDXi. A summary of several of these pilot tests is shown in Table I.

The other key component of the SmART Catalyst system is a high activity CoMo catalyst. The current catalyst is 420DX which has enjoyed great success in ULSD applications around the world since its introduction in 2008. 420DX benefitted from a new alumina support with modified surface acidity which ultimately results in better cobalt utilization and improved activity.2 The high activity of the catalyst is

<table>
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<th>Feed</th>
<th>Feed API</th>
<th>Feed Sulfur, wt.%</th>
<th>LHSV</th>
<th>H2 Pressure, Psi (Bar)</th>
<th>Activity Advantage at 10 wppm Sulfur</th>
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<td>1.5</td>
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</tr>
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</table>

TABLE I: 545DX Outperforms NDXi Over a Wide Variety of Feeds and Conditions
confirmed through independent catalyst testing which shows that 420DX has the highest activity among several leading CoMo catalysts for ULSD as shown in Table II.3

ART is constantly striving for continuous improvement of its products and services and, as part of that effort, initiated a program to develop a better CoMo catalyst specifically targeting lower pressure applications. That endeavor has resulted in the development of 425DX.

Figure 4 shows a comparison of the performance of 425DX relative to 420DX in a low pressure ULSD application. It is apparent from the chart that 425DX has significantly higher HDS activity compared to 420DX, especially when targeting ULSD. The activity advantage for 425DX is at least 10 °F (6 °C) when product sulfur is <50 ppm. An interesting feature of 425DX is that while it has higher HDS activity, it has lower HDN activity compared to 420DX. Therefore, the ULSD product from 425DX will contain slightly higher nitrogen and have slightly lower API than from 420DX. This translates to lower hydrogen consumption for 425DX relative to 420DX when making ULSD which is primarily due to a higher efficiency with the direct abstraction route for sulfur removal.

Another significant improvement with 425DX is stability. 425DX shows significantly better activity retention in accelerated aging tests compared to 420DX. This is demonstrated in Table III which summarizes an accelerated aging pilot plant test.

At the start of the test the HDS activity on a straight run feed is the same for 425DX and 420DX at 10 ppm product sulfur. After establishing the SOR activity, the H2 pressure is decreased and an LCO containing feed is introduced. The superior low pressure performance of 425DX is apparent. The accelerated aging period lasts for about two weeks, and then the unit is returned to the SOR feed and conditions. At this point 425DX has nearly 10 °F (6 °C) higher activity compared to 420DX.
As with 545DX, ART has completed a number of pilot plant tests for refiners demonstrating the better performance of 425DX over other CoMo catalysts. Table IV summarizes one set of results for a refiner who has enjoyed good success with ART’s CDXi catalyst. This refiner provided two feeds and operating conditions and asked that 425DX be compared to CDXi. The table shows that 425DX is nearly 15-20°F (8-11 °C) more active than CDXi. In this comparison the 425DX also has higher HDN and aromatic saturation activity than CDXi which is attributed to that fact that CDXi is a previous generation SmART component.

The data just discussed show that 545DX and 425DX represent State-of-the-Art technology for ULSD. 545DX offers significantly higher HDS, HDN and saturation activity compared to the previous generation of NiMo catalysts. For higher pressure applications this offers the opportunity for significantly higher product volume expansion along with higher cetane. For lower pressure applications, 425DX offers higher HDS activity and better stability compared to previous generation CoMo catalysts. Both examples demonstrate the flexibility of the SmART Catalyst System where a customized loading ensures that individual operating objectives are met within unit constraints.

Advanced Refining Technologies continues to develop high performance technologies aimed at helping refiners meet the ongoing challenges presented by clean fuels. 545DX and 425DX are merely the latest catalysts resulting from the dedicated effort to offer the best technology for refining today.

**References**

Don’t Be Medieval, Make More Diesel

Introduction

In a world of ever tighter fuels specifications, and ever fewer ways to process poor quality feedstocks, hydrotreating has become firmly entrenched as the lead refinery conversion process. Over the course of the last decade, hydrocrackers have been asked to produce greater volumes of distillate, including ULSD, and at higher levels of operating severity including increased throughput. Refineries with a hydrocracker generally are running well over original design capacity and at considerably higher operating severity than that of original design. Few refinery units can accommodate such a large variation in feeds, products, and throughputs while continuing to manufacture environmentally friendly products.

At the heart of a hydrocracker is the catalyst system. This typically consists of several carefully optimized individual catalysts working closely together. In the last 10 years, hydrocrackers have been asked to produce greater volumes of distillate, including ULSD, at these higher throughputs and higher levels of operating severity.

In early 2013, Advanced Refining Technologies (ART) and Chevron Lummus Global (CLG) announced an agreement in which ART has the exclusive rights to sell CLG’s hydrocracking and lubes hydrotreating catalysts to petroleum refiners worldwide for unit refills, while CLG continues to sell them in licensed units as first-fills. This agreement establishes ART as the single point of contact for all hydrotreating catalyst needs, which dramatically streamlines hydrotreating catalyst supply and the technical service focus for refining customers. CLG’s depth of technical expertise remains available for the refiner who requires process technology. As an illustration of the retained synergies between ART and CLG, this article addresses catalyst technology approaches and processing tactics that optimize hydrocracker unit operation in order to meet the future needs for diesel and gas oil production.

Increased Demand, Shift to Diesel

Despite fluctuating oil prices, the global consumption of petroleum products continues to grow, particularly as a result of the expanding Asian economies. Economic development in China and India has resulted in an increased number of cars and trucks, escalating the demand for transportation fuel.
As the inventor of the modern hydrocracking process, Chevron was the first global operating company to provide catalysts, hardware or both that afforded shifting existing hydrocracking units from maximum naphtha production to maximum middle distillate production. Since the 1980’s, Chevron has been the market leader in developing catalysts for maximum middle distillate production, (especially diesel) as the demand for these distillate fuels expanded in Europe, the Middle East, China, and India. Since the 1990’s, Chevron Lummus Global (CLG) has been the market leader in licensing new hydrocracking units geared toward maximum middle distillates production, being awarded more than 50% of the new licensed units. Key to Chevron’s early leadership in maximum middle distillate production was amorphous catalysts made by the so-called co-gelation technique (e.g. ICR 106, ICR 120). For many years these co-gel catalysts were the premier catalysts of choice in the industry for high-quality middle distillate production.

The commercialization of ICR 240 in the early 2000’s marked the completion of a portfolio of catalysts that represented a dramatic improvement over the co-gel catalyst technology. With the completion of the portfolio many improvements came to full fruition, comprising innovations to both the crystalline and the amorphous parts of the catalysts, innovations to the base metal emplacement process, and enhanced quality control.

Since the early 2000’s new generations of catalyst have been added. The current CLG-ART portfolio of catalysts affords fully optimizing a hydrocracking unit from maximum middle distillates production to maximum naphtha production within the unit’s operational envelope to meet the changing demands from the pertinent transportation fuels markets.

In the remainder of the article we will cover the technical developments that led to the creation of ICR 240 as the maximum distillate selective catalyst of choice by over a dozen commercial units, as well as the latest generation of maximum middle distillate catalyst, ICR 250.

**Chevron Diesel Selective Hydrocracking Catalysts**

Hydrocracking catalyst design involves the careful tuning of at least two key catalyst functionalities, a (de)hydrogenation function, and a cracking and isomerization function. The metallic active sites afford hydrogenation and dehydrogenation. These base metal sulfide sites are located in the ~10 nm pores of the bulk of the catalyst. The acidic sites afford cracking and isomerizing of hydrocarbons. These sites are located both in the ~1 nm pores of the zeolites and in the ~10 nm pores of amorphous silica-alumina components. Optimizing and varying the combination of these acidic catalyst components provides a tunable acidic strength and a tunable pore size for meeting a wide spectrum of fuels production of different molecular sizes, e.g. naphtha, jet, diesel, lube oil and combinations of these, to meet the needs of the dynamic world market.
Balancing the metal and acid activities, i.e. the hydrogenation and the cracking activities respectively, is the key to tailoring a catalyst for the desired product slate. Ideally, a hydrocracking catalyst preferentially converts heavier hydrocarbons to primary cracked products and avoids secondary cracking of the primary cracked products to undesirable lighter products. Ideal hydrocracking catalysts favor isomerizing paraffinic intermediates and retaining paraffinic branches of naphthenic components for improved cold flow properties of both middle distillates and unconverted oil. Unconverted oil can be utilized as a superior base oil feedstock for lubricant oil production.

The strength of the acidic sites and the pores that surround them, particularly the confined environments of zeolites and of amorphous silica-aluminas, offer controllable scission locations to tune the reactants and products at a molecular level. With decades of research experience in zeolite synthesis and application, Chevron mastered the art of controlling the location and strength of the acid sites to minimize undesirable secondary cracking. The development of the diesel-selective hydrocracking catalyst, ICR 240, is a demonstration of this breakthrough technology to convert heavy vacuum gas oil very selectively into diesel. The introduction of a tuned zeolite and a tuned amorphous silica-alumina to a hydrocracking catalyst significantly enhanced catalyst activity, life, and diesel selectivity in comparison with its predecessor catalyst, ICR 120. It is worth noting that the high diesel selectivity achieved with ICR 240 is without the requirements and safety concerns around ammonia titration throughout the operating cycle.

Results in Figure 3 and Figure 4 illustrate the benefits of utilizing ICR 240 in a commercial unit. As is typical, this hydrocracker was running at 110% throughput of the original design and it was near 100% utilization. As throughput increased over design rates, LPG and gasoline handling capability in the unit became the bottleneck limiting any increase in production. The replacement of the second stage hydrocracking catalyst ICR 120 by ICR 240 reduced the yield of LPG and naphtha by 10%. The implementation around 1800 days after initial startup yielded roughly 10 wt.% gross increase in distillate yield.

Recently, a new technology was introduced for manufacturing Chevron ISOCRACKING® catalysts. This technique allows optimizing the size, location and dispersion of the base metal sulfide nanoparticles. This advance resulted in commercialization of a new hydrocracking catalyst, ICR 250, in the early 2010’s with further performance enhancements.

Results in Table I, Table II and Figure 5 demonstrate that ICR 250 provides many advantages over ICR 240 including activity and distillate selectivity, aromatics’ saturation (particularly polycyclic aromatics’ saturation), and controlled hydrogen addition to desired products.

Compared to ICR 240, ICR 250 greatly enhances the activity and the selectivity toward middle distillate in the second stage hydrocracking application for high aromatics feed (Table I). ICR 250 enhances aromatics’ saturation resulting in an improved smoke point of the jet and a markedly improved stability of the viscosity (quantified by a higher viscosity index or VI) of the unconverted oil (UCO).
ICR 250 allows control of hydrogenation performance and manages where the hydrogen addition occurs and to what extent. It minimizes hydrogen addition to low-value products such as LPG and naphtha and provides value to product upgrade or unconverted oil (UCO). ICR 250 further enhances hydrogenation of polycyclic aromatics to prevent their accumulation in UCO. The accumulation rate of polycyclic aromatics of ICR 250 was reduced by more than 80% versus ICR 240 (Figure 5). This is particularly important in recycle operation resulting in improved catalyst life and reduced bleed rate of the recycle stream resulting in higher conversion. As a result, ICR 250 consumes significantly less hydrogen and provides for a longer operating cycle.

The enhanced activity and middle distillate selectivity of ICR 250 was also demonstrated with highly paraffinic feed as shown in Table II. The increased selectivity indicates that ICR 250 tends to not overcrack long-chain paraffins and/or to retain paraffinic branches of naphthenic components. It enhanced intermediate isomerization to improve diesel cold flow properties that was quantified by the diesel cloud point being lowered by 7 °F. Results of diesel density and viscosity and comparable carbon number distribution (not given) support the improved cold flow properties, which are illustrated when the diesel maintains its boiling range.

**TABLE I: Advanced Performance of ICR 250 Over ICR 240 for High Aromatics Feed in Recycle Operation**

<table>
<thead>
<tr>
<th>Property</th>
<th>ICR 250</th>
<th>ICR 240</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBAT, °F</td>
<td>-20</td>
<td></td>
</tr>
<tr>
<td>C4+, wt.%</td>
<td>-0.7</td>
<td></td>
</tr>
<tr>
<td>Naphtha (C5-250 °F), wt.%</td>
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<td></td>
</tr>
<tr>
<td>Kerosene (250-550 °F), wt.%</td>
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</tr>
<tr>
<td>Heavy Diesel (550-700 °F), wt.%</td>
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</tr>
<tr>
<td>Total Distillates (250-700 °F), wt.%</td>
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<td></td>
</tr>
<tr>
<td>H2 Consumption, SCF/B</td>
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<td></td>
</tr>
<tr>
<td>Kerosene Smoke Point, mm</td>
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<td>-4</td>
</tr>
<tr>
<td>Kerosene Freeze Point, °F</td>
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<td>Base</td>
</tr>
<tr>
<td>Heavy Diesel Cetane Index</td>
<td></td>
<td>Base</td>
</tr>
<tr>
<td>Heavy Diesel Cloud Point, °F</td>
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<td>Base</td>
</tr>
<tr>
<td>Dewaxed UCO VI</td>
<td></td>
<td>+4</td>
</tr>
</tbody>
</table>

**TABLE II: Advanced Performance of ICR 250 Over ICR 240 for High Paraffin Feed in Recycle Operation**

**FIGURE 5: Advanced hydrogenation performance of ICR 250 over ICR 240 in polycyclic aromatics’ saturation (quantified by polycyclic index (PCI) from UV adsorption measurement) for high aromatics feed in recycle operation.**

**Conclusions**

Deployment of a combination of an optimum catalyst system with major process design changes epitomizes how a combination of ART catalyst know-how and of CLG process knowledge represents a unique value proposition. In the Chevron tradition, ART continues to expand the ICR catalyst portfolio. ICR 250 is the latest addition to the portfolio. Through its careful design, this robust catalyst further enhances middle distillate yield and enhances run length at optimum hydrogen consumption.

**References**

Ebullating Bed Resid (EBR) Customer Needs

Refiners today are challenged to convert the bottom of the barrel to meet increasing demands for transportation fuels. Figure 1 shows the rapid growth in gasoline + diesel demand out to 2020, with a significant decline in fuel oil. In addition, there is a strong economic incentive to continue upgrading and converting heavy feeds based on the forecasted crack spreads between diesel and HSFO (Figure 2).

In the EBR hydrocracking process, the principle objective is to maximize conversion of 1000 °F+ (538 °C+) material into lighter and more valuable products like diesel and heavy gas oil. This process also removes sulfur and metals to make products more suitable for further processing and ultimate use in clean fuels. Because of the high temperatures at which the reactions occur (750 °F(399 °C)and higher), thermal cracking is pronounced and the unconverted heavy asphaltenes precipitate out of solution resulting in the formation of sludge - commonly known as organic sediment. The organic sediment causes fouling problems in the downstream circuits, requiring downtime to clean equipment. It also impacts the quality of the low sulfur resid product from the EBR unit.

EBR process profitability could be significantly enhanced with catalyst technology that would allow for maximum conversion while reducing the formation of organic sediment. This would allow for a reduction in downtime and the costs associated with cleaning of the equipment (exchangers, separation vessels, distillation units). Full profitability optimization of an EBR unit also requires consideration of feedstock type and individual unit constraints. To account for all these variables, ART has developed several technology platforms that can be used in dual catalyst systems to help refiners achieve their optimal profitability.

Catalyst Design for Low Sediment

Catalyst design for EBR catalysts leverages the technology strengths of both ART parents. Chevron and Grace each contributed significant residuum upgrading technology, with Chevron’s 30+ years of process and catalyst expertise in resid hydrotreating (including ARDS, VRDS, OCR®, and UFR® technology), and Grace’s 20 years background with catalysts for the EBR process.
The sharing of ideas from each parent provided leads with respect to new catalyst designs, specifically to address high conversion with minimum sediment formation - a problem common to both resid hydrotreating and hydrocracking.

For best performance with respect to sediment formation, it is critical to have the right balance of porosity in the meso- and macropore regions. The intrinsic reaction rate, which is inherently related to the mesopores (i.e., the catalyst surface area), controls the HDS, HDMCR, and resid conversion characteristics of the catalysts. The diffusivity, which is more related to the macropores (greater than 200 Å), controls the demetallation and the sedimentation functions of the catalyst. The optimization of both pore volume and pore size distribution (PSD) is critical to catalyst development as illustrated in Figure 3.1

- Pores in the < 200 Å range are most useful for HDS and HDMCR activity
- Pores in the 200 -1000 Å range are effective in allowing diffusion of the majority of the asphaltene molecules into the catalyst
- A select amount of pores >2000 Å is essential to allow the largest asphaltene molecules to readily enter the catalyst to achieve maximum HDM, while cracking the molecules with minimum sediment

The above characteristics are established via the proper combination of chemical composition and preparation technique.

The active metals, both molybdenum and the Group VIII promoters, are also extremely important to get proper catalyst performance. The correct amounts of the two (or more) elements throughout the pellet are necessary for full metal utilization. This requires exact control of the metals distribution and dispersion. Catalytic metals loading must often be tailored for different operating conditions and/or feedstock. Verification of the proper formulation must be done with pilot plant tests under the conditions of the application, and the catalyst cannot necessarily be extrapolated from other applications. The full life cycle of the catalyst must be considered, as the metals pick-up and pore volume reduction changes the performance with time.

FIGURE 1: Forcasted Global Refined Product Demand

FIGURE 2: Diesel-HSFO Crack Spread (Europe)

FIGURE 3: Pore Size Optimization in EBR Catalyst Development
The optimum catalyst is designed to allow maximum resid conversion, with emphasis on asphaltenes conversion, and acceptable HDS activity, for the lowest organic sediment formation. The feedstock plays an important role in delivering the key objectives.

**ART’s Technology Platform Development**

ART has developed several technology platforms to achieve different benefits within specific EBR unit constraints. The LS platform, developed in 2002, was the first commercially available EBR catalyst to provide low sediment on paraffinic type of feeds like Ural. Further development work in the area of low sediment technology led to the commercialization of the HSLS platform in 2007. The HSLS platform allows refiners to reach the next step in sediment control with improved stability and demetallation.

The HSLS technology incorporates a novel base structure, along with a unique process technology for efficient metals impregnation. This combination of proprietary alumina, leading to a very specific pore size distribution, and unique metals impregnation process technology allows efficient use of the active metals.

Key performance features of the HSLS technology platform are:

- Lower sediment formation (7-20%), allowing reduced frequency of clean out of downstream equipment, gives higher on-stream factor and lower maintenance costs. In 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 with higher HDM, which also means more value for metals recovery on spent catalyst.

In 2012, ART developed the step-out HCRC technology platform. This technology is based on a next generation alumina and base, and brings the flexibility to move to a lower reaction severity (less thermal conversion). This provides the opportunity to significantly reduce sediment/coke formation, and allow higher catalytic conversion in the EBR process.

At constant reaction severity, the HCRC platform yields:

- 4% Higher Resid Conversion
- Preferentially to Distillate and VGO
- 4% Higher HDS
- Lower sulfur in the bottoms and converted products
- 6% higher MCR removal
- 3% Higher HDN
- Lower Nitrogen in distillate and VGO

ART’s latest catalyst technology portfolio is summarized in Table I, with the description of its newest technologies.

### Dual Catalyst Systems

ART has tested both in their pilot plants and commercially the use of the dual catalyst systems in the EBR units. The use of a dual catalyst system as shown in Figure 4 allows optimizing the catalyst technology in Stage 1 and Stage 2/3 to achieve maximum resid conversion, HDS, HDCCR and HDM with good sediment control and to minimize catalyst costs. Various combinations of the dual catalyst systems shown in Table II, using the above listed catalyst technology platforms, are described in this paper.

### HCRC/HSLS Dual Catalyst System

The HCRC/HSLS dual catalyst system was designed to provide high resid conversion activity at identical operating conditions while maintaining good sediment control. This objective can be achieved in a single HCRC catalyst system, but the combination of the HCRC technology platform and the HSLS technology platform gives increased flexibility with respect to choice of feedstock and optimization of catalyst cost. The increased resid conversion, combined with
higher contaminant removal, gives higher yields of better quality products, and allows for options to maximize conversion at constant temperature. Refiners may also choose to improve selectivity by maintaining conversion and reducing temperature. Catalyst systems utilizing HCRC also display superior HDS, HDCCR and HDN activity, allowing refiners even more flexibility in operation.

The HCRC/HSLS dual catalyst system was pilot plant tested against the HCRC technology platform, using a Ural feedstock, in ART’s mini ebullating bed unit (MEBU) using a standard protocol operating at 0.26 LHSV, 815 °F (435 °C), and 2400 psig. The Ural feedstock properties are shown in Table III.

The HCRC/HSLS dual catalyst system also shows improved HDM activity over the full HCRC catalyst technology with small reductions in HDMCR, HDN and product API, as shown in Table IV.

Based on pilot plant work, the HCRC/HSLS dual catalyst system offers the following key opportunities at constant reaction severity:

- Excellent Resid Conversion/Sediment ratio is shown in Figure 5 with flexibility to enhance conversion by controlling reaction severity.
- Offers great flexibility of controlling the HDS, HDN and HDM (Cat Usage) with dual catalysts depending on feedstock and unit objectives
- Yields and product selectivities can be adjusted by individual catalyst optimization, catalyst mix ratio and reaction severity

The HCRC/HSLS dual catalyst system also brings a greater degree of flexibility to the EB refiner to allow a higher or lower reaction severity depending on the feedstock being processed, and also provides higher catalytic conversion and less thermal conversion in the EBR process.

HSLS/LS Dual Catalyst System

The HSLS/LS dual catalyst system was designed to provide excellent resid conversion activity for those units that run paraffinic feeds that are prone to sediment, thereby giving the ability to run at higher severity. This system offers a combination of a relatively high metals tolerance catalyst in the first stage with the relatively higher convers-
sion/low sediment system in the second stage. By allowing maximum metals removal in the first stage, the second stage can be operated at higher severity. By virtue of low metals on the second stage catalyst, this will result in maximizing the reactivity toward the difficult and unconverted feed components coming from the first stage. The catalyst addition rate split to the first and the second/third stages can be optimized, depending upon the feed contaminants levels, and the degree of the conversion reactions required in Stage 2/3. This system has been in commercial use very successfully for several years.

The HSLS/LS dual catalyst system was pilot plant tested in ART’s mini ebullating bed unit (MEBU) against the LS technology platform, using the same Ural feedstock as in Table 2, using a standard protocol operating at 0.26 LHSV, 815 °F (435 °C), and 2400 psig.

Figure 6 shows the excellent conversion that the HSLS/LS dual catalyst system has over the base LS system, with a significantly lower sediment.

The HSLS/LS dual catalyst system offers excellent resid conversion improvement, with exceptional sediment control compared to a full LS catalyst platform, with similar activity in HDS, HDCCR, HDN and product API, as shown in Table V.

**Summary**

All pilot plant data with various feeds shows that ART’s Dual Catalyst Systems offer increased ‘synergy’ in order to exploit the merits of each catalyst. The results of the two catalyst platforms, when used in the Dual System and in the optimum order, are better than the standalone catalysts in most cases. Each of these dual catalyst systems have been used commercially. In all trials, the results have been very positive, and confirm the pilot plant data presented here.

**References**

2. Lakhanpal, Klein, Chen; ART’s latest Catalyst Technology for EB RHC; *Catalagram*® 106, Fall 2009.
Introduction
Since its formation in March 2001, Advanced Refining Technologies, ART, has firmly established itself as the leading supplier of premium hydroprocessing catalysts to the refining industry worldwide. ART offers refiners the unique synergy derived from its parent partners W. R. Grace & Chevron, being the leaders in materials technologies & catalyst manufacturing and in hydroprocessing and heavy oil upgrading process technologies.

Chevron’s involvement in heavy oil upgrading began with the development and installation of the world’s first atmospheric resid desulfurization unit (ARDS) at the Richmond, California refinery in 1969, designed to make low sulfur fuel oil (LSFO). It was followed in 1977 by the first vacuum resid desulfurization unit (VRDS) at the El Segundo refinery also making LSFO. In 1983, Chevron started their third resid hydroprocessing unit at the Pascagoula, Mississippi refinery. Throughout the years, Chevron has accumulated extensive experience in both designing and operating ARDS and VRDS units, and in developing catalyst technologies for them. Combining Chevron’s strength in resid hydropyroprocessing with W. R. Grace’s expertise in coke selective resid FCC (RFCC) catalyst technologies, makes ART uniquely equipped to deliver powerful catalyst systems for refiners producing LSFO and for those that have integrated RDS/RFCC operations.

Growth in RDS Capacity
There has been significant growth in worldwide RDS capacity in the past 20 years to meet the growing global demand for fuels and petrochemicals, and from the increasingly heavy crudes being processed. Most of these new units are installed in refineries in Asia and the Middle East, so that more than 75% of worldwide RDS capacity is concentrated in these two regions. South Korea alone boasts of six large ARDS and VRDS units with a combined processing capacity of 400 MBPD of resid feed.

Chevron’s long success in resid hydropyroprocessing is continued today by Chevron Lummus Global (CLG), its joint venture for process technology licensing, and by ART for catalyst manufacture and sales. CLG has licensed >80% of all RDS units worldwide in the past 20 years, and in the same period 19 new CLG li-
censed RDS units have started up and are in operation today. ART supplies over half of all RDS catalysts used worldwide to produce LSFO and feed to the RFCC. A clear majority of those RDS units producing RFCC feed use ART catalysts, and these refiners place a premium on performance to produce low MCR, low metals RFCC feed to drive RFCC profitability.

ART catalysts are currently in use in CLG designed RDS units and also in units designed over the years by other licensors. ART’s success is evidenced in that its RDS catalyst sales have doubled in just the past eight years and, with several new CLG licensed RDS units slated to come on stream over the next five years, is expected to double again in that time. The success in retention and growth has come from the value refiners place on reliable and excellent catalyst performance and tangible continuous improvements delivered. ART is widely recognized for its technical service excellence and high credibility for delivering on projected catalyst performance.

Twenty five RDS units worldwide are currently using ART catalyst systems to process a wide range of AR and VR feeds for a range of product properties with the objectives of making fuel oil and RFCC feeds. (Table I) Several ART client refiners are on multi-year contracts and all twenty five are repeat users of ART catalysts.

<table>
<thead>
<tr>
<th>Unit</th>
<th>RDS Unit Label</th>
<th>Unit Capacity (MBPD)</th>
<th>Unit Type</th>
<th>Product</th>
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<td>1</td>
<td>F</td>
<td>83</td>
<td>RDS</td>
<td>RFCC Feed</td>
</tr>
<tr>
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<td>Q</td>
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<td>25</td>
<td>T</td>
<td>14</td>
<td>RDS</td>
<td>RFCC Feed</td>
</tr>
</tbody>
</table>

OCR = On Stream Catalyst Replacement UFR = Up Flow Reactor

TABLE I: 2013 Survey of 25 RDS Units Currently Using ART Catalysts

These units vary considerably in capacity, (Figure 1) ranging from the relatively small (<30 MBPD) older units to the more modern designs, most of which are in Asia with feed rates as high as 70 to 80 MBPD.

**Run Length**

Irrespective of capacity, most RDS units are designed for cycle times of nominally one year to coincide with scheduled annual turn-arounds in the refinery. However cycles can range from around 6 months to 18 months determined by a number of factors including unit design, operating severity, feed and product properties and catalyst system. Figure 2 shows the range of run lengths achieved by different refiners.

Important roles that the ART technical service engineers play are in designing optimum RDS catalyst systems for each refiner’s specific resid processing objectives, in monitoring the performance of the unit throughout the duration of the run, and in working closely with the client to overcome the technical challenges of processing difficult feeds and operating efficiently and reliably. This is even more important today where the price of crude oil is motivating refiners to
process less expensive but increasingly heavy, contaminant laden oil. Figure 3 shows the range of feed API gravities for these units. Most process resid with API gravity in the 13-16˚API range, however there are a few refiners processing feeds as heavy as 9-10˚API.

Feed Contaminants

In addition to feed heaviness, the level of feed contaminants and the difficulty of their removal vary considerably depending on the crude source. Figures 4, 5 and 6 show the range of metals (nickel and vanadium), sulfur and MCR content in the feed and product. Not surprisingly, these ranges are quite wide, emphasizing even more how critical the catalyst system designs need to be, with the optimum amounts of different functional catalysts to achieve the desired levels of HDM, HDS, HDMCR and HDN, and yet deliver the design run length at the specified feed rate.

ART has responded to the changing needs of the refiner and to the technical challenges of providing the refiner the needed ability and flexibility to process increasingly heavier and difficult crudes with focused R&D efforts. Guided by ART’s PRISM stage-gate process, these efforts have yielded a steady regular introduction of new RDS catalysts with the desired performance improvements. A third of ART’s RDS catalyst grades in use today were commercialized in just the past three years. The catalysts introduced have increasingly bet-
FIGURE 3: API Feed Properties for RDS Units Using ART Catalyst

FIGURE 4: Feed and Product Metals (Ni + V)

FIGURE 5: Feed and Product Sulfur
Delivering Continuous Improvements

While new improved catalysts are important, it is equally critical to have a well designed robust catalyst system comprising of several layers of different catalyst grades serving distinctly different catalytic functions to achieve each refiner’s specific objectives. Through the careful introduction of new improved catalyst grades, and optimizing the proportions in the catalyst system, ART successfully delivers run upon run performance improvements to RDS operators. Such continuous improvements delivered to an Asia Pacific refiner over the course of six consecutive RDS runs is presented in Figure 7. This refiner was able to meet RFCC feed specifications and maintain a one year cycle length for all six runs despite running progressively heavier feeds and accumulating more metals on the RDS catalyst systems.

Similar experience of continuous improvements delivered at two other Asia Pacific RDS units are presented in Figures 8 & 9. Thanks to the credibility from reliable RDS experiences, several clients have opted to enter into multi-year supply contracts with ART ranging from two to five years. These refiners estimate savings in excess of 60 man-days/year, that would otherwise have gone into evaluating multiple supplier proposals and catalyst selection without assured success.
RDS Operating Objective: RFCC Feed

14 Runs: 1998-2012

• Maintained 340-day run length despite an increase in the feed rate to the unit

• New ART RDS catalyst technologies introduced yielded run-over-run performance improvements with more stringent product specifications

• Increased profitability from running higher throughput, and greater amounts of cheaper-heavier crudes and low value opportunity crudes

Summary

In the twelve years since inception, ART has established itself as the leading supplier of resid hydrotreating catalysts worldwide. Focused R&D efforts and extensive experience from working closely with many RDS users have allowed ART to develop and commercialize catalysts in stride with refiners’ changing needs and challenges of processing progressively heavier crudes. These improved catalyst systems have delivered run upon run continuous performance improvements and increased profitability at several RDS units worldwide.
**Q31.** What is the threshold concentration of arsenic and phosphorus requiring a dedicated trap system? How are the arsenic and phosphorus trap systems specified and what are the controlling mechanisms?

**Arsenic**

Arsenic (As) is found in many crudes including some from West Africa and Russia as well as many synthetic crudes. It is becoming a common contaminant as use of these crudes, especially synthetic crudes, has been increasing in recent years. The arsenic is believed to bind with the metal sulfide sites, and in particular the active nickel on the catalyst forming nickel arsenide. This has a dramatic impact on catalyst activity. To demonstrate the impact of arsenic on catalyst activity, ART obtained a series of spent catalysts containing different levels of arsenic. These samples were carefully regenerated in the laboratory and were then activity tested using a diesel feed containing 50% cracked stocks under conditions producing <500 ppm sulfur. Figure 1 summarizes the results of that work. At 1000 ppm arsenic the catalyst shows 5 °F HDS activity loss and nearly 15 °F loss in HDN activity. The activity loss quickly increases to over 50 °F with 1 wt.% arsenic on the catalyst.

Canister data for a variety of catalysts also indicates that catalysts containing nickel are more effective for trapping arsenic. Figure 2 summarizes the arsenic pickup values for several NiMo catalysts. As this data shows, both high metals ULSD catalyst NDXI and AT580 as compared to our recent guard catalysts AT724G and AT734G which are quite effective for trapping arsenic. It also indicates that the active ring materials and demet catalysts used are also effective for trapping arsenic.

Other canister data also shows that the ultimate arsenic pick up is heavily dependent on temperature. Figure 3 shows the arsenic pickup as a function of temperature for a NiMo catalyst. These results were obtained by analyzing spent samples of a high metals NiMo catalyst 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 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 that a high nickel catalyst can pick up very high arsenic levels if the operating temperature and feed concentration are high enough.

Noting that there are a wide range of arsenic levels, unit operating conditions and expected cycle lengths, the ability to define a single set threshold for when a trap is needed is difficult. It is recommended that if arsenic is found to be a problem contaminant you consult your supplier to determine if it is impacting the cycle and to determine if and how much guard catalyst is needed.

**Phosphorous**

Phosphorous contamination in oil has been traced to fracturing fluids that are often used in crudes from the Western Canadian Sedimentary Basin. The source is diphosphate esters which are soluble in the crude oil. Refineries that run large percentages of light Western Canadian crude have reported crude column and crude furnace fouling for many years. Improvements made to crude columns to minimize fouling have transitioned the depositing of phosphorous to the downstream hydrotreaters.

Other sources of phosphorous include gasoline slop tanks, imported feeds and lube oil wastes. If phosphorous does manage to make its way into the hydrotreater it will poison the active sites of the catalyst causing a loss in activity. A level of 1 wt.% of phosphorous on the catalyst results in roughly 10 °F loss in activity. ART recommends that a feed content of < 0.5 wppm be maintained whenever possible as well as the use of feed filters to assist in trapping of phosphorous sediment.

An ART catalyst case study of the detrimental impacts of feed poisons on hydrotreater performance involved a ULSD unit which had recently started up with ART catalysts. Shortly after startup the unit began to experience extremely rapid catalyst deactivation. It was so severe that within a couple months the unit required an unplanned turnaround and fresh catalyst was installed. Samples of spent catalyst representing the whole catalyst charge were collected and analyzed in the laboratory. The results are summarized in Table I. It is apparent from these results that the catalysts were exposed to high levels of several poisons including arsenic, sodium, phosphorous and iron. The contaminants penetrated well into the catalyst bed. Catalyst at the bottom of the reactor was not yet poisoned, but the coke content was extremely high for catalyst which had been on stream such a short time. The level of contaminants indicates the catalyst in the top half of the bed lost over 60°F of activity while the...
bottom was providing most of the HDS conversion. This required very high temperatures, which is reflected in the high carbon content at the bottom of the bed.

ART has a suite of options in order to protect the main bed from these and other contaminants which may be present in the feed to a typical hydrotreater. The use of several of these materials combined together can adequately provide protection and extend the cycle life of your hydrotreater.

Q32. What is a typical range of HDM (metals removal) in a gas oil hydrotreater? Can HDM decline rapidly when metals in the feed becomes excessive relative to catalyst system design? Is there a point when metals in the feed are so high they “overwhelm” the demet and main bed catalyst, resulting in lower %HDM?

Traces of nickel (Ni) and vanadium (V) are present in most crudes although the amount is strongly dependant on crude type. They are concentrated in the heavier fractions, especially the bitumen and vacuum residue. Ni and V poisoning can be a significant problem in FCC pretreat and hydrocracker pretreat units which process heavier feeds, and they are not often encountered in diesel or lighter feeds. The primary deactivation mechanism of these poisons is pore mouth plugging. (Figure 1)

Nickel and vanadium are usually contained in large asphaltene-like molecules which are too large to penetrate into the pores of typical hydrotreating catalysts. Therefore, the nickel and vanadium end up depositing on the outside of the catalyst ultimately blocking access to the active sites within the pores. Pilot plant testing with heavy feeds on a widely used FCC pretreat catalyst suggests that 1 wt.% Ni+V on the catalyst results in 10 °F loss in activity. The activity loss will be greater for a smaller pore (diesel type/grade) catalyst. (Figure 2)

Dealing with nickel and vanadium requires specially designed catalysts for removing and storing the metals. These catalysts have very large pore size distributions which are tailored to provide very high capacities for nickel and vanadium.

There are demet catalysts available today that are capable of picking up as much as 100 wt.% (fresh catalyst basis) Ni + V in a gas oil hydrotreater. Much like other contaminants, the ability to pick up these metals is highly dependent on the reactor temperature as well as the concentration of Ni+V coming in with the feed. Generally speaking, if there is a sudden large spike in Ni+V in the feed there are other changes to the feed accompanying this (i.e. increased endpoint) that may be more detrimental to the catalyst performance.

The catalysts typically used for HDM in a gas oil hydrotreater are similar to the ones used in fixed bed resid hydrotreating where the concentration of metals is significantly higher than that found in gas

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<th>As, wt.%</th>
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<th>P, wt.%</th>
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<td>0.00</td>
<td>0.02</td>
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<td>11.1</td>
</tr>
</tbody>
</table>

Q31 TABLE I: Spent Catalyst Analysis

Q32 FIGURE 1: Pore Mouth Plugging of DeMet Catalyst

Q32 FIGURE 1: Pore Mouth Plugging of DeMet Catalyst
Iron readily precipitates out in the presence of heat and H₂S. These iron particulates fill the interstitial spaces in the catalyst bed which will result in a higher than expected pressure drop. To help mitigate the pressure drop associated with iron ART uses a series of grading materials which have high void space to accumulate and ‘store’ these particulates. Use of a specialized iron trapping material (GSK-9) which has high internal void space for trapping iron inside its large pore network is also valuable. (Figure 1)

If iron is known to be the cause of the pressure drop issues, then changes to larger diameter catalysts can also be used in an effort to allow for additional void space in the reactor. Sock loading a large portion of the top of the reactor will also greatly increase the effective void space allowing the smaller iron particles to move through the reactor.

Iron (Fe) works its way into hydrotreater feed as rust and iron scale from corrosion of upstream equipment and piping as well as unfiltered particulates present in the feed. Iron naphthenates can form from piping corrosion due to naphthenic acid in the feed, and the iron readily precipitates out in the presence of heat and H₂S. These iron particulates fill the interstitial spaces in the catalyst bed which will result in a higher than expected pressure drop. To help mitigate the pressure drop associated with iron ART uses a series of grading materials which have high void space to accumulate and ‘store’ these particulates. Use of a specialized iron trapping material (GSK-9) which has high internal void space for trapping iron inside its large pore network is also valuable. (Figure 1)

If iron is known to be the cause of the pressure drop issues, then changes to larger diameter catalysts can also be used in an effort to allow for additional void space in the reactor. Sock loading a large portion of the top of the reactor will also greatly increase the effective void space allowing the smaller iron particles to move through the reactor.
Another option are materials that are specially designed to dramatically increase the void fraction in the top bed of the reactor and are very good at trapping iron as well as other particulates and scale. These measures are helpful for delaying pressure drop buildup, but they do not prevent eventual pressure drop buildup. Effective feed filtration to remove particulates (at least 25 microns) provides a longer lasting solution in helping mitigate pressure drop buildup from these sources, as well as a way to identify the sources of iron that are present in the process.

Q34. When processing cracked naphtha what is done to ensure that polymerization of the diolefins/olefins will not result in pressure drop problems in a reactor or upstream equipment?

Processing coker naphtha can have several undesirable effects on the performance of the hydrotreater and the catalyst if the system was not properly designed to handle it. In general, coker stocks have a higher level of olefins present from the coking process. Once in the hydrotreater these olefins will quickly get saturated (Figure 1) resulting in high hydrogen consumption and generation of a lot of heat. As a general rule of thumb, one mole of hydrogen is required per mole of carbon-carbon double bonds, or between 5-10 times the Bromine number reduction in standard cubic feet of hydrogen per barrel (SCFB). This additional heat (130-160 Btu/SCF Hydrogen consumed), if not managed properly, will initiate additional reactions, quickly creating a very high temperature rise. The high temperatures can accelerate coking and can lead to olefin polymerization resulting in a dramatic increase in pressure drop. This can set an upper limit on how much coker naphtha can be processed based on the need to limit the heat rise or hydrogen consumption.

A system that is properly size and activity graded is be extremely important when processing coker. ART recommends utilizing a grading system to help mitigate pressure drop build-up. A large inert hold down ring (GSK-19) with a very high void fraction used for trapping large particulates is placed at the top of the catalyst bed. A smaller diameter macroporous ring (GSK-9) that traps iron as well as other fine particulates is typically used in the next layer. After that, two types of smaller rings are used as active grading. These materials have a low level of active metals which help to begin olefin saturation reactions as well as provide additional particulate space at the top part of the catalyst bed. Avoiding the use of any highly active catalyst at this point is also recommended. Below the grading system, it is recommended to use a layer of larger size (1/10” or 1/12”) catalyst which provides activity for olefin saturation and additional void space for pressure drop mitigation. This layer is often a catalyst which is suitable for trapping silicon (and arsenic) which is another concern when processing coker naphtha.

Another recommended practice to help prevent fouling and pressure drop build-up in coker naphtha units is to prevent contact of the coker feedstock with oxygen. It is preferred to bring the feed to the processing unit directly from the coker and avoid use of tankage. If this is not an option, then the alternative is to use a floating roof tank and purge the system to keep a nitrogen blanket over the feed in order to keep oxygen out.

Use of a di-olefin treating reactor can also be considered. A di-olefin reactor is operated at a much lower temperature in order to selectively catalyze the di-olefin saturation reaction and avoid any excess heat generation from sulfur and nitrogen removal.

Q37. How does the increased processing of tight oil (Eagle Ford, Bakken, etc) affect hydrotreating operations? With lighter feeds and less sulfur how can the hydrotreating reactors and catalyst systems be tailored to optimize performance? What other factors in economics replace volume gain when processing these lighter feeds (i.e. impact on FCC yields, gasoline blending, minimizing cetane giveaway, etc.)?

While tight oil trades at a discount compared to other sources, refineries with ready access to tight oil will be able to shift toward more hydrotreating, including demet and dewaxing and away from a hydrocracking focus. This is still primarily limited to U.S. mid-continent due to transportation limitation. If a refinery is gearing toward structurally processing sweeter crudes, then there is also an incentive to tweak the hydrocracking catalysts toward milder, more distillate selective part of ART’s hydrocracking catalyst portfolio. Since tight oil quality varies widely (even within the same area), it is advisable to continue to add additional demet and dewaxing capacity, and to continue to use advanced hydrotreating catalysts.

Looking at comparing a more naphthenic feed slate to one that is more paraffinic and understanding the impact on the various hydrotreating units in the refinery is important. The use of these tight oil, more paraffinic type crudes (Bakken and Eagle Ford) will lower the required severity on the average U.S. ULSD hydrotreater. Understanding how these changes will directionally affect the various processes is important in order to provide some planning, as there are both positive and negative effects with this change. The lower severity will reduce the required hydrotreating catalyst volume.
ration in order to remove the sulfur and nitrogen, hence increasing the hydrogen consumed. The increased aromatic content of these feeds also can influence the product cetane in ULSD. (Table I)

With higher aromatic concentration, however, there is a much greater potential for increased volume swell. (Figure 1) Additional detail on volume swell with aromatic saturation can be found in the AFPM paper "Understanding Catalyst Systems for Higher Yields of Diesel" AM 13-10.

Those feeds that are more paraffinic in nature, (Bakken and Eagle Ford) are much easier on the hydrotreating operations in the refinery. The sulfur and nitrogen molecules in these feeds are not as likely to be bound inside an aromatic ring and can be removed via direct abstraction which is significantly faster than having to complete a saturation step as well as the sulfur or nitrogen removal. This will provide either additional cycle time as the required temperatures assuming equal feed sulfur will be lower or there will be opportunity to process additional barrels per day in order to make up the loss in product yields.

These feeds also indicate an increase in light gas make as well. With higher paraffin content, comes less aromatic saturation opportunity, which will produce less volume swell per barrel than seen with a naphthenic feedstock. This also reduces the burden on the hydrogen system due to lower consumption. The high paraffin content of these feedstocks can also influence the cold flow properties requiring additional processing such as catalytic dewaxing or the blending of other valuable streams in order to meet these require-

<table>
<thead>
<tr>
<th>Compound</th>
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<th>Cetane Number</th>
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<tbody>
<tr>
<td>n-Decane</td>
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</tr>
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<td>n-Pentadecane</td>
<td>C_{15}H_{32}</td>
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<td>C_{20}H_{42}</td>
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</tr>
<tr>
<td>3-Ethyldecane</td>
<td>C_{12}H_{36}</td>
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</tr>
<tr>
<td>4,5-Diethyloctane</td>
<td>C_{10}H_{22}</td>
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<tr>
<td>Heptamethylnonane</td>
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<td>7,8-Diethyltetradecane</td>
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<td>n-Tetradecylnaphthalene</td>
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Q37 TABLE I: Cetane Number of Various Compounds

Q37 FIGURE 1: Aromatic Compounds Boiling in the Diesel Range

needed in order to achieve the same sulfur specification creating some additional catalyst volume which can be utilized to address some of the product property deficiencies resulting from these types of crudes. The use of tight oil crudes may also reduce the use and expense of using cetane improver to achieve the required cetane, as by nature, paraffins have higher cetane numbers (see Table I). More paraffinic feed stocks will decrease the hydrogen consumption of a hydrotreatment unit as well.

In general, a feedstock that is more naphthenic will have a higher hydrogen consumption per barrel due to the increased concentration of aromatic compounds. With this increased aromatic concentration, the likeliness that the sulfur or nitrogen is bound up in one of these molecules is greater making it more difficult to process in the hydrotreater. These feedstocks would require more aromatic ring satu-
There are several basic impacts that need to be understood when considering increasing the final boiling point of a particular feed stream in the refinery. With increases in the final boiling point of the feed, the total sulfur and nitrogen, the concentration of hard sulfur, and aromatics content all increase. This is independent of the source of feedstock. (Figure 1) In order to maintain the same product specifications, this will need to be compensated for by increasing the reactor temperature. Examining your available hydrotreaters and their processing capabilities as well the availability for an increased demand for hydrogen in one area or another in the refinery is important to avoid unexpected turnarounds.

In order to rank which feed source to consider for increasing the FBP, a good understanding of the current situation in the refinery and the ultimate impact of the change is important. In general, cracked stocks (Cokers and LCO’s) are more challenging to hydrotreat and require a higher weighted average bed temperature (WABT) compared to a straight run (SR) material at the same product targets. Coker stocks normally have higher sulfur and nitrogen content based on the nature of the feed to the coker and the coking process. These feeds also have a much higher olefin content (or bromine number) than SR feeds. The higher concentration of sulfur, nitrogen, and olefins will produce a higher heat release when operating to the same product targets giving rise to an increase in hydrogen consumption. When increasing overall diesel production by increasing feedstock endpoint coker stocks are probably the second best option for catalyst longevity behind straight run feeds.

Feeds from the fluid catalytic cracker (FCC) are much higher in aromatics than their SR counter parts and are especially concentrated in the poly aromatic content. This also gives these feeds a much lower API gravity relative to SR or coker stocks. The concentration of sulfur and nitrogen in these feeds are dependent on the presence of a pretreater upstream of the FCC which can help in lowering the total sulfur or nitrogen content. However, the sulfur and nitrogen compounds in FCC are usually the more difficult refractory species requiring a much higher required WABT to achieve the same product specification. (Figure 2)

Not all feedstock provide equal economic benefit. If your distillate hydrotreater has incremental hydrogen available and operates at high enough pressure, LCO may be the first choice for maximum economic return. LCO normally contains the highest amount of aromatics and therefore will provide the maximum volumetric expansion from hydrotreating. LCO will also undergo the largest increase in Cetane across the hydrotreater as shown in Figure 3.

Q39. There is a drive to target the highest end point possible on all distillate feed streams when maximizing overall diesel production. Are there feed streams that should be targeted first, considering operational impacts of such optimization, impacts to catalyst performance and life cycle, as well as cut point optimization between distillate units and the FCC?

There are several basic impacts that need to be understood when considering increasing the final boiling point of a particular feed stream in the refinery. With increases in the final boiling point of the feed, the total sulfur and nitrogen, the concentration of hard sulfur, and aromatics content all increase. This is independent of the source of feedstock. (Figure 1) In order to maintain the same product specifications, this will need to be compensated for by increasing the reactor temperature. Examining your available hydrotreaters and their processing capabilities as well the availability for an increased demand for hydrogen in one area or another in the refinery is important to avoid unexpected turnarounds.
As always ART is prepared to discuss these options and assist in making the best choice with the catalyst system already in use, and also to help prepare for the next catalyst load in order to take advantage of these various paths.

**Q40. Economic drivers dictate the need to process more difficult feed stocks such as cracked stocks and diesel feeds with high distillation end points. What are typical guidelines regarding minimum hydrogen partial pressure for a given feed stock?**

The question of what is the minimum allowable H₂ partial pressure for a hydrotreater has been asked frequently. The general answer is: it depends on how much the refiner is willing to sacrifice in cycle length.

As background for this discussion, H₂ partial pressure is set by the following parameters:

- Reactor Design Pressure
- Makeup Hydrogen Purity
- Recycle Gas Rate and Purity
- Bleed Rate
- Hydrogen Consumption
- Degree of Feed Vaporization

Typically, the reactor is operated at a constant inlet pressure near the design value and with a relatively stable feed quality; the hydrogen consumption and degree of feed vaporization are also essentially constant. Consequently, the variable parameters affecting H₂ partial pressure are makeup hydrogen purity, recycle gas rate and purity, and bleed rate. Of these, the independent variables are makeup hydrogen purity and bleed rate which set the recycle purity, and the recycle gas rate. Since many hydrotreaters have amine scrubbers to remove H₂S from the recycle gas, a bleed is not necessary and H₂ partial pressure is a function of makeup purity and recycle gas rate.

The H₂ partial pressure varies throughout the reactor with the highest partial pressure at the inlet and the lowest at the outlet. Since the operating conditions are the most severe at the outlet and strongly influence catalyst activity and stability, we will look at the impact of makeup purity and recycle gas rate on the H₂ partial pressure at the reactor outlet.

The following tables show the effect these parameters on unit performance for a diesel hydrotreater. The base case is:

- Inlet pressure: 760 psig
- Makeup gas purity: 99.9 vol.%
- Recycle gas rate: 1500 SCFB

Table I shows the effect of reducing makeup gas purity on reactor outlet conditions, cycle length, and start of run (SOR) weighted average bed temperature (WABT).

As the makeup gas purity drops, so does the outlet H₂ partial pressure. This leads to reduced cycle length and higher required SOR WABT. The impact of reducing makeup gas purity is essentially the same as reducing inlet pressure. Note, that as long as the recycle gas rate remains constant even though the H₂ purity is dropping, the outlet H₂S partial pressure is constant. In Table II, the impact of reducing the recycle gas rate is illustrated. Here the effect is more severe because as the outlet H₂ partial pressure drops, the outlet H₂S partial pressure increases. This further decreases catalyst activity and cycle length. The effect of the outlet H₂S partial pressure can be isolated by comparing the 90% makeup gas purity case with the

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<th>Recycle Gas Rate, SCFB</th>
<th>Makeup Gas Purity, vol.%</th>
<th>Outlet H₂, psi</th>
<th>Outlet H₂S, psi</th>
<th>Cycle Length, Months</th>
<th>SOR WABT, °F</th>
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**Q40 TABLE I: Effect of Reducing Makeup Gas Purity**

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<tr>
<th>Recycle Gas Rate, SCFB</th>
<th>Makeup Gas Purity, vol.%</th>
<th>Outlet H₂, psi</th>
<th>Outlet H₂S, psi</th>
<th>Cycle Length, Months</th>
<th>SOR WABT, °F</th>
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<tbody>
<tr>
<td>Base Case</td>
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<td>30.2</td>
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<td>406</td>
<td>46.9</td>
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</table>

**Q40 TABLE II: Impact of Reducing the Recycle Gas Rate**
Q49 FIGURE 1: Comparing a Mounded and Sloped Bed and the Effect on Relative LHSV

800 SCFB recycle gas rate case. The outlet H₂ partial pressure is similar, 408 vs 406 psi, but the cycle length is seven months shorter and the required WABT is 10 °F higher.

In conclusion, the minimum allowable H₂ partial pressure for a hydrotreater depends on the minimum acceptable cycle length and the method of reducing the outlet H₂ partial pressure.

Q47. What evaluations are required for hydrocracking units to increase conversion due to processing heavier feed stocks?

Evaluations for increased conversion of heavier feed stocks must consider catalytic, mechanical, and analytical capabilities. Depending upon catalyst choice, the operating cycle may decrease with increased conversion so it is important to work closely with your catalyst supplier. Depending upon feed type, increased conversion may result in an increase in hydrogen consumption and therefore may have an impact on hydrogen loop capacity and operating safety systems. An increase in conversion can also produce more light products which often requires mechanical modifications to ensure the process equipment can handle it. Finally, as feed endpoint increases, it is usually more difficult to maintain consistent feed properties. Be sure to consider increased analytical requirements and possibly upstream unit modifications to ensure that feed quality is maintained.

It is also a good idea to explore the need to improve the reactor internals in order to better handle the higher heat release that is likely to accompany the higher hydrogenation required by a more aromatic (heavier) feed.

Q49. What are the criteria for levelness during dense loading of a catalyst bed? What are the preferred monitoring techniques and what is the best approach to correct an uneven bed profile if it is detected?

For a level catalyst bed, ART recommends ensuring a slope of 5 degrees or less be maintained throughout the loading. This corresponds to a difference in catalyst bed height of one inch over a one foot distance across the bed. A slope in excess of 10 degrees needs to be corrected by vacuuming out catalyst down to a level bed, and then restarting the loading process at the corrected dense loader settings. It is not recommended that the unlevel bed be raked or pushed around in order to level it. This can lead to variable loading densities, which may lead to uneven gas and liquid flow.

Cold flow modeling shows that the oil and gas tends to flow along the slope of the catalyst bed as shown in Figures 1 & 2. For a mounded catalyst bed the liquid velocities are higher at the walls than in the center of the bed, and for a sloping bed the higher veloc-
ties are towards the downside of the slope. These figures clearly demonstrate the importance of a level catalyst bed to maximize catalyst utilization.

As bed densities are calculated, they should be compared to the expected density on the catalyst loading sheet. Normal differences are expected to be ± 5%. If the density varies by more than 5%, carefully recheck the calculation of the density. Verify that the bed is level since this will affect the outage and density. The dense loading machine should be adjusted as necessary to maintain an even, level bed and achieve the targeted density.

A few key items for measuring the outage:

- Check outages and bed levelness at each loading pause
- Always measure from the same reference point
- Always use the same measuring tape
- Use at least two points across the bed for an outage

Outages should be taken at reasonable intervals during the loading. Typically an outage may be taken after 10%, 25%, 50%, 75%, 90% and a final outage are good places. The depth of the bed or layer will determine if these outage points should be different as the loading should not be stopped too frequently for outage checks.

Refinery operations and the loading contractor should discuss how to handle TI installations. TIs should be removed prior to loading and then reinstalled when the dense loader is within six feet of the TI in order to minimize shadowing caused by TIs. This shadowing effect can create areas of lower density within the catalyst bed, causing an undesired re-direction of flow or possible hot spots.

It is important that the dense loading machine be set properly. Shimming the loader may be required in order to obtain a level bed and it is important for the loader to be centered in the manway.

Table I lists some examples of problems encountered while loading and suggestions on how to correct them.

<table>
<thead>
<tr>
<th>Problem Description</th>
<th>Solution Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density is too low, or there is a mound in the bed</td>
<td>It is necessary to increase the density. Talk with the contractor and verify that the catalyst is being distributed uniformly to the reactor walls. This probably requires reducing the velocity of the machine.</td>
</tr>
<tr>
<td>The bed has a slant</td>
<td>Verify the position of the machine and possibly add shims (talk with the contractor).</td>
</tr>
<tr>
<td>Density is too high, or there is a “hole” in the bed</td>
<td>It is necessary to decrease the density. Talk with the contractor and verify that the catalyst is being distributed evenly. This probably requires increasing the velocity of the machine.</td>
</tr>
<tr>
<td>Air pressure is erratic</td>
<td>There could be an obstruction in the machine. Stop loading and examine it.</td>
</tr>
</tbody>
</table>

Q49 TABLE 1: Loading Problems
Mike Zehender has been named General Manager, Americas and Segment Director, Distillate reporting to Scott Purnell. In this expanded role, Mike will assume sales leadership for the Americas region in addition to Distillate Segment leadership responsibilities. Mike will also continue to coordinate our global sales efforts for DHT and HCR/Lubes.

Chi-Wen Hung has been named General Manager, Asia Pacific. Chi-Wen joined Chevron in 1981 and has held a variety of roles across multiple divisions including: Technology Company, Technology Marketing, Corporate Major Transactions, Gas and Mid-stream Company, and most recently Asia Pacific Exploration and Production Company. Chi-Wen will report to Scott Purnell in this new role. Chi-Wen will be based in Singapore.

Dan Torchia has joined ART as Segment Director, Hydrocracking (HCR) and Lubes reporting functionally to Scott Purnell. Dan joined Chevron in 2005 and has been an integral member of CLG’s hydrocracking catalyst sales and marketing efforts. Prior to joining Chevron, Dan had a long career with BP working at both Lima and Toledo refineries, and finishing as Worldwide Hydrocracking Consultant. Following BP, Dan joined Akzo Nobel/Albemarle and worked to successfully develop a hydrocracking catalyst business to complement the existing hydrosprocessing catalyst business.

With the recent addition of hydrocracking and lubes hydrosprocessing catalyst sales to the ART portfolio, Woody Shiflett has assumed the new position of Business Director, Hydrocracking and Lubes. Woody will direct all aspects of the new HCR/Lubes business during this transition period in 2013 while continuing as Deputy Managing Director, ART.
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