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Gazprom Neft Omsk refinery has completed commercial testing of the first Russian-produced hydrotreating catalyst
Photo: Gazprom

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S
ince Standard Oil first demonstrated that mysterious materials called catalysts can deliver a lot more bucks from a barrel of crude, catalysis has played a key role in the development of petroleum refining as an efficient producer of fuels and much more besides. As this issue of PTQ Catalysis demonstrates, the level of innovation in the development of refining catalysis never slackens, whether the goal is to glean more – and more valuable – products from deeper and stickier post-distillation fractions, to achieve more efficient production of light olefins as petrochemicals feedstocks, or to achieve faster and more in-depth understanding of catalysts’ performance.

But for petroleum refiners there are always challenges to overcome other than more value and higher margin. Foremost and for the foreseeable future, one of the biggest of these is external pressure to reduce carbon dioxide emissions from refinery processes.

Perhaps catalysis also has a major role to play in tackling these emissions. For instance, a consortium of academic researchers from Europe and Australia has attracted some attention recently. The researchers reckon that they have developed a catalyst that will “significantly reduce” the amount of CO₂ produced by refiners. To sum up briefly, they have developed a type of aluminium silicate, the basis of zeolite structures, with acid activity that is stronger than any other silica-alumina material created. This, they reckon, could cut CO₂ emissions in refineries by 20%.

This is all well and good, but taking the academics’ work to commercial usefulness will be a much bigger step than simply devising a novel material.

Experts from the leading catalyst developers explain the issues with far greater eloquence in the pages of PTQ publications, but a summary of catalyst performance is this: all depends on pore structure and active sites. For a zeolite catalyst to be as effective as possible in its chosen role, access to its active sites and passage of feed and product through the catalyst must be as efficient as possible. Zeolites have a basic structure of micropores; appropriately designed with ‘mesopore’ or other inclusions, they can act more efficiently in the selective transport of feed and product.

The acid sites which catalyst feed encounters are important early stages in catalytic cracking reactions. Hence, their accessibility and location are fundamental to how useful a zeolite is as a catalytic performer. If the sites are on the outside surfaces of a zeolite, access to them is simple. Inside the zeolite, the pore structure is crucial to determining access. The chemical structure of the zeolite then comes into play. The distribution and function of acid sites can be altered by, for instance, changing the aluminum to silicon ratio, or by introducing alkaline earth metals.

The aluminium silicate material developed by the academics introduced earlier features high activity involving Bronsted acid sites which have been shown to be important if you want to avoid secondary reactions leading to unwanted products, CO₂ for instance.
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Q We have increased coke make and hydrogen production from our FCC. Is this a result of catalyst poisoning and how do we deal with it?

A Ann Benoit, Senior Principal FCC Technologist, Global Customer Technology, W. R. Grace & Co., ann.benoit@grace.com
Ann Benoit, Senior Principal FCC Technologist, Global Customer Technology, W. R. Grace & Co., ann.benoit@grace.com
Catalyst poisoning can increase hydrogen make and delta coke but does not greatly impact coke yield. Shifts in operating conditions such as reactor temperature, feed preheat temperature, catalyst cooler duty, or charge rate have a greater impact on coke make. Even though catalyst poisons do not greatly impact the coke make, they do have a major impact on the FCC unit.

Contaminant metals such as nickel (Ni), copper (Cu), vanadium (V), and iron (Fe) can drive dehydrogenation reactions, resulting in increased hydrogen yield in the FCC unit. Ni is a strong dehydrogenation catalyst and has been reported to be four times as strong as vanadium.

It is recommended to look at operating conditions and catalyst poisoning to determine the cause of the negative shifts in coke make, delta coke, and hydrogen.

If it is confirmed that poisons are causing the negative impact (higher delta coke and hydrogen) on the unit, they need to be appropriately managed. Several options can be considered when dealing with poisons. The first option is to locate the source and eliminate it. If the poisons are from an unwanted source such as an exchanger leak or line-up error, plans should be made to eliminate the source. Eliminating the source may not make sense if it is due to a crude slate which is profitable to run. If this is the case, other choices can be considered to mitigate the negative impacts of the poisons. One option is to flush the metals from the circulating inventory. This can be accomplished by increasing fresh catalyst addition rates, or by using purchased Ecat to control metals levels. If fresh catalyst additions are used, activity will have to be monitored to guarantee regenerator bed temperature stays within limitations or reformulate to a lower activity catalyst. Other options are passivators such as antimony or incorporating a nickel and/or vanadium trap into the catalyst formulation to alleviate the impacts of Ni and/or V respectively. The poison type, catalyst turnover, and length of time that is expected to be processing the higher poison feed will help determine the best possible option.

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There are a variety of types of contaminants that can cause poisoning of FCC catalyst, so even though the question does not exactly specify which contaminant caused the poisoning, common FCC knowledge helps to restrict the area of interest. If the poisoning was coming from metals that destroy zeolite crystals (like vanadium) or contaminants that occupy active sites like sodium or nitrogen, then the FCC riser would have seen lower Ecat activity and, given that Ecat activity is the main catalytic conversion driver and one of the largest delta coke contributors, the unit would not have seen increased coke make, but rather lower activity, lower conversion, and therefore lower coke make. This restricts the area to metals that do not affect the Ecat activity but do affect dehydrogenation reactions, like nickel, copper, iron (before it rises beyond the level or the ‘cliff’ when catalyst pore accessibility is highly restricted), and so on. Nickel can be controlled, in the short term, by adjusting (or initiating if not yet practised) the antimony (Sb) injection in the feed up to a point where no further benefit to the reduction of H/C ratio is observed. If Ni contamination incidents do happen more than once, then the use of dedicated Ni-trapping fresh catalysts (like BASF’s Boron Based Technology [BBT] catalysts) should be considered, so that the catalyst is ready – at any time – to adsorb these Ni excursions. Metals like Cu or Fe cannot easily be trapped or passivated, so a metals flushing strategy can be adopted by adding low-metals purchased Ecat (at times, reloading Ecat from the bottom of the spent catalyst hopper can help to quickly bring the inventory back to before the poisoning happened).

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Rainer Rakocy, Global Product Manager, Clariant Catalysts, and Arne Dinse, Senior Sales Account Manager, Clariant Catalysts, It is well known that the uptake of transition metals – especially nickel, chromium, and iron – from feed impurities can drastically influence the internal hydrogen household within an FCC cycle. In combination with a zeolite, dehydrocyclisation (aromatisation) is fostered, thus generating a bifunctional catalyst. The aromatisation is basically highly welcome to gain RON but, in parallel, aromatisation also promotes the generation of coke precursors, such as methylcyclopentadienyl cations. Most FCC catalyst suppliers offer additives or optimised main catalyst versions to dampen this effect introduced by the aforementioned transition metals.

A Steven van Vegten, FCC Technical Specialist, Albemarle, steven.vanvegten@albemarle.com
Contaminant metals like nickel can catalyse dehydrogenation reactions, yielding hydrogen and coke. Nickel is
not the only metal known for having this effect, which is why often the equivalent nickel level is calculated, see below. The analysis of the chemical composition of the Ecat sample will reveal how much nickel is on your catalyst. Has this level gone up? Please do bear in mind that fresh nickel is more active than old nickel.

Nickel can be passivated by using a catalyst that contains a nickel trapping matrix and/or by using an additive like antimony. Also, by increasing the catalyst addition rate, the nickel level on Ecat will be reduced, reducing its dehydrogenation effect.

Ni equivalent = Ni + V/4 + Cu*8 + Fe/7 – Sb

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First, inspect your equilibrium catalyst report to see if changes have taken place in contaminant metals. If metals are increasing slowly, determine if you are adding the proper amount of catalyst. If you use metals passivation, verify there are no major changes in the injection rates or measured levels on equilibrium catalyst.

Changes in hydrogen yield are usually indicative of major changes in metals contaminants or changes in metals trapping capabilities in the inventory. Nickel deposited from the feed onto the catalyst surface strongly promotes dehydrogenation reactions, causing increases in hydrogen make. Vanadium also promotes dehydrogenation but at a reduced rate as the same amount of nickel. However, vanadium is highly mobile under FCC conditions and reduces FCC catalyst activity by collapsing Y-zeolite structures of the FCC catalyst. With this loss of catalytically active surface area thermal reactions can occur in place of catalytic ones, increasing the amount of coke, in the form of delta coke. Copper is also very active for producing hydrogen and increasing delta coke.

If independent variables such as riser outlet temperature, feed preheat, CO/CO₂ ratio in partial burn, and catalyst cooler duty are kept constant, this increase in delta coke will reduce conversion through a reduction in catol.

Other contaminants can also cause catalyst poisoning through loss of catalyst activity; if operation is modified to recover conversion, delta coke and dry gas yields will suffer. Usual bad actors are sodium, iron, calcium, and potassium poisoning. All these contaminants enter the process in the feed so some level of improvement in feed conditioning, from improving desalter performance to hydrotreatment of the feed, will reduce this contaminant level.

Catalyst poisoning can also be caused by a change in the base catalyst formulation. Inspect the recent certificates of analysis for any changes.

FCC additives can be used to mitigate negative effects from metals poisoning. Ultra CokeBuster from G. W. Aru, LLC (sold under the Unicat brand outside of North America) is a metals trapping additive that will substantially reduce the coke and hydrogen make from a FCC unit, thus relieving current operating constraints, allowing a drive to further unit profitability and improved operation.

Q How do we best monitor FCC Ecat performance?

A Ann Benoit, Senior Principal FCC Technologist, Global Customer Technology, W. R. Grace & Co., ann.benoit@grace.com

It is recommended to take at least one equilibrium (Ecat) sample per week. Depending on the catalyst circulating inventory and consistency of feed and operations, more frequent Ecat samples may be necessary for proper FCC monitoring. In addition to Ecat samples, regenerator fines catch and slurry samples should be taken. The Ecat sample should be taken during the typical test run day which includes the battery of unit samples. This allows for a better understanding of catalyst health and the impact on overall unit performance. Refinery personnel should look for trends in the analysis and compare them to unit performance. One should pay close attention to activity, surface area, contaminant metals, and physical properties.

Catalyst activity and surface area should be closely monitored, as these can be key profitability drivers for the FCC. The unit yield performance may suffer if the catalyst activity drops below the optimum. Contaminant metals, fresh catalyst additions, and regenerator severity should be checked to understand the root cause of any activity shift.

In addition to activity, contaminant metals should be monitored along with FCC unit yield performance. Metals such as nickel (Ni), copper (Cu), vanadium (V) and iron (Fe) can yield higher hydrogen which could limit a wet gas compressor constrained unit. Metals can also increase delta coke, which has a major impact on FCC performance. In addition to a hydrogen increase, vanadium will destroy zeolite and cause surface area to decrease. The drop in catalyst activity can hurt overall unit conversion. Another significant metal to monitor is Fe, which will cause pore closure and negatively impact bottoms cracking and has the potential to cause catalyst circulation upsets.

When monitoring metals levels, it is important to look at contaminant metals on the Ecat and not absolute metals levels since additives and differences in clay can impact certain metals. SOx reducing additive will increase vanadium on Ecat, but this increase will not influence the catalyst health. Different fresh catalyst suppliers use different clay sources that vary in iron (Fe) content. The refinery should calculate the contaminant metals based on additive uses and fresh catalyst Fe content if the catalyst activity drops below the optimum. Contaminant metals, fresh catalyst additions, and regenerator severity should be checked to understand the root cause of any activity shift.

In addition to contaminant metals, physical properties should be monitored for shifts from typical operations. Physical properties such as particle size distribution and average particle size (APS) can give an indication if loss problems are due to attrition or mechanical/distribution issues.
CLG offers innovative technologies and catalyst solutions for the hydroprocessing industry through our collaboration with Advanced Refining Technologies, LLC a joint venture between Chevron and W. R. Grace & Co. To get the performance and flexibility needed to keep pace with changing market dynamics, start by visiting www.chevronlummus.com
In summary, Ecatal analysis in combination with unit data is extremely important in troubleshooting and monitoring the health of the FCC unit. The Ecatal analysis can aid in troubleshooting unit issues such as yield degradation and catalyst losses. The analysis should be monitored at least once a week so that necessary adjustments can be made.

Alexis Shackleford, Account Manager, BASF, alexis.shackleford@basf.com

The best way to monitor FCC Ecatal performance is through routine analysis by your catalyst vendor. Catalyst vendor testing includes physical properties, surface area, chemical analysis, and performance monitoring. While absolute values are useful, trends are equally, if not more, important for monitoring. Physical properties are useful for measuring fluidisation characteristics or determining if the unit is experiencing a loss problem. Variables to monitor include the particle size distribution (especially 0-45microns) and density. Surface area is analysed to monitor the activity and the stability of the catalyst. Chemical analysis tells you how much and what kinds of contaminants are on the catalyst such as nickel, vanadium, iron, sodium, calcium, and potassium which negatively impact unit performance. Other chemical analyses are useful for catalyst changeover calculating if switching catalyst types and additive monitoring. Carbon on regenerated catalyst is especially important for a partial burn unit, and even for full burn units it can indicate regenerator damage. Performance monitoring by catalyst vendors is done using a bench scale laboratory unit to measure the performance of the catalyst under controlled conditions including a standard feed, reaction temperature, and contact time. This shows the activity, yields, and selectivity of the catalyst for both undesirable products like coke, dry gas, LPG, gasoline, LCO, and slurry.

This description is a brief overview of what to look for to monitor FCC Ecatal performance. For a more in-depth look, please contact your catalyst vendor or refer to a previously published article: Shackleford A, Interpreting FCC equilibrium catalyst data, PTQ Catalysts 2018, 33-39.

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It is good practice to check Ecatal samples visually every day in the unit and send for analysis to your catalyst vendor at least once a week. From your vendor, you will get results indicating the activity, surface area, contaminant metals, and tracer elements. Each of these analyses will give valuable information about the operation of the unit, the catalyst addition rate, and the condition of certain equipment like cyclones, as well as additives. It is good practice to monitor the trends in Ecatal regularly, and adjust unit operations and catalyst or additive addition rate when deemed necessary. The physical properties of the Ecatal, together with the TSS, ESP or and slurry fines analysis, can be used for troubleshooting purposes when there is a problem with catalyst losses.

What are the advantages of a bulk material catalyst in hydrotreating?

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Self-supported catalysts, sometimes branded ‘bulk catalysts’, pack high hydrogenation activity into a small reactor volume. The superior hydrogenation activity of self-supported catalysts (as compared to alumina-supported catalysts) can enhance refinery margins by increasing a refinery’s flexibility to process reclaimer (for instance, resid-derived) feedstocks and extend run length.

In the past decades, applications of self-supported hydrotreating catalysts started in diesel hydrotreating to increase diesel volume swell. More recently, self-supported catalysts have expanded into hydrcracking applications to make more or better chemicals, fuels, and lubes. In addition, the superior hydrogenation activity of self-supported catalysts enables better and flexible integration of varying refinery processes, resulting in improved capital efficiency.

As with supported catalysts, there are many different self-supported catalysts, each with their unique chemical compositions, acid site densities, and pore size distributions. Through its enhanced hydrogenation ability and its carefully tuned pore structure, ART’s self-supported ICR 1000 catalyst platform has debottlenecked refineries and hydrcrackers by enabling higher conversion of vacuum gases (lower bleeder rates), by enabling conversion of opportunity or synthetic gases, and by enabling extension of hydrcracker run lengths. In addition, through its tailored acidity, ART’s self-supported ICR 1000 catalyst family has debottlenecked hydtrtreaters by improving the quality and value of base oil, improving the quality of steam cracker feedstocks, enabling the simplification of white oil production, and increasing diesel production volumes.

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In many cases, bulk catalyst types are preferred for hydrotreating and hydrogenation applications. Besides advantages in catalyst activity, the significantly higher availability of active metal species can provide outstanding tolerance towards catalyst poisons. It can also be utilised for hydrogenation reactions and as an adsorbent. The product cost is usually greater due to the higher metal content compared to supported catalyst types. However, this can be compensated by higher payback on the metal when sending the spent catalyst to metal reclaiming companies.

Stefano Melis, Global HPC Advisor, Albemarle, stefano.melis@albemarle.com

Bulk metal catalysts (BMC) are characterised by an exceptional activity, up to 3-4 times higher than conventional catalysts. Their activity derives both by the larger
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- High Metals Capacity Solutions for FCC Pretreat
- Distillate Selective Catalysts for Increasing Diesel Demand
- High Metals Capacity Hydrocracking Solutions
- High Metals Capacity Catalysts for Opportunity RDS and EBR Feeds
- Specialized Catalyst(s) for DAO Containing EBR Feeds

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of BMC can also lead to a significant improvement in yield structure. Other applications finally include the extension of the cycle length and, where applicable, the possibility to increase throughput without major revamps.

In conclusion, objectives apparently unthinkable can potentially come true thanks to the application of BMC. Application of BMC requires in-depth know-how and experience from your catalyst supplier. Albemarle has nearly 20 years of experience with BMC.

Table 1

<table>
<thead>
<tr>
<th>Sulphiding agent</th>
<th>wt% sulphur</th>
<th>Gallons of agent per lb of sulphur</th>
<th>Litres of agent per kg of sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl disulphide (DMDS)</td>
<td>68</td>
<td>0.166</td>
<td>1.385</td>
</tr>
<tr>
<td>Dimethyl sulphide (DMS)</td>
<td>51.5</td>
<td>0.275</td>
<td>2.295</td>
</tr>
<tr>
<td>Dimethyl sulphone (DMSO)</td>
<td>41</td>
<td>0.267</td>
<td>2.228</td>
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<tr>
<td>SulphrZol-54</td>
<td>54</td>
<td>0.204</td>
<td>1.702</td>
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<tr>
<td>TNPS</td>
<td>37</td>
<td>0.313</td>
<td>2.612</td>
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**Figure 1** Sulphiding conditions that contribute to low activity reduced metal sites

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<th>Sulphur content of common sulphiding agents</th>
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number of active sites as well as by their intrinsically high hydrogenation activity. Such excess activity is best exploited in the bottom part of the reactor where the most difficult reactions take place. In other words, BMC are best utilised for the removal of refractory sulphur and nitrogen or for the deep saturation of aromatics. We do not see specific advantages for removal of easy sulphur and nitrogen, which are often mass-transfer limited and where additional activity brings little benefits.

Applicability is not universal, still we see successful applications from naphtha hydrotreatment to HVGO hydrocracking pretreatment. Most frequent applications are diesel hydrotreatment and hydrocracking pretreatment, perhaps because these are the most challenging (and rewarding) hydrotreating units. From a fundamental point of view, BMC can be used when the coupling of feed properties and operating conditions leaves residual driving force for hydrogenation. This basically means that BMC application requires sufficient hydrogen pressure. There are not strict thresholds, and the preferential application remains to be medium to high pressure ULSD units (say, >50 bar) or high pressure HCPT units (say >100 bar).

In terms of application targets, BMC can be exploited in a large variety of ways. The most common case is the increase of the intake of highly distressed feedstocks (i.e. LCO, HCO, streams from visbreaking and/or coking units, Aromatic extracts, LC-Finate, and so on) with corresponding high margins. In our experience, we often see an increase by ca. of approximately 10-20% in the intake of such streams that completely changes the operating margin of the unit (and often of the entire refinery). BMC can also be used to enhance product quality. This practically means improving density and cetane in diesel units, smoke point in jet units and VI in lube units while, in the case of HC units, application

**Figure 1** Sulphiding conditions that contribute to low activity reduced metal sites

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Fueling sustainability

The conversion of biomass and waste materials into drop-in ultra-low sulfur diesel and A1 jet fuel, has become increasingly important due to regulatory and environmental challenges. These factors, as well as our commitment to sustainability, inspired us to develop HydroFlex™ process technology and catalysts. HydroFlex™ provides full feedstock flexibility and can be deployed either as stand-alone units or for co-processing with fossil feedstocks.

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The most common way to conduct sulphiding is to complete the reactor loading and then process a distillate range feed that is doped with a sulphiding agent. These sulphiding agents are high purity chemicals that have a high fraction of sulphur and readily decompose to hydrogen sulphide when heated. There are a number of sulphiding agents available, and Table 1 summarises a few of them.

As part of the preparation for catalyst sulphiding, the amount of sulphiding agent required to fully sulphide the catalyst will need to be calculated. The amount of sulphiding agent required can be calculated from equations 5-7 below for each catalyst independently and then summed:

\[ S_{\text{total}} = S_{\text{stoich,n}} \times m_n \]

\[ S_{\text{agent}} = \frac{S_{\text{total}}}{S_{\text{agent}}} \times m_n \]

\[ \text{Agent}_{\text{total}} = S_{\text{total}} \times S_{\text{agent}} \]

where:

- \( S_{\text{stoich,n}} \) = wet fraction stoichiometric sulphur for catalyst n
- \( S_{\text{total}} \) = total stoichiometric sulphur for all catalysts in catalyst system in pounds or kilograms
- \( S_{\text{agent}} \) = Sulphur content of the agent gallons per lb S or litres per kilogram S. See Table 1.
- \( m_n \) = mass of catalyst n in system

The choice of sulphiding agent will come down to individual refiners’ economic, safety, and environmental considerations. ART’s standard recommendation is to purchase 15% excess sulphiding agent to account for any upsets that may occur during the sulphiding procedure.

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Presulphiding agents react with hydrotreating catalysts to convert active metals in the oxide form to their sulphide form. To minimise undesirable reactions on the catalyst, such as coking, the presulphiding agent needs to completely decompose at low temperatures (220-230°C) in the presence of \( \text{H}_2 \) to hydrogen sulphide (\( \text{H}_2\text{S} \)). The \( \text{H}_2\text{S} \) reacts with the metallic oxides to give the corresponding sulphides. The sulphides formed are partially reduced by \( \text{H}_2 \) to generate the active form. The following reactions take place on the catalyst:

\[ \text{MoO}_3 + \text{H}_2 + 2\text{H}_2\text{S} \rightarrow \text{MoS}_2 + 3\text{H}_2 \text{O} \]

\[ 9\text{CoO} + \text{H}_2 + 8\text{H}_2\text{S} \rightarrow 9\text{CoS}_2 + 9\text{H}_2 \text{O} \]

\[ 3\text{NiO} + \text{H}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{NiS}_2 + 3\text{H}_2 \text{O} \]

\[ \text{WO}_3 + \text{H}_2 + 2\text{H}_2\text{S} \rightarrow W_2\text{S}_3 + 3\text{H}_2 \text{O} \]

Dimethyl disulphide (DMDS) is one of the most commonly used sulphiding agents. It has a high active sulphur content (68 wt%) and decomposes at relatively low temperatures to generate \( \text{H}_2\text{S} \). The amount of DMDS needed to sulphide a catalyst is directly proportional to (i) the amount of catalyst to be sulphided and (ii) the active metals content of the catalyst. Most catalyst manufacturers provide the percent sulphur uptake of the catalyst that is to be sulphided. This value can be in the range 5-15% of the weight of the catalyst loaded. Additionally, they recommend that the refiner order a 20% excess of the stoichiometric amount of the sulphiding agent needed. For instance, 100 t of catalyst that stoichiometrically requires 12% sulphur will need 17.6 t (12/0.68) of DMDS. Including the 20% excess the amount of DMDS procured should be 17.6 + (0.2 x 17.6) = 21.1 t. The stoichiometric quantity is calculated from the equations shown above.

The calculations do not take into account losses of sulphur during activation. These losses are dependent on the unit type (naphtha, diesel hydrotreater, and so on), gas or mixed gas-liquid phase sulphiding, design of the activation – with recycle of both liquid and gas phases, recycle of the liquid phase only, recycle of the gas phase only or once-through sulphiding with no recycle. If the sulphiding mode is once through, with no recycle, then several catalyst manufacturers recommend an additional 30% contingency of DMDS. For the above example, the amount of DMDS procured would be 26.4 t (17.6 + [0.2 + 0.3] x 17.6). Past operations are a precious help to size the right contingency, and verification with catalyst vendors is a good practice to follow. To minimise the risk of being short of sulphiding agent, suppliers like Arkema ship a further small excess of DMDS. As always, Arkema invoices only the injected amount of sulphiding agent. Generally, the refinery and sulphiding agent supplier discuss in advance a defined excess of DMDS to be delivered.

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A first efficient approach is to calculate the overall moles of metal on the catalyst, multiplied by 64 g/mole. This gives you a theoretical maximum uptake quantity of sulphur on the catalyst and an additional safety margin. Many sour service hydrotreating catalysts may require excess sulphur in the reactant fluid during the high temperature sulphiding step. There are multiple possibilities to recover sulphiding agent from the recycle liquid. Moreover, there are specialised companies that optimise the in-situ sulphiding procedure and provide on-site technical assistance and control equipment.

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From an operational point of view, the refinery can proceed with different options to activate its hydrotreating catalysts, namely:

1. ‘In-situ’ sulphiding which requires the injection of a sulphiding agent (DMDS, TNPS, and so on) during start-up or
2. ‘Ex-situ’ pre-sulphiding, such as UltraCAT practi-
viation, which does not require any sulphiding agents during start-up.

Sulphur requirement, both in-situ and ex-situ, is based on the active metals present on the hydroprocessing catalysts. Basically, the following reactions are taken into account to calculate the stoichiometric sulphur:

\[ 3\text{NiO} + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{Ni}_3\text{S}_2 + 3\text{H}_2\text{O} \]
\[ 9\text{CoO} + 8\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{Co}_9\text{S}_8 + 9\text{H}_2\text{O} \]
\[ \text{MoO}_3 + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{MoS}_2 + 3\text{H}_2\text{O} \]
\[ \text{WO}_3 + 2\text{H}_2\text{S} + \text{H}_2 \rightarrow \text{WS}_2 + 3\text{H}_2\text{O} \]

According to the molecular weight (MW) of the different elements and metal sulphides, it becomes easy to calculate the stoichiometric sulphur requirement. An example is given below for a NiMo catalyst containing 3 wt% Ni and 14 wt% Mo:

Stoichiometric sulphur = \( 3 \times [(2 \times 32.066)/(3 \times 58.71)] + 14 \times [(2 \times 32.066)/(95.95)] = 10.45 \text{ wt%} \)

where:
MW (Ni) = 58.71
MW (Mo) = 95.95
MW (S) = 32.066

If the refinery needs to inject DMDS to activate 100 t (expressed as dry basis) of hydrotreating catalyst, this leads to (100 000 x 10.45/100)/0.68 = 15 368 kg of DMDS. The weight percentage of sulphur present in the DMDS molecule is 68%. Typically, the refinery orders at least 10% of contingency to prevent any losses (leaks, upsets, for instance) during start-up activities.

By using ex-situ presulphiding, like UltraCAT preactivation, the refiner gets many advantages and benefits with respect to ‘in-situ’ sulphiding, namely:

No need to struggle with sulphur requirement calculation since the sulphur is already present
- Faster and easier start-ups: at least 18 hours of time savings
- Risk of temperature excursion is eliminated during start-up
- No sulphiding agents are required since the sulphur is already present
- Risk of metal reduction during the start-up is eliminated
- No minimum temperature requirement during start-up

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**A René Severens, Global HPC Advisor, Albemarle, rene.severens@albemarle.com**

A catalyst vendor will provide a ‘sulphur requirement’ expressed in wt% for each individual catalyst – the next paragraph details how that sulphur requirement is calculated. The total sulphur requirement for a unit is found by multiplying the sulphur requirement of each catalyst by its weight, and adding all the products. Example: a hydrotreating unit contains 50 t of catalyst A that has a sulphur requirement of 6 wt%, and another 150 t of catalyst B that has a sulphur requirement of 12 wt%. The total sulphur requirement for
the unit is 50 x 0.06 + 150 x 0.12 = 21 t of pure sulphur. Next, we look at the sulphur content of the sulphiding agent. Dimethylsulphide, or DMDS, a widely used compound, contains 68 wt% sulphur. For 21 t of pure sulphur we need 21/0.68 = 31 t of DMDS. This simple calculation assumes that there are no H₂S losses during the sulphiding step (due to gas once-through operation, significant purging or solution losses) and that there are no other sulphur sources (sulphur in the feed when operating in once-through mode or in recycle mode with a large inventory) – therefore, these may lead the required amount of sulphiding agent to be adjusted up or down somewhat.

Here is how the sulphur requirement of a catalyst is determined. Hydrotreating catalysts contain a combination of metal oxides such as MoO₃, CoO, NiO or WO. The active phase of the catalyst, however, consists of metal sulphides such as MoS₂, CoS₂, NiS or WS₂. To convert the oxides into sulphides, each mole of MoO₃ (which has a molecular weight of 96 + 3x16 = 144 g/mole) requires 2 moles of sulphur (MW = 32 g/mole) to become MoS₂. Similarly, each 9 moles of CoO (MW = 59 + 16 = 75 g/mole) require 8 moles of sulphur to become CoS₂, and so on. Expressed in weight: converting 1 g of MoO₃ to MoS₂ requires 2 x 32/144 = 0.444 g of sulphur, and converting 1 g of CoO to CoS₂ requires 8 x 32/9 x 75 = 0.379 g of sulphur. The sulphur requirement of a hypothetical catalyst that contains 20 wt% MoO₃ (that is 200g of MoO₃ per 1 kg of catalyst) and 5% CoO is 20 x 0.444 + 5 x 0.379 = 10.8 wt%.

Q What is the relative importance of catalysis matrix size and zeolite content in bottoms upgrading? What is an ideal balance of the two?

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The type of catalyst, FCC unit operating goals, and unit constraints all will influence what is the appropriate balance between catalyst matrix and zeolite when focused on bottoms upgrading. It is important to remember that not all zeolite and not all matrix is the same. Matrix surface area is defined as any material that is not zeolite. As a result, increasing matrix surface area will not always improve bottoms cracking. If the matrix material is an active matrix, increasing the matrix amount will increase bottoms cracking at constant cat-to-oil. However, the coke selectivity of the matrix must also be considered. Increasing matrix amount at the expense of zeolite often results in higher delta coke, thus any bottoms cracking improvements from higher matrix might not be realised as the unit must remain in heat balance by lowering catalyst circulation or Ecatal activity. Zeolite pore size is too small for most bottoms material to diffuse into and be cracked; however, depending on the catalyst type, a portion of the zeolite can exist outside the catalyst microsphere and crack bottoms material. Compared to an active matrix material, increasing zeolite content will not have the same increase on bottoms cracking. Zeolite plays an important role in the selectivity of LCO-dry gas products in the unit. In short, the ideal balance of matrix and zeolite depends on the type of catalyst used, desired unit product selectivity, and the unit constraints.

Both matrix and zeolite play important roles in cracking reactions. The hydrocarbon molecules present in the bottoms (CLO) are large size molecules which would require large pores to crack. In an FCC catalyst, matrix provides the meso- and macro-size pores (30–500 Å) to crack large molecules, whereas zeolite has a cage opening of 7.4 Å to which only small size hydrocarbon molecules can enter and crack. However, the cracking on the zeolite surface is more selective to produce high value lighter products as compared to matrix. Thus matrix does the primary cracking of the large molecules from the bottoms, and zeolite does the secondary cracking of the molecules to valuable products.

Properties of matrix regarding chemical composition, crystallinity, activity, pore size and pore size distribution, hydrothermal stability, and so on also play a role in the selectivity of matrix cracking and have an impact on its bottom upgrading capabilities. Some matrix also increases the metal tolerance of the catalyst by performing an additional function of trapping contaminant metals and basic nitrogen, thereby protecting zeolite and acid sites present in the catalyst. New generation matrix materials with optimised properties offer better selectivity and produce lower yields of coke and gas compared to the previous generation.

Thus, for maximum bottoms upgrading to desired high value products, an optimum combination of matrix and zeolite activity is required in the FCC catalyst. Typically, the relative proportion of zeolite and matrix in the catalyst formulation is measured in terms of Z/M ratio. As multiple properties of matrix and zeolite have an impact on bottoms upgrading, there is no simple answer to what is an ideal balance between the two. Generally, low Z/M catalyst formulation is preferred to maximise distillate yield from bottoms upgrading whereas high Z/M catalyst is more selective towards gasoline/LPG.

It is advisable to discuss specific applications and objectives with the catalyst supplier for catalyst design with optimised zeolite and matrix content. Typically, the catalyst supplier can optimise the Z/M for the specific application in consideration of its own catalyst technology as well as the unit configuration, feed quality, operating conditions, product yield requirements (LPG, gasoline or distillate), and so on. For example, for refineries who value bottoms upgrading with selectivity towards distillate, BASF recommends products based on Prox-SMZ technology platform or our new matrix technologies which contain matrix with better hydrothermal stability to preserve the low Z/M ratio and also have zeolite active sites in close proximity to matrix for better selective cracking. This synergy leads to higher LCO production with lower coke. For refineries who want to maximise LPG or gasoline yields from bottoms.
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Irrespective of the applied cracking technology, hydro-cracking (HC) or fluid catalytic cracking (FCC), a high zeolite content in the main operating catalyst will direct the product distribution towards too high a share of light ends.

A more efficient way is to build up secondary porosity on the zeolite crystals, combined with a highly porous matrix in the case of FCC catalysts. Optimising shape and size of the extrusions can be an efficient add-on in the case of HC. Today, the formation of secondary porosity by post-synthetic methods has reached an attractive level, also from a commercial perspective.

A Steven van Vegten, FCC Technical Specialist, Albemarle, steven.vanvegten@albemarle.com

Matrix activity is crucial to provide bottoms upgrading. A catalyst with high matrix activity typically comes with greater accessibility. Higher accessibility facilitates the diffusion of high molecular weight slurry molecules into the catalyst particle. Zeolite pores are too narrow for slurry molecules; it is the matrix active sites in the meso pores that upgrade slurry to LCO. Depending on the refiner’s objectives, the amount of zeolite activity can be chosen. For maximising gasoline, more zeolite activity will be preferred. While for maximising LCO, the zeolite activity should be modest.

Q If we hydrodesulphurise naphtha to meet fuel sulphur limits, is there a cost in lower octane?

A George Hoekstra, Hoekstra Trading, george.hoekstra@hoekstratradings.com

Yes, especially when desulphurising FCC and coker naphtha. The amount of octane loss varies from 1 to 10, depending on the desulphuriser feed, unit design, catalyst, and operating conditions. We did a three-year multi-client research project to quantify these effects. The project included pilot plant tests, side-by-side catalyst tests, commercial field tests, model development, and economic studies. We have field test data from 12 commercial FCC gasoline desulphurisers that show higher octane loss than has been anticipated by the industry when making Tier 3 (10 ppm sulphur) gasoline in the United States. The incremental octane loss when moving from Tier 2 to Tier 3 will likely be five times higher than was anticipated when the Tier 3 standard was enacted. None of the 12 commercial units in our field test data base indicates octane loss as low as that anticipated when the Tier 3 standard was enacted.

Octane will be lost when severity is increased in gasoline desulphurisers to lower the sulphur of FCC gasoline. In addition to octane loss, a lower product sulphur specification introduces new constraints on kinetic capacity, hydrogen availability, splitter effectiveness, feed flexibility, cycle life, synchronisation of unit downtime in the FCC train, and processing of orphan streams requiring desulphurisation. These constraints will surely come into play, especially in refineries that do not have FCC pretreaters and those with gasoline desulphurisers not designed for Tier 3 service.

The biggest cost factor for Tier 3 is replacement of the octane lost in gasoline desulphurisers. This will be mostly done by increasing alkylate or high-octane reformate in gasoline blends, which comes at a cost, and with capacity limits that depend on the refiner and feed. Some refineries in the USA are already paying $millions/month to replace lost octane with purchased alkylate.

When facing octane constraints, refiners can also reduce their production of premium gasoline and/or export non-compliant gasoline. But these remedies can really hurt profits of North American refiners because the retail value of octane in the US has tripled in recent years, making octane barrels an increasingly valuable commodity in the market.

Most US refineries have never made Tier 3 gasoline in substantial volume. Now, with the issue urgent, many unknowns must be worked out in real time. The costs and benefits will be widely distributed across US refiners.

Our pilot plant and field test studies have led to development of new tools and methods to reduce octane loss in gasoline desulphurisers which can be implemented immediately with no capital investment. These optimisation tools, and all the data on which they are based, are available at negligible cost through Hoekstra Trading.

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It goes without saying that the requirement for fluidised cracker and coker downstream naphtha HDS to meet global 10 wtppm sulphur standards for gasoline has an adverse effect on the anti-knock properties of the products: high RON components such as olefins – and in some cases even aromatics – are converted to lower RON molecules. To preserve as many as possible of the high RON components, a variety of selective HDS processes is available on the market. However, in some cases, caustic wash combined with a sulphur adsorption technology seems to have an economic benefit.

A René Severens, Global HPC Advisor, Albemarle, rene.severens@albemarle.com

Yes, there is. Aromatic molecules, branched iso-paraffins, and olefins all have high octane, whereas alkanes have low octane; compare, for instance, the following molecules that all have seven carbon atoms: toluene has an octane number of 120, trimethyl butane has 110, methyl hexane has 96, whereas heptane has zero octane. FCC naphtha is rich in aromatics and olefins, and hence has a high octane number. While aromatic naphtha molecules are quite stable in a hydrotreater, the olefins are easy to
We are meeting IMO 2020 rules but producing higher delta coke in our FCC. Will a change of catalyst help us?

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Although the question does not clearly explain what the refinery did to meet IMO 2020, it sounds like feed to the FCC got heavier since most likely they decided to pull the LSVGO out from the feed to sell it as low sulphur bunker fuel oil, and filled the FCC capacity with streams with higher sulphur. In general – at least for the same crude sources – FCC feed sulphur increases along with other contaminants (Ni, V, Fe), Concarbon, boiling point, and so on. Hence, not surprisingly, the unit has come to a coke constraint, so all aspects of the heat balance should be kept in consideration, including but not limited to the catalyst.

In general, there are four main contributors to coke formation which can be described as: feed coke, metals coke, stripping coke, and catalytic coke:

**Feed coke:** assuming that the new FCC feed diet is fixed, this is not really a variable. However, there are other aspects connected with feed preparation that need to be adjusted when (as probably happened in this case) the feed got heavier, particularly in connection with feed vapourisation. The atomisation steam should normally be increased to enhance feed vapourisation (it is best to perform a dedicated test run to increase the feed steam until no further benefit is observed). Uniform feed distribution across feed injectors should also be verified.

**Metals coke:** although, again, feed quality is not a variable, the overall metals balance can be modified: for instance, a reduction of the fresh catalyst activity together with an increased catalyst addition rate (to maintain constant Ecat activity) will help to flush more metals out and decrease the metals coke contribution.

The use of metals traps as a part of the catalyst formulation also helps to reduce the metals coke. BASF’s metal passivation or trapping technologies are an example: Boron Based Technology (BBT) commercially demonstrated high Ni trapping capability, thanks to the unique mobility of Boron within the catalyst to find and passivate more Ni, while Valor, BASF’s latest vanadium trapping technology, demonstrated superior activity maintenance.

**Stripping coke:** it is a no-brainer that any unstripped hydrocarbons will end up in the regenerator as incremental coke, so the optimum stripping steam rate should be reassessed by means of a dedicated test run, along with the optimum stripper level which determines the residence time for a given catalyst circulation rate. It is important to note that ‘catalyst strippability’ only refers to intra-particle vapours and not to the small portion of vapours that may still be trapped inside the catalyst particles, so differences in fresh catalyst total surface area (TSA) will not affect the catalyst strippability.

**Catalytic coke:** once the other three coke contributors are fixed, the catalytic coke will always be automatically adjusted to produce the remaining coke needed by the process (to vapourise the feed, crack it, preheat the air, compensate for heat losses, and so on) and the catalytic coke will show up proportionally to the feed conversion. Hence, the use of a low delta coke FCC catalyst will enable higher conversion per unit of coke produced, or allow lower delta coke for the same conversion.

Generally, the IMO 2020 regulation change increases the pricing differential between LSVGO and other higher sulphur heavy streams. Although the question does not specify what the refinery did to meet IMO 2020, it sounds like feed availability/economics have led the refinery to acquire heavier FCC feed, which is leading to increased tendency to produce delta coke. The four primary factors which contribute to coke formation are: feed quality (density, distillation, Concarbon); feed metals; stripper performance; and catalyst design.

For heavy feeds, good contacting between oil and catalyst is paramount to ensure maximum catalyst cracking (good coke and liquids selectivity) and minimum thermal cracking (poor coke and liquids selectivity). To produce good contacting, a few operating parameters can be checked:

- Optimal atomisation steam to ensure good dispersion and vapourisation of feed oil and to ensure reliable feed injector operation
- Mix zone temperature profiles should be adjusted to minimise feed/oil non-uniformity

Feed metals can be addressed through the use of feed additives as well as catalyst solutions. Nickel and vanadium strongly contribute to dehydrogenation and thus coke formation. Nickel can be passivated using feed additives (such as antimony) or catalyst solutions. Vanadium can be trapped and passivated with catalytic solutions as well. Examples of BASF’s metals control technologies are Boron Based Technology (BBT), a commercially proven unique nickel trap, and Valor commercially proven superior activity maintenance. Catalyst design can take advantage of inherent metals tolerance
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(rare earths, surface area, and so on) and also fine-tune activity/cost to enable metals flushing from the unit.

Stripper operations should be optimised by understanding the performance impacts of steam/catalyst ratio as well as catalyst residence time (stripper level and catalyst circulation rate). These important relationships can be studied with straightforward ‘step tests’. It is important to note that ‘catalyst strippability’ only refers to intra-particle vapours and not to the small portion of vapours that may still be trapped inside the catalyst particles, so differences in fresh catalyst total surface area (TSA) will not affect catalyst strippability.

When the FCC process is optimised to minimise coke making tendencies, catalyst design is effective in fine-tuning yields to ensure optimal operation. It is relatively obvious that the use of low delta coke FCC catalyst formulations is essential to address coke reduction. What is less obvious is that catalysts can be designed to produce favourable yield patterns which can deliver maximum value at desired conversion (coking yield) levels.

**A**

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Additional information is required to confirm a catalyst solution for your FCC unit and ensure you can further improve profitability and continue to meet your IMO objectives. Generally, optimising the FCC operation while meeting IMO 2020 regulations will depend on the local economics and the specific refinery configuration.

Higher delta coke can be a preferred operation for units limited by catalyst circulation and low regenerator temperature. High conversion and FCC unit charge rate can be achieved operating with a high delta coke operation using a FCC catalyst with high activity and superior coke selectivity for those units constrained by their air blower, coke yield, and catalyst circulation.

A lower delta coke catalyst, however, may be beneficial if your FCC unit has capacity to increase catalyst circulation and will benefit from a lower regenerator temperature. A catalyst with improved coke selectivity can be used to increase conversion and overall liquid yield through increased catalyst circulation and a lower regenerator bed temperature.

Sharing your objectives, operating conditions, constraints, and product priorities with your preferred catalyst supplier is essential to ensure an optimal solution is identified. Grace offers a wide FCC catalyst portfolio that complements FCC units processing light gasoil feedstocks, as well as high metal and Conradson carbon resid feedstocks. Catalysts can be specifically targeted to maximise distillate, gasoline or LPG olefins, in line with refinery economics and goals.

**A**

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Yes, switching to a delta coke selective catalyst will help in reducing delta coke as will changing to an optimum activity catalyst to get the optimum conversion in the unit. If high delta coke is caused by dehydrogenation reactions of contaminant metals, it would be good to add sufficient metal traps to the new catalyst to reduce delta coke and H₂. The new catalyst formulation should take into account the current feed slate in your unit and the desired product yields. Aiming to minimise delta coke, the catalyst vendors can also take the opportunity to design a new catalyst, increasing the most valuable products in your FCC unit.

**A**

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Without knowing the base case operation, it is impossible to say for certain, but it is very likely catalyst formulation changes are possible to reduce delta coke in your operating unit.

The exact change possible depends upon what exactly you have done to achieve IMO 2020 rules and you current operation.

Every year, catalyst and additives suppliers offer technology iterations to further drive down delta coke. Unless you have made a catalyst change very recently, it is highly likely you are not currently optimised. Numerous groups have reported the types of economic benefit from relentlessly optimising their FCC catalyst selection, with increased revenues approaching major hardware changes, but with no capital costs. It may even be possible to reduce operating cost depending upon your starting point.

**A**

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Historically, commercial oil-to-chemicals facilities converted a relatively small fraction (~30%) of crude oil into chemicals instead of fuels. The latest developments are facilities that convert appreciably more crude oil into chemicals at a larger scale. A key differentiator between the technologies that enable these higher chemicals yields is how the resid fraction is converted. Higher resid conversion improves economics by yielding more chemicals and fewer by-products.

A facility that aspires to convert about 50% of its crude intake into chemicals, and which has a market for propylene and aromatics, could opt for resid hydrotreating (RDS) followed by resid fluid catalytic cracking (RFCC) to produce feed for a steam cracker complex or aromatics complex, in addition to transportation fuels. This carbon-rejection route is attractive where hydrogen is in short supply and where the co-production of chemicals would lower the cost allocation for fuels production.

A facility that aspires to convert more than 70% of its crude into chemicals, and which focuses on ethylene and aromatics, would opt for resid hydrocracking (LC-Fining or LC-Slurry) followed by hydrotreating and
hydrocracking (HCR) of the residuum-derived products to produce feed for a steam cracker complex. This hydrogen injection route is attractive where a projected naphtha-crude differential (on a weight basis) sustainably supports low cost chemicals production.

The key value driver in resid to chemicals conversion is the degree of process integration and intensification. Integration includes processes and catalysts. CLG has had many highly integrated resid conversion designs in commercial operation for many years and is the first and only licensor that has had a LC-Fining unit integrated with a hydrotreating and hydrocracking facility in reliable commercial operation for more than a dozen years. Lummus’s heavy oil processing system (HOPS) is the lowest investment, most efficient option to steam crack RDS/FCC or LC/HCR feeds into chemicals. The step-out catalyst technology and resid experience provided by ART Hydroprocessing are a critical ingredient in the high operational reliability and on-stream time of these highly integrated process configurations.

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When the fluid catalytic cracker (FCC) is operated in a propylene maximisation mode, it can be a critical part of a refiner’s strategy to maximise petrochemicals from crude as confirmed by ART in the previous response. In a maximum propylene operation, the propylene yield from the FCC is impacted by the following:

- FCC equipment technology
- Operating conditions
- Feedstock type: resid vs VGO
- Catalyst and additives

Many recent heavy resid to propylene grassroots projects have included a resid fluid catalytic cracking (RFCC) unit to produce increased light olefin yields over traditional transportation fuels. Many of these RFCCs use two stage regeneration with and without catalyst coolers, allowing high conversion of the resid feedstocks and ensuring high yields of propylene, ethylene, and butylenes. A dedicated external riser to process recycled naphthas, C₅s or polynaphtha from an oligomerisation unit to further increase propylene yields can also be included.

In addition, auxiliary equipment to the RFCC can be installed to further enhance C₅s for example, using a metathesis unit processing ethylene and butylene to produce additional propylene.

Higher riser outlet temperature (ROT) is required in a maximum propylene RFCC operation which comes with trade-offs including higher dry gas and coke yield. A catalyst cooler, if required, to maintain the regeneration temperature to acceptable levels will also increase coke yield. A RFCC unit operating in maximum propylene mode often operates at a lower hydrocarbon partial pressure to increase propylene selectivity and improve coke selectivity.

Grace is committed to further development of crude to chemical technology to meet the growing demand and further enhance on our leading light olefin FCC catalyst and additive position. As part of that commitment Grace and TechnipFMC recently signed an agreement to jointly develop improved catalyst and process technology related to TechnipFMC’s PropyleneMax catalytic cracking (PMcc) technology. PMcc is a high-severity fluid catalytic cracking process licensed by TechnipFMC that can provide up to 10 wt% crude to propylene, ethylene, and butylene. The collaboration will leverage Grace’s knowledge as a supplier of FCC catalysts and light olefins additives as well as TechnipFMC’s significant experience in maximum propylene projects including process and mechanical know-how.

In terms of feedstock, propylene yield increases when using feedstocks with high hydrogen content and low naphthenic and aromatic content. It is common to incorporate resid hydrotreating (RDS) to treat the heavy resid feedstock ahead of the RFCC unit to ensure high conversion and C₅s as mentioned by the prior response from our colleagues at ART. Hydroprocessing reduces nickel, vanadium, nitrogen, and Conradson carbon and increases the hydrogen content, improving the light olefin yield from the RFCC unit.

Optimising the catalyst formulation for containment metals and elevated Conradson carbon is essential to maximise propylene yield while staying within the wet gas compressor, air blower, and regenerator temperatures constraints.

The design of RFCC catalyst for maximum C₅s balances the need for conversion against minimising hydrogen transfer reactions to ensure high C₅s selectivity. Traditionally, a catalyst designed for maximising propylene from a resid feedstock is designed with low hydrogen transfer and features the following:

- Nickel and vanadium traps to improve selectivities
- Pore structure to accommodate high iron levels
- Coke selective matrix for low slurry yield and coke selectivity

Rive catalysts containing Molecular Highway Zeolite technology (MHY) offer a different approach to minimise hydrogen transfer reactions while maintaining catalytic activity. The MHY zeolite in Rive catalysts improves the diffusion of reactants into and products out of the MHY zeolite compared with conventional Y-zeolite, and therefore minimises undesirable hydrogen transfer reactions. These catalysts are a powerful tool to maximise propylene from the RFCC.

Finally, the maximum propylene catalyst generally includes a ZSM-5 additive to crack gasoline olefins into LPG olefins. As a result of the high LPG olefin yields in maximum C₅s RFCC applications (11 wt% or higher C₅s targets are common for resid to propylene applications), a high addition rate of ZSM-5 is used. By using the highest activity ZSM-5 additive, a lower amount of ZSM-5 additive can be used for a similar LPG olefin yield. Since ZSM-5 can only crack gasoline range molecules, minimising the amount of ZSM-5 additive avoids dilution of the zeolite catalyst activity. To maximise C₅s, Grace recommends using ZSM-5 additives from the family of OlefinsUltra additives or our newest ZSM-5 technology, Zavanti catalysts.
A variety of process licensor technologies to enhance olefins production from the FCC are available. New designs and technology have been introduced to the market to achieve very high yields of chemicals from crude oil and eliminate or reduce transport fuel products. The specific unit objectives and economics are a driver for the catalyst selection, and the market has a wide variety of options available. These high performance systems require close integration of any new FCC catalyst technology with the specific unit objectives and feed constraints. Crude to chemicals FCC units often require high zeolite surface area and tailored matrix technologies. Most utilise speciality zeolites such as ZSM-5 to drive the high olefin selectivity for chemical production. The specific process and catalyst technology will depend on your specific economics and design case.

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In the 1950s and 1960s, technologies were developed to generate ‘active’ starting molecules (such as ethylene, acetylene, and propylene) by thermal methods directly from crude. One example is the HTP process by the former Hoechst company. Due to their high energy demand, these technologies were substituted by more efficient steam cracking on naphtha and wet natural gas in the 1970s and 1980s. Regarding heavier feedstock utilisation: state-of-the-art coking technologies allow the generation of more valuable light olefins even from highly asphaltic crude sources. The solution can be progressive hydrocracking technologies in combination with downstream upgrading hydroprocessing technologies for further deep saturation or viscosity adjustment. This can open an attractive chemicals portfolio beyond fuel: white oils, high performance lubricants, heat and power transmission fluids and solvents.

Steven van Vegten, FCC technical specialist, Albemarle, steven.vanvegten@albemarle.com

Many modern FCC units are designed to process residue feed while maximising light olefins yield, notably propylene. These units use high amounts of ZSM-5 type zeolite. In these applications, the selection of the base catalyst is critical. Using a conventional catalyst, the unit would quickly reach a plateau in propylene make and adding more ZSM-5 does not give higher \( C_3 = \) yields. However, when using a high matrix, high accessibility, low hydrogen transfer base catalyst, more gasoline olefins are produced. The increased amount of gasoline olefins, which are the precursors to making \( C_3 = \), allows for truly maximising \( C_3 = \). In addition, high unit severity and notably higher riser outlet temperature will increase \( C_3 = \) make.

In the future, we foresee the increase of interest in BTX. For this application, selecting an aromatic feed and high level of hydrogen transfer from the host catalyst would be most suitable.
Modern Crude Distillation, Modularized

Global interest in modular refinery construction is surging. Small modular refineries are attractive to investors for several important reasons:

**SPEED**
Project time from contract execution to start-up can be as short as 18-24 months.

**LOGISTICAL ADVANTAGES**
Modular refineries can be built in remote locations to realize efficiencies in supply and transportation of raw crude and refined products.

**LOW INITIAL COST**
Small relative size makes initial capital cost more manageable. Modules can be constructed in the shop with nearly 100% productive time, and turnkey fabrication and construction services lower the likelihood of project delays or cost overruns.

For a project to realize the benefits listed above, it has to start up and run reliably. Saving initial capital by cutting corners is a doomed strategy. Cost savings should result from clever flow schemes that minimize equipment and module count without sacrificing product yields or unit reliability.

With the right expertise, it is possible to design industrially proven, reliable equipment to be easily modularized.

Process Consulting Services has engineered over 100 crude/vacuum unit revamps and over 4 MMBPD of grassroots crude unit capacity. We have drawn on all of this experience to develop a unique flow scheme for modular crude/vacuum units. Our modular crude distillation process is fully modern, incorporating time-tested technologies to eliminate common reliability issues. Some of these features, developed in much larger units, have been re-thought to be affordable on a modular scale.

No matter how low the initial cost of a crude unit is, the investment will not pay off if the unit is plagued by avoidable problems. Poor desalting (corrosion), pre-flash tower foaming (off-spec naphtha), tray plugging (poor fractionation and product quality), etc. can all be mitigated by thoughtful front-end design.

Through creative flowsheet and equipment design, PCS is able to significantly reduce the number of modules required to build a modern crude distillation unit that maximizes valuable product yield, energy efficiency, and reliability.

*Photo Credit: Honeywell UOP*
FCC catalyst accelerates bottoms upgrading

A competitive FCC catalyst trial demonstrated that improved diffusion of feed and products boosts unit performance when residence time is short

HEATHER MORRIS Shell Canada
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CLINT COOPER W. R. Grace & Co.

Maximising diffusion of feed into and products out of an FCC catalyst is critical to unlocking the full value potential of an FCC unit in which the riser residence time is only a few seconds. Rive FCC catalysts incorporate Molecular Highway Y-zeolite (MHY) technology, which engineers a precise series of mesopores into the Y-zeolite framework, the primary active component of all FCC catalysts. This technology enhances diffusion of molecules into and out of the catalyst.

Building on the success of Rive Technology (Rive) and W.R. Grace & Co. (Grace) at a Shell US Gulf Coast refinery in 2016, a customised catalyst solution incorporating MHY zeolite was designed and trialled at a second North American Shell refinery. The primary objective of this trial was to increase FCC bottoms upgrading into valuable gasoline and diesel products.

The trial results again demonstrated the value of this technology, which can provide to an FCC unit. During the trial, Shell was able to realise uplift in the range $1.45-1.80/bbl (within the boundary of the FCC unit), depending on the market economics.

This article will further investigate the technology and how it was used to improve performance at this refinery.

Molecular Highway Y-zeolite technology

Since 2010, Rive and Grace have jointly developed and commercialised MHY zeolite technology for use in FCC units throughout the world. The MHY zeolite process introduces a network of intermediate-sized (∼40 Å) mesopores into the zeolite, which significantly enhances diffusion of the feed and cracked products.

The interconnected network of mesopores permits access for larger feed molecules that vaporise in the FCC unit at temperatures above 950°F (410°C) to the strong acid sites in the zeolite framework. These acid sites are able to crack the larger feed molecules much more selectively than conventional active matrix materials. The improved diffusion within the zeolite drives bottoms upgrading into LPG olefins, gasoline, and LCO, without coke or gas penalties that are often associated with alternate technologies. Additionally, the MHY zeolite helps to channel valuable cracked products out of the catalyst before the products succumb to potentially undesirable reactions such as overcracking into dry gas, olefin saturation via hydrogen transfer, or coke formation via condensation reactions.

In June 2019 (after conclusion of the trial), Grace acquired the assets of Rive, including its patented MHY zeolite technology. This strengthened Grace’s catalyst portfolio by enabling more rapid deployment of the technology across new catalyst frameworks. Through flexible manufacturing technology, Grace can control the amount of mesoporosity in MHY zeolite to help refiners optimise their profitability.

MHY zeolite technology is protected by more than 40 patents and has been applied successfully to more than 10 FCC units globally since 2011. Catalysts containing these zeolites typically provide the highest value in FCC units processing heavier feedstocks, particularly if the refinery is challenged by unit constraints such as maximum regenerator temperature, wet gas compressor rate, or air blower rate. However, refineries processing lighter feeds have still gained substantial uplift (>$0.50/bbl) from the diffusional improvements facilitated by the technology.

The catalyst used at the Shell refinery was customised to meet specific objectives and constraints – namely, using improved diffusion to upgrade slurry into valuable gasoline plus distillate.

In Figure 1, the image on the left shows a scanning electron microscope (SEM) image of a conven-

Figure 1 Micrographs of conventional zeolite (left) and MHY zeolite (right). At similar magnifications, micropores in conventional zeolite are not viewable (left image), while the 40 Å network of mesopores within MHY zeolite are viewable (right image).
Catalysis and LPG production are usually objectives to maximise gasoline production. Catalyst circulation rate typically maximises feed rate to the air blower limit. The primary product is gasoline in partial burn, and the unit typically processes low sulphur VGO. The regenerator operates revamped Kellogg design which was awarded a trial at the refinery. Grace and Rive together were awarded a trial at the refinery based on pilot testing results from a competitor and proven performance at another Shell refinery using a Rive FCC catalyst. While some of the objectives and constraints differed between these Shell FCCs, both units were able to benefit from improved hydrocarbon diffusion through the catalyst. The primary objective of this trial was to increase product revenue while maintaining the physical properties of the catalyst. Avenues to increasing FCC revenue included:

- Increase conversion and liquid volume
- Decrease slurry yield
- Increase gasoline and diesel yield
- Reduce dry gas yield
- Maintain LPG yield
- Maintain or reduce catalyst addition rate

Through a comprehensive ACE testing program and subsequent modelling and optimisation, Grace and Rive designed a catalyst to meet the refinery’s objectives. Value uplift was predicted to be approximately $0.92/bbl using RFP pricing. Catalyst improvement projections were independently confirmed via laboratory testing at Shell’s Technology Center (Houston) and modelling with Shell’s proprietary Sharc model.

Trial analysis and evaluation was a joint effort by Rive, Grace, Shell’s technology group, and the refinery’s personnel. Several different methods were used to analyse the trial and determine the catalyst’s uplift, including:

- Operating data evaluation (cross-plots; comparing similar time periods)
- Ecat data evaluation (cross-plots; ACE testing at, before and after Ecat turnover to the Rive FCC catalyst)
- FCC kinetic modelling

Risk mitigation and technical service
Prior to the trial, the combined team worked to create a risk management plan. Key risk management items included:

- Ensuring C8 olefinicity remained above minimum specifications
- No increase to catalyst attrition/losses
- Regenerator bed temperature would remain within specified limits

For each risk, the team created a detailed monitoring plan and mitigation plan. Near the start of each review throughout the trial, each of these risk management items was discussed. With a high level of attention and frequency of review, each item was maintained or improved during the trial.

Collaboration between Rive, Grace, Shell’s technology group, and refinery personnel ensured a successful trial. The team worked to push the unit to significantly improved profitability by leveraging the catalyst’s benefits at optimised operating conditions. Grace was also able to utilise technical expertise from its Global Customer Technology group to assist with fine tuning operating variables during the trial.

Evaluating operating data
The combined team monitored daily operating data throughout the trial to evaluate the effects of the catalyst change. Updated process data was shared by the refinery on a weekly basis. Comparisons of operating data were made between the incum-
bent catalyst and Rive FCC catalyst at >30% T/O in unit inventory and normal partial burn operation.

It was important to the refinery that the catalyst addition rate did not increase during the trial. During the trial, it decreased by approximately 0.03 lb/bbl.

The feed was slightly heavier during the Rive FCC catalyst trial compared to pre-trial operation. This degradation of feed quality typically makes slurry upgrading into valuable products more challenging. Because of the reduced fresh catalyst addition rate and heavier feed quality, the metals on Ecat increased. Compared to pre-trial operation, nickel on Ecat was 300 mg/kg higher and vanadium on Ecat was 500 mg/kg higher. Also, the refiner reduced the ratio of Sb/Ni by approximately 20% intentionally, as lower gas factors were observed during the trial.

Despite the higher Ecat Ni and V and lower Sb/Ni ratio, the dry gas selectivity (see Figure 2) was only slightly higher for the Rive FCC catalyst. Had the unit maintained Ecat metals and Sb in a similar range to the pre-trial period, reduced dry gas production would have been expected.

Based on economics and unit constraints, it was desirable for LPG production to be near the same levels as pre-trial operation. As Figure 3 shows, LPG selectivity was approximately the same as the incumbent catalyst.

The most valuable products at the refinery, on a per-barrel of product basis, were gasoline and light gas oil (LGO, similar to the lighter range of typical light cycle oil), and the main trial objective was to maximise slurry upgrading into these products. As the gasoline cut point changed frequently, Figure 4 shows the selectivity of the combined ‘gasoline + LGO’ product. At a given conversion, the Rive FCC catalyst provided approximately 2.0 vol% higher yield.

Figure 5 shows the slurry product selectivity. For a given conversion, the Rive FCC catalyst provided approximately 0.6 vol% lower slurry yield. Consistent with the improved slurry selectivity shown in Figure 5, the slurry gravity decreased during the trial by about 2.5 °API, which was the lowest historical slurry gravity noted by this Shell site during periods of normal operation. Slurry upgrading was so improved that, during the trial when lighter feed was processed, Shell altered cut points to ensure slurry gravity did not fall below the minimum requirement.

Evaluating similar periods of operation
To better understand the effects of the catalyst change, similar summer periods of operation were compared between the catalysts. Table 1 provides a comparison of Ecat metals during these periods. As was noted previously, Ni and V were significantly higher during the Rive FCC catalyst period, while the ratio of Sb/Ni on Ecat was notably lower.
Table 2 provides the yields (vol%) for these two periods of operation. Despite having higher Ecat metals, bottoms upgrading improved dramatically, resulting in an additional 2.0 vol% of gasoline and diesel range products.

**Evaluating Ecat data**
Grace performed ACE testing to benchmark the trial Ecat against the incumbent Ecat using Shell feed collected just prior to the trial. Testing Ecat samples on this feed removes variation in commercial feed and operational impacts and isolates the effects of the catalyst change. However, differences in Ecat metals and test unit residence time still affect the ACE testing results.

The ACE study evaluated the following Ecat samples:
• Pre-trial incumbent Ecat
• 80% turnover Rive FCC catalyst

Consistent with observations previously noted in operating data, slurry upgrading improved, driving yields of gasoline + LCO, at constant coke. Dry gas yield was the same, despite higher Ecat metals. LPG yield and LPG olefinicity were similar to the incumbent, as desired. The results of this ACE study are provided in Table 3.

The ability to maintain LPG olefins is a particularly notable point in this application. In other applications of MHY zeolite technology, an increase in LPG olefinicity is often noted. However, due to the unique catalyst design employed in the Shell trial, the Rive FCC catalyst was able to hold LPG olefins at a constant level. This demonstrates the flexibility inherent in MHY zeolite technology.

**Modelling highlights**
Using a variety of test run cases, Rive Technology and Grace used kinetic modelling to estimate more accurate yield/uplift comparison, while Shell independently used the Sharc kinetic model to evaluate the results.

Both models agreed that the Rive FCC catalyst provided significant improvement in value for Shell. Contributors to value improvement
Looking forward

Based on the positive results observed at the unit and through the evaluation described here, Shell continues to use a Rive FCC catalyst. Based on mutual learnings from the combined team, as well as predicted changes to feed quality and product pricing, an optimised formulation was developed for the refinery, which is projected to further increase uplift by $>0.40/bbl.

Conclusions

The results from this commercial FCC catalyst trial support the fundamental principle that improving diffusion of feed into and product molecules out of active zeolite crystals is critical to unlocking the full value potential of an FCC unit in which the riser residence time is only a few seconds.

In line with the refinery’s objectives, the following FCC performance improvements were documented at normal operating conditions, relative to pre-trial conditions comparing the Rive FCC catalyst to the incumbent base catalyst:

a. Total \( C_{\text{C}+} \) liquid volume increased by 1.15 vol% 
b. Slurry yield decreased by 0.65 vol% 
c. Gasoline yield increased by 0.90 vol% 
d. LGO/HGO yield increased by 1.10 vol% 
e. Dry gas remained approximately the same with significantly higher Ni and V and reduced Sb on Ecats.

Extensive FCC modelling with multiple kinetic models, Ecats benchmark ACE testing, and operating data comparison between periods of similar operating conditions, confirmed uplift in the range $1.45-1.80/bbl (within the boundary of the FCC unit), depending on feed quality and market economics.

Performance improvements, strong technical service, and a collaborative relationship resulted in continued use of the catalyst after the trial, and an enhancement to the catalyst which is expected to drive even more value from the FCC.

References


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Developments in refining catalysts

New catalyst technologies underpin increasing flexibility in refineries’ response to changes in demand for their output

MICHAEL CLEVELAND
Honeywell UOP

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tunning technological advances have occurred since UOP introduced catalysis to the refining industry in 1933. It graduated the science of refining from a series of processes governed by pressure, temperature, and time to one where catalysts could be employed to perform specific functions, to break and rearrange molecular bonds to make predetermined products. As catalytic science became more sophisticated, catalysts could be engineered to perform those functions more selectively and efficiently.

By merely coming into contact with a catalyst, hydrocarbon molecules can be induced to break apart, join together, and rearrange themselves into intended new forms. But despite all the achievements in catalytic science in the last 87 years, the industry still has only scratched the surface of what catalysts can do.

Most of the developments in catalysts resulted from the invention of new materials that do not exist naturally. These materials were designed to be manufactured with repeating crystalline structures with advanced properties. For example, acid catalysts were developed with greater acid site density and strength, lower diffusion paths, and other qualities to make them more efficient. Novel metal catalysts featured new nanomaterials, or atomic-level compositions, with superior electronics that gave them new capabilities. All of these developments are the product of highly developed core competencies in the design of new materials, and the manufacturing expertise to uniformly synthesize them.

While the industry has developed thousands of new materials, including hundreds of new zeolites, a second competency is necessary to scale up production from a few grams in a lab to continuous quantities that may number in the hundreds of metric tons.

Today, much of the development in catalysts focuses on process intensification – designing catalysts that are more efficient than existing catalysts, or that perform more than one chemical conversion in a single step. This allows them to process more feedstock with fewer and smaller units, requiring less land, steel, and energy.

Because catalysts are integral to process technology, this profoundly improves the economics of refineries and petrochemical plants by reducing their utilities requirements and water use, avoiding production of low value byproducts, and even allowing them to use a wider range of feedstocks. These processes, enabled by more capable and efficient catalysts, can lower capital requirements and operating costs.

Catalysts also are at the heart of the Refinery of the Future, a framework of asset development and molecule management that helps ensure optimal economic efficiency, profitability, and environmental leadership over time. It is an approach to capital investment that is unique to each refinery. Different combinations of technologies are built in carefully timed stages to meet changing market conditions, take advantage of changing feedstocks, and meet evolving regulatory constraints and competitive threats – with the goal of maintaining optimal profitability.

One of the overriding trends in the industry today is the widely forecast peak in global demand for transportation fuels in the mid-2030s, due to the introduction of more fuel-efficient engines and the growing number of vehicles powered by alternative fuels. At the same time, new environmental regulations threaten to strand refining capacity for fuels that do not meet stricter emissions standards.

This has caused many refiners to upgrade their fuels refining capacity while bridging into petrochemicals, where product demand and margins remain strong, due to 4% growth in global GDP driven in part by population growth in developing economies.

More efficient processes – based on more sophisticated catalysts – offer great competitive advantages in terms of operating margins and slate flexibility, with the ability to direct molecules to processes where they can produce the greatest value. The best solutions are catalysts that are designed to operate under these new conditions using existing capital assets. In this sense, they are akin to reprogramming a refinery, in the same way you would install a software upgrade to a computer. The refinery is essentially the same, but now it can do more.

For example, a new catalyst – with some modifications to operating conditions – can change a hydrocracking unit from production of distillate to production of naphtha. With the staged investment of a CCR Platforming unit, the naphtha can be converted into aromatics – and LPG which, with the addition of a PDH unit, can be the feed for producing olefins.

While existing refineries are investigating these paths, new world-scale refineries already are being built that will convert half or more of their feedstock into petrochemicals. In fact, refineries that
produce only petrochemicals probably are not far behind. Where economics favour larger operations, new catalyst designs also make it possible to design larger units with greater capacities. In cases where processes are hydrodynamically limited, a catalyst can be made denser or stronger, or given a more efficient shape or some other property to accommodate greater production capacity, without risking pressure drop, pinning, or void blowing. The design of advanced catalysts today requires advanced characterisation techniques, employing electron microscopes to verify the composition of the material and even ensure metals have been properly dispersed. Without the ability to actually inspect what has been created, we cannot know exactly why a new catalyst formulation behaves the way it does.

Aromatics conversion
One of the processes used to selectively convert lower value toluene and C5 aromatics into benzene and xylene products is the Tatoray process. In this process, toluene is combined with C5 and C6 aromatics and converted to benzene and xylenes in a simple transalkylation reactor system, more than doubling the yield of paraxylene from a given naphtha feedstock.

But to further increase yields of paraxylene from an aromatics complex – and allow the use of even heavier feeds – UOP developed the TA-42 catalyst for the Tatoray process. This catalyst employs a true nano-zeolite which is highly stable, active, and selective because the reactions are controlled by mass transfer. The dimensions of the zeolite pores are smaller, giving it more active sites and greater selectivity to the molecules without getting clogged by heavier C5 and C6 aromatics. As a result of its higher activity, yields of paraxylene per unit of energy – and overall processing capacity – are higher. The ability to scale up this zeolite was made possible by the invention of a new material.

Bottoms upgrading
One of the persistent problems with upgrading vacuum residue, or so-called ‘bottoms’, is the volume of carbon byproduct, or pet coke. Conventional coking converts this residue to naphtha and diesel-range products, but also generates large quantities of low value coke.

UOP introduced a new slurry upgrading process using MicroCat catalyst. The Uniflex MC process works by thermal conversion of heavy hydrocarbons in the presence of hydrogen. The stabilised light oil products are used for fuels and as feed for petrochemical manufacturing. Uniflex MC converts more than 95% of its vacuum residue into light vacuum gasoil and distillate which are ideal feeds for an FCC or hydrocracking unit, respectively. These light feeds are more easily converted to distillates and naphtha with less energy intensity than would otherwise be required.

It can easily be integrated into existing refining facilities, and can process even high sulphur residues and highly aromatic streams such as FCC cycle oils while producing only small amounts of VGO that can be fed to an existing hydrocracker or FCC unit. This is especially consequential as the industry continues to rebalance in the wake of new MARPOL regulations on marine fuels.

Hydroprocessing developments
UOP also introduced the ULTIMet hydrotreating catalyst, an unsupported VGO pretreat catalyst, to more cost-effectively produce fuels that meet tightening quality specifications. As an unsupported catalyst, it has a higher metals content per unit of volume, making it far more active than a catalyst with an alumina binder. As a result, it improves sulphur and nitrogen removal while raising cetane levels. The catalyst is designed to work in existing units, eliminating the need to build additional reactor space or operate at higher pressures. Utilisation benefits from higher feed rates, and there are typically longer periods between catalyst changeouts. For refiners with available hydrogen, an added advantage is the volume swell the ULTIMet process provides.

Because refiners and petrochemical producers are looking for new ways to produce heavy naphtha from diesel and VGO feeds, UOP developed HC-680/682/685 hydrocracking catalysts that convert VGO, diesel, and light coker gasoil to naphtha, which can be tailored for aromatics production with the new R-364 Platforming catalyst.

Advances in alkylation
The alkylation process upgrades low value refinery butanes and olefins to a high value blend component which helps to offset combinations of gasoline pool vapour pressure, sulphur, octane, aromatic, and olefin content limitations present in today’s gasoline pool.

One of the most significant new catalysts to be introduced in the current period is the ionic liquid catalyst used in the Isoalky process for production of alkylate. The ionic liquid catalyst is far simpler to handle than conventional liquid acid catalysts. Essentially a salt in liquid state, it is far less corrosive to skin than hydrofluoric or sulphuric acids, eliminating the need for special personal protective equipment required for acid catalysts. Its low vapour pressure allows it to remain a liquid at ambient temperatures, allowing it to drop into a containment basin in the event of a leak, rather than into a vapour cloud. Due to its higher activity and on-site regeneration, far smaller inventories are required for an alkylation unit.

The Isoalky process produces a higher octane alkylate – typically 99 RON – allowing more of a lower octane blend stock to be used to produce 93-octane motor fuels. It operates at lower temperatures than conventional acids and has greater feed flexibility while producing almost no acid soluble oil byproduct. Because it can process C5 to C8 olefins, it eliminates the need for additional reactors to separate these hydrocarbons, and the steel and utilities required to operate them.

A revolution in managing catalysts
Historically, the purchase of a catalyst has been a one-time transaction, where the catalyst provider responds to a customer’s request
for a proposal with the best possible solution at that time. In the future, catalyst management will become an ongoing transaction based on the achievement of a prescribed outcome where catalyst performance is actively and continuously managed.

The catalyst supplier actively monitors unit performance through connected plant technologies, providing operational recommendations to the customer over the lifecycle of the catalyst. Optimisation recommendations are provided proactively and in real time, rather than in periodic health checks, or when a customer suspects performance problems, potentially protecting millions of dollars of production from being lost to under-performance.

While this benefits the customer, it also creates a cost for the catalyst supplier, and this demands a new payment model. Instead of merely purchasing a catalyst and managing its performance, the customer pays on the basis of performance. If the catalyst fails to meet certain performance criteria, the supplier is owed less. But if the catalyst meets – or even exceeds – those criteria, the supplier earns a portion of the additional profit.

Essentially a risk-sharing programme, it puts the supplier and the customer on the same side with fully aligned economic incentives. From the supplier’s standpoint, the more successful the customer is, the more the supplier will benefit. Conversely, if the customer suffers, the supplier will suffer equally.

This is a revolutionary paradigm in the refining industry today, but indexing cost to performance is a common model in other industries. Construction projects are guaranteed on-time completion, with late financial penalties for delays, shipments of goods are guaranteed for on-time fulfilment also with penalties for late delivery, and investment advisors are compensated on how much their clients profit from their services. In many industries, suppliers are incentivised to reduce costs by sharing a portion of the savings.

This model is most likely to demonstrate recurring economic benefits to the customer over a period of years, as new catalysts are developed and experience with them is gained. It also eliminates periodic capital expense by aligning the cost of the catalyst to production over time. Instead of simply paying for a catalyst, the customer pays only for what the catalyst does.

This model is not for everyone but, perhaps counter-intuitively, it is likely to gain traction first with sophisticated operators, or ‘optimisers’ for whom the added benefits and risk sharing are most attractive.

Michael Cleveland is Vice President and General Manager of Honeywell UOP’s refining catalysts business. He has held key positions within UOP, spanning research and development, manufacturing, and business management, and was critical in the commercialisation of new hydrocracking catalysts, isomerisation catalysts, and on-purpose propylene process technology. He holds a bachelor’s degree in chemical engineering from Michigan Technological University and is a licensed professional engineer in the States of Michigan and Illinois.

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Flawless project execution will not prevent a unit shutdown due to selecting the wrong metallurgy for a challenging crude slate.

No matter how well it is fabricated and installed, a shell and tube exchanger with cold, high viscosity vacuum resid on the tube side will have poor heat transfer performance.

On-time shipping and installation of a too-small desalter will not prevent crude column overhead corrosion if the centerline velocity is overly optimistic for the design crude.

A high labor efficiency factor for installation of tower internals will not increase vacuum resid cut point, but properly designed stripping trays will.

Managing major projects such as grassroots crude, coker, and FCC unit construction is hard work. Large revamps are even harder. In projects costing tens of millions to billions of dollars, detailed engineering and construction are monumental tasks that consume most of the overall project budget and schedule. As a project advances from a design on paper to steel on the ground, success requires relentless focus on meeting cost and schedule expectations, leading project management to seem an end in itself. However, the success of a project rests upon the foundation that is built during conceptual design and front-end engineering.

With surprising regularity, a unit’s failure to meet performance expectations does not stem from the detailed engineering and construction phases or faulty equipment manufacturing. Instead, project failure is often the result of poor front-end flow scheme design and initial process equipment specification.

A well-defined, early phase activity that consumes only a few percent of the overall project budget may seem trivial. In reality, solid front-end flow scheme development and equipment design are prerequisites for successful project execution. Rework and late stage process modifications usually reside at the top of the list of post-audit culprits in late and over budget projects.

Unit startup can quickly re-designate a project from shining success to haunting failure. Selecting a partner with an extensive experience list and a specialized understanding of the unit at hand can ensure startup goals are met while minimally impacting the overall project budget.
Boosting hydrocracker heavy feed conversion

**New pore structure in nano-engineered zeolites helps to improve conversion efficiency of heavy molecules, improving product yields and qualities**

SAL TORRISI and JOHAN DEN BREEJEN  
Shell Catalysts & Technologies

To remain competitive, refiners must continuously adapt to emerging trends or risk an undesirable performance drop. This continuous quest for improvement has driven them to process ever-more difficult feeds and advantaged crudes, to produce more and differentiated fuels and to generate valuable lubricant base oils or petrochemical products. The hydrocracker has emerged as an important unit for providing the refinery with the flexibility to adapt quickly to market changes. However, a key constraint for the unit has been in the all-important cracking reaction: specifically the ability to get larger molecules into the zeolite catalyst’s narrow micropores and quickly remove them after cracking.

As refiners increase processing severity in response to emerging requirements, the limitations of the catalytic material have diminished molecular conversion efficiency and reduced product yields. This article reveals how a new nano-engineered technology, Shell’s Molecular Access Catalysts for Hydrocracking (MACH), has unlocked this constraint and describes the opportunities this creates for refiners.

**Strategic objectives for refiners**

As the pressure on margins continues to intensify, the reality is that refiners must continue to find ways to adapt to today’s increasingly dynamic business landscape.

Many refiners are processing lower priced opportunity crudes and very heavy residue type feeds that can be extremely difficult to deal with. Others are striving to find ways to elevate the value of the product slate by moving away from bulk commodity products to more differentiated products such as lubricant base oils and petrochemicals.

And, as a consequence of the International Maritime Organization’s 2020 fuel sulphur cap and because it has a clear link with competitiveness, some refiners are striving to minimise the amount of bottoms they send to the bunker fuel pool.

For all these objectives, the hydrocracker and its catalysts are key.

**The need for an enhanced zeolite**

Almost all hydrocracking catalysts contain Y-zeolites: 3D, crystalline solids with well-defined structures and micropores that provide a high number of acidic catalytic sites for inducing cracking reactions.

In a conventional hydrocracker processing lighter feeds, the relatively small molecules can get in and out of the zeolite adequately and the cracking reaction is unrestricted. However, getting the heavier molecules in challenging feeds, or even typical vacuum gasoil (VGO) molecules, into the zeolite’s narrow micropores and quickly removing them as the processing severity increases has long been a key limitation. Any extra time that the molecules spend inside the ‘sizeable’ zeolite structure leads to over-cracking and, consequently, lower yields of liquid products and catalyst deactivation.

To address this, Shell Catalysts & Technologies sought improved materials that would offer better accessibility for larger molecules. Following a five-year research and development journey, the result is MACH, a nano-engineered technology that enables feed molecules to be converted more efficiently into high quality fuels, lubricants, and petrochemical products, which thereby helps refiners to meet the strategic objectives described above.

**Figure 1** A conventional zeolite has micropores that can constrain the molecules’ access, whereas MACH technology introduces mesopores that enhance their diffusion.

**Figure 2** A conventional Y-zeolite contains micropores (pore mouth 0.4 nm) whereas MACH technology introduces mesopores (~4 nm) that enhance their diffusion.

The transmission electron microscopy images in **Figure 2** contrast a conventional microporous Y-zeolite having a few macroporous (large port) feeder ports in the microporous Y-zeolite crystal with a MACH Y-zeolite. The MACH Y-zeolite’s...
The whole pore structure is engineered to incorporate a mesoporous arrangement that has a finely tuned pore size distribution that accommodates the largest VGO molecules better. This contrasts with other mesopore incorporation techniques that have a more random approach and yield a broader distribution.

In addition, the introduction of mesopores decreases the distance molecules need to travel between acidic and metal sites. This also helps to improve hydrogenation and, therefore, to enhance the middle distillate yield and aromatics saturation.

The MACH zeolite provides step-out performance in the conversion of VGO and heavier molecules because the molecules:

• Travel one-third the distance to reach active sites, providing improved diffusion rates via the extra entrances and exits to the cracking sites; and
• Diffuse nine times better for the largest VGO molecules (see Figure 4).

Hydrocracking catalyst portfolio
Shell Catalysts & Technologies collaborates with PQ Corporation through its Zeolyst International (Zeolyst) joint venture to create hydrocracking and specialty chemical catalysts. The two organisations worked together on the MACH research and development programme.

This relationship began in 1990. Since then, Shell Catalysts & Technologies has produced three generations of hydrocracking catalysts recognised for their stability and good balance of activity and selectivity, which result in long run lengths and slow yield declines. Key to this is the organisation’s ability to develop, synthesise and manufacture new zeolites of high quality and specific molecular design.

Figure 5 shows the full portfolio of Shell Catalysts & Technologies and Zeolyst’s hydrocracking catalysts. These have been used in more than 100 hydrocrackers, mild hydrocrackers, and distillate upgrading units around the world.

The new fourth generation products based on MACH technology have been commercialised and are available in the high selectivity structure is transformed to have a high volume of well-defined mesopores with a uniform distribution while maintaining the key features of high acidity, microporous structure, and hydrothermal stability.

In a MACH zeolite, the actual cracking reactions still take place predominantly in the microporous structure. However, the number of entry points is very much higher because of mesopore introduction. Thus, the flux of reactants and products in and out the micropores is also higher.

The cracking reaction itself is a three-step reaction in which the first and third steps happen over the metal function in the catalyst’s amorphous phase outside the zeolitic structure. The mesoporous MACH zeolite increases molecular speed to and from the metal sites that initiate and terminate the cracking reactions. Ultimately, this fosters the desired cracking reactions and reduces the likelihood of overcracking that generates undesirable light products.

Figure 3 shows the difference in the pore distributions of a conventional Y-zeolite compared with a MACH zeolite containing mesopores (the macropores are not shown).
portion of the portfolio as Z-HD27, Z-MD07, and Z-MD17. Extension of the portfolio to the higher activity space is under way and anticipated soon.

In the original premise for developing the technology, the primary economic driver was to increase valuable liquid yields such as diesel (see Figure 5). However, Shell Catalysts & Technologies discovered many additional benefits that translate into significant economic gains for each application of a MACH product in place of a conventional product. The following section describes three diverse, real-world applications of these MACH products and the multiple economic benefits they provide that can help refiners to realise the full potential of a hydrocracker and enhance overall refinery profitability.

**Case 1: enhancing middle distillate yield and product properties**

A growing number of refiners have hydrocrackers that produce multiple fuel and lubricant products. Hydrocracking can be highly profitable, especially if it is possible to maximise both the yields and product qualities simultaneously, which can be challenging.

In this example, the refiner’s key objectives were to maximise middle distillate yield and produce good quality unconverted oil (UCO) for lubricant base oil production from its series flow hydrocracker. The feedstock was heavy VGO with high ammonia and hydrogen sulphide contents in the recycle gas. The comparative testing was done at 140 bar operating pressure. MACH Z-MD17 was compared with a third generation cracking catalyst, Z-MD10, to assess the differences in performance.

MACH Z-MD17 outperformed the Z-MD10 reference catalyst with about a 1.5% higher middle distillate yield (see Figure 6), which was mainly due to the lower light naphtha and light ends production, thereby reinforcing that the new technology minimises overcracking.

The UCO product properties also improved (see Figure 7). The MACH catalyst enabled a higher viscosity index (VI) and a higher hydrogen content, which indicate that it facilitates the selective upgrading of these heavier molecules to produce high quality lubricants feedstock.

Furthermore, the additional upgrading of product yield and quality required no additional hydrogen consumption. This is a significant improvement in hydrogen utilisation and efficiency, as the higher hydrogen consumption for aromatics saturation that drives yield and product quality improvements is offset by the avoidance of hydrogen consumption through less lower value light gas production. This improved hydrogen utilisation could also enable the refiner to bring in lower quality, cheaper feeds and thus improve the overall refinery margin.

For a 50 000 b/d refinery in northwestern Europe with a three-year cycle, estimates indicate that the

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**Figure 5** The Shell Catalysts & Technologies and Zeolyst hydrocracking catalyst portfolio

**Figure 6** The middle distillate selectivity of MACH Z-MD17 was about 1.5% higher than the previous generation Z-MD10 catalyst

**Figure 7** The VI (left) and hydrogen content (right) were both higher with the MACH catalyst compared with the previous generation one
improved yield and product quality delivered by the MACH technology could improve the bottom line by $10-30 million per cycle, compared with the conventional catalyst.

Case 2: processing heavy feeds
A second European refiner had a high incentive to process deasphalted oil (DAO) as part of its solution for minimising fuel oil production. The challenge was to have an acceptable cycle length while also maintaining key product quality targets using a feed blend containing 30% DAO having a T90 of 566°C and a final boiling point of 690°C. To evaluate this opportunity, a base catalyst system containing Z-MD10 (current generation) was compared with the new MACH Z-MD17 in a series flow configuration operating at 150 barg.

Similar to Case 1, a middle distillate yield benefit of +1 wt% was observed for MACH Z-MD17. In addition, Figure 8 shows that the MACH catalyst had a lower deactivation rate. Figure 9 reinforces that observation as the spent catalyst analysis showed both lower and easier (higher H/C content) coke levels. As both catalysts were operating in a dual-barrel pilot plant reactor and at the same weighted average bed temperature and conversion, the lower deactivation rate can be attributed to a lower coking rate, related to the ability to convert more of the heavy feed coke precursors into valuable liquid products.

Lastly, higher heavy ends conversion is achieved by the MACH catalyst (see Figure 10). Thus, the large, heavy DAO molecules that have the propensity to coke in conventional catalysts can be upgraded into valuable middle distillate products by the MACH catalyst. This demonstrates that MACH technology enables step-out hydrocracking catalyst performance by providing:

- Increased middle distillate selectivity, hydrogenation, and volume swell
- Effective upgrading of hard to convert residue boiling molecules into valuable middle distillates
- Lower catalyst coking rates with heavy boiling feeds such as DAO, which improves cracking catalyst stability and cycle length.

For a 300 t/h hydrocracker operating on a two-year cycle, estimates indicate that MACH technology could improve the bottom line by up to $10 million per cycle. This is associated with its ability to upgrade more difficult feeds and generate better yields while still maintaining an acceptable cycle length.

Case 3: maximising conversion while managing heavy ends
The last case study focuses on opportunities to apply MACH catalyst in the second stage of a high conversion, two-stage hydrocracker operating at 130 barg. These units can be limited in their ability to convert the last and most refractory molecules which can sometimes build up in the recycle loop and cause product quality issues, equipment fouling, and significant increases in catalyst deactivation.

Comparing a MACH catalyst optimised for diesel production, Z-HD27, with a similar third generation catalyst, Z-HD20, in a second stage reactor during a recycle pilot plant test, clearly demonstrates the...
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When refiners use UCO recycle to either increase conversion or improve product selectivity, there is the risk that large, refractory polycyclic aromatic (PCA) molecules will build up in the recycle loop if they or their precursor molecules are not converted effectively to lighter products. Thus, cracking conversion and second stage catalyst cycle life can be negatively affected by elevated PCA concentrations.

However, the enhanced accessibility and improved hydrogenation of the MACH catalyst inhibits PCA build-up by converting these molecules more effectively into

ability to convert these most difficult molecules.

Again, the first evidence is the significantly higher heavy ends conversion (540°C+) (see Figure 11) that helped to improve the middle distillate yield.

In addition, an analysis of the various products found a significant reduction in aromatics (see Figure 12) in all the products, particularly the diesel fraction. There was also an increase in product hydrogen content and a decrease in product densities that demonstrated MACH Z-HD27’s improved hydrogenation function and its contribution to an increased volume swell of 0.6%.
lighter products. This is evidenced by the decreased olefins (a characteristic PCA molecule) content in the recycle stream (see Figure 13) which is at about half the concentration as that observed in the pilot test and in the commercial unit using Z-HD20.

For a European refiner operating a 300 t/h two-stage with recycle hydrocracker having a three-year cycle, estimates indicate that MACH technology could improve the bottom line by $10–20 million per cycle.

Conclusion
Shell Catalysts & Technologies, in collaboration with Zeolyst, has developed a new nano-engineered zeolite hydrocracking catalyst technology, MACH, featuring mesopores that enable VGO molecules and those of heavier feeds to enter it more efficiently.

Refiners can leverage MACH technology to respond to today’s strategic objectives because, compared with the previous generation products, it can:
- Provide better yield stability throughout the run and higher margins. Its improved diffusion characteristics enable the hydrocracker to produce more liquid fuels and less light naphtha/gas.
- Enable the production of lubricant base oils or petrochemicals. Its increased aromatic saturation characteristics and ring opening functionality mean the UCO will have higher hydrogen content (vital for the steam cracker) and a higher VI (essential for lubricants). In addition, it enables higher conversion capability, which means more heavy naphtha for petrochemical aromatics.
- Increase the efficient use of hydrogen for conversion for better economics.
- Help refiners to reduce fuel oil production and meet the International Maritime Organization’s 2020 fuel sulphur cap. Because MACH technology increases the conversion of heavy molecules, the UCO will have fewer heavy PCAs, which will enable the processing of feeds such as deep cut heavy VGO, heavy coker gasoil, DAO, ebullated bed products, and heavy fluidised catalytic cracking products.
- Process advantaged crudes. The ability to upgrade products beyond the ability of conventional catalysts with MACH zeolites also enables processing of more difficult or higher margin, lower quality feeds while still producing the desired products in specification.
- Increase product quality (diesel cetane number and jet smoke point) and yields. The higher hydrogenation characteristic of MACH catalyst helps to convert more aromatics, thereby improving product properties, and increasing volume swell.
- Increase the yield of premium fuels through the increased conversion of heavy molecules.

MACH technology therefore provides valuable opportunities for any hydrocracker centric refinery and could have a major impact on its bottom line. Furthermore, it is already available.

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It’s the same as Sulfiding. Right?

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Sulfiding is only part of the story.

To ensure complete activation of your entire catalyst charge, you really need precise and up-to-the-minute information on the spiking agent injection and recycle gas concentration. Without accurate and timely data, you’re simply pumping a chemical into your reactor with no assurance that the catalyst is being totally activated. This “blind” approach leads to wasted product, dangerously high H₂S levels, purging of sour gas, and emission issues from non-decomposed mercaptans.

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Pilot plant studies of hydrotreating catalysts

Studies of catalysts for hydrotreating lubricant base oil delivered similar results from conventional and high throughput pilot plants

TIAGO VILELA, GRAHAM ORMSBY, JOSÉ CASTRO and HENDRIK DATHE Avantium
ANDREW MICHAEL LEE GIBBS and MARY ANN ABNEY Ergon
PAUL ROBINSON Independent Consultant

Proposed catalyst systems for a lubricant base oil hydrotreater were evaluated with two pilot plant studies. Both studies compared two different catalyst loading schemes – System A and System B – where System A outperformed System B for hydrodesulphurisation (HDS) and hydrogenation (HDN).

One pilot plant is a conventional unit with a single reactor pilot and an available catalyst volume of above 500ml. The second is an Avantium Flowrence unit with 16 parallel single pellet string reactors (SPSRs), each of which has an internal diameter (ID) of 2.6mm and an available catalyst volume of 1.0ml. In the conventional unit, the catalyst schemes were tested one at a time, without replication, while in the Avantium Flowrence unit, the schemes were tested in parallel – at two different space velocities and in quadruplicate for increased accuracy.

The SPSRs in the Avantium unit were fitted into a commercially available Flowrence XR³ system, which ensures stable and highly accurate control of gas flow, liquid flow, and pressure across all reactors. Performance data like hydrogen consumptions and liquid product properties were determined independently per reactor. For this, the products from each SPSR were collected separately and various offline analyses performed, for instance for distillation, sulphur, nitrogen, and aromatics.

Due to the excellent hydrodynamics,¹² of the SPSR and sophisticated process control, the Avantium unit achieved high reproducibility, resulting in average deviations of less than 0.2 wtppm for HDS and HDN across the quadruple reactors with the same loading scheme.

Results from the conventional pilot plant corresponded closely to results from the Avantium pilot plant. For Catalyst System A, the relative average deviations were less than 1% for HDS and HDN. For Catalyst System B, all relative HDS deviations and two of three HDN deviations were less than 1%.

These observations indicate transitively that the Avantium unit is a suitable alternative to the conventional pilot plant for the customer’s lube oil hydrotreater. It is in fact preferable if one accounts for the advantages of high throughput technology: parallel testing, lower cost and feed amounts, and increased flexibility on testing more options. Moreover, due to the small scale of testing, safe operation can be accomplished in a laboratory setting which would be difficult to achieve with the same number of reactors at conventional scale.

This particular study considered base oil hydrotreating for a single feedstock, but Avantium equipment and methodology also can be employed to evaluate several feedstocks simultaneously. Moreover, the same technology has been used successfully to examine other fixed bed catalytic processes, including hydrocracking, hydroisomerisation, catalytic reforming, and hydroisomerisation.

Lubricant base oil classification and preparation routes

Depending on the preparation, lubricant base stocks are classified into different groups.³ Groups I, II, and III are manufactured from paraffinic crudes in refineries. They are commonly called mineral base oils or petroleum base stocks to differentiate them from synthetic base stocks, such as those prepared with polyalphaolefins (PAO, Group IV). Group V stocks include all remaining pale oils (naphthenic base oils), which are manufactured from naphthenic crudes, and other synthetic base materials (see Table 1).

The vast majority of lubricants contain Group I or II base stocks. In 1999, the National Advertising Division of the United States Better Business Bureau declared that automotive lubricants made using Group III base stocks could be labelled ‘synthetic’ due to the very severe processing conditions required to produce them, and because the performance of Group III lubricants was comparable to that provided by PAO. Table 1 compares important properties: sulphur content, satu-

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**Table 1**

<table>
<thead>
<tr>
<th>Group</th>
<th>Sulfur, wt%</th>
<th>Saturates, wt%</th>
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<tr>
<td>I</td>
<td>&gt;0.03</td>
<td>&lt;90</td>
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<tr>
<td>II</td>
<td>≤0.03</td>
<td>≥90</td>
</tr>
<tr>
<td>III</td>
<td>≤0.03</td>
<td>≥90</td>
</tr>
<tr>
<td>IV</td>
<td>All polyalphaolefins (PAOs)</td>
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</tr>
<tr>
<td>V</td>
<td>All stock not included in Groups I-IV. Includes pale oils and non-PAO synthetics</td>
<td></td>
</tr>
</tbody>
</table>

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¹¹ Comparison of lubricant base oil groups

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rates content, and viscosity index (VI) for all five major groups.

Figure 1 illustrates different routes for preparing Groups I-III base stocks; note that hydroprocessing plays at least some role in each route. Preparation of Group I base oils entails distillation to set viscosity, solvent extraction to remove aromatics and other low-VI molecules, wax removal — by extraction or crystallisation — to improve cold-flow properties, and finishing, which removes remaining impurities and improves both colour and colour stability. Preparation of Groups II and III stocks, often called premium base stocks, relies extensively on hydroprocessing where aromatics are removed with saturation, and wax is removed either with selective hydrocracking or hydroisomerisation.

‘Plus’ categories are recognised informally for marketing reasons. Group I+ has VIs from 103 to 108. Group II+ has VIs from 111 to 119. Group III+ has VIs >130 for light oils, and Group IV+ has VIs from 5 to 15 higher than conventional 1-decene.

Premium base stocks are preferred because they have:
• Lower viscosity, which increases fuel economy during cold starts and reduces engine friction
• Lower volatility, which reduces oil losses and, consequently, reduces emissions
• Improved oxidative and thermal stability
• Improved lubricant performance across a wide range of temperatures, allowing an engine to crank at sub-zero temperatures and also provide superior lubrication during high temperature operation

Hydroprocessing in lubricant feedstock conversion
Traditional solvent based lube oil plants are designed for a specific range of crude oils due to the inherent limitations of solvent extraction units. If the aromatics content of a crude oil is too high, aromatics extraction will be a bottleneck, and the distillation, dewaxing, and hydrofinishing sections of the production train will be under-utilised, resulting in a low base stock yield. On the other hand, if the wax content is too low, a wax crystalliser may not function efficiently.

Applying hydroprocessing technologies adds feedstock flexibility by increasing the practical range of crude oil properties.

Figure 2 illustrates important chemical reactions in base oil hydroprocessing. While HDS and HDN remove reactive heteroatoms, which accelerate oxidative degradation, saturation and ring opening convert low VI molecules into high VI molecules. Hydrodewaxing removes waxy n-paraffins by converting them into lighter molecules, such as diesel and naphtha constituents, over catalysts containing ZSM-5 or similar materials. Isomerisation converts n-paraffins into i-paraffins and by this removing waxy molecules.

One considers a lube stock preparation plant in which aromatics removal is accomplished by saturation, that is hydrodearomatisation (HDA). Up to a point — below the aromatics crossover temperature and with guidelines for safe operation — HDA can be increased simply by raising the average catalyst temperature in the hydroprocessing unit. The same applies if wax removal is accomplished by hydrodewaxing. Higher temperature is not necessarily beneficial in hydroisomerisation, where cracking is undesirable.

Base oil pilot plant studies
For lube base stock production, modest differences in feedstocks, catalysts, and process configuration can have a major impact on product quality. Refiners and catalyst vendors conduct pilot plant studies to ensure that changes are practical and economically viable. Relevant and scalable test data are required.
and test results from pilot plant studies should enable the reliable prediction of the performance of commercial scale units.

Conventional hydroprocessing pilot plant studies are relatively expensive to build and operate. They employ relatively large reactors, typically with an inside diameter (ID) ranging from 1.2-2.5cm and a catalyst bed length of 30-80cm. Consequently, it becomes impractical to evaluate more than a few alternative catalyst loading schemes or different sets of process conditions within a given time frame. Moreover, replicate tests are seldom even considered, which makes these tests simply spot measurements of catalyst activity.

Regardless of size, pilot plant reactors have inherent limitations for testing catalysts with commercial sizes and shapes. To compensate for channeling, wall effects, and back mixing, catalysts are diluted with non-porous inert particles of suitable size. The impact of diluent size has been identified experimentally. Even with a suitable diluent, reactors must be carefully packed to ensure even flow of fluids through the bed, to approximate plug-flow behaviour.

It is intuitive to expect that larger reactors are less susceptible to size-related limitations. However, recent research by Moonen et al. shows that SPSRs are no more susceptible to wall effects, channeling, and back mixing than properly utilised bench-scale reactors. With experiments, they showed an excellent correspondence for gasoil HDS between an Avantium SPSR unit and a bench-scale unit with a catalyst volume of 225ml – more than 300 times more than the volume of an SPSR. This particular study looked at base oil hydro treating – specifically HDS, HDN, and HDA. It is also possible to apply high throughput pilot plant equipment and methodology to other base oil processes, including hydrocracking, hydro de waxing, catalytic reforming, and hydroisomerisation.

Advantages of single pellet string reactors

SPSR units have many advantages. They require far less catalyst and feed. They provide excellent temperature control and reproducible reactor loading due to the fact that the diameter of the extrudates is just slightly smaller than the reactor diameter. In addition, extrudates automatically align as a string of extrudates (see Figure 3) which, in combination with the narrow reactor, avoids maldistribution of gas and liquid over the catalyst bed, thereby eliminating catalyst bed channeling and incomplete catalyst wetting. When an inert diluent is used, it can be introduced after catalyst pellets are loaded over the full length of the tube, resulting in embedded extrudates while not going between them.

Due to the size and feedstock consumption of such small-scale reactor systems, it becomes feasible to implement these in a compact platform while still being able to operate under relevant conditions. This enables not only testing of multiple options under identical conditions, but also allows true replication of tests. This increases data quality and allows the estimation of

Figure 3 Extrudates automatically line up in a string when loaded into a single pellet string reactor

Figure 4 Schematic representation of the Avantium pilot plant with 16 parallel SPSRs

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confidence intervals, thus improving over the more common ‘single point’ tests.

Experimental

Purpose

The primary aim of this experiment was to evaluate two catalyst systems for a commercial lubricant base oil hydrotreater. A secondary aim was to compare the performance of a single reactor conventional pilot plant with an Avantium pilot plant system employing 16 SPSRs.

Equipment, feedstock and reactor loading

Figure 4 presents an overview of the Avantium Flowrence XR unit. Hydrogen feed gas was equally distributed to 16 reactors, and the pressure of each channel was measured before and after the catalyst bed by using electronic pressure sensors. Based on these measurements, the reactor pressures were individually controlled to ensure equal process conditions. The oil feed (see properties in Table 2) was uniformly distributed to all 16 channels. The exact liquid flow rate of each of the individual liquid feed lines was measured and actively controlled to ensure even distribution of the oil feed to each of the reactors within 0.5% relative standard deviation between the reactors. When necessary for sulphiding or passivation, the feed can be dosed with additives from a separate pump.

The SPSRs are made of a stainless steel tube with 2.6mm inside diameter, a maximum catalyst bed volume of 1.0ml, and 560mm length including a conditioning zone at the top of the reactor.

As mentioned above, the loaded extrudates automatically aligned as a string of extrudates (see Figure 3), and porous ceramic beads with diameters of 0.07mm were used to embed them.

The reactor tubes were inserted into four separate isothermal heating blocks. Each reactor block was loaded with four reactor tubes which can be operated at the same temperature without impact on any other block. All process control data were recorded per reactor while liquid products were collected in separate sample vials for 12 reaction conditions (2 catalyst systems * 3 temperatures * 2 LHSVs). Online gas chromatography was used to analyse and quantify the light gas content.

In both studies, two catalyst configurations were tested: System A and System B. The commercial catalysts were loaded to match the recommendations of the catalyst vendors. Note that for each condition catalysts were loaded in quadruplicate. Total catalyst volume was varied to achieve the low and high desired LHSV.

Experimental protocol

The experimental protocol is summarised in Figure 5 and is based on customer requirements. The first step is sulphidation to convert the catalyst (typically metal oxides supported on a high surface area Al2O3) into sulphides via reactions with hydrogen and H2S. For this study, a liquid activation was chosen, where the H2S for sulphiding comes from organic sulphur compounds in feedstocks augmented by dimethyldisulphide (DMDS) or butyl sulphides such as Lubrizol’s SulphrZol 54.

In this case, for sulphiding the test feedstock was spiked with sufficient DMDS to bring the sulphur concentration to 2.0 wt%. The reactor pressure (hydrogen partial pressure) was maintained constant in a moderate-to-high range. Temperatures were as specified by the catalyst vendor.

During the 14-day catalyst conditioning phase, normal test feed passed through the reactors under vendor specified conditions. At the end of the conditioning phase came three successive periods of line out (24 hours) at a given temperature followed by liquid product collection (88 hours) at that temperature. Compositions of gaseous products were determined online. Liquid effluent was collected at each condition for fractionation and analysis. Daily sulphur and nitrogen analyses were performed to track HDS and HDN activity.

Customer’s single reactor experimental protocol

The customer’s conventional single reactor protocol is very similar to the Avantium unit, differing in the number of parallel reactors, scale of testing/volume processing, and process complexity. Like in the

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Table 2

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</table>

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Avantium unit, the first step is sulphidation to convert the catalyst (metal oxides supported on a high surface area Al₂O₃) into sulphides via reactions with hydrogen and H₂S. For this study, a liquid activation was chosen, where the H₂S for sulphiding come from organic sulphur compounds in feedstocks augmented by dimethyl disulphide (DMDS) or butyl sulphides such as Lubrizol’s SulphrZol 54.

In this case, for sulphiding the test feedstock was spiked with sufficient SulphrZol 54 to increase the sulphur concentration. The reactor pressure (hydrogen partial pressure) was moderate-to-high, while temperatures were as specified by the catalyst vendor.

During the 14-day catalyst conditioning phase, normal test feed passed through the reactors under customer specified conditions. At the end of the conditioning phase came three successive periods of line out at a given temperature followed by liquid product collection at that temperature. Liquid effluent was collected at each condition for further product analysis.

Results and discussion
Temperature and pressure
Figure 6 presents the time on stream, temperatures, and pressures used for the experiment. Note the ramp to a peak temperature during the second stage of sulphiding. All temperatures were controlled within 0.5°C while maintaining target inlet pressure.

Figure 7 presents the box plot of the inlet reactor pressure per reactor. As mentioned above, each reactor pressure was actively controlled using Avantium’s proprietary reactor pressure control (RPC) technology, leading to a bandwidth within +/-0.01 bar across all 16 reactors.

Material balance
Figure 8 depicts the mass balances for all 16 reactors separated by the catalyst system with a more detailed statistical analysis in Figure 9. The average mass balance obtained was 99.5% with 95% of the data falling within a range of +/-1.5% (please note that two reactors have some minor outliers), which indicates that lube oils such as this can be controlled and distributed evenly over all 16 reactors using Avantium’s advanced liquid distribution (ALD) technology.

Hydrogen consumption
Figure 10 shows the hydrogen consumption data for all 16 reactors. The values are based on online gas chromatography measurement. The colours correspond to the different LHSV’s applied while the green line shows the temperature profile applied. The data show that H₂ consumption increases with temperature and decreases with LHSV,
which is consistent with the expectations. H₂ consumption is higher for catalyst System B compared to System A, which could indicate a higher activity for HDS, HDN, and HDA. Note the very high H₂ consumption for catalyst System B at the peak sulphiding temperature.

It is important to note that samples were measured in quadruplicates for statistical purposes. The average bandwidth is well within +/-20 scf/bbl, indicating very good reproducibility.

Sulphur and nitrogen removal
Liquid samples were collected and analysed offline. As mentioned, 12 composite samples were produced (2 catalyst systems * 3 temperatures

"2 LHSVs). An example is shown in Figure 11 where the lighter colour is observed at higher severity, which corresponds to greater HDS and HDA. Please note that the composites were analysed by the customer for different properties such as distillation, aromatics, and delta aniline point.

Sulphur and nitrogen in the liquid products were analysed daily and used to calculate percent HDS and HDN (see Figures 12 and 13). Expected trends are observed: sulphur and nitrogen removal increases with increasing temperature and at lower LHSV. The observed values for conversion are in line with client results from the conventional pilot plant.

It is important to note that the high discriminatory power of Avantium’s reactor technology can also be observed in the HDS activity shown in Figure 14. For catalyst System B, at the highest temperature the conversion at high LHSV is 99%, whereas at the low LHSV it is 99.999%. Moreover, reproducibility between the quadruples is excellent and consistent with the perfect hydrodynamic achieved in the unit. Please note that the HDN activity shows a similar result.

Comparison of results with the customer’s single reactor unit
The customer executed a similar study on a larger scale without duplications. Figures 15 and 16 show a comparison of the results from these tests and indicate that results from the Avantium unit are in line with client data obtained from much larger scale reactors. Results from the two pilot plants corresponded closely. For catalyst System A, average deviations were less than 1% for HDS and HDN. For catalyst System B, all HDS deviations and two of three HDN deviations were less than 1%.

Conclusions
Two catalyst loading schemes were evaluated for a change-out in a commercial lubricant base oil hydrotreater. The tests were executed in a unit with single pellet string reactors (SPSRs) from Avantium as well as in a conven-
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Figure 12 %HDS in dependence of time on stream. The blue line represents the high LHSV while the red one the low LHSV. The green line represents the temperature pattern applied.

Figure 13 %HDN in dependence of time on stream. The blue line represents the high LHSV while the red one the low LHSV. The green line represents the temperature pattern applied.

Figure 14 Statistical analysis of HDS capacity at the three selected temperature levels measured.

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Resid to propylene: the two-step approach

For maximum propylene from the FCC unit, refiners should customise their catalyst for properties best suited to deep conversion that can handle residue feeds

MELISSA CLOUGH MASTRY, HERNANDO SALGADO, Baha Eren and Wei Sheun Gan
BASF

The fluid catalytic cracker (FCC) remains one of the most important conversion units within a refinery for the generation of transportation fuels (i.e. gasoline and diesel precursors). However, in certain markets, especially where integration between refineries and petrochemical plants is high, there is great incentive to maximise propylene over other products, including gasoline. In these regions, mainly in Asia and the Middle East, the financial incentive of propylene over gasoline and other liquid products is clear and is driving many of the new project builds. Furthermore, new hardware technologies are advancing, including new unit designs. For these reasons, catalyst technologies must also contribute to advancements in this field.

Catalyst technologies and performance are monitored on a weekly basis from most refineries in the world. The performance can be compiled over many years to demonstrate trends in FCC. Historical equilibrium catalyst (Ecat) yields demonstrate an upward global trend in propylene, particularly in the Asia, EMEA, and Latin American regions (see Figure 1). This trend supports further utilisation of the FCC that will produce propylene from resid reliant regions and how important it is to design an optimal catalyst.

The FCC utilises a fluidised solid catalyst to crack oils into valuable products. The main contributor of catalyst activity is the zeolite Y, an important ingredient in all FCC catalysts. The zeolite Y is critical for generating a mix of products, including LPG olefins, naphtha (a gasoline precursor), and light cycle oil (a diesel precursor). Most FCC catalyst manufacturers employ ultra-stable zeolite Y, or USY, an outcome of careful calcination in the manufacturing process. A second and important zeolite in the maximum propylene FCC is ZSM-5. ZSM-5 is a very shape selective zeolite, capable of cracking near-linear naphtha range olefins. For this reason, ZSM-5 is very selective and cracks mainly C5-C9 linear or near-linear olefins. Without these temporary precursors in the FCC reaction, the ZSM-5 would contribute nothing to the FCC process. Therefore, the balance of high activity USY zeolite and ZSM-5 zeolite is critical. For example, with too much ZSM-5 in the FCC system, one might dilute the USY, penalising catalyst activity to an extent that there no longer remain C5-C9 linear or near-linear olefins for the ZSM-5 to crack.

Furthermore, for resid FCC applications there are additional challenges. For instance, resid feeds bring contaminant metals that can disrupt the FCC process, either catalytically or through the generation of unwanted byproducts. The most critical contaminants that come in with resid feeds include vanadium (V), nickel (Ni), sodium (Na), and iron (Fe). Vanadium is well known to destroy USY within an FCC catalyst, attacking the Si-O bonds and resulting in zeolite collapse. Ultimately, this leads to a loss in catalyst activity and thus will result in lower conversion, with all things constant. Lower conversion means lower naphtha, lower feed for the ZSM-5 zeolite, and ultimately lower propylene. Nickel, on the other hand, operates with a very different mechanism. Instead of destroying catalyst activity, nickel promotes dehydrogenation side reactions. Nickel is a very strong dehydrogenation agent, and thus will result in the generation of H2 and coke, two byproducts that are unwanted in resid applications. Higher H2 means higher loading on the wet gas compressor, which can often be a constraint for FCC units.

Figure 1 Historical Ecat propylene yield trend; EMEA: Europe, Middle East, and Africa; NA: North America; LA: Latin America
Higher coke generation means lower generation of other valuable products, including naphtha and LPG.

Sodium is a very detrimental contaminant and much like other alkali and alkaline earth metals will work to neutralise the acid sites on USY with the positive charge. This immediately and irreversibly results in a loss in catalyst activity, with results similar to those of V poisoning. However, it takes very little Na contamination to see an effect on activity, so keeping Na out of the FCC unit is critical.

The last contaminant on the list is iron. Iron deposition occurs on the outside surface of the catalyst and in some cases can lead to pore blockage, acting as a physical barrier between feed and the important USY cracking sites. This too will lead to a loss in conversion on the FCC unit, resulting in lower naphtha and ultimately lower propylene.

In most cases, the deposition of contaminant metals occurs on the active catalyst itself (containing USY), and not on the ZSM-5 material. For this reason, the focus of contaminant metals technology should be on the base catalyst.

As a result of the very well understood mechanisms of USY cracking, ZSM-5 cracking, and metal contamination pathways, the science behind maximising propylene from resid feed to propylene product, the main contaminants and their effects in the USY catalyst system, the catalytic solutions to mitigate contaminants, and strategies to maximise propylene by ZSM-5 cracking. Thereafter, case studies are offered to demonstrate a two-step approach for propylene maximisation. These cases will further highlight the fact that, for each refinery, there exists a different solution for propylene maximisation, which highlights the need for a highly customised approach at every refinery.

**Catalytic cracking mechanisms**

**First step: primary cracking using Y-zeolite**

Catalytic cracking on USY zeolite is a complex process with multiple reactions occurring on the zeolitic acid sites, under the well accepted mechanism of carbenium and carbonium ion formation plus β-scission, leading to smaller molecules compared to molecules in the feed. A simplistic approximation of these primary reactions is shown in Figure 2.

Other secondary reactions such as hydrogen transfer and isomerisation also take place, affecting the quality of the products in terms of paraffins, olefins, and aromatics content. Since the catalytic cracking process was originally developed to convert VGO into gasoline through reactions 1, 2, and 3, most olefins are in the range 6 to 12 carbon atoms. Reaction 4 yields aromatic compounds containing two, three, or more rings in addition to small olefins and coke. Although β-scission can yield LPG molecules by itself, including propylene, due to the unit cell size of the Y-zeolite and contact time, most products from reactions 1, 2, and 3 are within the range of gasoline.

In this first step, the matrix also plays an important role, providing cracking of the biggest feed molecules and accessibility to the acid sites of the zeolite to maximise bottoms cracking and naphtha yield. Matrix, in addition to other important parameters such as metals passivation, imparts important physical characteristics to the catalyst architecture by defining the pore network connectivity.

**Second step: secondary cracking of naphtha to smaller molecules**

The lighter range gasoline molecules, from 6 to 9 carbons, coming from cracking on Y-zeolite or matrix can further crack in a secondary set of reactions to be converted into smaller molecules, including propylene. However, a different active zeolite with smaller pore openings is required: the ZSM-5 zeolite. An added advantage of the secondary reactions comes from the fact that linear olefins are more reactive, leaving highly branched olefins and paraffins in the gasoline fraction, thus improving its octane number.

The two steps are shown in Figure 3. After introducing the two-step approach, with propylene being produced in both steps, it is clear that more light naphtha produced in the first step (feed cracking over Y-zeolite) leads to higher potential for more propylene in the second step (naphtha cracking over ZSM-5). Therefore, one of the key factors is how to maximise naphtha in the first step, which is more challenging when the feed contains residue streams such as demetalised oil, atmospheric residue, or vacuum residue.

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**Figure 2 Main cracking reactions on Y-zeolite**

The following sections are dedicated to explanation of the cracking mechanisms from resid feed to propylene product, the main contaminants and their effects in the USY catalyst system, the catalytic solutions to mitigate contaminants, and strategies to maximise propylene by ZSM-5 cracking. Thereafter, case studies are offered to demonstrate a two-step approach for propylene maximisation. These cases will further highlight the fact that, for each refinery, there exists a different solution for propylene maximisation, which highlights the need for a highly customised approach at every refinery.

**Figure 3 The two-step approach to produce light olefins in an FCC**

---

**Table 1 Paraffins + Olefins**

1. Paraffins + Olefins
2. Olefins + Olefins
3. Naphthenes + Olefins
4. Aromatics + Olefins

**Figure 3** The two-step approach to produce light olefins in an FCC.
Challenges of cracking residue feeds

The main challenges to cracking residual feeds are their high content of carbon residue (measured as Conradson carbon or Concarbon, Micro Carbon or Ramsbottom Carbon), and Ni, V, Na and Fe.

The heat balance in an FCC unit is highly sensitive to the concentration of carbon residue or asphaltenes in the feed. Although the catalyst can help to minimise coke selectivity in several ways, most of the heat balance effects need to be addressed from the hardware point of view through solutions including minimising coke formation during feed injection (feed nozzle design), minimising thermal cracking (riser termination design), improving the stripping of heavy hydrocarbons in the circulating catalyst (stripper design), or removing heat from the regenerator through flexible catalyst coolers.

On the other hand, catalyst technology plays a major role in dealing with metallic contaminants. This will be addressed in the following sections.

Controlling the effects of nickel

Metals are present in the heaviest feed molecules, especially in asphaltene molecules or porphyrins. Ni is a hydrogenation catalyst widely used for hydrotreating applications, however under typical FCC conditions (low pressures and high temperatures) it behaves as a dehydrogenation agent, promoting hydrogen and coke formation (see Figure 4).

Ni deposits on the outer region of the catalyst surface, generally on the matrix. Ni is immobile once deposited and becomes deactivated over time. However, the presence of chlorides in the FCC environment can promote its reactivation.

Conventional Ni-trapping technologies are based on the use of specialty aluminas. The effectiveness of these technologies will depend on the alumina used and its dispersion characteristics, among other factors. A novel approach called Boron Based Technology (BBT) can also be employed. With BBT, a higher portion of contaminant Ni is kept in an electron-deficient state under FCC conditions, essentially providing a higher passivation efficiency and lowering unwanted dehydrogenation activity. In addition, boron does not induce NOx emissions as antimony injection (another common Ni-passivation strategy) does.

Controlling the effects of vanadium

Vanadium is also present in asphaltene molecules or porphyrins but, unlike Ni, it is mobile under typical FCC conditions and can migrate to the active sites on the zeolite (see Figure 5). Although it is also a mild dehydrogenation agent (with activity about 25% that of Ni), its major effect is on zeolite activity. In combination with Na and steam at high temperatures, V forms acidic compounds (sodium vanadates) that destroy the zeolite framework, decreasing catalyst activity. Therefore, sodium needs to be avoided when processing residue feeds which are highly contaminated with vanadium. Furthermore, a less active catalyst will lead to more thermal cracking over catalytic cracking, promoting coke making reactions.

To combat the effect of vanadium, effort should be focused on keeping Na out of the FCC. This can be done through efficient desalting operations, also the amount of sodium in the fresh catalyst should be minimised. For example, depending on the catalyst manufacturing technique, fresh sodium content can be as low as 0.15 wt%, or as high as 0.35 wt%. In addition, vanadium passivation technologies can be employed. Technologies are available which react with V and render it immobile and inactive through various chemical reactions. One aspect of vanadium passivation technology is its sulphur tolerance; thus employing a vanadium passivation technology that is tolerant to sulphur such as the novel Valor technology will give the best protection against contaminant vanadium.

Understanding the role of iron

Like Na, Fe can be present in fresh FCC catalyst since it is present in raw
In the second step, the catalytic properties of the ZSM-5 material are also important. The ZSM-5 material is ideal to deal with added Fe to prevent pore blockage due to the different forms of Fe deposition. Other effects of Fe include: 1) changes in average bulk density (ABD), which can affect fluidisation and circulation; 2) mild dehydrogenation, leading to higher hydrogen and coke; and 3) increased SOx emissions, acting as an inverse SOx additive.

The full pathway from resid to propylene: the two-step approach
Summarising the proposed approach (see Figure 7) to convert residue feeds to propylene, from the catalytic point of view the first step is tolerance to metal contaminants, especially metals including Ni, V, Na, and Fe. Coke selectivity characteristics are also important to minimise coke yields and therefore minimise heat balance effects.

In addition to metals tolerance and coke selectivity, bottoms conversion to gasoline (the propylene precursor in the second step) and rare earth hydrogen transfer reactions are also important catalytic characteristics to be considered.

In the second step, besides the catalytic properties of the ZSM-5 material, the reaction severity needs to be carefully defined since too high severity might increase thermal cracking and therefore over-cracking of naphtha to dry gas.

Case studies
Because the answer to each resid FCC unit’s maximum propylene approach is different, case studies are provided to demonstrate the multitude of challenges and approaches.

Figure 6 Ecat particle with 0.68 wt% added iron

Case 1: resid FCC struggling with delta coke
A refinery in the Asia Pacific region was struggling with delta coke and was looking to further maximise propylene from the FCC unit. This refinery historically runs feeds with a CCR content of up to 4.5 wt%. The FCC unit used external ZSM-5 and processed resid feeds that contributed to the refinery’s challenges by introducing contaminant metals and high Concarbon content. To aid decision-making, this refinery network underwent an extensive catalytic selection process that included catalyst testing in a pilot plant. The pilot plant and modelling results suggested that a change in the base catalyst could provide the benefits described above. For the best ‘apples to apples’ comparison, the trial plan included maintaining the same external ZSM-5 additions to focus on changing the base catalyst itself. To minimise risk in switching from a non-BASF catalyst to the BASF resid catalyst technology, an extensive trial plan was jointly prepared between the refinery, the central corporate group, and BASF. The trial plan included multiple mitigation steps, a common practice for BASF to help refineries minimise risk when opting for higher profit yielding solutions. The trial went as planned, with delta coke benefits being a step-out performance indicator, leading to high propylene selectivity (see Figure 8). The BASF resid technology focused on mitigating the contaminant metals effects (Ni, V, Na, Fe) while delivering high catalyst activity. As a result, the refinery saw higher product yields at constant ZSM-5 additions. The analysis done for this catalyst change resulted in an annual economic benefit of approximately $5.5 million for the refinery, driven through coke selectivity.

Case 2: resid FCC defines turnaround objectives to increase CCR capacity
This refinery’s objective was to process more and heavier resid feeds while maintaining propylene. The FCC, prior to the turnaround, was processing feed CCR of around 4 wt%. After the turnaround, the refinery introduced new resid streams into the FCC, with caution. Knowing

Figure 7 Main considerations in the two-step approach to maximising light olefins
that the resid streams contained higher amounts of metals (including Ca, Fe, Ni, Na), the streams also contained higher basic nitrogen, which deactivates FCC catalysts in a reversible way. The resid streams also introduced new chemistry into the FCC unit by delivering higher aromatics. Despite this, the refinery continued to push resid into the FCC unit while maintaining the maximum feed rate target.

Ultimately, the refinery reached a new record for feed CCR processing, with values nearing 7 wt%. At the same time, the catalyst pre- and post-turnaround was kept consistent. The BoroCat catalyst was designed to withstand big swings in feed metals and to maintain activity despite the introduction of deleterious poisons. Because of this, catalyst activity before and after the turnaround was maintained, allowing for the formation of sufficient gasoline olefin precursors for ZSM-5. The amount of ZSM-5 before and after the turnaround did increase from 4.5% to 5.2%, but the response in propylene was phenomenal. The refinery reached a maximum propylene processing limit of around 7 wt% due to a hydraulic limit design for propylene recovery. These results are shown in Table 1 and Figure 8.

9. Despite the heavier feed with higher CCR and metals, the catalyst addition rate per unit of feed was maintained before and after the turnaround.

This turnaround, and the introduction of new and heavier feeds, has changed the way the refinery operates and has defined new operating limits around feed CCR and what is possible with LPG generation from the FCC. With the change in operating window and the new limits that the refinery reached after the turnaround, in combination with a flexible catalyst, this resulted in improved profitability for the refinery.

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Table 1: Post- vs pre-turnaround conditions

<table>
<thead>
<tr>
<th>Feed rate, t/d</th>
<th>Change, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed basic N</td>
<td>11.6</td>
</tr>
<tr>
<td>Feed Ca</td>
<td>29.7</td>
</tr>
<tr>
<td>Feed density (15°C)</td>
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</tr>
<tr>
<td>Feed di-aromatics</td>
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</tr>
<tr>
<td>Feed Fe</td>
<td>168.1</td>
</tr>
<tr>
<td>Feed Ni</td>
<td>-14.9</td>
</tr>
<tr>
<td>Feed Na</td>
<td>43.7</td>
</tr>
<tr>
<td>CO, vol%</td>
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</tr>
<tr>
<td>ROT, °C</td>
<td>0.0</td>
</tr>
<tr>
<td>Regen bed, °C</td>
<td>-0.1</td>
</tr>
<tr>
<td>Cat cooler duty, MW</td>
<td>-17.1</td>
</tr>
</tbody>
</table>

Figure 8 Post audit results of a catalyst trial leading to lower delta coke and higher propylene selectivity

Case 3: resid FCC looking to optimise catalyst solution

This refinery’s main objective was to maximise propylene while processing heavier resid feeds. The FCC utilises BASF’s MPS catalyst, which has high activity and high selectivity towards propylene. A combination of in situ manufacturing technology and the use of Valor vanadium passivation technology allowed the use of a lower rare earth catalyst to boost propylene selectivity. The FCC was processing feed CCR of around 2.8 wt%, which increased to 4 wt% during the trial. At the same time, the feed got much heavier and API decreased from 24.0 to 21.4. Feed vanadium more than doubled from 2.5 ppm to 5.4 ppm. Despite the heavier feed with higher CCR and metals, the catalyst addition rate per unit of feed was maintained.

This turnaround, and the introduction of new and heavier feeds, has changed the way the refinery operates and has defined new operating limits around feed CCR and what is possible with LPG generation from the FCC. With the change in operating window and the new limits that the refinery reached after the turnaround, in combination with a flexible catalyst, this resulted in improved profitability for the refinery.

Table 2: Feed CCR and FCCU propylene yields before and after turnaround

<table>
<thead>
<tr>
<th>Date</th>
<th>Refinery’s new max feed CCR</th>
<th>Date</th>
<th>Propylene, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turnaround</td>
<td>7.8</td>
<td>Turnaround</td>
<td>8.0</td>
</tr>
<tr>
<td>2.8</td>
<td></td>
<td>3.4</td>
<td>Max C₃ yield limit</td>
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<td>5.8</td>
<td></td>
<td>5.0</td>
<td>ZSM-5 content</td>
</tr>
<tr>
<td>4.8</td>
<td></td>
<td>4.5%</td>
<td>4.5%</td>
</tr>
<tr>
<td>6.8</td>
<td></td>
<td>5.2%</td>
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<td></td>
<td>7.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

These results are demonstrated in Table 2 and Figure 10. No external ZSM-5 was added before or during the trial.
Conclusions
Refiners who seek to reap the financial incentives of maximising their propylene yields from resid feeds are primarily located in Asia and the Middle East. These emerging markets and developing regions have created an environment for a high demand for propylene, where many of the refineries and petrochemical plants are integrated. While most propylene demand will be met by steam cracking, a significant portion of propylene demand can be fulfilled through optimising the FCC.

Several challenges exist for the FCC to produce the optimal yield slate needed by the refinery. A few of those challenges include: operating within primary constraints, optimal catalytic properties for deep conversion, and finally cracking residue feeds. Refiners should seek to increase their severity, activity, and cat-to-oil ratio for optimal propylene production. However, operational improvements are limited to a narrow window of optimisation, often limited to downstream capabilities. Ultimately, refiners should resort to customising their catalyst solution for properties that are suited to deep conversion and are capable of handling residual feeds.

BASF catalyst solutions for achieving maximum propylene yields have several characteristics which aid in the two-step process in accomplishing the optimum yield pattern and hence economic optimisation of FCC units.

The catalyst must be metals tolerant in order to prevent activity and conversion loss due to the increased vanadium, iron, and sodium found in residual feeds. Maintaining and improving coke selectivity allows for more flexibility in the heat balance around the unit and minimises impacts from feed effects. Protecting against dehydrogenation effects from nickel will give the flexibility needed in the downstream wet gas compressor and will give a more profitable yield structure.

Increasing bottoms conversion is necessary to produce more light naphtha which is the precursor for propylene. Improving bottoms conversion relies on optimal hydrogen transfer characteristics and zeolite acidity topology. Additionally, ZSM-5 must be attrition resistant and offer high activity in order to be effective in cracking.

In each of the cases cited, BASF proposed tailored resid catalyst solutions to minimise operational risk when processing residue feeds to maximise unit profitability. In each case, the solution for maximum propylene was different. In one, delta coke was the key. In the second, a flexible catalyst that could handle increases in metals and high CCR was needed. In the third, a complete catalyst solution was needed to overhaul the operation. Through understanding the two-step solution in resid processing, BASF successfully increased propylene yields in several resid environments that pose a variety of unique challenges and has shown improved annual profitability in one example of over $5 million.

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The fluidised catalytic cracking unit is a highly complex multivariable operation. The conversion of feed to petrochemical feedstocks and/or motor fuels is primarily a function of feed quality, independent operating parameters, and catalyst composition. Perhaps the single most powerful tool for understanding unit performance is the equilibrium catalyst analysis provided by catalyst vendors.

The intent of this article is to provide the process engineer with advanced Ecat analysis techniques to assist in understanding unit performance. These techniques span the range from measuring the resistance to mass transfer in the catalyst circulating inventory to analysing the subtle shifts in catalyst composition imparting measurable impacts on yield selectivities.

Catalyst diffusion

The ability of FCC catalyst to diffuse high molecular weight, sterically hindered molecules into the catalyst particle has been debated and marketed by catalyst suppliers for decades. This article offers no claim that one catalyst technology is superior to other technologies. It is expected that each refiner has selected the best available catalyst for their feed slate, providing the desired product slate. The focus is to assist the FCC operator to understand where an inflection point may exist in their operation at which point a barrier to mass transfer into the catalyst is measurable.

The simplest technique is to plot the slurry yield vs total equilibrium metals. Total metals include nickel, vanadium, sodium, iron, and calcium. The highest accuracy will be achieved by calculating the ‘add-on’ sodium and iron as both sodium and iron are present in the fresh catalyst. However, since the concentration of these elements in fresh catalyst is consistent between batches, the error incorporated by using total sodium and iron is systematic and may be ignored.

As the amount of contaminant metals increases on the Ecat particles, a barrier to mass transfer builds in the form of a crust. The more sterically hindered feed molecules will not be able to access the particle pore structure as the thickness of this crust increases, resulting in an increase in slurry yield. Cross plotting slurry yield vs total metals provides a simple indication of where this barrier begins for your feedstock and catalyst technology. In general, the author has observed that the inflection point is frequently observed at approximately 10 000-12 000 ppm for most units.

Refiner #1 has a typical metal loading of 13 000-15000 ppm total metals. The data demonstrate a significant step change increase to
28 000 ppm metals beginning at day 600 (see Figure 1). Figure 2 presents the response of slurry yield to the typical metals level observed in the first portion of the curve from day 0 to about day 600. The slurry yield increases by approximately 2.0 wt% for every 1000 ppm increase in contaminant metals. An inflection point appears at approximately 15 000 ppm. Figure 3 presents the slurry response for the peak observed beginning at day 600. It is interesting to note that a clear inflection point occurs with this feedstock at approximately 21 000 ppm.

Feed quality shifts
Approximately 75% of all yield selectivity shifts are the result of feed quality variation for most units not involved in a catalyst change-out. The two simplest methods to determine the root cause of the yield selectivity shift resulting from feed quality variation is the direct measurement of feed quality and monitoring the Ecat nickel-to-vanadium (Ni-to-V) ratio. Feed quality parameters include density, nitrogen, CCR, UOP K, and so on.

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The catalyst circulating inventory is very sensitive to feed quality shifts. The simplest measurement available to the process engineer to monitor subtle changes in feed quality and correlates well with many yield selectivities such as conversion, gasoline, and slurry. Figure 4 demonstrates that the typical Ni-to-V ratio for Refiner #2 is from 1.0-1.4. However, beginning at approximately day 95, a lower density feed slate was processed in the unit (dark red data points). Figure 5 indicates the normal response of conversion to the Ni-to-V ratio. The lighter feedstock clearly does not follow the same response curve as observed with the refiner’s more typical feeds.

Please note that each unit responds differently to changes in the Ni-to-V ratio. It is essential that the process engineer determines the response, if any, to the typical variation in their unit.
Fresh catalyst composition

Fresh catalyst composition is critical to optimal conversion with desired yield selectivities. However, the fresh catalyst certificate of analysis (COA) often contains limited data, making detailed catalyst quality analysis difficult. It is recommended that the process engineer correlates key Ecatty properties and ratios vs important yield selectivities.

For refiners targeting maximum light olefin yield, it is recommended to plot propylene yield or propylene olefinicity vs Ecatty sodium. For additional yields, the engineer is recommended to plot the desired yield vs the Ecatty zeolite-to-matrix (Z-to-M) ratio. As with all analyses, it is important to verify each unit’s response to these variable shifts. Not all units respond alike. It is also suggested that the refiner negotiate tighter upper and lower limits for those units whose yield selectivities are sensitive to catalyst composition.

Figures 6 and 7 demonstrate the gasoline yield response of Refiner #3 to normal variations in the equilibrium catalyst Z-to-M ratio. It is important to note the degree of gasoline yield variation in this period of normal operations. Analyses such as these enable the FCC operator to understand the root cause in ‘typical’ yield variation or scatter.

Catalyst stability

The engineer is encouraged to monitor the Z-to-M ratio as an indicator of catalyst stability. A decreasing trend in the Z-to-M ratio that is not correlated to decreased catalyst additions but is correlated to an anticipated long-term increase in regenerator temperature or equilibrium catalyst metals is encouraged to discuss potential catalyst reformulation with their catalyst supplier.

As the regenerator increases in temperature, the hydrothermal deactivation of the catalyst increases. The zeolite portion of the catalyst is much more sensitive to regenerator temperature than the active alumina, resulting in dealumination of the zeolite crystal structure. This loss in activity leads to increased slurry yield. The process engineer is encouraged to evaluate the effect of regenerator temperature effects on Z-to-M and yield selectivity on their unit.

Catalyst attrition resistance

The refiner is recommended to regularly monitor and record catalyst fines for surface area and metals content. An increase in Ecatty fines surface area combined with a decrease in total metals is an indicator of softer catalyst. An increase in catalyst fines production not demonstrating increased surface area or decreased metals is an indicator of a new attrition source in the unit. Please note that reports of soft catalyst by any catalyst manufacturer is very rare.

Cyclone mechanical integrity

It is strongly recommended that regular catalyst fines samples be
acquired and measured for particle size distribution (PSD) on a frequency of at least once monthly. The refiner is advised to request a more detailed PSD for the fines than for the circulating inventory. The suggested PSD is a one-micron scale for 0-10 µ particles (1, 2, 3 ... 10), every two microns for 12-40 µ and every five microns for particles greater than 40 µ. Plot wt% capture vs PSD using a semi-log plot for each sample taken. Keep a monthly record of these plots through each operating cycle and for the life of the cyclones.

A well-designed, mechanically sound unit will present a peak at approximately 35-40 µ with a small peak between 0-3 µ (see Figure 8). The peak observed between 0-3 µ represents attrition in the unit. A bimodal distribution with an abnormal secondary peak appearing between approximately 10-25 µ is an indication of a crack or hole in a primary cyclone or plenum. A bimodal distribution with an abnormal secondary peak appearing at a PSD greater than the ‘normal’ peak is an indication of a hole or crack in a secondary cyclone (see Figure 9). Monitor these abnormal peaks closely as they will not disappear after time. Cyclone weld cracks or holes will get progressively worse, eventually requiring a shutdown to control catalyst losses.

A large increase in the 0-3 µ peak is an indication of a new attrition source in the unit or soft catalyst (see Figure 10). Please note that soft catalyst will result in increased losses on both the reactor and regenerator sides of the unit while an attrition source will present higher losses primarily on the side of the unit where the attrition source exists. Reference 1 provides a detailed description of this methodology.

Summary
In is recommended that the process engineer monitors specific values and ratios in the FCC ecat data sheet in addition to standard time plots of the data. Several recommended plots include:
- Total contaminant metals as an indication of mass transfer
- Ni-to-V ratio as an indication of shifts in feed quality
- Z-to-M ratio as an indication of fresh catalyst stability
- Ecatal sodium for maximum propylene production
- Crack or hole in a secondary cyclone
- Capture, wt% vs PSD as an indication of cyclone integrity and attrition

These analyses lend themselves well to automatic calculation in Excel and will provide the engineer with important indications of catalyst performance, cyclone mechanical integrity, and attrition.

Reference

Ray Fletcher is a co-founder of Inovato, deploying a new fixed bed naphtha-to-olefins process for maximum propylene. He also conducts FCC training for engineers and operators. With over 32 years of refining experience, he has worked nearly every process in a typical fuels based refinery, and spent 19 years with Albemarle and Johnson Matthey focusing on FCC troubleshooting, optimisation, and catalysis. He holds a bachelor’s degree from the University of Washington.
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Pre-reformer catalyst in a hydrogen plant

Good operation following recommended practice with technical support highlight the successful performance of a pre-reformer catalyst

K R RAMAKUMAR Johnson Matthey
SULTAN ORMAN and ISMAIL BAHA DIR KARA Tüp āş

Pre-reforming is the process by which methane and heavier hydrocarbons are steam reformed and the products of the heavier hydrocarbon reforming are methanated. The adiabatic pre-reformer is usually positioned upstream of the main steam reformer and uses a catalyst with high nickel content.

Three reactions occur in the pre-reformer and each of them will reach equilibrium:

Steam reforming reaction

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \] (endothermic)

\[ \text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + (n+m/2)\text{H}_2 \] (endothermic)

Water gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \] (exothermic)

Methanation

\[ \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \] (exothermic)

The overall reaction is endothermic for light (natural gas) feeds while for LPG there is an exotherm. For naphtha, there is an endotherm followed by an exotherm. Overall, for heavier feeds the reaction is exothermic.

The benefits of having a pre-reformer are:

- Flexibility to operate with different feeds, especially in refineries where it is important to use the most available and economic feed which might vary at different times of the year
- When the plant is designed to operate at a very low steam to carbon ratio, such as HyCO units where the main objective is to have more CO (and also a specific ratio of \( \text{H}_2/\text{CO} \)) in the reformed gas
- Having a pre-reformer can lead to lower capex due to the smaller size of the steam reformer

- Having a pre-reformer can also lead to lower opex due to less fuel consumption in the steam reformer and less steam requirement
- A pre-reformer is also an excellent revamp option for increased hydrogen production as it would typically add about 10-15% additional capacity

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- The overall excess steam production (steam export) with the pre-reformer in the flowsheet will be less
- The pre-reformer also facilitates operating the reformer at a higher inlet temperature without any preheat coil cracking issues as the higher hydrocarbons are already converted to methane and hydrogen
- A pre-reformer also acts as a poison buffer, protecting the downstream reformer catalyst in case of any poison slip across the purification section

The hydrogen plant in Tüpraş’s residue upgradation project block, PLT-147, supplies hydrogen for the integrated hydrotreating unit in Izmit refinery. The block consists of vacuum distillation, hydrotreater, and hydrocracker units.

PLT-147 has a design capacity of 160 kNm³/h and mainly processes natural gas along with hydrogen rich gas from the CCR unit. The unit also processes naphtha and LPG when there is a shortage of natural gas, especially during the winter. Natural gas contains up to 3.5 vppm \( \text{H}_2\text{S} \) and 7.5 vppm of organic sulphur.

The unit consists of a purification section (hydrodesulphurisation, \( \text{H}_2\text{S} \) absorption, and ultra-purification), pre-reformer, steam reformer, medium temperature shift converter, and a 14-bed PSA system for hydrogen purification.

The feed gas first goes through the hydrodesulphurisation reactor. This has a Ni-Mo catalyst installed which does all the functions of HDS (see **Figure 1**). The temperature is normally maintained in the range...
The temperature profiles 1 and 4 in Figure 3 correspond to the typical profiles at SOR and EOR respectively. Gradual deactivation of the catalyst due to poisoning sets in from the top. As the catalyst ages, the bed depth at which the reforming reaction begins also increases. Deactivation of the pre-reformer can be monitored by drawing a Z-90 plot. A Z-90 plot is a method to monitor and trend the temperature profile movement throughout the pre-reformer catalyst bed, whereby the 90% point of total endotherm is plotted. Typically, the Z-90 over time will increase owing to gradual deactivation of the bed from top. Figure 4 depicts the gradual increase in Z-90 for the bed profile represented in Figure 3.

Deactivation by sintering
Sintering is deactivation due to gradual ageing of the catalyst whereby small crystallites of active metal increase in size, thus reducing the effective surface area and therefore relative activity. The effect of sintering can be known by monitoring the bed temperature profile. The slope of the bed temperature profile is slightly different for catalyst subjected to sintering (see Figure 5). This difference in bed profile assumes that the plant is at the same rate.

Pre-reformer performance in PLT-147
The PLT-147 hydrogen manufacturing unit of the residue upgradation project has a design capacity of 160 kNm³/h and was commissioned in 2015. The unit supplies H₂ for the integrated hydrocracker and diesel hydrotreater units and is designed to operate with flexible feeds ranging from heavy naphtha to natural gas. The plant runs close to design feed rate most of the time.

PLT-147’s pre-reformer catalyst is a pre-reduced, high-Ni based catalyst and is operated with the objective of minimising C₂+ slip. The pre-reformer catalyst was loaded in February 2015. There are about 40 temperature measurement points, of three sets, within the catalyst bed; these are placed equally round the circumference of the reactor shell. The three thermowell sets...
are installed vertically down the reactor length.

With a steam to carbon ratio at the inlet of the pre-reformer of normally less than 2.5 mol/mol, the catalyst has been performing exceptionally well for more than four years from the time it was taken in-line. The bed temperature profile has not exhibited any significant change since SOR, which is evident from a very low Z-90 point.

The normalised bed temperature profile along the bed depth is shown in Figure 6.

The Z-90 point is still at 12% of bed depth after 1400 days of operation, which indicates that the catalyst’s performance is still good. There has been no sign of any deactivation by poisoning or sintering.

The key reasons contributing to the performance of pre-reformer catalyst at Tüpraş Izmit refinery are:

- **Robust upstream purification system**: sulphur in the feed has always been minimal and the overall purification system with an ultra-purification layer ensured that the pre-reformer catalyst life was greatly enhanced due to very low levels of sulphur in the inlet stream to the pre-reformer.

- **Monitoring of key parameters**: the inlet temperature to the pre-reformer was maintained low and steady, below 450°C, without any excursion during upsets. This greatly decreased the rate of catalyst sintering. The steam to carbon ratio was also maintained steady at 2.5 mol/mol. Our timely evaluation of operational datasets helped Tüpraş keep track of the plant’s overall performance.

- **Smooth changeover of feed**: Normally, the pre-reformer catalyst is subjected to a ‘shock’ when feeds are switched over (for instance, from natural gas to naphtha, or vice versa), as different feeds have significantly different temperature profiles and sudden switching of the feed may stress the catalyst, resulting in loss of activity. The operations team of Tüpraş has always ensured that the feed changeover was smooth and have followed our recommendations.

- **Clean source of steam**: steam may also contain contaminants such as sulphides, metals, chlorides, and silica which are poisons to the downstream pre-reforming catalyst. From the temperature profiles, it is evident that the steam source was free from all such contaminants.

- **Use of appropriate support/hold-down balls**: high purity alumina balls (for hold-down and support layers) are always recommended for pre-reformer service. The high purity of the supports is required to avoid leaching of the silica from standard inert supports, which may lead to catalyst poisoning and weaken the support itself.

- **Following the correct procedure**: during upsets, the standard operating procedure was followed. This meant that, despite plant upsets, the pre-reformer catalyst was not affected and its performance remained robust.

This case study of excellent catalyst performance in a critical pre-reformer duty is an example of how good operation following recommended practice with technical expertise can help realise the true potential of assets.

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