A Better Perspective on Hydroprocessing Solutions

In the refining industry, market conditions are always evolving with new regulatory requirements, global demand shifts, and the use of heavier feedstocks among other factors. ART Hydroprocessing can help you take a better perspective on these challenges based on our deep understanding of refinery operations and a full spectrum of hydroprocessing catalysts solutions that maximize profits by balancing run length, severity, feed flexibility, contaminants, and operating constraints.

ART is a joint venture of Chevron and W. R. Grace & Co., created to bring you state-of-the-art hydproprocessing catalyst solutions for petroleum refining applications worldwide. We collaborate with the industry’s leading licensor, CLG, to provide complete solutions to address your needs to extract more value from every barrel of oil. Combined with our unparalleled technical customer service, we deliver results for you.

Contact your ART representative today for more information.
Investments in Innovation

Scott Purnell, Vice President, Marketing, Refining Technologies, W. R. Grace & Co.

When people today hear the word “innovation,” they likely think of the high-tech industry and the rapidly evolving hardware and software that continues to make us more productive and more connected every day. For a mature industry like refining, with a modern history of more than 150 years, one might expect a slow pace of change. I’m pretty sure that not many people would immediately associate refining or refining catalysts with innovation. But I would attest that innovation is one of the key reasons that fossil fuels still dominate our energy supply and refining is still an important industry. Innovation has allowed refiners to meet each new challenge and to do so in a profitable way.

Today’s refiner continues to face even more hurdles – ever-tightening fuel sulfur regulations, increased need for heavy oil upgrading, compliance with air emission requirements, and IMO marine fuel specifications are just a few examples. At Grace and ART we are investing in catalyst innovation to help our customers meet this challenge. We are investing in research to develop and launch next generation catalysts and additives. In this issue you will find success stories describing the value these innovations have delivered through improved yields, reduced emissions, increased catalyst activity, and longer run lengths. At Rompetrol we increased profitability by generating FCCU propylene yields among the highest in EMEA with our ACHIEVE® 100 catalyst and OlefinsUltra® HZ additive. At Hellenic Petroleum we reduced FCC NOx emissions by 65% through the combination of our CP®P and DENOX® additives. Finally, ART’s ICR® 1000 catalyst system improved the economics of a major refiner’s recycle operation by improving the production rate of transportation fuels.

Our investments go beyond new products. We are investing in manufacturing assets to produce these new products as well as in infrastructure capabilities to further support our customers. As of this writing, we are in the process of starting up a production line to produce our industry-leading MIDAS® catalysts in our Worms, Germany facility. We have previously announced logistics investments in the UAE, and this year we have opened the region’s first FCC equilibrium catalyst laboratory through a partnership with Sohar University in Oman to further demonstrate our commitment to the Arabian Gulf region. We have also announced the signing of a framework agreement including planned investments to support Kazakhstan’s refining sector and potentially the broader CIS region. Meanwhile progress continues to be made on the construction of ART’s new world-class resid hydroprocessing catalyst plant in Lake Charles, Louisiana, USA.

We are committed to helping our customers meet today’s challenges and whatever new ones might lay around the corner. We aren’t successful unless you are successful. As always, we look forward to your feedback and continuing the journey together.

“I would attest that innovation is one of the key reasons that fossil fuels still dominate our energy supply and refining is still an important industry.”

Scott Purnell
Vice President, Marketing, Refining Technologies
IN THIS ISSUE of Catalagram®, our experts demonstrate the value of doing business with Grace. From improved product performance to increased profitability, Grace’s FCC catalysts and additives and ART’s hydrotreatment catalysts and catalysts systems deliver significant value in today’s challenging refining environment.

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Collaboration with Customers Creates Opportunities for Improved Refinery Operations

ART Hydroprocessing hosted a technical workshop at Chevron’s Technology Center in Richmond, California, USA for customers currently using ART’s Online Catalyst Replacement (OCR) technology. Engineering teams from KNPC’s Mina Abdullah refinery and IKC’s Aichi and Hokkaido refiners attended the workshop, which was held June 25-27, 2018. During the three days, ART’s RDS technical experts addressed operational and maintenance aspects of OCR units, the latest advances in RDS catalyst technology and deployment of new OCR and RDS catalysts. In addition, KNPC and IKC participants toured the state of the art R&D facilities.

The sessions were conducted by Robert Wade, ART’s subject matter expert for Resid Technology, with contributions from Technical Service leaders Mike Smith, Steven Song, Srihari Narisetty, Mathew Yu, Chris Dillon, and R&D leaders Viorel Duma and Rong He.

The workshop is example of ART’s ability to utilize its experience in operating Chevron units and superior hydproprocessing knowledge and data analysis capabilities to collaborate with customers to improve cycle length and other performance measures. It is also one of the ways ART’s local and global technical service engineers provide support to customers to improve unit reliability. Claudia Janse van Rensburg, KNPC Technical Service Engineer, remarked “This workshop provided a valuable opportunity for KNPC, IKC, and ART Hydroprocessing to share their experiences, best practices and research. Critical to the success of this event was the open and willing communication between IKC and KNPC, which can be built on for continued knowledge sharing.” ART, KNPC, and IKC look forward to exploring resid catalyst solutions together to improve overall refinery economics and operations.

Engineering teams from KNPC’s Mina Abdullah refinery and IKC’s Aichi and Hokkaido refiners learn from ART Hydroprocessing experts at Chevron’s Technology Center in Richmond, California, USA.

Workshop participants explore operational and maintenance aspects of OCR units and discuss the latest advances in catalyst technology.
**FCC Workshops Deliver Fundamental Value**

In May of this year, catalyst experts from Grace helped engineers from customer refineries to understand better the fundamentals of FCC unit operation and the role catalysts play in optimizing output for greater efficiency and profitability.

Twenty-one engineers and operators from companies such as Phillips 66, Shell, and Philadelphia Energy Solutions gathered at Grace’s corporate headquarters in Columbia, Maryland, USA to attend the semi-annual FCC Technology Workshop organized by Ann Benoit, Senior Technical Service Manager, FCC.

Over three and a half days, attendees heard presentations from our top FCC researchers and technical service team on topics ranging from understanding FCC heat balance to troubleshooting conversion shifts. In addition, they had the opportunity to visit R&D labs on the Columbia campus and take a tour of Grace’s Curtis Bay operations. Evenings included a chance to relax and socialize along with opportunities to discuss further challenges at their units.

Also in May, a group of engineers at BP’s Castellón, Spain facility attended an on-site FCC Fundamentals Workshop organized by Rafael Gonzalez, Technical Sales Manager, FCC. Similar to the Columbia workshop, but designed for a specific customer, the FCC Fundamentals Workshop is one of several hosted by Grace and held at customers’ refineries to address their unique needs. The workshops are part of Grace’s ongoing commitment to helping customers create the highest value possible from their refinery operations.

**ART and CLG Experts Conduct Hydroprocessing Workshop**

ART Hydroprocessing (ART) and its licensing partner, Chevron Lummus Global (CLG), which is a joint venture between Chevron and McDermott, conducted an extensive three-day Operations and Process training workshop at SATORP in Jubail, Saudi Arabia on July 2-4, 2018. The training was led by technical experts Michael Salyer (CLG), Atanu Chakraborty (ART), and Alok Srivastava (ART) and was attended by an energetic group of SATORP refinery engineers.

Participants at the highly interactive workshop benefited from the 80+ years of experience provided by ART’s and CLG’s technical experts as well as the deep knowledge of SATORP’s HCR units, which were licensed by CLG. The workshop covered a wide range of topics including Hydroprocessing Chemistry and Fundamentals, Unit Start-up and Operational Excellence. In addition to the theoretical content, the participants shared real life experiences and case study reviews that highlighted methods to optimize cycle length product yields.

ART and CLG’s practical approach to developing technology and optimizing operations and SATORP’s commendable approach to achieving high levels of refinery productivity and results complemented each other well and resulted in a successful workshop. ART and CLG look forward to conducting future workshops with SATORP as they continue to pursue excellence in their operations.
SOx emission control has long been a requirement for many refineries worldwide, but refiners in certain regions and countries will continue to face more stringent SOx targets in the coming years. There are various SOx emissions abatement measures available for refiners, including the purchase of low sulfur crude feedstocks, the use of catalytic feed hydrotreaters or the installation of wet gas scrubbers (WGS). Although highly effective for reducing SOx emissions, these options can result in high OPEX costs and high CAPEX investments.

FCC SOx reduction additives however, represent a CAPEX-free approach with lower OPEX costs, and provide refiners with a high degree of flexibility for controlling SOx emissions across a wide range of operational conditions. For this reason, FCC SOx reduction additives have long been considered as being extremely cost-effective and versatile, and are well established as one of the best available technologies for many refineries. This is highlighted by the fact that more than 130 refiners globally have used Grace’s Super DESOX® additives.
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WGS versus FCC SOx Reduction Additives

Two of the main regions currently using SOx additives are the US and EMEA (Europe, Middle East and Africa). Grace recently analyzed these markets to compare the use of WGS versus the use of FCC SOx reduction additives. Figure 1 shows the US market, and it can be seen that proportion of refiners using WGS compared to SOx additives differs considerably according to the Petroleum Administration for Defense District (PADD), perhaps reflecting the cost of caustic in each district. The Rocky Mountains has the highest proportion of refiners using SOx additives and lowest proportion of refineries using WGS. In contrast, the East Coast and Gulf Coast has the lowest proportion of refiners using SOx additives and highest proportion of refineries using WGS. The Midwest and West Coast have a more balanced proportion of refiners using WGS and SOx additives. Interestingly in most of the regions there are a handful of refiners using a combination of both technologies.

As highlighted in Figure 2, a much lower proportion of refiners in EMEA are using WGS compared to their US counterparts. The use of SOx additives is particularly prevalent in South Europe, but is also common in North Europe and the Middle East. A handful of refiners in Eastern Europe are using SOx additives, while there is a much smaller amount of SOx additive users in Africa, Russia and the CIS. The EMEA analysis conservatively takes into account the refiners expected to start using SOx additive later in 2018 in connection with the new European BREF legislation.

Figure 1: US SOx Reduction Market by PADD

Figure 2: EMEA SOx Reduction Market by Region
Economic Benefits of Using SOx Additives

Over the past two years global caustic pricing has increased considerably, which for those refineries operating a WGS will be having a significant impact on OPEX costs. Figure 3 highlights caustic pricing in the US West Coast, US Midwest, US Northeast, US Southeast, NW Europe, and NE Asia. The pricing varies considerably by region, but in each example a significant increase in caustic price has been observed in the last two years.

Because SOx reduction additives are a well-established, robust, and reliable route to achieve emissions targets, it is possible to make an accurate estimation of the potential cost savings associated with using an optimum combination of caustic WGS with SOx additives. The factors that impact the overall economic evaluation include the level of uncontrolled SOx emissions (i.e., the SOx levels that would be obtained without the use of any SOx reduction technology), the target SOx levels, the caustic soda price, the effectiveness of SOx additives for a given operation, and the price of the SOx additive.

Figure 4 highlights the potential cost savings for a typical refiner operating a caustic WGS when deciding also to use SOx additives to reduce caustic consumption requirements. It assumes uncontrolled SOx emissions of 800 ppmv, with a target SOx level of 25 ppmv, and a flue gas flow rate of 100,000 SCFM (158 kNm3/hr, which would typically represent an FCC unit processing 60-65 kBPD feedstock). It considers a caustic soda price range of 500 to 600 $/MT, and incorporates typical market pricing for SOx additives. The analysis considers that SOx additives can be used to achieve different levels of the SOx reduction required. For example:

- Case 1 is based on the additive being used for 75% of the SOx reduction, while caustic is used for the remaining 25% SOx reduction.
- Case 2 is based on the additive being used for 50% of the SOx reduction, while caustic is used for the remaining 50% SOx reduction.
- Case 3 is based on the additive being used for 25% of the SOx reduction, while caustic is used for the remaining 75% SOx reduction.

It also takes into account that SOx additive efficiency will decrease slightly for higher targets of SOx reduction. For example, at an uncontrolled SOx level of 800 ppmv, the SOx additive Pick Up

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**Figure 3: Caustic Soda Market Pricing**

**Figure 4: Potential Cost Savings for Optimum Combination of Caustic WGS and SOx Reduction Additives**

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Factor (PUF, mass of SO\textsubscript{x} captured per mass of SO\textsubscript{x} additive used) will be lower when targeting 75% SO\textsubscript{x} reduction through use of additive compared to a target of 25% SO\textsubscript{x} reduction. It can be clearly seen that high levels of cost savings are possible even when using SO\textsubscript{x} additives to only achieve 25% of the required SO\textsubscript{x} reduction. However, the cost benefits are considerably higher again when using SO\textsubscript{x} additives to achieve 75% of the required SO\textsubscript{x} reduction, with savings of up to $1 million per year achievable. Another way of looking at this is that refiners can save between 20 to 40% of their caustic costs by using SO\textsubscript{x} additives. An additional advantage for refiners will be a reduction in caustic disposal costs, which has not been taken into account in this analysis.

**Grace SO\textsubscript{x} Reduction Technology**

Grace’s Super DESOX\textsuperscript{®} additives are designed to reduce flue gas SO\textsubscript{x} emissions from the FCCU regenerator. They are unique in that they incorporate a patented magnesium spinel platform, resulting in an optimized system for SO\textsubscript{2} oxidation, the capture of SO\textsubscript{3}, and additive regeneration. Super DESOX\textsuperscript{®} additives are typically used at dosing rates of 2-10 wt.% of fresh catalyst additions, and are effective for controlling emissions well below 25 ppmv SO\textsubscript{x}. Super DESOX\textsuperscript{®} additives can be preblended with fresh catalyst or delivered separately, to provide refiners with a full flexibility of options. In addition to benefits of reducing WGS caustic consumption, SO\textsubscript{x} additives also allow refiners to balance refinery wide SO\textsubscript{x} emissions when operating under bubble limits, they provide economic flexibility to process feeds high in sulfur, and can relieve pressure on FCC feed hydrotreaters.

**Reducing Caustic Usage and OPEX at Refinery A with Super DESOX\textsuperscript{®} Additives**

The following case study features an FCC unit from Refinery A in the Asia Pacific region, which processes residue with a typical sulfur content of 0.35 wt.%. The FCCU is equipped with a flue gas scrubber using caustic water, as well as a Third-Stage Separator (TSS) for catalyst fine recovery after the primary and secondary regenerator cyclones. The refinery recently decided to trial Grace’s Super DESOX\textsuperscript{®} additive due to more stringent regulations on SO\textsubscript{x} emissions. Refinery A use FCC catalyst from Grace, and after an initial base loading period of SO\textsubscript{x} additive, moved to a continuous addition of 3 wt.% of Super DESOX\textsuperscript{®} additive during the trial.

The wet gas scrubber (WGS), as depicted in Figure 6, enables the removal of mainly SO\textsubscript{2}, as well as SO\textsubscript{3}, gaseous pollutants and catalyst particulates by contacting the flue gas with a caustic water solution. The WGS efficiency is impacted by several factors including the inlet temperature, pressure, caustic concentration and caustic water flowrate. The operating conditions of the WGS were maintained constant before and during the additive trial period, with the exception of the caustic usage. The key target and requirement was to comply with the SO\textsubscript{x} emission limits at 25 ppm in the stack after the WGS.

Prior to the SO\textsubscript{x} additive trial, SO\textsubscript{x} emissions were in the range of 80-100 ppmv. As highlighted in Figure 7, upon addition of Super DESOX\textsuperscript{®} additive, a rapid decrease in SO\textsubscript{x} emissions was observed, and the target limit of 25 ppmv was comfortably met with SO\textsubscript{x} levels as low as 5-10 ppmv achieved. After stopping the Super DESOX\textsuperscript{®} additive injection, the SO\textsubscript{x} emissions remained below the regulatory limit for a period of seven days, demonstrating the excellent activity retention of the additive.

Besides the noticeable impact on SO\textsubscript{x} levels, Super DESOX\textsuperscript{®} additive allowed a considerable reduction of caustic usage in the WGS operation. By the latter part of the additive trial, caustic consumption had been reduced by 60% through use of the SO\textsubscript{x} reduction additive.

In addition to lower SO\textsubscript{x} levels and lower caustic usage, the refinery observed an improvement in the level of particulates in the stack emissions, resulting in an estimated 10% lower level of fines in the TSS. This presents the refinery with a wider operating flexibility while complying with particulates emissions regulations.
In order to quantify the benefits for the refinery, a caustic price of $600 per metric ton was used in the evaluation, and a 60% reduction of the caustic water washing flowrate used prior to the SOx additive trial. Based on this OPEX costs were reduced by $4,500 on a daily basis, corresponding to yearly savings of approximately $1.6M. Local caustic pricing has even exceeded $600 per metric ton in the meantime, so the economic savings using SOx additives to offset caustic costs are on the conservative side.

The use of SOx reduction additives offer refiners an opportunity to reduce OPEX costs during periods of high caustic prices. A case study from Refinery A in Asia Pacific has been used to highlight this, in which Super DESOX® additive demonstrated excellent levels of SOx reduction to meet environmental requirements, with SOx emissions reduced from 80-100 to as as low as 5-15 ppmv.

Moreover, the use of Super DESOX® additive provided the refinery with the opportunity to decrease the consumption of caustic water in the wet gas scrubber, which was estimated to have provided a reduction in OPEX costs by approximately $1.6M on an annual basis.

Figure 6: Representative Scheme of the Wet Gas Scrubber

Figure 7: Lower SOx Emissions and Lower Caustic Usage Using Super DESOX® Additive
A refinery’s flexibility and responsiveness to market dynamics and regulatory environments has a major impact on its competitive position. Several factors drive this need for responsiveness including the availability of inexpensive opportunity crudes and compatible cutter stocks, tightening regulations on residual fuel oil, and price differentials between petrochemical feedstocks, base oil and transportation fuels. Tighter specifications on refinery process schemes combined with more robust catalyst systems affords more sustainably turning a larger portfolio of opportunity feedstocks into a product slate that is more in sync with the market dynamics¹.
Dealing with Refinery Constraints

Refineries impose constraints on operations to maximize operational reliability. Recent process and catalyst options have been developed that significantly reduce and refine these constraints postures. With the production of light crudes and heavy crudes increasing and with medium crudes in decline, more and more refineries are feeding opportunity blends of light and heavy crudes. These crude blends raise compatibility concerns, and they can challenge the distillation train, which frequently exacerbates entrainment of residual oil in the hydrocracker feed. Entrained residual oil has a deleterious impact on hydrocracker performance even if the entrainment is so small that it is close to the detection limit of standard analytical techniques (Table 1). If capital is available, one can invest in improved process options to improve the hydrocracker feedstock, and thereby mitigate the exposure to the negative impact of opportunity crudes. A capital-neutral solution is a catalyst system that can mitigate the risk associated with only a minor increase in end boiling point of the feedstock to the hydrocracker.

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Table 1: Entrainment of residual oil (i.e. oil boiling above 1050 °F) often goes undetected by a single fractionation method, such as simulated distillation by gas chromatography. Fractionation into saturates, aromatics and resins by liquid chromatography (ASTM D2007) followed by simulated distillation frequently brings residual oil entrainment into sharp contrast.

How to Mitigate the Impact of Incompatibilities During Hydroprocessing

Residual oil entrained in the feed to a hydrocracker designed to hydrometer vacuum gas oil is a problem, because parts of the residual oil frequently do not maintain their compatibility once the feed starts to be hydrometered. Compatibility is lost because hydrometering strips the complex residual oil molecules initially dissolved in the feed down to polycyclic aromatic cores, whilst simultaneously saturating the feed into a less aromatic stream that is less hospitable to large aromatics. Compatibility is further reduced by the condensation of smaller aromatics into thermodynamically more favored larger configurations. This simultaneous formation of a more aromatic solvent inside a less aromatic solvent can create nano-emulsions, which can form mesophases (liquid crystals) that can ultimately sediment out either inside the reactor or inside equipment downstream from the reactor. A recent catalyst system has been designed that disrupts this sedimentation process by saturating key feed components before these are stripped into their incompatible aromatic cores. The efficacy of this disruptive catalyst system is best illustrated in a hydrocracker configuration that runs in recycle operation.

How to Disrupt Sedimentation

Sedimentation of molecules that have become incompatible with the gas oil as it is being hydrometered is a particularly acute problem in hydrocrackers running in recycle (Figure 1). Recycle operation augments the impact of incompatibility because this operation concentrates the polycyclic aromatic solute by hydrometering the solvent into transportation fuels, and by distilling these fuels away as products. This concentrates the already not overly compatible aromatic solute, and concentration further enhances the risk of bringing the aromatic solute well above its solubility limit. The associated risk of a catastrophic seizure of the run through sedimentation inside the recycle loop is well known. Sedimentation is typically controlled by carefully monitoring the recycle loop for the buildup of sediment-forming heavy aromatics and by bleeding the appropriate fraction of unconverted oil to keep these aromatics under their solubility limit. There are several monitoring options: i) by color, visually; ii) by UV Vis spectroscopy from which one can derive a PolyCyclic Aromatic Index (or PCI, a marker for incompatibility risk); iii) by spot checking the buildup of aromatic compounds with high-resolution mass spectrometry (Figure 2). This reactive approach to mitigating incompatible

Figure 1: Converting more of the bleed stream into product is a major way of improving the economics of recycle operation. The most refractory compounds left unconverted would accumulate in the recycle loop if it were not for a bleed to e.g. an FCC unit.

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aromatics accumulation generates a low-value bleed stream of unconverted oil, which misses an opportunity to hydprocess this oil into high-value transportation fuel (Figure 1). We have demonstrated the efficacy of a more proactive approach that mitigates the risk of the buildup of incompatible compounds before it gets started. We show how this proactive approach minimizes the bleed stream and commensurately improves the production rate of transportation fuel without a major impact on run length.

One can proactively counteract sedimentation by selectively keeping the polycyclic aromatics in the hydprocessing streams at their hydrogenation equilibrium before they have an opportunity to agglomerate, to emulsify or to become recalcitrant to hydprocessing in other ways. Since the incompatible large aromatic compounds agglomerate already at low concentrations and since they boil toward and above the tail end of typical hydcracker feedstock boiling range, traditional hydrotreating catalysts focus at saturation of the majority of the feedstock (the solvent) and do not start to saturate the low concentration of polycyclic aromatics (the solute) until it has built up to appreciable (and undesirable) levels (Figure 3A/B). In marked contrast, the unique pore structure and high hydrogenation activity of the new ICR® 1000 catalyst affords it to selectively target the polycyclic aromatics even at concentration well below the level at which they start to agglomerate. A comparison of the efficacy of a catalyst system with ICR® 1000 as compared

Figure 2: To assure that a recycling hydcracker run does not fail catastrophically by refractory compounds settling out in the recycle loop, the color and polycyclic aromatic index (PCI) are regularly monitored and maintained within an acceptable range bleeding part of the recycle stream.

Figure 3A: Traditional hydrotreating catalyst systems first hydrotreat the bulk of the vacuum gas oil (VGO) solvent and only start bringing the heavy polynuclear aromatics (HPNA's) solute to hydrogenation equilibrium when this solute is at appreciable concentrations. By contrast, hydrotreating catalyst systems with sufficient ICR 1000 focus at hydrogenating the HPNA solute first.

Figure 3B: Typical catalyst systems hydcrack the high-boiling vacuum gas oil (VGO) solvent into a lower transportation fuel range, which concentrates the refractory sediment precursors in the unconverted oil. Hydcracking systems containing ICR 1000 convert some of the sediment precursors, which results in a lower polynuclear aromatics Index or PCI.
to a typical catalyst system illustrates the selective hydrogenation of a representative polycyclic aromatic compound doped into a typical vacuum gas oil (Figure 3A). Another illustration is the significant reduction of PCI (a marker for incompatibility risk) by adding ICR® 1000 to a catalyst system deployed to hydroprocess a vacuum gas oil (VGO) feed derived nearly exclusively from residue desulfurization (RDS) in once-through operation (Figure 3B).

### A Commercial Example

The most powerful illustration is what happens when this concept is taken into practice at a commercial hydrocracker that hydroprocesses RDS VGO in recycle operation (Figure 1) Interestingly, the bulk properties (more saturated, lower boiling range) of RDS VGO suggest that it should be significantly more amenable to hyd processing than a typical Straight-Run (SR) VGO (Table 2), whereas the exact opposite is true in that RDS VGO is significantly more recalcitrant to hyd processing.

A refiner recently deployed the ICR® 1000 technology to sustainably minimize the low-value bleed of UnConverted Oil(UCO) and produce commensurately more value-added fuel.

This refiner has two virtually identical hydrocrackers which have the same configuration, operating conditions and feed. The feed consists of RDS VGO, SR VGO and Coker Gas Oil (CGO). The hydrocrackers are targeting maximum middle distillate product yield (mainly jet) and maximum overall conversion of the feed. The feed conversion has been limited by the need to bleed UCO from the recycle loop so as to assure that the heavy polycyclic aromatic sediment precursors stay at an acceptable level.

Recently, ICR® 1000 was added to the catalyst system of one hydrocracker to catalytically disrupt the buildup of sediment precursors in the UCO, and the results are compared with the other hydrocracker’s most recent two cycles which use virtually the same catalyst system but without ICR® 1000. Due to changes in the refinery stock balance, the refiner had to increase the feed end boiling point (Figure 4), and had to add some highly aromatic CGO (Figure 5) to the cycle containing ICR® 1000. As a result, feed nitrogen content increased (Figure 6), feed PCI increased (Figure 7), and the feed became more aromatic. Even at about 450 days on stream the refiner kept the feed more aromatic as compared to the cycles without ICR® 1000 (Figures 4-7). Even though the properties of the feed for the ICR® 1000 run suggest that it is considerably more challenging, the PCI of the UCO in the recycle stream of the ICR® 1000 run remained at a similar level, if not lower than the runs without ICR® 1000 (Figure 8).

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Table 2: Typical physical properties suggest that a vacuum gas oil (VGO) derived from an residual oil hydrodesulfurization (RDS) unit is more saturated and should hyd process with more ease than a straight run VGO, whereas the reverse is true.

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</tr>
</tbody>
</table>

**SimDist (wt-%) F**

| 0.5 | SR VGO | 624 | 595 |
|     | RDS VGO | 689 | 680 |
| 5   | SR VGO | 689 | 680 |
| 10  | SR VGO | 723 | 710 |
| 30  | SR VGO | 793 | 775 |
| 50  | SR VGO | 845 | 825 |
| 70  | SR VGO | 899 | 880 |
| 90  | SR VGO | 979 | 950 |
| 95  | SR VGO | 1018 | 975 |
| 99  | SR VGO | 1092 | 1035 |

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Figure 4: For the ICR® 1000 cycle the feed end boiling point was increased.

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Continued on Page 16
In addition to addressing stock balance issues, (and more impactfully), the refiner increased the product value by significantly reducing the bleed rate (Figure 9A). This bleed reduction appears not to have reduced the cycle length. The total UCO bleed reduction in the ICR® 1000 cycle is projected to be approximately 2,000 Mbbl over the three years’ cycle length, and the corresponding middle distillate production increase is estimated to be approximately 1,500 Mbbl (Figure 9B). The resulting economics can vary widely depending on the specific refinery’s situation and the local, regional and global market conditions. However, if we assume an average $10/bbl differential between middle distillates and UCO, the impact of the bleed reduction alone easily amounts to $15-16 MM for the current cycle.

Operating hydrocrackers in recycle operation with RDS VGO and CGO feed is a major challenge due to the risk of high polycyclic aromatics build-up and sedimentation terminating the run prematurely. Controlling the buildup of refractory aromatics becomes more challenging as the hydrocracker is running more toward full conversion of the feed to maximize diesel or jet production. Typically, the buildup of polycyclic aromatic sediment precursors and run length is thereby maintained by the judicious bleeding of unconverted oil.

Here we demonstrate how a close cooperation with a client led to the commercial introduction of a catalytic solution, ICR® 1000, by Advanced Refining Technology (ART) that converts more feed into jet by lowering the bleed rate without impacting run length.

References

1. U Mukherjee, D. Gillis, PQT Q1 2018 75-83
Figure 8: Despite the higher PCI of the feed, the unconverted oil maintains PCI.

Figure 9A: Despite the more challenging feed, there is less unconverted oil (less bleed) and commensurately more product.

Figure 9B: Despite the more challenging feed and the lower bleed rate, the unit is slated to make it usual cycle length.
Improving Operating Profitability at the Refinery with ACHIEVE® Technology

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KMG Rompetrol are addressing current market challenges through a strategy of downstream integration with petrochemicals, taking advantage of the flexibility that the Fluid Catalytic Cracking (FCC) unit offers for maximum light olefins production. In this article, KMG Rompetrol and Grace provide an overview on how refineries can increase the profitability of their FCC operation by maximizing the production of propylene and iso-butylene using the latest FCC catalyst and additive technology. ACHIEVE® technology from Grace has contributed sustaining the refinery’s profitability, as well as improving its competitive position in the marketplace. This technology has resulted in yields of 11 wt% propylene, which ranks the refinery’s FCC unit among the top five propylene producers in EMEA.
Maximization of propylene production has become the focus of many refineries because propylene consumption continues to grow and there is a supply shortage, resulting in a supply-demand gap. Demand for propylene is driven mainly by the global polypropylene industry, which has seen historical growth of 5.0-6.0 %/year\(^1\). As shown in Figure 1, by 2035 petrochemical products will account for almost 50% of the expected growth in demand for crude-oil based products, of which a significant portion will be propylene.

In Asia-Pacific (and to a large but slightly lesser extent in the EMEA region) propylene demand is high; therefore, many refineries that have the potential to produce more propylene are enjoying a competitive edge in the industry. There are different ways for refineries to increase production of light olefins, for example through a revamping and debottlenecking of the entire FCC unit. However, using the latest catalyst and additive technology offers a reliable, quick, and flexible route.

**KMG Rompetrol Unit and Operating Focus**

The KMG Rompetrol company operates two production facilities: Petromidia, consisting of a refinery and a petrochemical complex, as well as the Vega refinery. Petromidia is located in Constanța close to the Black Sea, which gives KMG Rompetrol several strategic advantages. The Petromidia Refinery Nelson Complexity Index is 10.5 and is usually processing URAL crudes but also blends with other crudes such as Kirkuk, Azeri, and Siberian. The FCC unit is a 24,000 bbl./day UOP Side-by-Side design and is processing 100% hydro-treated feed coming from a Mild Hydrocracking Unit.
SUCCESS STORIES

Solomon Benchmark Related Figures

Every two years, Rompetrol Rafinare participates in the Solomon Worldwide Fuels Refinery Performance Analysis (Fuels Study) and receives the graphs below, which shows the Conversion Units’ performance.

Figure 3 highlights the FCC unit performance related to the 1st quartile / 2nd quartile break (black line), and with respect to the world’s top 10% of performers (green line). FCC unit performance is based on SOLOMON methodology, using a correlation between Dynamic Activity (measure of catalyst performance) and Feed UOP K Factor. The graph demonstrates that the Rompetrol FCC unit (red dot ‘2016’) is placed in the 1st quartile and close to world’s top 10% performers.

Figure 3: Solomon - FCC Yield Gaps

This gap in yield performance, as measured by a Dynamic Activity gap compared to world’s top 25% of performers, can then be translated to a gap in product yields and then into a gap in USD/bbl. Figure 4 shows that in both 2014 and 2016 Solomon Worldwide Fuels Studies, the Rompetrol FCC Unit is placed at the border between 1st and the 2nd quartile from a total of approximately 300 FCC units in the Solomon Worldwide Fuels Study.

In Figure 4 each FCC Unit is placed in one of the 4 quartiles (red color represents the 4th quartile and the green color represents the 1st quartile).

Figure 4: Solomon – Yield Gap Quartile of Performance

Improved Performance through FCC Catalyst Optimization

The refining market is more global and more competitive than ever and Grace recognizes the importance of providing value to its customers through new product development. The KMG Rompetrol and Grace teams have worked closely together to better identify refinery opportunities, as well as to understand challenges and limitations in more depth, which has been essential for overall success. The following objectives were identified as the main drivers to help increase FCC unit profitability²:

- Maximum propylene yield (min.10 wt% of FF)
- Maximum iso-butylene yield
- Maximize LCO
- High RON
- Higher delta coke
- Minimize dry gas

Maximum propylene is driven by demand from the nearby petrochemical plant, while maximum iso-butylene is highly desired to boost MTBE unit capacity. Grace executed a rigorous process to qualify and verify selected catalyst performance, including ACE™ pilot plant testing, which minimizes the financial risk associated with unsuccessful catalyst trials in the unit ³,⁴.

Based on extensive ACE™ pilot plant testing utilizing a representative feedstock from the KMG Rompetrol Petromidia refinery, various new catalyst formulations were screened versus the base catalyst. This enabled Grace to identify a combination of the ACHIEVE® 100 catalyst and OlefinsUltra® HZ light olefins additive as the leading formulation to provide the optimum performance in terms of the desired operating targets. As shown in Figure 5, this catalyst system resulted in a significantly higher propylene and iso-butylene yields, as well as higher LCO and lower slurry (decanted oil), which demonstrates a clear improvement in bottoms upgrading.

Figure 5: ACE Performance Deltas (wt.%)
ACHIEVE® and OlefinsUltra® HZ Technologies

The ACHIEVE® catalyst series comprises state-of-the-art technologies designed to maximize refinery profitability for a wide range of FCC feedstocks and yield objectives. When processing lighter feedstocks, insufficient catalytic activity requires that the catalyst circulation rate increase so that conversion, and thus the coke yield from the catalyst, increases to satisfy the FCC heat balance. If the FCCU cannot physically circulate enough catalyst, it will be necessary to reduce the unit charge rate or the reaction severity to stay within the FCC catalyst circulation limit. Use of a high activity catalyst can counter the effects of low delta coke, highlighting the importance to select a catalyst with the proper coke selectivity (coke to conversion relationship).

ACHIEVE® 100 catalyst is designed for use with hydro treated and light VGO feedstocks, with a low-to-moderate level of contaminant metals. ACHIEVE® 100 catalysts are formulated with ultra high activity zeolite to support conversion and counter the effects of low delta coke, while delivering the proper coke selectivity. The high diffusivity of ACHIEVE® 100 catalyst increases distillate yield, while an optimized rare earth exchange results in the required hydrogen transfer activity to balance LPG and gasoline production.

Launched in 2010, OlefinsUltra® HZ additive is part of Grace’s OlefinsUltra® family of propylene maximization additives. The family includes OlefinsUltra® additive for moderate-to-high propylene yields, OlefinsUltra® HZ additive for high propylene yields, and OlefinsUltra® MZ additive with industry leading activity, for very high propylene yields.

The entire OlefinsUltra® family of additives is manufactured with excellent attrition resistance and low 0–40%. Our testing has demonstrated that OlefinsUltra® HZ shows excellent activity retention achieving required maximum unit performance.

Validating Catalyst and Additive Performance

When the ACHIEVE® 100 catalyst preblended with OlefinsUltra® HZ additive was added to the FCC unit, the turnover of the circulating inventory to the new catalyst was carefully evaluated. Typically, the impact of new catalyst grades on FCC product yields can be observed by the time 60% catalyst turnover is achieved. In parallel to this, E-cat analysis was performed using samples received from the refinery on a weekly basis. This allows catalyst performance to be evaluated independently of the daily variations that occur in FCC unit, as the testing is performed using standard feedstock and constant operating conditions. ACE™ E-cat testing is shown in Figures 6 and 7. At constant conversion, the new catalyst system delivered higher selectivity towards propylene and iso-butylene.
As shown in Figures 8, 9, and 10, the trends observed in ACE™ testing of equilibrium catalyst were also observed in the FCC unit. Using the combination of ACHIEVE® 100 and OlefinsUltra® HZ technologies, both propylene and iso-butylene yields were increased significantly at constant conversion.

Gasoline yields are reduced using ZSM-5 additive due to the cracking of gasoline range olefins into lighter olefins. However, the enhanced activity of ACHIEVE® 100 catalyst enabled a deeper cracking of heavier molecules into gasoline, therefore minimizing the loss of valuable gasoline despite the higher light olefin yields (Figure 11). The gasoline octane RON and MON also slightly improved as a result of the new catalyst system. The improved bottoms cracking obtained through the ACHIEVE® 100 catalyst in the commercial unit is shown in Figure 12 and 13.
Unit Test Run

KBC’s FCC-SIM® simulation tool was used to evaluate the performance of ACHIEVE® 100 catalyst vs. the base catalyst at constant coke. The test runs selection criteria to obtain calibration factors were based on the following:

- Complete and robust set of feed, operating and product data
- Heat of cracking ratio within acceptable range (0.7-1.3) and consistent kinetic coke make and conversion kinetic parameters.
- Calibration of selected FCC unit weekly test data to obtain a reliable set of calibration factors

In the simulation exercise, the ex-reactor product standard yields were considered: (gasoline C5-221°C, LCO 221-343°C and FCC Bottoms +343°C). The yields shifts with operation parameters and equilibrium catalyst physical and chemical properties are given in Table 1.

<table>
<thead>
<tr>
<th>Performance</th>
<th>ACHIEVE® vs. Base</th>
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<tr>
<td>Conversion, wt%</td>
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<tr>
<td>Dry Gas, wt%</td>
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<tr>
<td>Slurry, wt%</td>
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<td>Coke, wt%</td>
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<tr>
<td>ZSM-5-additive, %</td>
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<table>
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<tr>
<th>ECAT Properties</th>
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<td>Activity (wt%)</td>
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<td>UCS (Å)</td>
<td>24.26</td>
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<tr>
<td>Make-up Rate (MT/d)</td>
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</tr>
</tbody>
</table>

Table 1: FCC Unit Test Run Data

PIMS Value added Calculation

Figure 14 outlines what steps are accomplished from catalyst selection using ACE™ testing to the unit performance evaluation using refinery PIMS model. As already said the lab scale-testing goal is to match the commercial FCC unit performance estimate. However, the refinery is only focusing on real unit performance results.

The benefit calculation coming from the new re-formulated ACHIEVE® 100 catalyst vs the base catalyst was performed by running two scenarios with the help of AspenTech PIMS™ Model. PIMS (Process Industry Modelling System) is the refinery production optimization tool based on linear programming.

Main assumptions of the two scenarios were:
- similar refinery run rate and similar FCC Unit Feed Rate both in terms of quantity and quality;
- similar FCC Unit Operating Conditions: Reactor Overhead Temperature & ZSM-5 additive injection;
- degrees of freedom were provided to the Finished Products selling operations to capture the impact of new FCC Unit re-formulated ACHIEVE® 100 catalyst in refinery operation;

After running the two scenarios, an annualized benefit of ~ $2.3 MM USD has been obtained. The benefit is mainly coming from higher Light Olefins production — higher content of Propylene in C3 Cut and higher content of iso-butylene in Light C4 cut. Since the Light C4 Cut is the feed to MTBE (Methyl-Tertiary-Buthyl-Ether) unit, increased content of iso-butylene led to increased MTBE production (MTBE product is the “octane booster” used within the gasoline pool). As the refinery is integrated with a petrochemical complex, increased content of propylene in the C3 cut and the increased production of the C3 cut, helped in debottlenecking the C3 splitter column and allowed Rompetrol to sell chemical grade propylene on the domestic market. A benefit is also coming from slightly higher LCO (Light Cycle Oil) production and lower production of slurry (decanted oil), and Heavy C4 cut.

The above benefit was calculated in a 2017 price scenario with a crude oil quotation of about 55 $/bbl, this being in line with 2017 average price, a price difference between propylene and MTBE vs gasoline of ~170 $/t and a price difference between slurry (decanted oil) vs. auto diesel of ~250 $/t.
Continued Innovation Enhances Profitability

Evolving market drivers continue to provide refiners with opportunities to improve refining margins. The FCC unit is the most flexible unit in the refinery in terms of capability to process different feeds, and achieve different yields. The more flexible the FCCU operation is, the greater the potential to take advantage of market opportunities.

KMG Rompetrol and Grace worked closely on enhancing unit performance through incorporation of high-performance catalytic solutions, and optimizing operational parameters within the unit constraints. Continued innovation in FCC catalyst and additive technology, as illustrated in this article, enables refineries to enhance refinery profitability. Combining ACHIEVE® 100 state-of-the-art catalyst technology with OlefinsUltra® HZ additive enabled the refinery to capture opportunities in a dynamic market, achieving higher propylene and iso-butylene yields. Test run results at maximum unit throughput and maximum unit severity demonstrate improved refinery profitability of $2.3 MM USD/yr.

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Grace offers customers a custom portal for troubleshooting with sample analysis and other tools to help you manage catalysts in your FCC unit.

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Reducing NOx Emissions from the Hellenic Petroleum FCC Unit

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Refinery processes account for a considerable share of the overall emissions of air pollutants in Europe. The Industrial Emissions Directive (IED) is the main EU instrument regulating pollutant emissions from industrial installations. The IED entered into force in 2011 and had to be transposed by Member States by 2013. As a result, many refiners in the EU are facing more stringent SOx and NOx emissions with additional emission reduction targets coming into effect in 2018. One such refinery is Hellenic Petroleum’s, Aspropyrgos Refinery in Greece who have successfully managed to reduce NOx emissions using Grace FCC additive technology.
Options for NOx Reduction

One route to lower NOx is through choice of feedstock, which is a costly approach and not particularly flexible. Regenerator conditions also play a big role in NOx formation and can present an easier route for NOx reduction. For example, lower oxygen levels and regen temperatures typically help to reduce NOx. In addition, optimizing air distribution and regen bed levels can be beneficial.

The use of platinum based combustion promoters can lead to excessive NOx formation, with many refiners switching from platinum to palladium based promoters, such as Grace’s CP® P combustion promoter in recent years. After combustion promoter usage has been optimized, specific NOx reduction additives such as DENOX® additives can provide additional levels of NOx reduction.

Decreasing NOx Emissions at Aspropyrgos Refinery Petroleum

The FCC unit at Aspropyrgos Refinery is an Exxon® FlexiCrackeR® design operating in full burn with close-coupled cyclones and modern feed nozzles. The unit processes a combination of hydrocracker unconverted oil and atmospheric residue. Hellenic and Grace initiated a NOx reduction project at the start of 2017, involving commercial trials of FCC additive technology. The objective was to determine the lowest achievable emissions of NOx, to avoid the future need for high CAPEX modifications such as retrofitting furnaces with low-NOx burners, while remaining within compliance of future BREF NOx emission legislation.

Until 2017, Aspropyrgos Refinery had been using Grace’s traditional platinum based combustion promoter technology for afterburn control. The first step of the NOx reduction project was to transition to CP® P, a non platinum based low-NOx combustion promoter. A key consideration in addition to NOx reduction was not to compromise the level of afterburn in the regenerator. NOx emissions from the FCC unit are measured using a portable flue gas analyser, and based on a 5-year period of operational data the baseline NOx emission levels could be determined.

During the switch from a platinum to a palladium based combustion promoter, elemental analysis of the equilibrium catalyst (E-cat) enabled the technology change out to be monitored. Once complete change out was achieved, a NOx emission reduction of 45% was consistently noted using the CP® P combustion promoter. Importantly, the catalyst remained well promoted using CP® P with no afterburn issues observed.

The next step of the project was to examine the additional benefits of combining the low NOx combustion promoter with Grace’s DENOX® technology, a standalone additive for NOx reduction. The target was to reduce the NOx emissions as low as possible. The DENOX® additive was preblended with the fresh catalyst to ensure consistent additive injection. Elemental analysis of the E-cat was again used to monitor the level of additive technology in the circulating inventory. The target level of DENOX® additive was 0.6 wt.%, and this was achieved over a 4-month period without the use of a baseloading period. During this time the frequency of NOx measurement was increased to ensure the performance of the additive was determined in the most accurate way possible. Using a combination of CP® P and DENOX® technologies enabled NOx emissions to be reduced by 65% fully meeting the ambitious expectations of the refinery.

The 45% reduction of NOx using CP® P, followed by the additional NOx reduction through the use of DENOX® additive is shown in Figure 1.

The use of the NOx reduction technologies described had no negative impact on unit performance or the FCC products yield structure.

By establishing the levels of NOx emissions achievable using Grace’s CP® P and DENOX® technologies, Aspropyrgos refinery are well prepared for the upcoming impact from BREF limitations and expect to be able to mitigate any potential CAPEX impact.

Continued from Page 25
REDUCING NOX EMISSIONS FROM THE HELLENIC PETROLEUM FCC UNIT

Figure 1: NOx Reduction Achieved with CP® P and DENOX® Additives

Miss an Issue?

For more than 50 years, Catalagram® has featured articles from Grace and ART’s technical experts and strategic business partners that demonstrate the value of doing business with Grace.

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Newest Additions to SmART Catalyst System® Technology Achieve Longer Run Lengths Through Increased Activity, Improved Stability

John Cunningham
Technical Service Specialist
Advanced Refining Technologies (ART)

Refiners demand higher activity catalysts as global sulfur specifications continue to tighten. Advanced Refining Technologies (ART) continues to expand its portfolio of ultra-high activity catalysts to meet oil refiner’s needs. ART’s DX® Catalyst Series has demonstrated superior performance in ULSD applications, exceeding expectations for many years. ART’s 425DX® and 545DX® catalysts continue to excel in middle distillate after worldwide acceptance. Responding to the need to balance feedstock flexibility, cycle length, and product flexibility, ART developed ICR® 316 and 548DX®, the newest catalysts in a long line of innovation. The addition of ICR® 316 and 548DX® allows refiners to process tougher feeds, meet tighter specifications, improve product quality, and expand capacity with no additional capital costs.

ICR® 316 and 548DX® catalysts capture recent advancements in alumina technologies made by the ART research team. Innovations in surface chemistry and new pore structures provide a significant boost in HDS, HDN, and HDA activity, with improvements exceeding 20% in some applications. Chelate enhancements also make each catalyst more robust and forgiving for start-up. Both catalysts will excel as stand-alone catalysts or as an integral part of the SmART Catalyst System® technology.
**ICR® 316**

ICR® 316 offers improvement opportunity to every diesel hydrotreating unit. Its benefits have been demonstrated on both straight run and cracked stocks, and at low and high operating pressures. Figure 1 shows a comparison of ICR® 316 to its predecessor, 425DX®, in a ULSD protocol using a feed containing 15% cracked stocks. ICR® 316 shows a clear activity gain in the low-pressure ULSD test, and further extends its advantage in the higher-pressure test. This increased activity enables refiners to process more opportunity feed stocks and increase hydrotreater cycle length.

**548DX®**

548DX® utilizes ART’s newest technology in advanced chelate enhancement and alumina surface modification to provide the highest activity for HDS, HDN, and HDA, making it ideal for use in both ULSD and other applications. It is commercially proven and is currently in use in units around the world. High pressure ULSD testing reveals a substantial improvement for both sulfur and nitrogen removal, as shown in Figure 2.

The same ULSD testing protocol also shows a significant boost in aromatic saturation activity for 548DX® relative to its predecessor, 545DX® catalyst. This is readily demonstrated by the significant gains in API gravity and Cetane Index at ULSD conditions, as shown in Figure 3. This translates directly into increased volume swell and refinery profitability.

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**Figure 1:** Relative Volume Activity (RVA) of ICR® 316 significantly exceeds 425DX® in both low and medium pressure ULSD applications.

**Figure 2:** 548DX® offers significant advantages in HDS and HDN activity in high-pressure ULSD testing (1000 psig).

**Figure 3:** 548DX® shows a significant improvement in product quality in high pressure ULSD testing (1000 psig).
SmART Catalyst System® Technology

Platform

ICR® 316 and 548DX® are the newest high-activity catalysts for use in the SmART Catalyst System® technology. ART pioneered the combined use CoMo and NiMo catalysts with the introduction of the SmART Catalyst System® technology in the early 2000s. It has since become widely accepted as the premier method to fully utilize existing assets within a refinery’s individual constraints. Figure 4 shows how catalyst selection and placement can be tailored to provide the optimum balance of maximum HDS and hydrogen consumption.

![Figure 4: ART uses its SmART Catalyst System® technology to optimize activity with hydrogen consumption and product quality for maximum refinery profit.](image)

The SmART Catalyst System® technology design is the culmination of an extensive effort put towards understanding the chemistry and process conditions required for ultra-low sulfur fuels. ART has devoted significant resources to designing the most active and robust ULSD catalysts for use in the SmART Catalyst System® technology. This effort has led to the recent commercialization of ART’s new CoMo catalyst, ICR® 316, and new NiMo catalyst, 548DX®. These new technologies capitalize on the extensive material science and catalyst knowledge encompassed in the ART joint venture.

Contact your ART representative today to learn more about ICR® 316, 548DX®, the SmART Catalyst System® technology, and how our hydroprocessing expertise can maximize your refinery profitability. ☝️
Let’s do the math.

Grace custom catalyst solutions, co-developed with you, are about more than performance—and more than chemistry. They’re designed to add to your bottom line.

In some cases, the difference between our refinery customers’ financial return on Grace technologies versus the alternative has reached into eight figures.

If you’re ready to put Grace chemistry to work to strengthen your business, we’re ready to show you how we can help. Call us to get started with the calculations.
