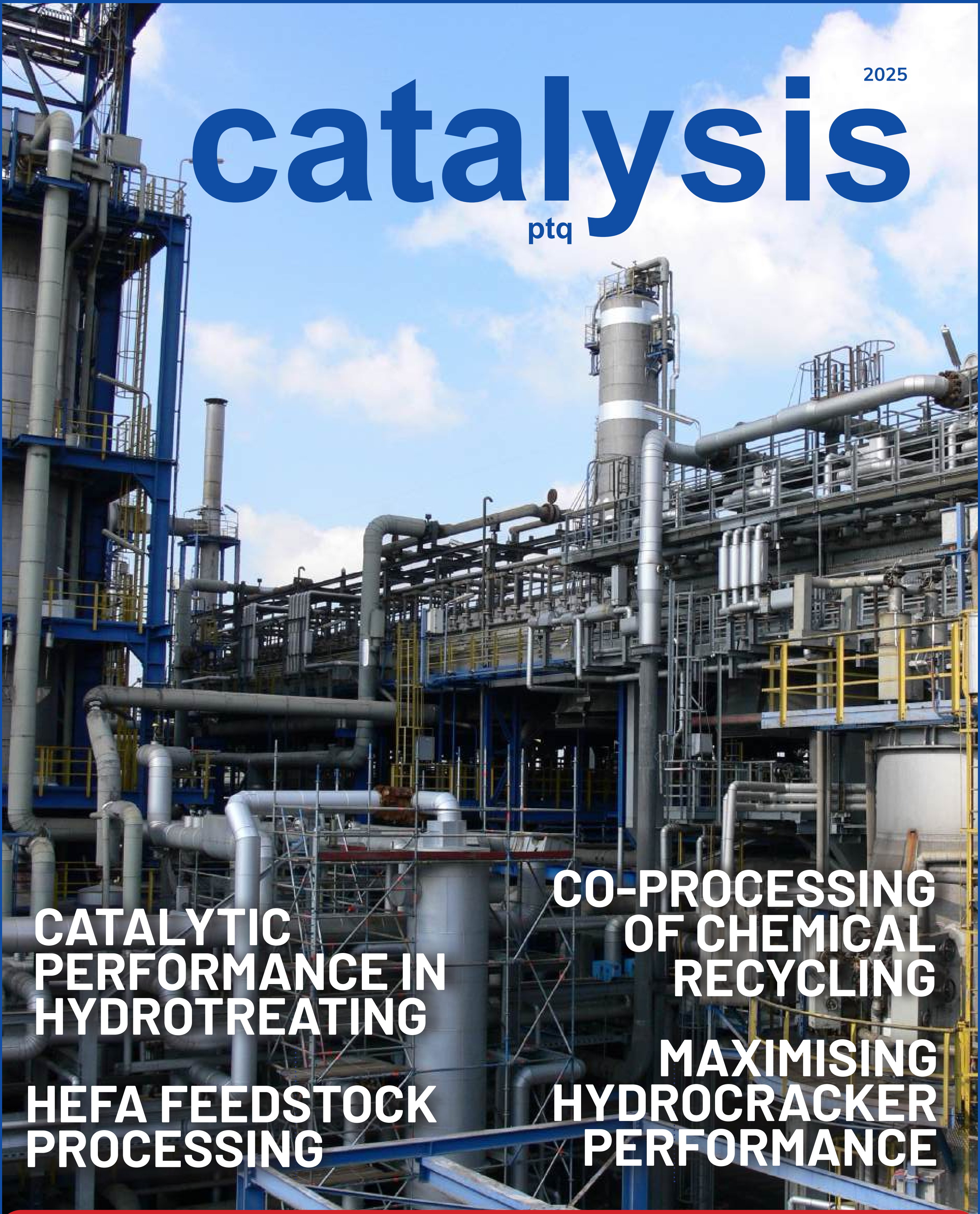

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Cover: The BP Gelsenkirchen Hydrocracker unit, one of the most pivotal units in almost every refining facility's operation. *Courtesy: Kurita Europe GmbH*

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Catalysts provide seamless integration

The refinery catalyst market is expected to maintain steady growth to meet demand for clean gasoline, diesel, jet fuel, and petrochemical feedstocks. High-compression, high-efficiency engines will increase catalyst demand for production of high-octane components such as butylene. Meanwhile, increased use of biomass feeds and pyrolysis oils co-processed with fossil feeds benefit from single- or two-stage hydrotreating and hydrocracking reactor configurations loaded with advanced catalyst formulations.

Tailored catalysts promote specific reactions, increasing the yield of desired products while minimising unwanted byproducts like coke and light gases, and reducing carbon dioxide (CO_2) emissions. Advanced catalyst formulations influence operating conditions, compressor operation, hydrogen requirements, pretreatment strategies, corrosion and fouling, cycle length, refractory feeds, tighter product specifications, and other emerging concerns, such as a wider array of contaminants affecting return on investment (ROI). Demand estimates vary among industry consultants. MarketsandMarkets estimated that the catalyst market was valued at approximately $5.6 billion in 2024 and is projected to reach $6.8 billion by 2029, exhibiting a compound annual growth rate (CAGR) of 4% during this period.

Another estimate from Fortune Business Insights projects market growth from $5.01 billion in 2024 to $6.77 billion by 2032, with a CAGR of 3.8% during the forecast period. The US Department of Energy (DOE) projects global gasoline market growth from more than $1.5 billion in 2024 to more than $1.8 billion by 2029. Regardless, gasoline consumption is expected to level off by 2033, but petrochemical demand ranging from olefins to aromatics will deliver higher margins for hydrocarbon processors.

For example, at the 2024 AFPM Annual Meeting, Keith Couch, Senior Director, Business Development at Honeywell UOP, spoke about certain refiners repositioning their business towards petrochemicals. In those cases, Couch said: “There are five things you need to be talking about: benzene, toluene, xylene, ethylene, and propylene.” Petrochemical catalyst growth for these basic petrochemical building blocks is expected to accelerate. As discussed in this issue of *Catalysis* 2025, major areas benefitting from catalysts include alkylation, catalytic reforming, hydroprocessing, plastics ‘re-circularity,’ blue hydrogen, and an expanding range of olefins and aromatics.

The process additives market, which includes chemicals formulated to enhance refinery operations and mitigate challenges, was valued at around $2.1 billion in 2022. It is projected to grow at a CAGR of 4.1%, reaching roughly $2.7 billion by 2027. Additional types of additives are used to remove poisons from catalyst active sites, ranging from metals and oxygen from biomass feeds to chloride contaminants affecting catalysts designed for hydrocracking plastics waste-derived pyrolysis oils.

Increasing conversion unit run length and operating costs justify additive programmes. For example, effective carbon disulphide (CS_2) removal in light naphtha or petrochemical naphtha (PCN: in the C_5-C_6 range) is necessary to compete in the high-margins polymer chain market. Next to hydrogen sulphide (H_2S), CS_2 has the second strongest catalyst poisoning effect, requiring a limit of less than 0.1 ppm CS_2 to protect catalysts loaded in reactors yielding C_5-based streams (such as isoprene and cyclopentadiene), which are building blocks for synthetic rubber production and a range of fine chemicals.

These challenges and opportunities are captured in this issue’s articles supplied by catalyst and refinery reactor experts.

Rene Gonzalez

Q What evolving methanol-to-olefins configurations are feasible for SAF production?

A Scott Sayles, Manager, Renewable Fuels and Alternate Feeds, Becht, ssayles@becht.com

Methanol processes that emit a minimal amount of greenhouse gas (GHG) are bio-methanol (sustainable biomass) and e-methanol (CO_2 and renewable hydrogen). eMeOH or BioMeOH are viable synthetic liquid fuels. Both are used directly for transportation fuel, mainly in maritime service today.

The concept of converting methanol-to-olefins (MTO) followed by polymerisation to sustainable aviation fuel (SAF) is referred to as methanol-to-jet (MTJ). The individual steps are commercially proven, while the combination of technologies to produce MTJ is new (see **Figure 1**).

Converting eMeOH to olefins is a proven technology with many licence providers. Each licensor is readily improving their technologies to increase yield and selectivity. The eMeOH production is an exothermic reaction requiring heat removal. The catalyst also deactivates, requiring regeneration. Fixed-bed designs use a cyclic design, with some reactors in regeneration while others are in service. Newer reactor system designs utilise a fluidised bed reactor with integrated regeneration.

MTJ is a mixture of oxygen-free hydrocarbon chains and is a 'drop-in fuel'. The blend is typical of a Fischer-Tropsch (FT) synthesis consisting of paraffins, cycloparaffins (naphthene), and a smaller concentration of naphthene/aromatics. FT synthesis allows for customising the hydrocarbon chain length range to the jet fuel range of C_9 to C_{16}. The chemical composition is different from fossil fuel, and the performance in jet engines requires ASTM certification. The unit designs are focused on energy and carbon efficiency to maximise renewable carbon in SAF.

Commercial fixed-bed reactors designed for methanol-to-gasoline (MTG) have been in operation in New Zealand (now shut down) and China. Catalyst is regenerated in a batch process, in situ. Heat removal is via recycled gas exchange, and the exchangers are large as gases are exchanged. An improved MTG reactor design is a fluidised bed reactor similar to a fluid catalytic cracker (FCC). The fluidised process allows continuous catalyst addition and regeneration. Heat removal is accomplished by generating steam. Extension of this technology to methanol-to-jet (MTJ) production is possible with changes in operating conditions and fractionation.

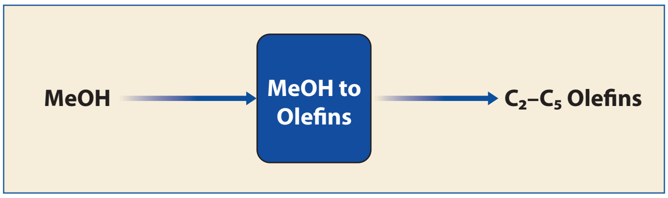


Figure 1 Converting methanol to olefins is a proven technology with many licence providers

The emerging technology is directional, progressing from MTG to MTJ, and focused on lower investment cost. Using fluidised bed reactors allows smaller systems and lower investment. Approval for MTJ as aircraft fuel is being evaluated by ASTM to ensure safe performance. ASTM International's aviation fuel subcommittee developed the ASTM D4054 standard practice to outline the data needed to assess a fuel's performance and composition. ASTM is fast-tracking the approval, but at the time of writing it had still not been approved. The ASTM subcommittee approved the establishment of a task force to oversee the work leading to the qualification of new SAF. In addition to chairing the ASTM MTJ Task Force, ExxonMobil has produced and submitted test batches of MTJ for evaluation by the ASTM D4054 Clearinghouse. Provided the fuel passes as a blendstock with fossil jet, the results of the work would update ASTM D7566.

A Woody Shiflett, President, Blue Ridge Consulting, blueridgeconsulting2020@outlook.com

The framing of the question precludes any discussion of the various methanol feed source processes that can ultimately yield net-zero or even sub-net-zero carbon footprints, so in this instance the focus will be on the MTO process itself as well as the necessary oligomerisation and hydrogenation steps required for viable SAF production. Until very recent years, MTO processes were geared towards light olefin production, with ethylene and propylene, and development work followed that path toward petrochemical applications. Oligomerisation as a fuels production process is nearly 90 years old, and innovation in that process has been at a pace commensurate with such a mature process until recently. So, with respect to SAF, what is needed, and what are recent developments?

Several opportunities exist under the needs list:

- MTO process selectivity to higher carbon chain products beyond light olefins.
- Oligomerisation processes that are specifically selective to the carbon chain molecules required in the jet fuel range.
- Some means to reduce the energy required and associated carbon intensity of existing MTO processes that utilise fluidised bed reactors and associated regeneration configurations to deal with the coke fouling issues of existing MTO catalysts.
- Process consolidation and optimisation to mitigate the heritage path to jet fuel involving MTO, oligomerisation, hydrogenation, hydrocracking, and hydroisomerisation required for drop-in SAF with appropriate molecular distribution and cold flow properties.

The perusal of recent patent applications and grants shows progress in a number of these areas. It is no surprise that innovation is based on catalysis in most cases. Catalyst development in MTO focuses on shape-selective catalysts of varying structure and acidity to promote larger carbon chain olefins to be produced as well as even isoparaffins. More coke-resistant catalysts promise to offer less energy input for regeneration. They could even stretch to a departure from the complexity of operation and energy needed in the current fluidised bed/regenerator configurations. Changes in the mode of MTO operation have revealed certain unexpected benefits in product distributions and operating conditions.

The oligomerisation area has likewise seen catalyst development expand the selectivity envelope to home in on SAF yield maximisation. Technology to combine both oligomerisation and hydrogenation functions in a single reactor is demonstrated in the laboratory at a minimum. In more conventional process flows, consolidation of hydrocracking and hydroisomerisation functions in a single step are outlined.

The key enabler will be to efficiently marry the MTO and oligomerisation selectivities as a combined process that ideally produces the isoparaffin content and molecular chain length to meet SAF requirements. Predominant technology providers are clearly active in these efforts.

A **Rob Snoeijs, Communication Specialist,** **rob.snoeijs@zeopore.com**

A variety of conversions are available to convert methanol (or other alcohols) to olefinic products, which, through further upgrading, may be used as SAF.

The first option relates to methanol conversion to ethylene and propylene using zeolite-based catalyst in an MTP (ZSM-5-based) or MTO-type (SAPO-34-based) configuration. The resulting small olefins may then be oligomerised towards larger carbon numbers suitable for the SAF boiling range, a conversion for which zeolite catalysts have shown selectivity and lifetime benefits (particularly based on ZSM-23 zeolites). Finally, the resulting stream may be hydrogenated using a standard hydrogenation catalyst towards the required levels to suit SAF.

An alternative pathway relates to the conversion of methanol directly towards larger olefinic species, for example using a ZSM-5-based catalyst in an MTG-type configuration. Here, too, the ZSM-23 zeolite has shown remarkable selectivity and lifetime benefits. Also, after this reaction, hydrogenation is required to yield an acceptable SAF.

Importantly, reactions involving small alcohols and olefins tend to coke and deactivate the zeolite catalysts rapidly, hampering selectivity and catalyst lifetime. To overcome this challenge, various solutions have been developed, such as diluting the reactive feed, adding additives to the zeolite, and importantly increasing the external surface of zeolite, giving rise to the family of more accessible (mesoporous) zeolites.

Mesoporous zeolites have suffered a bad reputation when it comes to industrial applications based on the high cost commonly associated with their production. However, efforts at Zeopore have demonstrated that these cost challenges can be overcome through capitalising on the synergy between conventional hydrothermal zeolite and post-synthetic workup. This can be seen in the associated Zeopore article in this issue of *PTQ Catalysis 2025*, that sizeable benefits can be attained in this domain (specifically for ZSM-5 and ZSM-23 zeolites), and that combining mesoporisation with simultaneous additive addition yields sizeable benefits (*PTQ Catalysis 2023*, pp55-58).

Q How is contamination of FCC catalysts being resolved to increase yields and cycle length?

A **Mark Schmalfeld, Global Marketing Manager, BASF Refinery Catalysts,** **mark.schmalfeld@basf.com**

FCC catalysts, specifically BASF FCC catalysts, are specifically designed to enhance the operation of fluid catalytic cracking (FCC) units. Catalyst design considers the context of contamination management expected for the feed types used by the FCC unit. Here are several ways in which FCC catalysts contribute to improved FCC performance, even in the presence of catalyst feed contamination.

FCC catalysts have been developed with enhanced metal tolerance, allowing them to maintain activity and selectivity even when exposed to feedstocks containing metals such as nickel and vanadium. This capability helps mitigate the negative effects of these contaminants, leading to more stable operation and improved yields, in addition to catalysts with near-zero levels of chlorides. Low sodium levels in FCC catalyst improve the zeolite stability. Use of an in situ manufacturing process designs the pore volume distribution to ensure a high level of iron tolerance.

FCC catalysts often incorporate advanced zeolite structures engineered to resist the deposition of contaminants. These optimised structures provide greater surface area and improved diffusion pathways, allowing for better hydrocarbon access and reduced accumulation of coke and other contaminants.

FCC catalysts are designed to facilitate effective regeneration as coke and hydrocarbon deposits are combusted in the FCC regenerator. Their design allows for the efficient removal of carbon deposits and some contaminants during the regeneration process, helping to restore and maintain the catalyst activity. This means that even in the presence of contamination, the catalysts can be regenerated more effectively when tailored to the specific unit constraints and targeted operating conditions.

FCC catalysts may include proprietary additives and design elements that specifically target and mitigate the effects of contaminants. For example, these additives can help neutralise harmful compounds or enhance the catalyst's ability to cope with specific impurities, thus maintaining performance levels. Enhanced catalysts and activity can help offset the impact of contamination by ensuring that the FCC unit operates efficiently, even when feed quality fluctuates. An optimised activity level is required based on unit constraints and economics.

BASF's FCC technical team can adjust catalyst design to provide refiners with operational flexibility to manage unexpected changes in feed quality. Additionally, catalyst design can be utilised to adjust how contaminated metals are removed from the FCC unit over time. This adaptability is crucial in maintaining stable performance and ensuring that the FCC unit can respond effectively to variations in contamination levels.

Equilibrium catalyst (Ecat) analysis is conducted and combined with operating data for refiners to enable continuous improvements in operational adjustments, troubleshooting, and opportunity development. This collaboration and partnership approach allows for ongoing optimisation of catalyst usage and operational practices, further enhancing overall performance.

A Scott Sayles, Manager, Renewable Fuels and Alternate Feeds, Becht, ssayles@becht.com
Contamination in FCC feeds is minimised by endpoint control and hydrotreating to remove catalyst fouling. The newer catalysts can tolerate higher levels of metal contamination, allowing the ability to either process higher endpoint feeds or lower hydrotreating severity. The balance between hydrotreating, yields, naphtha/light cycle oil (LCO) sulphur, and catalyst replacement requires consideration of the interactions between the variables.

In general, an economic balance is reached between these variables at the highest C_4+ liquid yields. An economic optimum is reached for two separate conditions:

- Maximum gasoline or the naphtha peak point conversion.
- Maximum distillate occurs at a lower conversion, further augmented by fractionator cut points.

The two optimums require separate operating conditions, feedstock quality, and catalyst replacement strategies. These conditions are best controlled via an online advanced control system. Catalyst selection will also improve selectivity to naphtha or distillate but is a longer-term change and does not capture seasonal effects. Recent strategies are to optimise distillate production using a distillate selective catalyst.

A Darrell Rainer, Global FCC VGO Specialist, Ketjen Corporation, darrell.rainer@ketjen.com
The contaminants exerting the most significant impacts on FCC catalyst and unit performance, along with commonly employed mitigation measures, are as follows:

- **Nickel** is present in all feeds, with higher concentrations in resids and nickel deposits, and remains in the outer shell of the catalyst particle, promoting dehydrogenation reactions that increase delta coke and hydrogen yield. Many catalysts feature components designed to minimise active nickel surface area on the Ecat, as well as influence the chemical state, limiting the overall dehydrogenation increase. Newer nickel has more dehydrogen effects than older nickel on Ecat.
- **Antimony** (Sb) has nickel (Ni) passivating properties and can be added to the riser as a liquid stream. Typical Sb/Ni ratio targets would be in the 0.25-0.35 range, which might be lowered according to the intrinsic nickel tolerance of the catalyst. For nickel and other contaminants, the use of purchased Ecat is an option to minimise levels in the circulating inventory by increasing the overall catalyst addition rate. Refiners sometimes resort to the systematic addition of purchased Ecat higher CAR (catalyst addition rate) at a lower cost than fresh catalyst alone. This frequently comes with attendant performance deficits that factor in the decision.
- **Vanadium** in the fully oxidised state (V_2O_5) is highly mobile and distributes throughout the catalyst particle. Full combustion units with excess O_2 will have elevated V_2O_5 levels. While the dehydrogenation activity is a fraction of that of nickel (~25%), vanadium also interacts destructively with Y-zeolite. This impact can be mitigated with the inclusion of vanadium traps in the circulating inventory and the use of a high matrix activity catalyst, hedging against activity loss through zeolite destruction by providing significant catalyst matrix cracking.

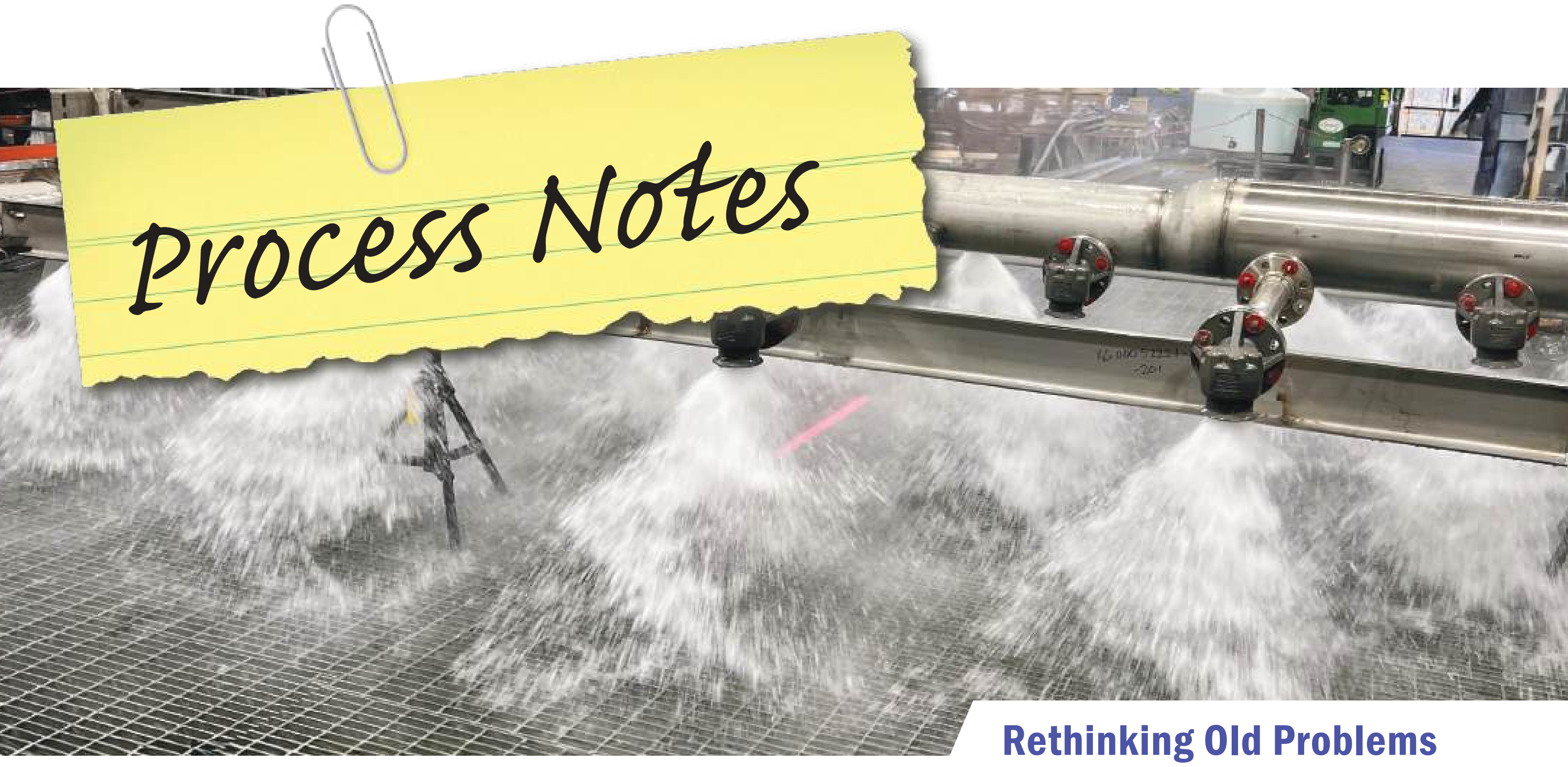
With iron, the spatial deposition profile of iron is similar to that of nickel, but the impact on particle surface morphology/porosity is significantly greater. Iron interacts with silica (originating both in the catalyst and from the feed) in the presence of other fluxing metals (calcium, sodium, and vanadium) to form eutectics under regenerator conditions that result in the formation of a densified shell in the outer layer of the catalyst particle. This results in a loss of porosity in the surface region, imposing a diffusional barrier that can greatly diminish the accessibility of larger molecules to the interior cracking sites, increasing slurry yields.

Catalyst selection is key in managing the impacts of iron contamination. Employing a high-accessibility catalyst expands the operating safety margin (in terms of avoiding 'the cliff' at which point the catalyst accessibility drops sufficiently to cause a precipitous drop in bottoms upgrading), allowing a higher add-on iron on Ecat level to be safely tolerated. Catalysts such as Ketjen's proprietary SaFeGuard, specifically designed in their chemistry to minimise the surface reactions with iron, calcium, and sodium that result in densification and accessibility loss can play an important role in managing iron risk. Fluidisation issues can also develop with iron contamination, originating from 'nodulation' and the attendant drop in apparent bulk density (ABD). This varies significantly from unit to unit.

Catalyst selection is key in managing the impacts of iron contamination. Employing a high-accessibility catalyst expands the operating safety margin, allowing a higher add-on iron on Ecat level to be safely tolerated

Sodium attacks zeolite and is also a fluxing metal that promotes the formation of the eutectics associated with the harmful morphological changes that occur in iron poisoning. Mitigation strategies in the FCC unit would mostly be limited to increasing catalyst addition rate and upstream remedies, such as improved desalting of crude.

Calcium also attacks zeolite, though not so severely as sodium. However, it plays a much more significant role in exacerbating the damaging impact of iron poisoning and is frequently implicated in the worst cases. Mitigation approaches would be the same as for sodium.



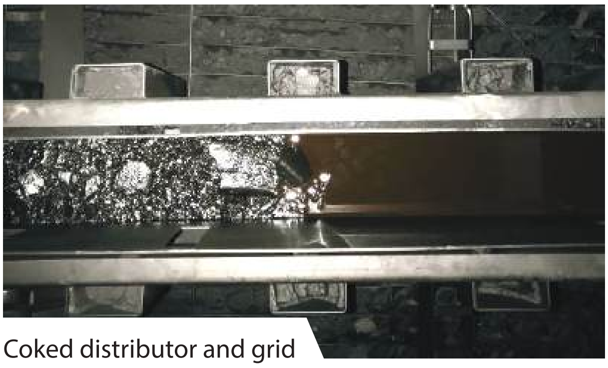
Rethinking Old Problems

New design improves FCC slurry pumparound

Rising global demand for transportation fuels and propylene as a chemical feedstock will require new and revamped FCC units to increase supply. Technology enhancements have historically focused on improved or new catalyst formulations, updated feed nozzles, and reactor/regenerator designs.

FCC charge rate and reactor temperature are often limited by performance of the main column and bottoms system. To fully capture benefits associated with tailored catalyst formulation or new reactor/regenerator designs, the main column and slurry pumparound system must be up to the task.

For many refiners, problems in the main column and bottoms section are a common occurrence. Rapid fouling in slurry pumparound exchangers requires frequent cleanings and added maintenance costs. Coking in the slurry pumparound bed leads to poor product quality, increased column pressure drop, and shortened run length. However, many chronic problems can be mitigated with innovative designs driven by a proper understanding of the root cause.



Coked distributor and grid

Slurry Pumparound Bed

Many FCCs are expected to operate 5-7 years between planned maintenance turnarounds. Modern grid packings have been used in this severe service with success. Even so, there have been times when the combination of high temperature, high liquid rate, and high vapor rate have caused severe coking.

Trough distributors have been the go-to device to distribute liquid to the slurry pumparound bed. Special design features are used to mitigate risk of catalyst and coke particle accumulation in the troughs. The features that make the distributor more forgiving also make it more sensitive to liquid gradient and out-of-levelness. Even with the most careful design, slurry beds have experienced premature coking and shortened run lengths.

In order to solve old problems, sometimes new thinking is needed. The engineers at Process Consulting Services, Inc. have revamped high severity, highly-loaded slurry pumparound sections with innovative solutions. A new twist on a classic distributor design improves reliability while eliminating inherent problems of old designs. Patented solutions to highly loaded grid-beds offer needed breathing room. Contact us today to learn how PCS designs can improve your FCC.

Chlorides originating either in the feed or in the catalyst can introduce various complications, including intensifying corrosion concerns (NH_4Cl), forming unwanted deposits in the fractionator and enhancing the dehydrogenation activity of nickel deposited on the catalyst. Mitigation approaches would include sound catalyst selection (avoiding high chloride-containing catalysts if there is an issue) and upstream solutions, such as (again) improving desalter efficiency.

Silicon (silica) contamination does not get much discussion or attention as it is essentially undetectable against the background of silica in the catalyst itself, and the impacts have not been thoroughly documented and quantified. It is reasonable to assume that silicon introduced in the feed (for example, from such sources as defoaming agents employed in the delayed coker) might interact with iron in a similar way as silica originating with the catalyst. While the total amount of silica contaminant is going to be very low relative to the catalyst baseline, mobile silica is the real issue. That ratio is going to be significantly higher. So, while it is tempting to draw the conclusion that silica in the feed is simply not present in large enough quantities to have an impact, this has not rigorously been shown to be true. In fact, Ketjen has lab data indicating the opposite. A catalyst specifically designed to minimise iron and silica interactions (SaFeGuard) can alleviate this impact.

A Berthold Otzisk, Senior Product Manager, Process Chemicals, Kurita Europe, Berthold.otzisk@kurita-water.com

In recent years, FCC catalysts have been developed that are much more tolerant of catalyst poisons (contaminants). Nevertheless, contamination of the FCC catalyst still leads to reduced product quantities or shorter cycle lengths. Contaminants act as competitive catalysts to dehydrogenate the hydrocarbons, leading to excess hydrogen production and coke. They reach the FCC catalyst with the feed material and irreversibly destroy the zeolite crystallinity and/or the acidity. Classical impurities are metals such as nickel (Ni), vanadium (V), iron (Fe), copper (Cu), sodium (Na), calcium (Ca), or magnesium (Mg). Nickel (also Cu, V, and Fe) enters the system in the form of large porphyrin molecules, which crack onto the FCC catalyst, leaving the nickel behind.

Nitrogen (N) or carbon (C) are catalyst poisons that deactivate or cover cracking sites on FCC catalysts. However, this is only temporary, and the catalyst activity is recovered. Catalyst destruction by metals is more pronounced and permanent, where catalyst bed activity can only be recovered by adding fresh catalyst.

Nickel is the primary competitive catalyst in the FCC, acting as a dehydrogenation catalyst. Dehydrogenation of hydrocarbons leads to loss of gasoline selectivity and a slight reduction in catalyst activity. By plugging catalyst pores, the conversion is reduced with the negative effects of increased delta coke on FCC heat balance. Nickel should always be considered if the process unit is running against a limit. If nickel on Ecat exceeds around 500 ppm, a chemical treatment programme should be started. A nickel passivation programme reduces the negative effect of nickel by 50-70%. Alongside nickel, vanadium is another metal that causes problems and production losses. Vanadium acts as a competitive catalyst and a true catalyst poison. Besides dehydrogenation reactions, it may oxidise, becoming mobile and migrate to the zeolite catalyst, permanently destroying it.

There are various passivation programmes with which a reduction of nickel or vanadium dehydrogenation can be achieved. The negative influence of these metals is reduced, and the conversion and yield are increased in addition to the improved gasoline and C_3/C_4 selectivity and longer cycle length.

Best known in the industry is the use of antimony or bismuth (Bi) to mitigate the effects of nickel. Aqueous antimony pentoxide solution (Sb_2O_5) is preferred as it works much faster compared to bismuth and is easier to control. Care should be taken to ensure that the particle size of Sb_2O_5 is preferably <5 nm in order to obtain a stable colloidal dispersion. The more stable dispersion avoids settling problems in storage. Sodium is a catalyst poison, and residual sodium or byproducts such as Sb_2O_3 (suspected to be carcinogenic) should not be present.

When dosing Sb_2O_5, an average ratio of 0.35 Sb:Ni should be set. The typical base load to saturate active nickel is reached after five to seven days. An overdose of Sb_2O_5 must be avoided because Sb in LCO can poison downstream Ni-Mo hydrotreater catalysts.

Q Can you discuss your experience with using CFD for hydroprocessing reactor troubleshooting?

A Zumao Chen, Engineering Fellow, Becht, zchen@becht.com

The application of computational fluid dynamics (CFD) for troubleshooting hydroprocessing reactors has proven invaluable in diagnosing complex operational challenges, optimising designs, and enhancing reactor performance. CFD, often coupled with kinetic modelling, is particularly effective in addressing flow maldistribution in hydrotreating and hydrocracking reactors. For example, modelling the inlet distributor through the catalyst beds of a downflow reactor allows for improved distribution and mixing in both radial and vertical directions (see **Figure 1**).

CFD analysis also enables the modelling of complex reactor configurations, such as ebullated bed reactors, where

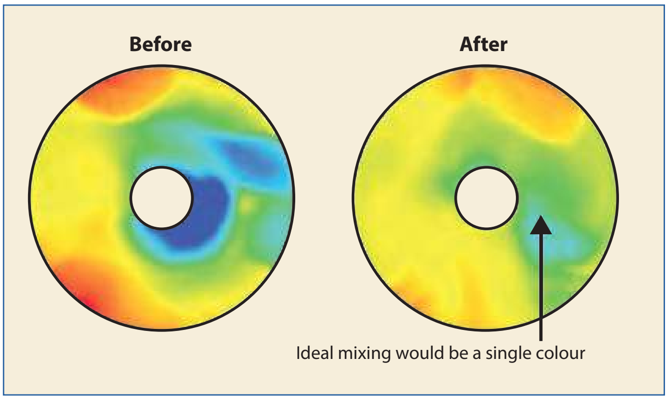


Figure 1 CFD analysis can improve distribution and mixing in radial and vertical directions in reactors

the catalyst bed is fluidised by the upward flow of liquid feed, gas, and recycle liquid. By analysing catalyst, oil, and gas residence times and mixing, CFD provides critical data for evaluating and quantifying the effectiveness of various design configurations. This facilitates targeted design modifications to resolve maldistribution and improve overall reactor performance.

In troubleshooting scenarios, such as operational upsets or dynamic process changes, CFD offers a powerful tool for analysing time-dependent behaviours. Breaking the timeline into discrete periods and simulating each phase provides insights into the causes of process disruptions and supports the development of effective solutions.

CFD's utility extends beyond reactors to associated systems. For example, it has been used to address flow distribution issues in complex geometries like elbows and tees in coke drum dual inlet piping systems, where design adjustments, such as adding wedges, successfully balance vapour and liquid flow rates to reduce thermal and mechanical stresses. Similarly, CFD has been applied to optimise steam distribution in hydrocarbon outlet headers of proprietary Catofin reactors, minimising coke formation and damage to liners. Additionally, in high-velocity environments like waste heat boilers, CFD accurately predicts erosion rates and identifies critical failure zones, enabling targeted design enhancements and improved inspection protocols.

CFD has also addressed thermal management challenges, such as optimising heat transfer in storage tanks. Simulations can lead to adjustments like closer steam coil spacing in molten sulphur tanks, which maintain wall temperatures above the acid dew point, preventing corrosion and improving system reliability.

Overall, CFD has consistently demonstrated its predictive power by validating design changes, reducing downtime, and ensuring long-term equipment integrity. Its role in troubleshooting and optimisation underscores its importance in enhancing process safety and performance in hydroprocessing reactors and their associated systems.

A Rainer Rakoczy, Technical Advisor, Fuels, Clariant, **rainer.rakoczy@clariant.com**

The role of numerical methods for the simulation of fluid flows has become key for understanding and optimisation in uncountable areas in technology and engineering. Fixed catalyst bed hydrogenation calls beside an appropriate catalyst solution for the optimum dispersion of the desired feed and the applied hydrogen. The design of reactor dimensions, grading, and internals such as flow distributors or quench lines needs immense support from CFD, especially on the process engineering side.

As a catalyst vendor, the shape of the applied materials can be key. Therefore, Clariant started to look into optimising shapes as well. Some decades ago, for some hydroprocessing applications, a unique computer design shape (CDS) was developed and commercialised in several product series as CDS material, and the advantages, especially from the macroscopic surface area, are very much enjoyed by the applicants.

A Louise Jivan Shah, Senior R&D Manager | Mechanical Concepts, Topsoe, **ljsh@topsoe.com**

Topsoe recognises the importance of CFD in the design, development, and troubleshooting of our reactors, and we have successfully integrated it into our workflows from an early stage.

Despite the challenges associated with multiphase models in CFD, these limitations have been addressed by validating our CFD models for critical assumptions using in-house measurements and literature information. This validation process ensures that our simulations closely represent the real-world behaviour of our reactors, giving us confidence in the results. Thanks to our in-house 2,000+ central processing unit (CPU) cores high-performance computing cluster for running these computationally demanding CFD simulations.

One of the major benefits we have experienced is the ability of CFD to provide meaningful insights and information that are difficult to obtain through plant-scale measurements. Troubleshooting in hydroprocessing reactors often involves identifying the root cause of observed deviations, such as temperature radials in the reactor beds. With CFD, we have been able to strengthen our hypotheses by analysing the impact of different design and process deviations on the observed deviations.

For instance, when we observed a temperature radial in our reactor, we utilised CFD to understand how various factors contributed to the observed deviations. These included design deviations (for example, as-intended vs as-built) and process deviations (for example, actual operating vs design-basis conditions). By simulating different scenarios and analysing the results, we gained a better understanding of the underlying causes and were able to develop targeted solutions.

Overall, the implementation of CFD for hydroprocessing reactor troubleshooting has been highly beneficial for Topsoe. It has allowed us to address issues more effectively, improve reactor performance, and optimise our processes. The insights and information generated through CFD have proven invaluable in enhancing our understanding and decision-making capabilities.

Q To what extent is pretreatment needed to protect hydrotreaters/hydrocrackers from impurities when upgrading WPO to petrochemical feedstocks?

A Scott Sayles, Manager, Renewable Fuels and Alternate Feeds, Becht, **ssayles@becht.com**

Waste plastic oil (WPO) has potential impurities that cause catalyst deactivation. The types of impurities depend on the plastic type being fed to the liquefaction device. Typical feed contaminants are nitrogen, oxygen, olefins, phosphorus, silicon, and chlorides. For example, polyvinyl chloride (PVC) has the most difficult composition, mainly due to the chloride concentration and some metal stabilisers, while polypropylene has the least. The waste plastic received is a mixture of all plastic types. Some sorting is used to remove the hardest-to-process plastics, but the resulting feed is typically a mix of plastic types.

The level of contamination that reaches the hydroprocessing reactors determines the rate of catalyst deactivation. The higher the contamination, the shorter the run length that is observed; this is similar to fossil fuel deactivation. The individual contaminants have individual deactivation rates, and they are also cumulative. The contaminants are at higher concentrations and lower boiling ranges than the equivalent fossil fuels, resulting in higher overall catalyst deactivation. The plastic liquefaction step does not seem to impact the contaminant concentration. However, a pretreatment unit such as that used for renewable feeds is not required.

The method of producing the plastic oil also determines the level of contamination, with hydroliquefaction (HTL) removing more contaminants and pyrolysis retaining more contaminants in the liquid phase.

A **Woody Shiflett, President, Blue Ridge Consulting,** **blueridgeconsulting2020@outlook.com**

WPOs contain a myriad of contaminants that are highly variable depending on what waste plastics constitute the pyrolysis process feedstock and what type of pyrolysis process is employed (thermal and catalytic). Some of these contaminants are in the form of particulates. Many of these contaminants can be removed simply by depth filtration in pretreatment reactors or beds, as has been reported in a joint Ghent University/Pall Corporation study. Mixed polyolefin pyrolysis oils tested have shown some 80% of metals removed in this manner and exhibit 40-60% less coke formation downstream.

Fossil fuel feed contaminants tend to be limited to Ni and V in the heaviest stocks (vacuum gasoil [VGO], deasphalted oil [DAO], and residue), Fe in many feeds from upstream corrosion products, or Si in lighter coker-derived feeds (naphtha and kero). WPO can introduce high levels of Na (as 10s-100s ppm), higher levels of Si and Fe (10s of ppm), some Pb (~ <10 ppm), and significantly high levels of chlorine (Cl) (100s of ppm). Clearly, in any case, some significant pretreatment is and will be required.

Most technology providers and catalyst suppliers actively engage in guard catalyst and 'hydrodemetallisation' catalyst development to meet the needs of emerging feedstocks, with the renewables co-processing and hydroprocessing area being a somewhat recent example over the prior decade or two.

WPO processing guard catalyst development is and will be following. Speciality guard material innovators and suppliers, such as Crystaphase (Houston, TX), are and will be tailoring specialised trapping guard systems to address these needs. As WPO processes enter full commercial-scale applications, more detailed physical and chemical characterisation of contaminants will be needed in order to design and optimise appropriate pretreatment and guard material processes and products.

A **Chris Ploetz, Process Technology Manager at Burns & McDonnell,** **cploetz@burnsmcd.com**

When used as a petrochemical feedstock, the composition and physical properties of raw WPO, also called waste plastic pyrolysis oil (WPPO) or plastic pyrolysis oil (PPO), can cause various challenges in downstream processes. The nature of these challenges varies depending on the disposition of the oil as steam cracker feed, FCC feed, or hydroprocessing unit feed. Usage of these oils in a steam cracker or FCC supports circularity in the polyolefins market (for example, high-density polyethylene [HDPE], low-density polyethylene [LDPE], and polypropylene [PP]), whereas usage in a hydroprocessing unit (with subsequent processing through a reformer and aromatics complex) supports circularity in the aromatic derivatives market (for example, polyethylene terephthalate [PET], polystyrene, and nylon).

From the perspective of downstream processing as a petrochemical feedstock, notable characteristics of WPO include the following: high vapour pressure, low flash point, wide boiling range with heavy tail, high pour point, high levels of unsaturation (including diolefins), chemically bound oxygen and nitrogen, chemically bound halogens (primarily chlorine due to PVC in waste plastic), metals and other heteroatoms (for example, silicon and phosphorus), and particulates (reactor solids consisting of carbonaceous char and calcium halides).

All of these properties can be problematic in downstream processing, but the issues are magnified if the feed is to be 100% pyrolysis oil. In lieu of this, many refinery and petrochemical operators are considering pyrolysis oil blending at relatively small fractions with traditional feedstocks in order to reduce the adverse impacts of raw pyrolysis oil while still gaining credit for recycled content via certification from International Sustainability and Carbon Certification (ISCC) Plus or other third parties.

Specific pretreatment needs upstream of a hydroprocessing unit should focus on addressing diolefins, metals, silicon, phosphorus, and particulates. Diolefins should be saturated in a selective hydrogenation unit (SHU) to avoid oligomerisation at high temperatures in the reactor feed preheat train. Metals, silicon, and phosphorus should be removed using guard beds to avoid poisoning and pluggage/fouling of the main reactor catalyst bed.

Primary particulate removal should be accomplished at the pyrolysis facility, but users of WPO should also install filtration systems to prevent plugging of exchangers, catalyst beds, and control valves. Within the hydroprocessing unit, metallurgy should be evaluated for the presence of chemically bound chlorine and other halogens, which will react to form hydrochloric acid (HCl) and hydrofluoric acid (HF) within the reactor. These acidic compounds will ultimately be removed with the acidic sour water decant streams at the cold separator vessels downstream from the reactor.

Additionally, any user of WPO needs to consider the high vapour pressure (if unstabilised), low flash point, and high pour point. The vapour pressure of unstabilised pyrolysis oil can preclude storage in atmospheric tanks. The low flash point (typically <<100°F) requires pyrolysis oils to be treated as a flammable liquid despite being relatively heavy. The high pour point (substantially above summer ambient temperatures) requires heat tracing or other methods of maintaining adequate storage and process temperatures to avoid pluggage due to wax build-up.

Although these pretreatment steps add cost to a project, new technology is not required; all these strategies are within the general experience of the refining and petrochemical industry. Catalyst and adsorbent providers are actively working to optimise their products and services to meet the needs of the pyrolysis oil market. Each WPO user should craft these considerations into a tailored pretreatment scheme that meets the needs of their specific application, considering the actual properties of the candidate pyrolysis oil and the needs of the downstream process.

A Rainer Rakoczy, Technical Advisor, Fuels, Clariant, rainer.rakoczy@clariant.com
Utilisation and conversion of waste plastic pyrolysis oil is of increasing industrial interest. There are multiple options from a technical standpoint utilising these materials with the highest desire to get the materials back to steam crackers to follow a circular economy concept. Nevertheless, a low-hanging fruit may be the utilisation of older or smaller process equipment in a refinery or a refinery complex with certain access to petrochemical equipment utilising small quantities of an available WPO source to treat or pretreat it for application through coprocessing in the hydrocracker or catalytic cracker. Clariant has expanded the proprietary Clarity, HDMax, and even Hydex portfolio to handle this demanding feedstock and convert it towards feedstock for the aforementioned processes.

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Raw WPOs are highly contaminated and, therefore, can be fed directly to FCC or steam crackers only at very high dilution rates. To increase the recycled content in a feed stream, hydrotreating and, optionally also, hydrocracking are required to bring the WPO onto specification for downstream processing. These hydrotreating and hydrocracking steps must be tailored for contaminant removal and property adjustment to enable the processing of this new type of feedstock. These steps (upgrading via hydroprocessing) can be understood as a pretreatment necessary to integrate WPO into the existing production facilities.

However, some caution is needed when using the term pretreatment, as several of the steps in plastic recycling require some kind of pretreatment. This can, for example, be the sorting and cleaning steps required for plastic waste before pyrolysis, or it can be post-pyrolysis single contaminant clean-up steps, as is the case for use of sorbents. The contaminant levels in common mixed plastic WPO can be successfully upgraded via tailored hydroprocessing without any additional pretreatment steps required, but a combination of different steps could have economic benefits.

Q In what situations do advanced catalyst formulations and technical support affect/benefit downstream product investment, such as when separating olefins?

A Mark Schmalfeld, Global Marketing Manager, BASF Refinery Catalysts, mark.schmalfeld@basf.com
Advanced catalyst formulation and technical support can significantly influence investment decisions and operational efficiencies in various chemical processes, including the generation of olefins and the equipment required for the separation of olefins. Here are several situations in which these factors provide substantial benefits:

- **Enhanced selectivity and yield**

Situation: In processes such as the separation of olefins from mixed hydrocarbon streams, advanced FCC catalyst formulations can improve selectivity towards desired olefins (for example, ethylene, propylene, and butylenes) while minimising byproducts. Targeted catalyst design and additive use improve olefins selectivity. Examples are specific lower unit cell size for the Ultrastable Y zeolite, speciality zeolites (such as ZSM-5), and other types of zeolites that increase yields of olefins (often targeting propylene and butylenes), which helps to define goals for investment decisions.
Benefit: Higher selectivity results in increased yields of target products, reducing the need for additional downstream processing, thus saving on capital and operational expenditure.

- **Integration with process technology**

Situation: The integration of advanced catalysts with proprietary process technologies or reactor designs can lead to synergies that enhance olefin separation efficiency. Working with catalyst suppliers and equipment process licensors can improve the effectiveness of investment decisions for olefins separation.
Benefit: Technical support that aids in integrating these technologies can lead to a smoother implementation process and quicker realisation of economic benefits.

- **Tailored solutions for specific feedstocks**

Situation: Different feedstocks can have varying compositions and impurities that affect olefin separation. Advanced catalyst formulations can be tailored to specific feedstocks (for example, resid feedstocks requiring metals-resistant catalyst designs, VGO feedstocks, or alternative feedstocks for the FCC such as pyoils from plastics vs pyoils from biomass materials all have alternative catalyst designs to support olefins production and enable improved yields from separation units).
Benefit: This customisation can lead to optimal performance and yields, justifying higher initial investments in catalysts tailored to specific operational needs.

- **Technical support for process optimisation**

Situation: Ongoing technical support from catalyst manufacturers can provide refiners with insights into optimising operating conditions and troubleshooting issues during olefin separation.
Benefit: This support can enhance operational efficiency, reduce costs, and increase profitability, making the initial investment in advanced catalyst technology more appealing.

- **Sustainability considerations:**

Situation: As sustainability becomes increasingly important,

advanced catalyst formulations that enable the production of olefins from renewable feedstocks can provide a competitive edge.
Benefit: Investments in these catalysts not only improve economic outcomes but also align with corporate sustainability goals, enhancing their attractiveness to investors.

In summary, advanced catalyst formulations and technical support play critical roles in enhancing the efficiency, yield, and sustainability of processes such as olefin separation. By addressing issues such as selectivity, catalyst stability, and process integration, these advancements can significantly benefit investment decisions and overall operational performance.

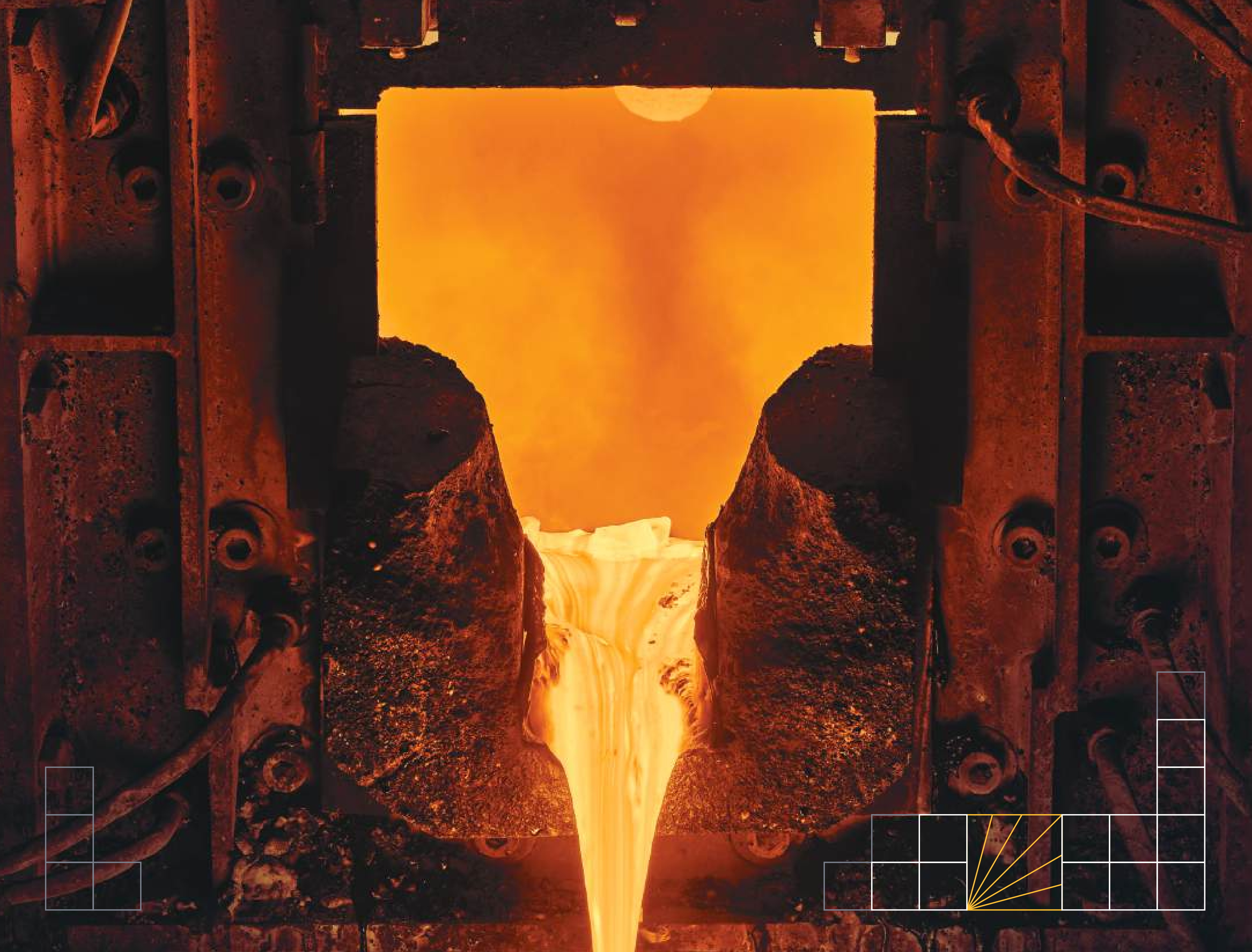
A **Wolf Spaether, Head of Strategic Marketing & Product Development Ethylene, Clariant,** wolf.spaether@clariant.com
The complexity of large-scale olefin product separation correlates with the compositional complexity of the product raw stream mixtures. Well-established fractionation technologies will quantitatively separate the different 'C-cuts' (C_1, C_2, C_3, C_4) due to their distinctively different molecular weights.

However, olefinic mixtures, dependent on their source (such as steam crackers, refineries, FCC, and deep catalytic cracking), typically contain additional impurities and poisons such as acetylenes, organic sulphur species, phosphines, and various heavy metals that cannot easily be removed by means of fractionated distillation. It is, however, imperative to remove those impurities and poisons to render the olefin product usable for further downstream conversion, such as polyethylene, polypropylene, and other base chemical processes.

In a conventional configuration, the contaminated feed streams would be passed over several adsorbents to individually remove heavy metals, sulphur, and phosphines, followed by selective hydrogenation catalysts to convert acetylenes into their corresponding olefins. This would require capital-intensive flow sheets and cause undesired operational complexity.

Advanced catalyst formulations should be able to conduct the clean-up over significantly fewer steps, even down to a one-reactor single-pass operation. A good example is Clariant's OleMax 101 catalyst series, which simultaneously cleans refinery offgas from oxygen, nitrous oxides, acetylenes, and heavy metals contamination in a single reactor design. The purified olefinic mixture can be combined with other olefin streams or directly processed in a downstream olefin recovery section. The employed capital could be significantly reduced in comparison to a conventional multi-reactor design.

Support should be provided beginning with the design phase, catalyst loading, start-up, and continued operation, as well as state-of-the-art digital data collection and analysis. Against this backdrop, a team of experienced global experts supports our clients during the entire life cycle of the catalyst, including regeneration to facilitate maximum on-stream availability.



Co-processing of chemical recycling products in FCC units

To perform a techno-economic assessment it is important to determine the crackability and the yield structure effects of alternative feedstocks

Rafael Orejas Contreras **Repsol**
María Bescansa Leirós **Grace GmbH & Co. KG Spain**
Nelson Olong and Stefan Brandt **Grace GmbH**

Advanced chemical recycling is projected to increase over the coming years and decades to improve the circularity of plastics, reduce environmental pollution, and decrease the dependency on fossil crude. The use of unconventional feedstocks, such as waste-derived streams in refinery processes, continues to be evaluated from an economic, regulatory, and environmental perspective.

As **Figure 1** shows, it is projected that the availability of plastic waste for chemical recycling will increase to about 7-20 million tons by 2030, with continued growth thereafter. Ideally, mixed plastic waste is converted by advanced chemical recycling processes to monomers as feedstocks for new plastic production to maximise carbon circularity. However, suitable conversion processes are not yet commercially available at scale. Pyrolysis technologies are finding increased application for advanced chemical recycling, producing a liquid product, plastics-derived pyrolysis oil (PDPO), which requires secondary conversion in existing refining or petrochemical assets for valorisation.

The fluid catalytic cracking (FCC) unit is one of the most flexible units in a crude oil refinery. The unique properties of the FCC unit allow significant adjustments to unit operation and, therefore, yield patterns within short periods of time. The daily catalyst addition allows for catalyst optimisation while the unit is operational.

Severe catalyst deactivation can be proactively mitigated by increased catalyst additions within the catalyst management strategy of the refinery. Longer term catalyst deactivation factors will require catalyst reformulation in collaboration with the FCC catalyst supplier. However, any significant feedstock change requires a thorough risk assessment regarding its consequences on unit operation, conversion, yield pattern, catalyst inventory and, if possible, downstream processing.

Risk assessment considerations

Determination of the physical and chemical attributes of respective feedstocks will provide a basic understanding of potential conversion and yield impacts and indicate contaminants that might affect catalyst management as well as downstream equipment. Physical attributes include density, viscosity, refractive index, boiling point distribution, and moisture content, influencing handling, transport, and processing. Chemical attributes involve elemental composition, molecular structure, and the presence of specific compounds, which determine reactivity, conversion efficiency, and compatibility with catalysts.

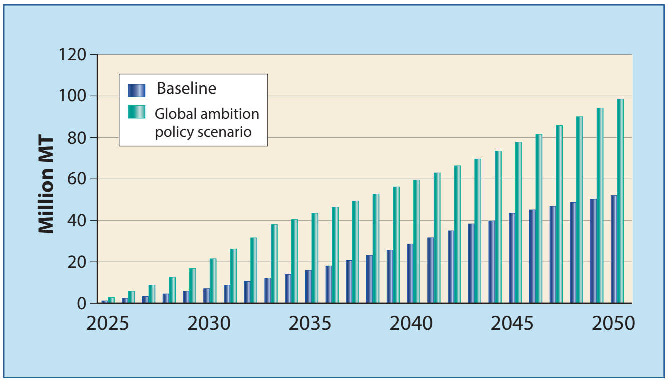


Figure 1 Outlook of plastic waste potential for chemical recycling by pyrolysis *Based on OECD data*[1]

For example, **Figure 2** depicts results from different plastics-derived feed samples received by Grace. The data proves the heterogeneity of the received samples in terms of contaminant and heteroatom contents and allows an initial assessment of impacts on FCC catalyst, operation, conversion, yield structure, and emissions.

Any significant feedstock change requires a thorough risk assessment regarding its consequences on unit operation, conversion, yield pattern, catalyst inventory and, if possible, downstream processing

Some of the feedstocks with very high Calcium (Ca) or Conradson carbon content will have an impact on catalyst deactivation and unit operation. Calcium is a known poison to the FCC catalyst, which deposits on the external surface

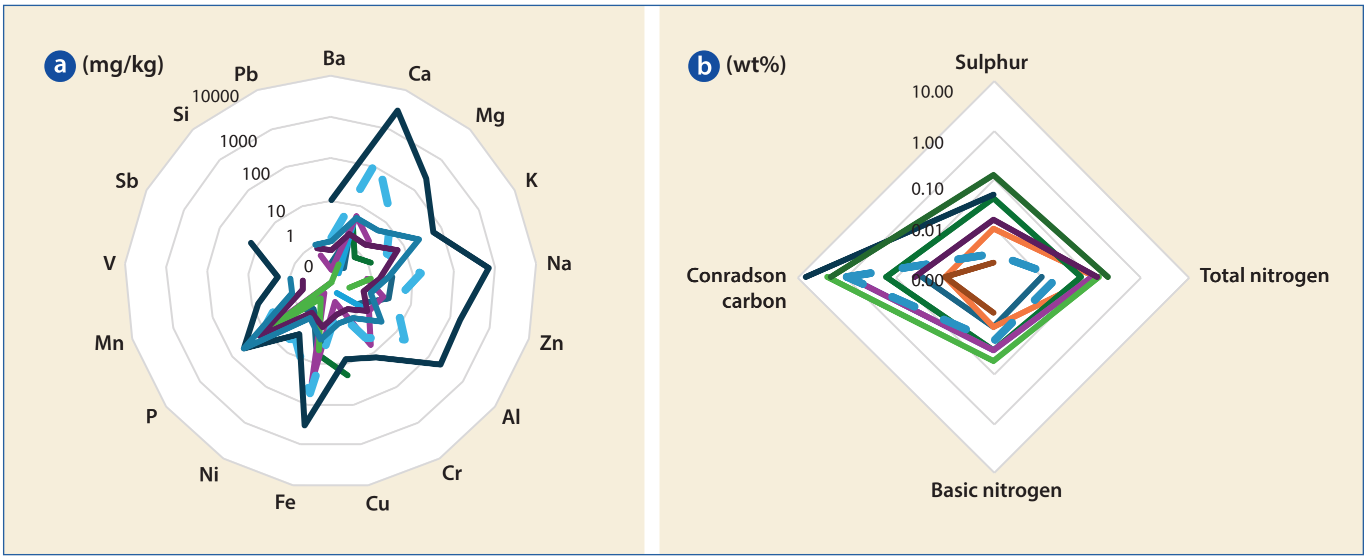


Figure 2a Contaminant contents in PDPO samples; **2b** Heteroatom and concarbon contents in PDPO samples

Physical/chemical properties of VGO, PDPO A and PDPO B			
	Standard VGO	**PDPO A**	**PDPO B**
API (15°C)	22.9	26.0	37.1
Density, 15°C (g/cm³)	0.916	0.898	0.838
Refractive Index, 60°C	1.5003	1.4720	1.4529
Sulphur (wt%)	0.09	0.01	0.13
Conradson carbon (wt%)	0.23	0.04	2.1

Table 1

of the catalyst particle, blocks feed molecule entry to the catalyst pore system and, therefore, affects the diffusion of feed or intermediate molecules to the active cracking sites (see **Figure 3**).

In addition, calcium is known to contribute to zeolite Y destruction by catalysing the dealumination processes, leading to the collapse or degradation of the zeolite framework. This results in a loss of surface area, pore volume, and catalytic activity, significantly impairing the catalyst's performance. The presence of calcium not only reduces cracking efficiency but also increases the likelihood of deactivation and fouling, necessitating frequent regeneration or replacement of the catalyst. These effects make calcium a critical contaminant to monitor and manage in FCC feedstocks.

Based on the chemical determination of contaminants in alternative feed samples, a steady-state equilibrium catalyst (Ecat) metals calculator might be used to allow an understanding of potential catalyst deactivation effects.

To perform a techno-economic assessment, it is important to determine the crackability and yield structure effects of alternative feedstocks too. For this purpose, different scales of pilot plant equipment are available, such as fixed bed, fixed fluidised bed, and fully circulating riser pilot plants. An example of such an evaluation of catalytic testing results is described in the following discussion.

Project scope

Repsol is a leading multi-energy company that works to advance the energy transition using different technologies

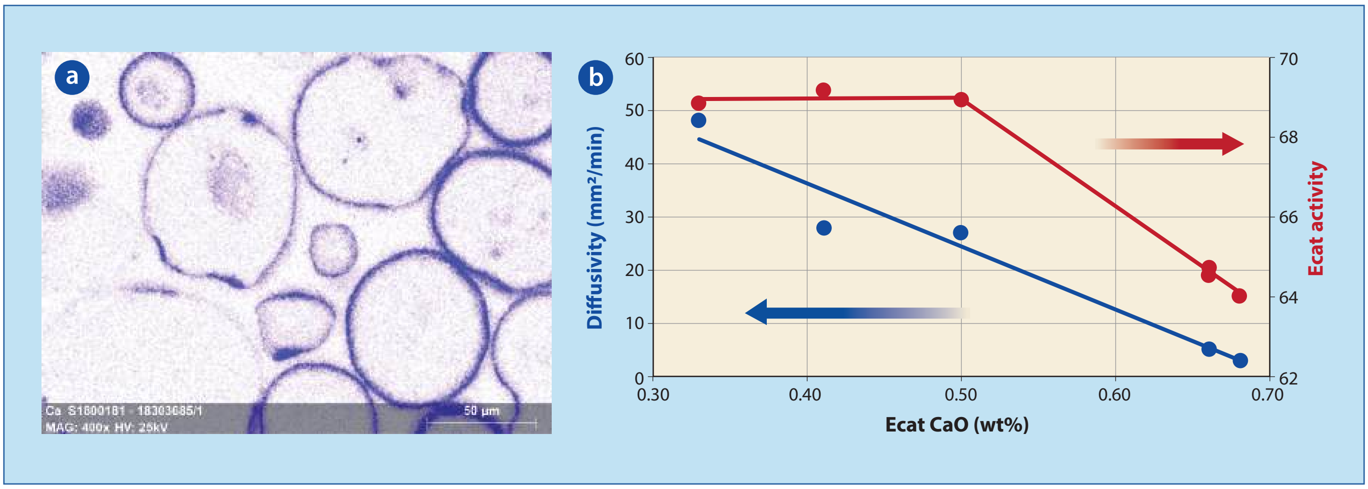
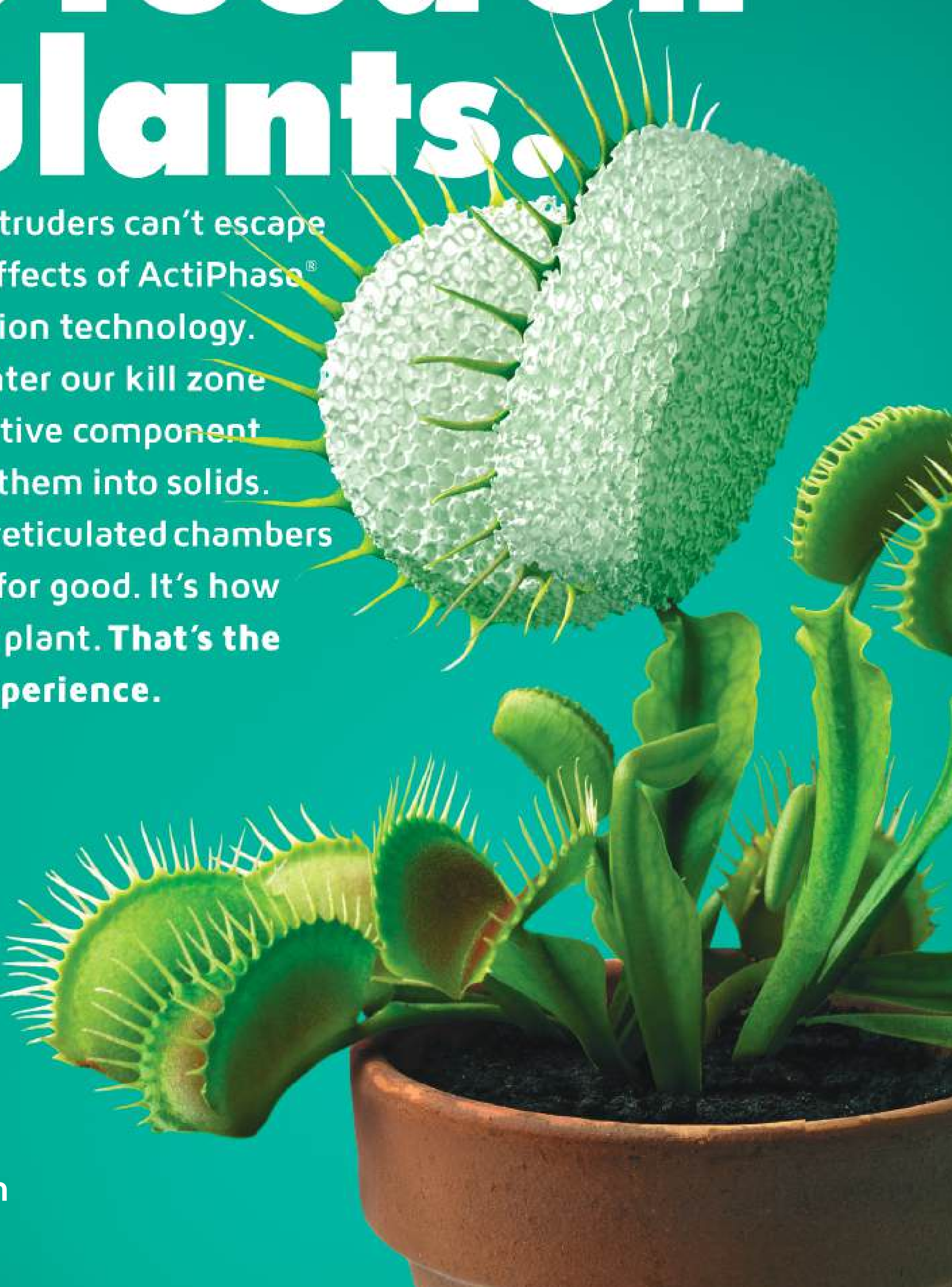


Figure 3a Cross-sectional SEM-EDX Ca mapping of Ca contaminated FCC Ecat sample; **3b** Effect of Ecat CaO content on Ecat mass transfer resistance for Ecat samples



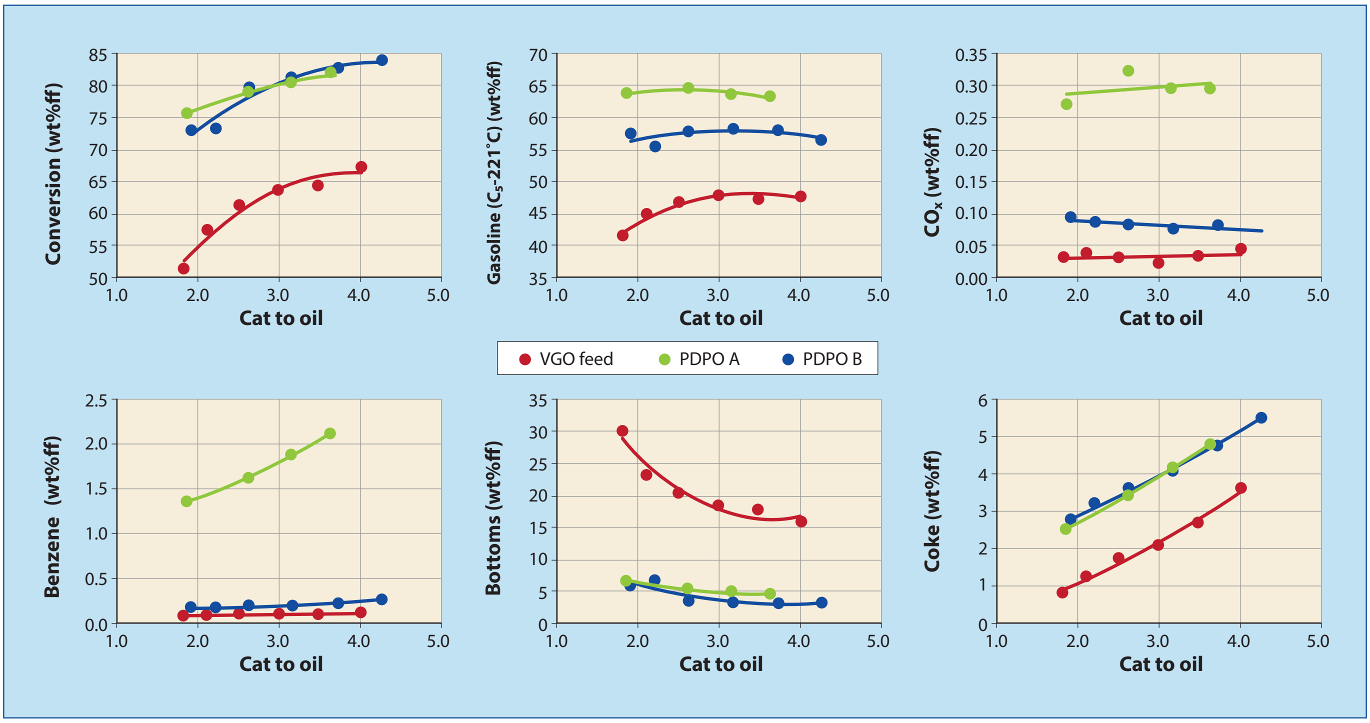


Figure 4 Conversion/yield responses for VGO and PDPO A and B feed samples from SR-SCT MAT testing

that contribute to reducing the carbon footprint. With its commitment to a sustainable world and the vision to be a global energy company that relies on innovation, efficiency, and respect to create sustainable value in the service of societal progress,[2] Repsol believes that the current energy transition should be urgently rethought and a new, fairer model set up so as to involve all of society and leave no one behind.[3]

In connection with the company's vision for the energy transition, Repsol is considering the potential of processing lower carbon intensity feedstocks in FCC units. Such feedstocks can be of biogenic origin or waste-derived feedstocks.

Repsol and Grace collaborated on the assessment of yield structure effects of waste plastics-derived feedstocks. The refining company provided two plastics-derived pyrolysis oil samples (PDPO A and PDPO B) to support an initial techno-economic assessment (TEA) of processing such feed streams in an FCC unit (see **Table 1**).

Though unconventional feedstocks like bio- or waste-derived feed streams are co-processed in the refinery, the yield structure from such feed streams is of high interest in assessing the respective margin uplift. In most cases, pilot plant co-processing experiments in blends with fossil feed components are performed to assess the incremental yields from the alternative feed component.[4] However, testing the alternative feedstock pure allows for similar information, if not limited by processing challenges in FCC pilot plant equipment.

Test programme

Waste plastics, when cracked, might yield more light olefins or aromatic compounds depending on the polymer type. To evaluate the crackability and resulting yield effects of cracking the plastics-derived pyrolysis oil samples, Grace's proprietary single-receiver short-contact microactivity test unit (SR-SCT MAT)[5] was selected. The SR-SCT MAT unit has proven its versatility in screening unconventional FCC feedstocks where impacts on testing equipment and process cannot be ruled out.

The respective samples of PDPO were compared to a typical vacuum gas oil (VGO) reference feed and converted in the SR-SCT MAT unit using a standard equilibrium catalyst sample from a VGO processing FCC unit.

Test results

The catalytic testing of the pure PDPO samples in comparison to a typical VGO highlights the different nature of the

SR-SCT MAT results from VGO and PDPO A and B samples at constant C/O

	Standard VGO	PDPO A	PDPO B
Conversion (wt%FF)	62.6	79.5	79.3
Dry gas (wt%FF)	0.9	1.0	1.3
Propylene (wt%FF)	3.6	3.6	4.7
i-C_4 (wt%FF)	2.7	1.6	3.2
i-C_4= (wt%FF)	1.2	1.3	2.2
LPG (wt%FF)	12.4	10.7	16.5
LPG olefinicity (%)	71	78	74
Gasoline (wt%FF)	47.3	64.2	57.8
LCO (wt%FF)	18.6	15.4	16.6
Bottoms (wt%FF)	18.9	5.1	4.1
Coke (wt%FF)	1.9	3.6	3.7
CO_x (wt%FF)	0.03	0.29	0.09
G-CON RON	88.8	84.7	84.9
G-CON MON	78.4	76.0	74.9
Gasoline benzene Content (wt%)	0.2	2.7	0.3

Table 2

molecular structures in the PDPO samples (see **Figure 4**). Both PDPO samples gave significantly higher conversion levels at the selected conditions, and while both samples resulted in elevated gasoline yield, PDPO A showed highest gasoline selectivity. Further, gasoline octane numbers decreased due to the higher hydrogen content of the two feeds (see **Table 2**).

The higher conversion is reflected in the very low bottoms yields from the two PDPO samples. Both samples yielded somewhat elevated coke levels, which needs to be considered in view of the commercial FCC unit's heat balance. PDPO A made a significantly higher benzene yield and somewhat higher $CO+CO_2$ (CO_x) yield. These observations indicate that the feed to the upstream pyrolysis process might be higher in monoaromatics precursors and oxygen content for PDPO A.

Catalytic testing of the respective plastics-derived pyrolysis oils A and B showed high crackability with favourable gasoline and bottoms yield. PDPO B yielded more LPG than sample A at somewhat higher LPG olefins yields like propylene and butylene. The gasoline fractions from both samples contained reduced research octane number (RON) and motor octane number (MON) quality, which needs consideration in the techno-economic assessment. Additionally, the higher coke yield for the samples needs to be included in the required modelling of FCC unit effects. The complete yield structure data allow an initial assessment of the margin uplift from the plastics-derived pyrolysis oil types.

> **By fully understanding the yield structure and addressing associated challenges, refineries can unlock the potential of waste-derived feedstocks, achieving both financial and environmental benefits**

Conclusion

By fully understanding the yield structure and addressing associated challenges, refineries can unlock the potential of waste-derived feedstocks, achieving both financial and environmental benefits. Against this backdrop, collaboration is key to accelerating the assessment of challenges and opportunities that arise with the energy transition and new developing circular value chains.

Repsol and Grace collaborated to investigate the crackability and yield structure from catalytic cracking of two different plastics-derived pyrolysis oils in pilot plant equipment. The resulting yield delta to a reference VGO sample allows an initial assessment of yield shifts but also indicates areas that might need more attention in a commercial trial, like oxygen in the PDPO or the effect on gasoline quality.

The combination of Repsol and Grace competencies in the evaluation of two plastics-derived pyrolysis oils is an example of a successful collaboration to assess opportunities and challenges associated with the processing of advanced chemical recycling feed streams in the refining industry.

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Stefan Brandt is Market Development Director Energy Transition for Grace's FCC business. He is based in Worms, Germany. He has more than 25 years of experience in FCC catalyst technology and its application, holding positions in quality control, R&D, and technical sales and service. Throughout his tenure in R&D, he was involved in various EU-funded projects for processing and co-processing of bio-based feedstocks. Brandt holds a Diploma in chemistry from the University of Bochum, Germany and a PhD in chemistry from the same university. He is the co-inventor of several patents and the co-author of peer-reviewed journals and numerous trade press articles.

Nelson Olong is Principal Scientist in the Catalyst Evaluations Research and Services group for Grace FCC. He started his career at Grace in 2007 in the FCC catalyst synthesis group and later joined the process technology department. He is currently one of the R&D partners for resid conversion, serving as Strategic Marketing Manager and responsible for catalysts evaluation. During Olong's career, he has been involved in the development of many new FCC catalysts and manufacturing processes. He holds a PhD in chemical engineering from the University of Saarland, Germany.

Advancing catalytic performance in hydrotreating: Part 1

Review of chemistry and catalysts determining performance in low- and medium-pressure distillate hydrotreating and FCC-PT

Andrea Battiston
Ketjen

Oil demand is going to be tempered by the transition to renewable energy.[1,2,3] According to the 2024 IEA's *World Energy Outlook*, worldwide fossil fuel demand is projected to peak in 2030 across all scenarios. Global consumption of refined products from oil and biofuels combined is also expected to peak at the beginning of the 2030s. However, rather than a sharp decline, a fluctuating pattern is expected, with the true peak being recognisable only years after it has occurred. On average, over the next 10 years, combined global consumption of refined liquid products from fossil and renewable origins will likely remain close to the 2024 levels.

In this evolving landscape, where hydrotreating technology maintains a primary role, innovation in catalysts is crucial for the refining industry to stay competitive, meet market demand, and allow a sustainable energy transition.

The development of advanced hydrotreating catalysts for both conventional (fossil) and renewable feedstocks, such as waste oils and fats,[4,5] and waste plastics oils,[6] benefits from the latest technological advancements in high-throughput experimentation, including machine learning and combinatorial chemistry. These tools enable a novel approach to catalyst development by helping identify deeper relationships between the properties of the catalysts' active phase and performance. The effectiveness of this approach is demonstrated by the launch over the last five years of the Pulsar and Quasar catalyst platforms, along with eight hydrotreating grades, including those within the ReNewFine renewables catalyst platform (see **Table 1**), enabling increased intake of distressed feedstock and extended cycle lengths.

Achieving enhanced performance also requires a continuous focus on developing new analytical techniques and kinetic models to gain a deeper understanding of the chemistry at play in the hydrotreaters for both existing and emerging technologies. This approach allows for a rational development and selection of catalysts based on their properties and the reactions occurring in the multiple reactor zones of the hydrotreaters. Consequently, this method promotes maximum overall unit profitability, increases operating flexibility, and reduces operational risks.

Conventional fuels hydrotreating and operating regimes

Hydrotreater performance is influenced by several factors, including feedstock characteristics, operating conditions, catalyst type, and catalyst loading configuration in the reactor. The operating objective and type of feedstock, along with its distillation properties, aromatic content, sulphur/nitrogen speciation, unsaturated compounds, and contaminants, set the challenge. The main operating conditions, particularly partial pressure of hydrogen (PPH_2) and temperature, also determined by reactor design and quench systems, define the intrinsic potential of the operation. Ultimately, the properties of the catalyst, with its activity, stability, and catalyst loading configuration that allow

Ketjen's new hydrotreating catalyst platforms and grades introduced in the market in the last five years

Platform	Grades	Application	Introduction
Stars	KF 862	Medium- and high-pressure distillate HT; HC-PT	2023
	KF 787	Low- and medium-pressure distillate HT	2019
Pulsar	KF 774	Medium-pressure distillate HT	2021
	KF 917	**FCC-PT**	**2024**
Quasar	KF 882	Medium- and high-pressure distillate HT; 100% LCO-HT	2023
	KF 872	**HC-PT**	**2024**
ReNewFine	**RNF 102**	**Renewables – phosphorous-trapping**	**2024**
	RNF 204	**Renewables – hydro-deoxygenation (HDO)**	**2024**

The latest catalysts, introduced in 2024, are indicated in bold

Table 1

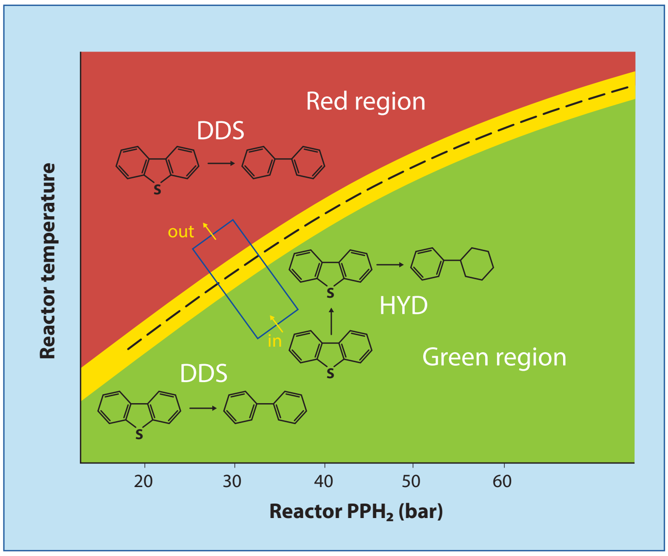

Figure 1 Operating regions in a hydrotreater as a function of the operating H_2 pressure and temperature

catalysts to operate in synergy, turn the operating potential of a hydrotreater into actual performance.

In conventional (fossil) hydrotreating, catalysts are selected to achieve two primary objectives: controlling poisons (such as sodium, silicon, iron, arsenic, nickel and vanadium) using a guard bed; and optimising hydrodesulphurisation (HDS), hydrodenitrogenation (HDN), and hydrodearomatisation (HDA) throughout the cycle with the main catalyst system.

The HDS reaction proceeds via two pathways: direct desulphurisation (DDS) and hydrogenation (HYD). The DDS pathway primarily removes easy sulphur species, is usually the fastest route at low hydrogen pressure (< ca. 30 bar/450 psig), and is not affected by nitrogen and aromatics inhibition or by thermodynamic equilibrium for hydrogenation. In contrast, the HYD pathway removes refractory sulphur species and is favoured at higher hydrogen pressure, but it is also severely affected by nitrogen inhibition and thermodynamic equilibrium. Note that the last step in the HYD reaction pathway is a DDS step, so HYD also requires the presence of DDS active sites in the catalyst to be able to proceed.

HDN and HDA proceed via a hydrogenation step like HYD. Refractory (basic) nitrogen, in particular, inhibits the HYD and HDA reactions. The ability to remove refractory nitrogen allows for boosting HDS and HDA, resulting in a significant operational advantage. So, HDN activity is key, especially in distillate hydrotreating operations at medium and high pressure. HYD is potentially the fastest HDS reaction pathway. However, it is only effective if PPH_2 is sufficiently high (> ca. 35 bar/500 psig), inhibition by refractory nitrogen and polynuclear aromatics (PNAs) is not too high, and the proper combination of PPH_2 and temperature is met.

Based on these observations, three operating regimes (regions) can be identified for a hydrotreating reactor (see **Figure 1**). The effectiveness of different reaction routes and the type of catalysts applied varies across these regions:

❶ In the green operating region, characterised by a low temperature-to-hydrogen pressure ratio, all reactions (DDS, HYD, HDN, and HDA) are effective. DDS is the dominant route for HDS at low pressure or when inhibition by nitrogen and PNAs is severe. HYD, HDN, and HDA become increasingly favoured at higher pressure. The green region is the safest from an operational perspective, leading to the highest volume swell and hydrogen consumption. Also depending on nitrogen and PNAs inhibition, the green region allows applying both DDS- and HYD-selective catalysts, with HYD catalysts being more effective and thus preferred at higher pressure and when hydrogen consumption is not a limitation.

❷ In the intermediate (yellow) region, the reaction rates of HDN, HYD, and HDA begin to slow down due to limitations on the hydrogenation steps imposed by the thermodynamic equilibrium. When operating in this regime, either DDS- or HYD-selective catalysts could potentially be applied. However, DDS-selective catalysts are usually preferred in view of the risk of slipping into the red region, where a high HYD-selective catalyst is not suited.

❸ In the red region, which has the highest temperature-to-hydrogen pressure ratio, all hydrogenation-assisted reaction routes (HYD, HDN, and HDA) are hindered. In this region, the rates of sulphur and nitrogen removal are significantly lower, and HDS proceeds almost exclusively via the DDS route. In this regime, dehydrogenation and condensation reactions are thermodynamically favoured, and coking and deactivation can occur if a catalyst with too high selectivity for hydrogenation is applied. Operating in this regime requires caution and the use of a highly DDS-selective catalyst.

As commercial hydrotreaters are characterised by an increasing temperature profile and a decreasing pressure profile when moving from the reactor top (inlet) to the bottom (outlet) (Figure 1), the bottom section of the reactor is more likely to be exposed to thermodynamic limitation for hydrogenation (red region). This is often the case for moderate pressure hydrotreaters processing difficult feedstocks. The top section of the reactor, in contrast, is typically affected by nitrogen and PNAs inhibition. A specific function of the quenches, by decreasing the temperature locally in the reactor, is to increase the fraction of the catalyst operating in the green region, providing a larger window for exploiting the hydrogenation reaction pathway for HDS, HDN, and HDA.

Catalyst design and performance

The performance of a catalyst can be optimised by modifying the properties of the support and the active metal phase. These include the active metal phase's accessibility for the reactants, composition, morphology, and interaction with the support. Catalysts with a strong interaction between the metals and the support are often referred to as Type I, while those with a weak interaction are called Type II. The strength of the interaction is determined by the manufacturing procedure.

The morphology of the metal slabs and their interaction with the support determine the DDS or HYD character of a catalyst. This, in turn, influences the catalyst's activity and stability depending on the operating regime of the hydrotreater, as discussed in the previous section. High DDS selectivity, which leads to lower nitrogen and PNAs

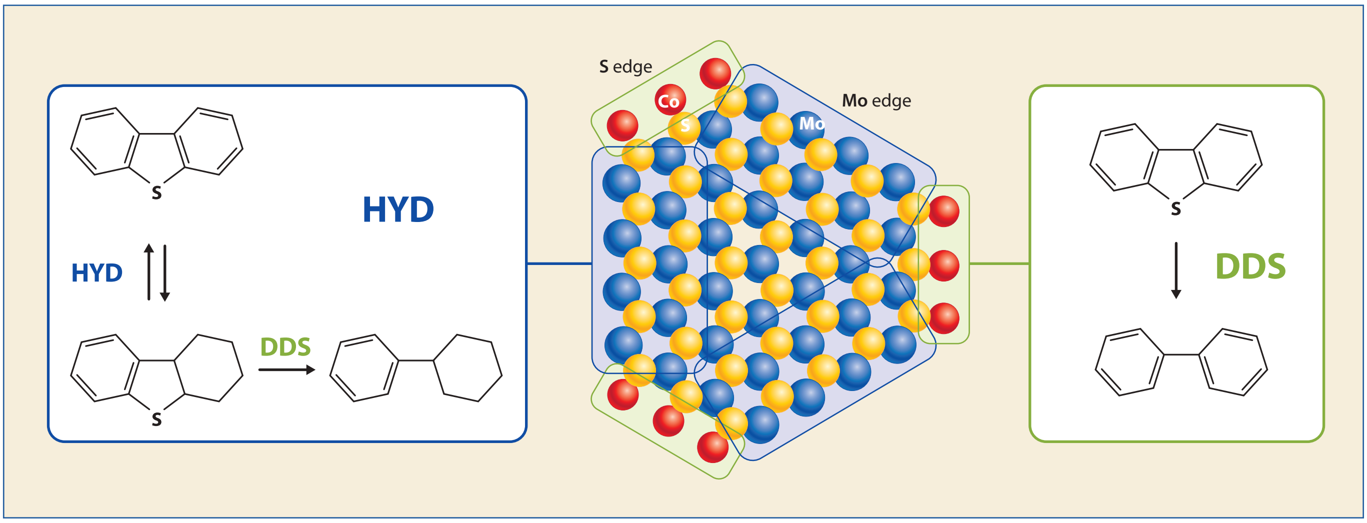

Figure 2 Model of the DDS (light green frames) and the HYD (blue frames) active sites in CoMo hydrotreating catalysts

inhibition, and overall better performance at low pressure and in the red operating region, is typical of catalysts with smaller metal slabs and stronger metal-support interaction (Type I). HYD selectivity, on the other hand, is enhanced by lower metal-support interaction (Type II). Notably, NiMo catalysts have higher HYD selectivity than CoMo catalysts, regardless of other characteristics.

The relationship between the morphology of the active metal phase and the DDS and HYD activity/selectivity is visualised in **Figure 2** for a CoMo catalyst. The DDS reaction pathway occurs at the positions available for the cobalt (Co) atoms at the slabs' sulphur edges (light green frames). Conversely, all hydrogenation reactions, including the HYD pathway for HDS, take place on the molybdenum (Mo) atoms adjacent to the slabs' edges (blue frames). Smaller metal slabs possess more DDS sites relative to HYD sites and are thus more DDS selective. At equal metal slabs size, a catalyst's HYD character can be further increased by lowering the interaction between the metal slabs and the support.

In general, smaller and better-dispersed metal slabs are highly beneficial for the hydrotreaters' performance in all applications and operating regions. They lead to higher efficiency with more activity provided for the same amount of metal. They also provide higher stability thanks to their greater tolerance to nitrogen and PNAs and lower tendency to coking, metal mobility, and sintering. The advantage of smaller and better-dispersed metal slabs is greater for applications that rely heavily on the DDS reaction pathway for HDS, such as low- and medium-pressure distillate hydrotreating and fluid catalytic cracking pretreatment (FCC-PT).

Low- and medium-pressure distillate hydrotreating

Pulsar is Ketjen's latest catalyst platform alongside Quasar. Initially introduced for distillate hydrotreating, this technology has now been further developed for FCC-PT applications in partnership with Nippon Ketjen. This collaboration led to the market introduction of KF 917 Pulsar at the end of 2024. Two grades are applied for distillate hydrotreating, KF 787 and KF 774. The two catalysts combined cover all types of distillate applications from low to medium-to-high pressure (typically, 10-60 bar/150-900 psig PPH_2).

Despite their recent introduction, distillate hydrotreating Pulsar grades have already become a standard in the industry, with more than 7,000 tons of catalyst applied and 60 commercial cycles. One of the key features of the Pulsar technology is its advanced active phase morphology. Pulsar metal slabs are significantly better dispersed and approximately 40% smaller than in previous generation catalysts.

Their size distribution is also very narrow. **Figure 3**

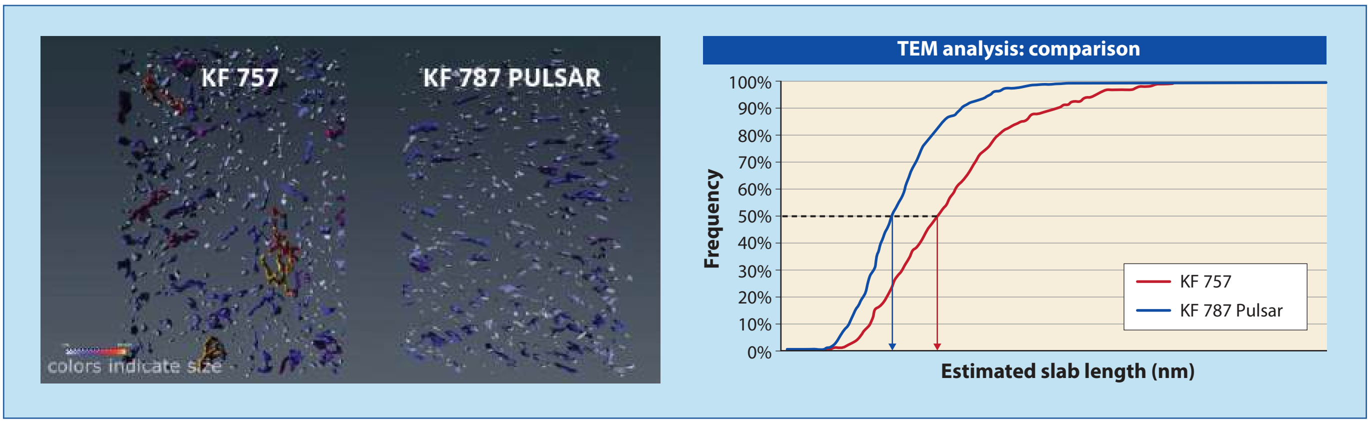

Figure 3 Statistical analysis of the metal slabs' length in spent KF 787 Pulsar after operating with cracked feedstock at high temperature (3D-STEM study)

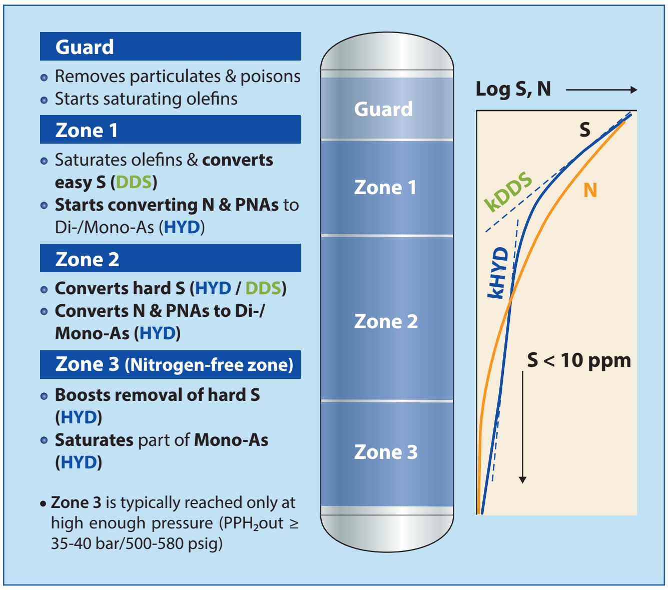

Figure 4 Reactor zones and the function of DDS vs HYD activity in distillate hydrotreaters

illustrates the results of a statistical analysis of the metal slab lengths measured using 3D scanning transmission electron microscopy (3D-STEM) after testing KF 787 alongside reference catalyst KF 757. The 40-day activity test was conducted to produce ultra-low sulphur diesel (ULSD) while feeding cracked feedstock at low pressure, including the red operating regime (Figure 1), with temperatures as high as 380°C/715°F. Despite the severe operating conditions, the small size and the excellent dispersion of the metal slabs in KF 787 were very well preserved.

The benefits of applying KF 787 and KF 774 in distillate applications can be explained by considering the reactions occurring in a diesel hydrotreater and by recalling the observations on the operating regimes and the effect on the catalyst properties on performance, as discussed in the previous sections. As illustrated in **Figure 4**, two or three operating zones exist in a distillate hydrotreater below the guard bed section. The third zone at the reactor bottom is present only if nitrogen is (almost) completely removed. This typically occurs in applications with a PPH₂ outlet above 35-40 bar (500-580 psig), where the entire reactor, including the bottom section, operates in the green region.

Zone 1, at the top, is usually affected by the inhibitory effect on HDS by refractory nitrogen and PNAs, which is particularly strong at moderate pressure and when upgrading distressed and cracked feedstock. A catalyst with high DDS selectivity is preferred in Zone 1 unless PPH₂ is high enough for the inhibition effects to be sufficiently low.

Zone 2 is the part of the reactor where the inhibition by nitrogen and PNAs is low enough for the HYD function to become effective. In this zone, a catalyst with higher HDN activity and HYD selectivity is preferred when operating in the green regime, as it can lower nitrogen more quickly and is more effective at removing refractory sulphur to meet ULSD specifications. Conversely, in the yellow and red regimes, a higher DDS-selective catalyst is necessary. Note that operations at low or medium pressure with a very high intake of cracked feedstock usually do not reach Zone 3.

Zone 3 is reached only if product nitrogen is low enough, typically close to zero ppmwt when operating at low and medium pressure. The benefit of Zone 3 compared to Zone 2 is the drastically reduced inhibition on hydrogenation reactions, which boosts HDS and HDA activity, thereby maximising volume swell. Since Zone 3 requires favourable thermodynamic conditions for hydrogenation, it can only exist when the bottom section of the reactor operates in the green region (Figure 1). Note that Zone 3 is easier to reach in the earlier part of the operating cycle, when the weighted average bed temperature (WABT) is lower and the HYD and HDN/HDS selectivity of the catalyst is higher.

KF 787 has very high DDS selectivity and delivers superior HDS and HDN activity and stability in both low- and medium-pressure applications, allowing the processing of a wide range of feedstocks, including straight-run gasoil (SRGO) and cracked feedstock. KF 787 is suited for any zone of the reactor. Depending on H₂ availability, it can be applied standalone or in combination with KF 774, with

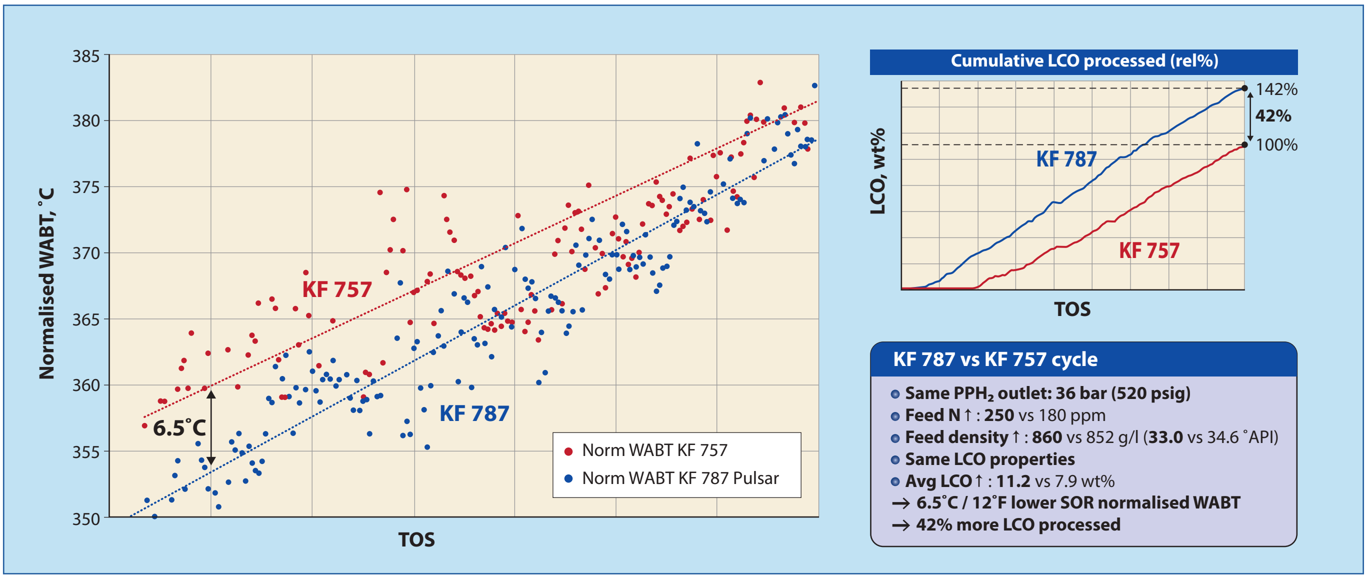

Figure 5 Low-to-medium pressure KF 787 commercial case: 6.5°C /12°F lower normalised SOR WABT and 42% more LCO processed

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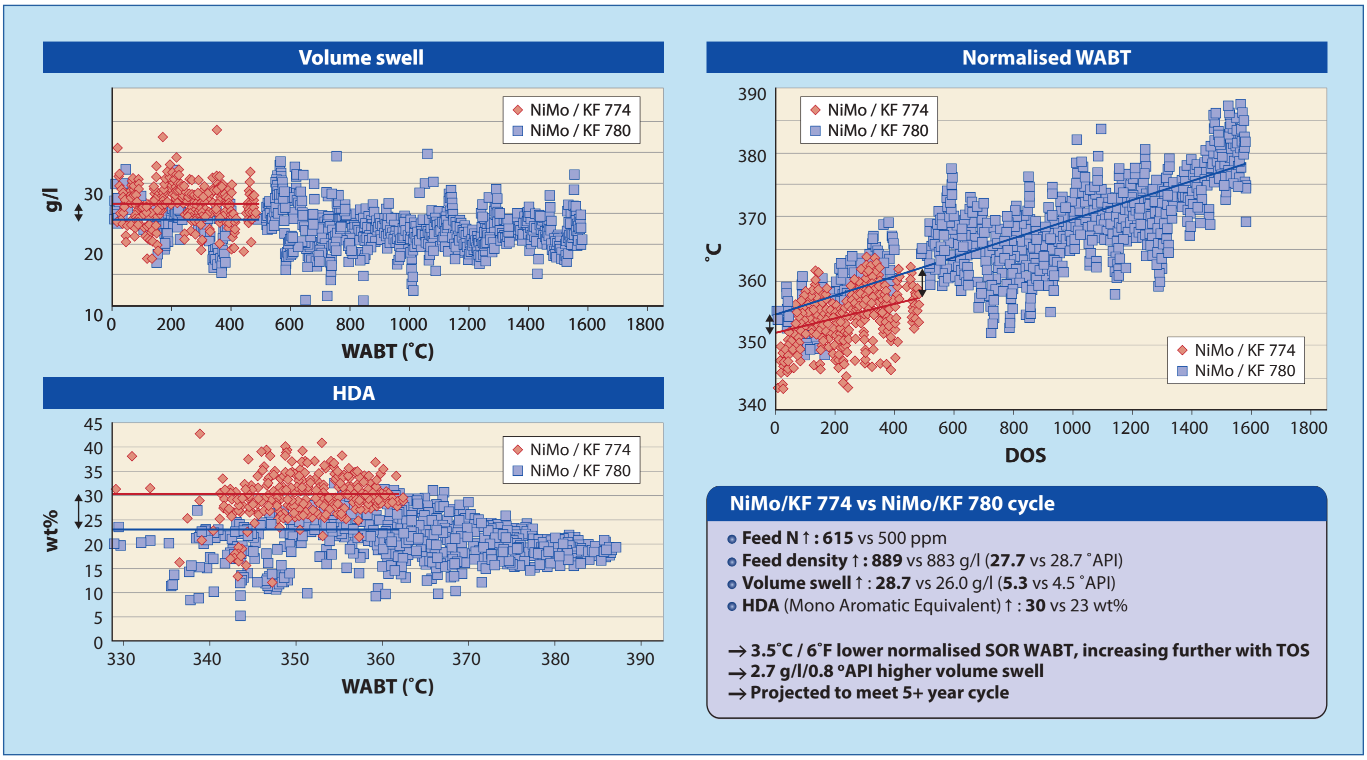


NiMo/KF 774 vs NiMo/KF 780 cycle

- **Feed N ↑ : 615** vs 500 ppm
- **Feed density ↑ : 889** vs 883 g/l (**27.7** vs 28.7 ˚API)
- **Volume swell ↑ : 28.7** vs 26.0 g/l (**5.3** vs 4.5 ˚API)
- **HDA** (Mono Aromatic Equivalent) ↑ : **30** vs 23 wt%

→ 3.5˚C / 6˚F lower normalised SOR WABT, increasing further with TOS
→ 2.7 g/l/0.8 °API higher volume swell
→ Projected to meet 5+ year cycle

Figure 6 High-pressure NiMo/KF 774 commercial case: 3.5°C/6°F lower normalised SOR WABT and 2.7 g/l/0.8°API higher volume swell. The NiMo/KF 774 Stax system is running more stable than the previous catalyst and is projected to meet more than a five-year cycle

KF 774 applied in Zone 2 to boost HDN and HDS further, allowing an even higher intake of distressed feedstock.

KF 774 has higher HYD selectivity compared to KF 787 and is designed for medium and medium-to-high pressure applications, processing even more difficult feed, including high-nitrogen cracked components. KF 774 can be applied standalone at medium pressure. For applications with low PPH$_2$ outlet or close to the yellow operating regime (Figure 1), KF 787 is typically applied under KF 774 (KF 774/KF 787) to boost DDS selectivity at the reactor bottom and, with it, reduce hydrogen consumption and increase operating stability. In contrast, for medium-to-high applications with good H$_2$ coverage and low enough inhibition by nitrogen and PNAs in Zone 1, KF 774 can be loaded in combination with a NiMo catalyst on top. NiMo/KF 774 loading configurations can further boost overall performance, with KF 774 allowing for reduced hydrogen consumption and improved stability compared to a full NiMo loading system.

Case studies

Refiners are leveraging the Pulsar catalyst technology in distillate hydrotreating to achieve various objectives by lifting performance constraints. Key achievements include upgrading significantly more distressed feedstock and achieving longer cycles. As the Pulsar technology is applicable across a broad range of pressure and feedstocks, it also enables high operational flexibility and simplifies catalyst pool management. Additionally, it offers economic advantage through energy savings from lowered WABT.

Three cases illustrate the benefits of the Pulsar platform for distillate hydrotreating in commercial practice. In the first one, KF 787 was loaded as the main catalyst in a particularly challenging low-to-medium pressure ULSD operation (PPH$_2$ outlet = 36 bar/520 psig) targeting maximum LCO intake (see **Figure 5**). Compared to the previous cycle with earlier generation KF 757, KF 787 allowed for a reduction in the normalised start-of-run (SOR) WABT of 6.5°C/12°F and for an increase of the average intake of light cycle oil (LCO) from 7.9 to 11.2 wt%, leading to 42% more LCO being processed. The main operating conditions in the two cycles were the same as the quality of LCO treated (density = 950 g/l/17.4°API, T95% = 369°C/696°F). Based on its performance, KF 787 has been confirmed in the unit for three cycles.

A second notable commercial case, given the significant value generated, involves a medium-pressure ULSD unit loaded with a KF 774/KF 787 system (PPH$_2$ outlet = 44 bar/640 psig). In this catalyst configuration, defined through Stax, Ketjen's proprietary kinetic model and reactor load optimisation technology, the specific function of KF 774 is to convert nitrogen more quickly and increase HYD activity in Zone 2, allowing for more effective removal of refractory sulphur.

The unit is operated to maximise cracked stock intake, including low-value thermally cracked gasoil. A specific target when loading the Pulsar catalyst system was to prolong the cycle length at equal cracked stock intake from the usual two to three years, providing the refinery with the option to synchronise the change-out with that of other units. Thanks to increased catalytic activity and stability, the cycle has successfully passed more than two years on stream with the same cracked stock intake as previous cycles, but with also sufficient activity to meet the targeted three-year cycle length. In view of the excellent performance, the same catalyst system has been confirmed for the next cycle.

The third case consists of a high-pressure ULSD hydrotreater, operating with an outlet PPH$_2$ of 66 bar/960 psig and processing a feedstock primarily composed of SRGO, LCO, and coker gasoil (CGO). The unit is hydrogen-constrained due to limitations of the make-up gas compressor. The primary objective is to extend cycle length to consistently achieve a five-year cycle while also increasing volume swell. This is being accomplished by applying a NiMo/KF 774 catalyst Stax configuration. KF 774 has been positioned at the reactor bottom with the dual objective of maximising HDS activity without consuming too much hydrogen and safeguarding stability for the entire five-year cycle.

The catalyst system has successfully achieved both objectives thus far in the cycle. This is highlighted in **Figure 6** by the 3.5°C/6°F lower SOR WABT, 0.1°C/0.2°F lower monthly deactivation rate, and the 2.7 g/ml/0.8°API volume swell increase compared to the first 15 months on stream of the previous cycle, which was loaded with NiMo/KF 780. The unit is expected to exceed the five-year target cycle length.

FCC-Pretreat

The economic value of FCC-PT depends on its ability to enhance the yields and quality of FCC unit products. The main objectives in FCC-PT include minimising sulphur levels through HDS, reducing nitrogen and aromatic content by optimising HDN and HDA, and increasing the conversion of vacuum gasoil (VGO) to diesel-range products.

Figure 7, analogous to Figure 4 for distillate hydrotreating, illustrates the main operating zones and the role of the DDS and HYD functionalities of the catalyst in a low- and medium-pressure FCC-PT unit (inlet PPH$_2$ < 90 bar/1,300 psig).

Unlike in distillate hydrotreaters, in FCC-PT units Zone 3 (nitrogen-free zone) is never reached due to the significantly higher presence of refractory nitrogen and PNAs in VGO and heavy coker gasoil (HCGO), owing to their higher boiling points. Consequently, FCC-PT reactors operate either entirely in Zone 1, or in Zones 1 and 2.

Zone 1 in FCC-PT is defined as the part of the reactor where predominantly olefins and easy sulphur are converted. In Zone 1, the main limiting factor for performance is the inhibition by refractory nitrogen and PNAs, particularly on the removal of hard sulphur. HDN and HDA reactions tend to be further constrained by the relatively low hydrogen pressure.

Loading a catalyst with high DDS activity in Zone 1 is crucial for two reasons: DDS is the fastest reaction route to remove sulphur and helps limit coke formation on the active metal phase. Additionally, good pore accessibility is important to allow the deposition of coke and metals without significantly impacting reactants' mass transfer.

When the intermediate product nitrogen falls to a sufficiently low level, Zone 2 is reached. Refractory sulphur also starts being converted as HDS proceeds via both the DDS and HYD routes. Due to the reduced inhibition, HDN of refractory nitrogen and HDA are also favoured. While the exact nitrogen and corresponding sulphur levels marking the transition from Zone 1 to Zone 2 vary by operation, it is generally assumed that Zone 2 starts below a product sulphur level of approximately 1,500 ppmwt.

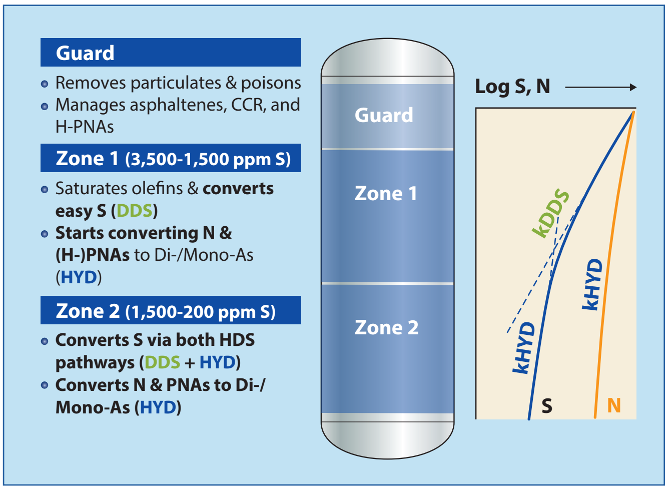


Figure 7 Reactor zones and role of the catalyst's DDS and HYD functionalities in a low- and medium-pressure FCC-PT hydrotreater

A catalyst for Zone 2 still requires high DDS activity but also needs sufficiently high HYD activity. An open pore structure is highly beneficial also in Zone 2, especially when the main operating target is increased conversion of VGO feed to diesel, as it provides better stability against coke deposition, particularly at the high temperatures where maximum conversion is achieved.

The features that make Pulsar technology excel in distillate hydrotreating also make it effective in low- and medium-pressure FCC-PT operations in Zones 1 and 2, both in HDS and conversion mode. The small size of the Pulsar metal slabs provides very high DDS activity, low nitrogen and PNAs inhibition, and low tendency to coking. Their high dispersion and narrow size distribution increase stability by reducing the likelihood of metal migration and sintering.

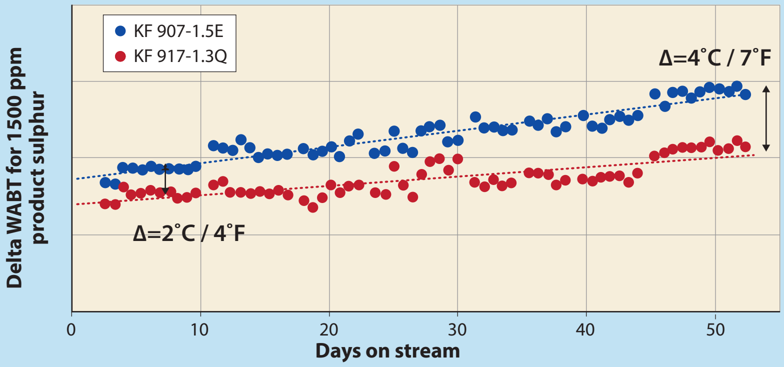
The first catalyst developed for FCC-PT using Pulsar technology is KF 917, a high-performance NiCoMo grade for low- and medium-pressure operations, created in collaboration with Nippon Ketjen's R&D centre in Niihama, Japan. Launched in the last quarter of 2024, it already has a commercial application. Its active phase provides high DDS selectivity and nitrogen tolerance, leading to high HDS activity and stability, as well as improved HDN and HDA activity with moderate hydrogen consumption.

KF 917 is highly effective in both Zones 1 and 2 of the reactor. Its performance advantage can be monetised by refiners by increasing the intake of more distressed feedstock and/or through lowering operating WABT and increasing cycle length. Additional benefits include operational flexibility and robustness. KF 917 can treat a broad range of feedstocks, including high percentages of HCGO, with increased resistance to operational upsets. Its advantage over previous generation KF 907 is demonstrated through two comprehensive pilot plant tests, as summarised in **Figure 8,** highlighting advantages in terms of SOR activity, enhanced stability, and its capability to process more challenging feedstock.

The first test consisted of a side-by-side comparison of the two catalysts at low pressure fed with VGO and operating at a constant product sulphur level of 1,500 ppmwt. To

Test 1: VGO

Test 1		
PPH$_2$ in	(bar / psig)	**45-50 / 650-725**
H$_2$/oil	(Nl/l / scf/b)	**200-300 / 1200-1800**
LHSV	(h-1)	**0.6-4.0**
Feed properties		**VGO**
Sulphur	(wt%)	**2.26**
Nitrogen	(ppmwt)	**934**
Density	(g/l / °API)	**918 / 22.6**
T10%	(°C / °F)	**338 / 640**
T50%	(°C / °F)	**433 / 811**
T90%	(°C / °F)	**511 / 952**



Test 2: VGO + VGO/HCGO

Test 2				
PPH$_2$ in	(bar / psig)	**42-51 / 610-740**		
H$_2$/oil	(Nl/l / scf/b)	**285-350 / 1700-2100**		
LHSV	(h-1)	**1.9-2.3**		
Feed properties		**VGO**	**VGO-1**	**VGO-2**
Blending ratio (vol%)	**VGO**	**100**	**39**	**21**
	HCGO-1	**–**	**54**	**77**
	HCGO-2	**–**	**7**	**2**
Sulphur	(wt%)	**1.76**	**2.53**	**2.58**
Total nitrogen (Basic)	(ppmwt)	**868 (240)**	**1638 (478)**	**1843 (593)**
Density	(g/l / °API)	**909 / 24.2**	**933 / 20.2**	**942 / 18.7**
T10%	(°C / °F)	**328 / 622**	**310 / 590**	**306 / 583**
T50%	(°C / °F)	**431 / 608**	**418 / 784**	**418 / 784**
T90%	(°C / °F)	**516 / 961**	**507 / 945**	**509 / 948**
Product S/ N	(ppmwt)	**1500 / 540**	**1700 / 1050**	**1800 / 1200**

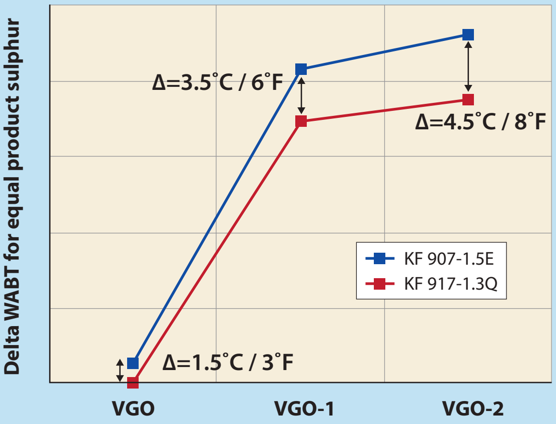


Figure 8 Performance advantage of KF 917 in FCC-PT when processing VGO and VGO/HCGO blends. KF 917's activity advantage increases with both time-on-stream (TOS) and with the higher intake of more challenging feedstock

maintain both catalysts at the same target product sulphur, the WABT of the two reactors was varied independently, while all the other operating parameters were kept the same.

The HDS activity advantage of KF 917 increased from 2°C/4°F at SOR to 4°C/7°F after 50 days-on-stream (DOS), demonstrating its higher activity and stability and thus its ability to prolong cycle length. In the second test, the ability of the two catalysts to treat more difficult feedstock was compared. Three feedstocks were screened: VGO and two blends of VGO with increasing amounts of refractory HCGO components, blend VGO1 (61 wt% total HCGO), and blend VGO2 (79 wt% total HCGO).

Increased intake of HCGO led to higher sulphur, basic nitrogen, and density of the feed blend. Also in this test, the WABT of the two catalysts was varied independently in the reactors to meet the same target product sulphur, which was 1,500, 1,700 and 1,800 ppmwt for feeds VGO, VGO1, and VGO2, respectively. The results of the second test prove that KF 917 is not only more active when treating VGO (1.5°C/3°F lower WABT) but also that its activity advantage increases with increasingly higher intake of HCGO (3.5°C/6°F lower WABT with blend VGO1, and 4.5°C/8°F lower WABT with blend VGO2). Additionally, its hydrogen consumption for the same product sulphur level was slightly lower (average of 2-3 Nl/l/10-15 scf/b across the three feedstocks) compared to KF 907, as KF 917 was able to meet the product sulphur target at a lower temperature thanks to its higher activity and stability.

Going forward

Part 2 of the article will appear in *PTQ* Q3 2025 and discuss Ketjen's latest catalyst technology developments and their benefits in conventional high-pressure distillate hydrotreating and HC-PT, and in distillate renewables co-processing applications. Key reactions and factors determining performance will be examined, along with solutions to increase operating flexibility, robustness, and maximise profitability.

Acknowledgment

The author would like to express his gratitude to everyone at Ketjen and Nippon Ketjen who contributed to the development and introduction in the market of the catalysts discussed in this paper.

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Renewables Part 2: A focus on SAF

Review of HEFA technologies as well as alcohol-to-jet and Fischer-Tropsch synthetic paraffinic kerosene processes and the impact of feedstock and process choices

Woody Shiflett
Blue Ridge Consulting LLC

In Part 1 of this article published in *PTQ* Q1 2025,[1] the potential for renewable diesel (RD) and sustainable aviation fuel (SAF) was reviewed, with a particular focus on SAF. The chemistry of hydrotreated esters and fatty acids (HEFA) processes, the current predominant technology employed for RD and SAF, was overviewed along with the types of catalysts used. Co-processing opportunities were explained as a lower barrier means to entering SAF production with existing fossil fuel assets.

In this article, a detailed look is taken at existing HEFA technologies as well as alcohol-to-jet (ATJ) and Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK) processes. A brief, high-level assessment is made of the dependence of carbon intensity (CI) and greenhouse gas (GHG) emissions on feedstock and process choices. Additionally, the impact of the complexity of governmental regulations and incentives on production economics is shown by example.

RD and SAF hydroprocessing processes

All technology providers of renewables hydroprocessing offer two-stage systems, and some also offer single-stage systems. Single-stage systems have lower capital expense (Capex) but less flexibility and yield. As noted in the co-processing discussion, such systems are also limited in their ability to produce SAF and primarily produce RD. Triglycerides typically yield C_{16}, C_{18}, C_{20}, and C_{22} normal alkanes via strict hydrodeoxygenation (HDO) mechanisms, and C_{15}, C_{17}, C_{19}, and C_{21} via decarboxylation, placing the compounds in the diesel boiling range.

The jet fuel boiling range is in the carbon range of C_8 to C_{16} alkanes, dictating that the hydrotreated vegetable oil (HVO) product will need to be hydrocracked into the range appropriate for SAF. In a two-stage unit, this is readily facilitated by incorporating hydrocracking functionality into the dewaxing catalyst or employing hydrocracking catalyst along with dewaxing catalyst in the second-stage reactor. Otherwise, HVO will need to be directed to a separate hydrocracking unit in order to produce SAF. In maximum SAF production mode, these processes can yield about 75-80% SAF.

Neste developed its own proprietary process, NExBTL, for the production of renewable fuels. It received a patent for it in 1997 and subsequently commercialised its first plant in its Porvoo, Finland refinery in 2007. NExBTL technology allows Neste to convert a wide range of renewable raw materials into premium-quality renewable products, including fuels for road transport and aviation, as well as for renewable products for chemicals and plastics feedstocks.

Since 2007, Neste has added production capacity in Rotterdam (2010) and Singapore (2011) using its proprietary MY Renewable Diesel and MY Sustainable Aviation Fuel brands, making it one of the largest global renewable fuels producers. After a planned expansion at the Singapore refinery, completed in 2023, the total global renewable product capacity will be close to 4.5 million ton/annum (1,500 million US gal/year, 100,000 bbl/day). Approximately one-third of this is estimated to be SAF. In addition, Neste has formed a joint venture with Marathon to produce renewable fuels at Marathon's Martinez, California refinery, adding a nameplate capacity of 2.1 million tons per annum (700 million US gal/year, 45,000bbl/day) at the end of 2023. This is expected to be largely RD at the time of writing.

> **The jet fuel boiling range is in the carbon range of C_8 to C_{16} alkanes, dictating that the HVO product will need to be hydrocracked into the range appropriate for SAF**

Neste's proprietary NExBTL technology is closely held and is stated to contain both an HDO step and an isomerisation step after preliminary pretreatment to remove contaminants. Patent activity shows that a counter-current flow isomerisation step could be an innovative part of the process. Ketjen supplies catalyst for the NExBTL process. Of note are SAF offtake or supply agreements with more than a dozen airlines, including Singapore Airlines, Air New Zealand, Air France-KLM, JAL, DHL, VivaAerobus, Boeing, Avfuel (US West Coast), American, Alaska, Air Canada, Emirates, United, and Ryanair.

Technology supplier approaches

There is a plethora of information regarding technology suppliers and licensors available on their respective websites and in industry publications. Most use similar approaches to HEFA processing and employ catalyst systems based fundamentally on hydroprocessing catalyst technology. Hence, only overview and summary information will be covered in this article.

Honeywell UOP collaborated with Eni SpA in the early 2000s to address evolving EU renewable fuels requirements, with subsequent patent activity in 2007 and 2008

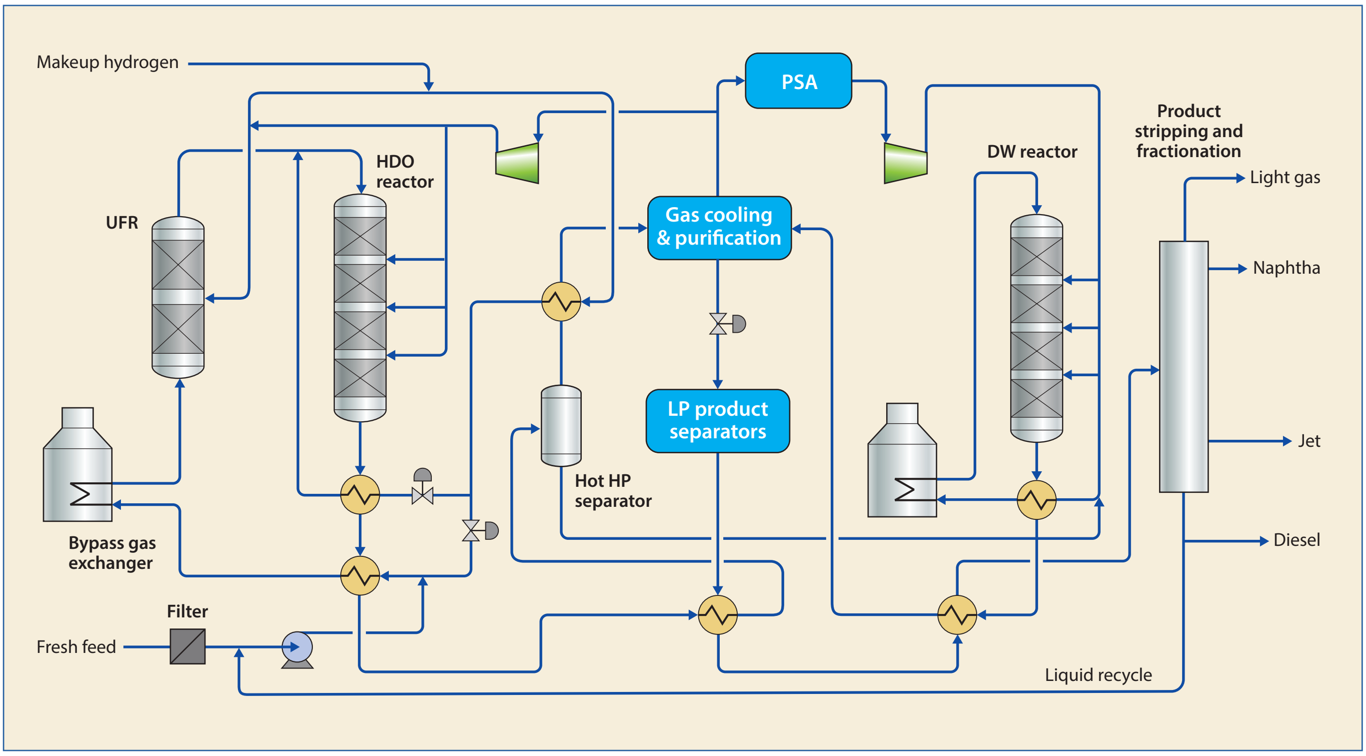

Figure 1 Chevron Lummus Global two-stage Isoterra Process²

forming the foundation for its proprietary Ecofining process for the production of RD and jet fuels. The first process licence ensued in 2013, and commercialisation followed at Eni's Venice refinery in 2014. Since that time, more than 150,000 barrels per stream day (BPSD) of Ecofining capacity has been placed into operation across 13 individual units that range in size up to 35,000 barrels per day (BPD) as of January 2025. Five of those are repurposed assets, according to Honeywell UOP sources.

Ecofining is offered in two options: a lower Capex single-stage design to produce Honeywell's proprietary RD, and a two-stage option to optimise the production of UOP's proprietary Green Jet Fuel, a SAF blend component. The two-stage option includes the flexibility to produce RD with changing market needs.

There are more than 50 Ecofining licences as of January 2025. One of Diamond Green Diesel's Port Arthur, Texas, Ecofining units was modified to produce 235 million gal/year (900 million litres/year or 15,000 bbl/day) by the end of 2024. Diamond Green Diesel announced a supply agreement with JetBlue. World Energy Paramount, one of the larger SAF producers at 240 million gal/year (900 million litres/year or 16,000 bbl/day), licensed the Ecofining process. World Energy has offtake agreements with United, Air France-KLM, JetBlue, SAS, and DHL.

UOP also offers co-processing revamps of existing hydrotreating units, particularly distillate hydrotreating units. Other UOP routes to SAF include eFuels with methanol-to-jet (eFining), ethanol-to-jet, and FT routes with FT Unicracking to be covered later.

Topsoe's proprietary HydroFlex process addresses the production of RD and SAF with both single-stage and two-stage units. Commercial application of the process began in 2010, and 20+ co-processing units plus some 60+ fully renewable units have been licensed, of which some 75% are two-stage units according to industry sources. Topsoe uses a graded catalyst activity and selectivity approach with a variety of catalysts. Topsoe uses formulations other than the standard NiMo/alumina catalysts employed in general hydroprocessing to achieve improved selectivity towards HDO, up to 97%. Patent literature points to a Mo/alumina formulation for such high HDO selectivity.

Montana Renewables employs HydroFlex technology to produce some 30 million gal/year (110 million litres/year or 2,000 bbl/day) SAF, as does Phillips 66 Rodeo, California to produce some 800 million gal/year (3 billion litres/year or 53,000 bbl/day) of RD and SAF, of which about 20-25% will be SAF at the time of writing. Montana Renewables has announced a multiyear SAF offtake agreement with Shell, and Phillips has a supply agreement with British Airways.

Axens' proprietary Vegan process is applicable for producing RD and SAF through the hydrotreatment of a wide range of lipids. The process incorporates an HDO step and an isomerisation step, and it can be adapted to revamps and co-processing units. The process has been operating at the TotalEnergies La Mède biorefinery for more than three years, and seven additional units have been licensed as of 2023. Total has an offtake agreement for SAF with Air France-KLM.

Chevron Lummus Global (CLG) offers proprietary Isoterra and Isoconversion processes for renewable fuels production (see **Figure 1**). Isoconversion is a jointly developed hydrothermolysis technology employing CLG and Applied Research Associates (ARA) technologies. Only the post-hydrothermolysis portion of the process involves HEFA-type technologies, specifically hydrodeoxygenation of the FFA intermediate feed, followed by dewaxing to meet final cold flow property specifications.

The dewaxing step uses CLG's proprietary fifth-generation

Isodewaxing catalyst. In addition, the trademarked ReadiJet and ReadiDiesel, produced from the biofuels Isoconversion technology, contain a uniform distribution of all hydrocarbon types observed in petroleum fuels, including aromatic, cycloparaffin, isoparaffin, and normal paraffin compounds, and can be directly blended with petroleum fuels. The process is differentiated from a pure hydroprocessing approach by the production of glycerine rather than propane as a side product.

The Isoterra process is an all-hydroprocessing route that can be operated to maximise yields of ASTM-approved RD or SAF. The two-step process involves hydrodeoxygenation of the feed followed by dewaxing to meet final cold flow property specifications. The dewaxing step likewise uses CLG's Isodewaxing catalyst. The Isoterra process is suited for revamping existing hydrotreaters to renewables service as the process can be implemented in either one or two-stage configurations. CLG and Grace's proprietary Hydroprocessing (ART) have introduced catalysts to the marketplace branded as Endeavor systems, which will include the proprietary EnRich HDO catalysts and the proprietary EnHance dewaxing and hydrocracking catalysts for general application to renewable feedstock applications. Figure 1, other than the upflow reactor (UFR) component, is illustrative for most two-stage HEFA processes and clearly indicates recycle liquid flows for quench and selectivity purposes.[2]

Shell Catalysts & Technologies licenses the Shell Renewable Refining Process, incorporating the Shell SRC portfolio of renewables hydroprocessing catalysts. The process is a two-stage process, which Shell maintains offers multiple benefits over single-stage units, including higher diesel and SAF yields, longer cycles and slower yield decline, and the ability to produce a range of cloud points that qualify for any RD market in any season, plus the flexibility to swing between diesel and SAF.

ExxonMobil Catalysts & Licensing offers its proprietary ExxonMobil Renewable Diesel (EMRD) two-stage process for RD production. It can produce jet if fractionation is added. The process was introduced in September 2021 and incorporates ExxonMobil's Bio-Isomerization Dewaxing (BIDW) dewaxing catalyst suite. ExxonMobil notes that its BIDW dewaxing catalyst suite provides solutions that meet cold-flow specifications for RD to improve yield in either two-stage or single-stage service applications.

Alcohol-to-jet technology

Ethanol-to-jet processes are seeing more imminent commercialisation. The technologies involved, including ethanol dehydration, olefin oligomerisation, and olefin hydrogenation, are all mature catalytic technologies. Solid phosphoric acid catalyst (SPA) was developed in the 1930s for the UOP CatPoly oligomerisation process, and homogeneous Ziegler-type catalysts for oligomerisation were developed in the early 1950s.

A variety of solid acidic catalysts can be used for dehydration, ranging from γ-alumina and silica-aluminas to mixed oxides and zeolites. Oligomerisation can either be carried out in heterogeneous systems utilising SPA-based, acid ion exchange resin-based catalysts or zeolite-based catalysts or conversely in homogeneous systems employing nickel and aluminum alkyl-based catalysts. Hydrogenation of the linear and branched oligomer olefin products is straightforward, basic hydroprocessing. Technology providers for the dehydration step include:

- Axens*: Atol ATO-201 catalyst (ZSM-5 based).
- Lummus-Braskem: SynDol catalyst (Al_2O_3-MgO/SiO_2).
- Technip: Hummingbird (supported heteropoly acid catalyst).
- KBR-Petron: K-SEET (likely γ-alumina-based catalyst)
- Honeywell UOP.

Oligomerisation technology providers include:

- Axens*: Dimersol, Polynaphtha (homogeneous Ziegler-type nickel hydride and aluminum alkyl system, heterogeneous amorphous silica-alumina IP 811 catalyst).
- UOP: CatPoly, InAlk, Catolene components (SPA or acid resin catalyst).
- Lummus: Dimer Process, Light Olefins Oligomerisation (homogeneous butenes production, subsequent oligomerisation not specified).

* Axens refers to its combined process as Jetanol.

The first small commercial-scale ethanol-to-jet operation is the LanzaJet facility in Soperton, Georgia, which started up early in 2024, benefiting from funding from the US DOE. It has a capacity of 10 million gal/year (38 million litres/year, 660 bbl/day) SAF produced from low-carbon intensity ethanol. Ethanol from sugarcane is approved by the US EPA for the facility and is being sourced from Brazil. It employs the Technip Hummingbird dehydration process and a two-component oligomerisation process developed at the Pacific Northwest National Laboratory (PNNL). The first step utilises a mixed Zn-Zr oxide catalyst developed at PNNL, and the second likely employs either a zeolite catalyst or an acid resin catalyst. LanzaJet has SAF offtake agreements with British Airways and ANA.

Ethanol-to-jet facilities will generally require a greenfield or brownfield site owing to limited opportunities to repurpose existing infrastructure and equipment.

Processes for SAF via FT-SPK

The starting point will typically be the conversion of lignocellulosic material, such as biomass waste from agricultural or forestry production or municipal solid waste (MSW) by gasification, a mature technology. The resultant syngas (CO + H_2) will have significant impurities and typically a low H_2/CO ratio (~0.5 vs >2 desired), requiring appreciable pretreatment efforts to remove impurities prior to catalytic steps.

Adjustment of the H_2/CO ratio is affected through high-temperature and low-temperature water gas shift (WGS) reactors using catalyst technologies that have been proven for decades in the hydrogen and ammonia production industries. The high-temperature shift catalyst is typically a promoted Fe-Cr oxide-based catalyst, and the low-temperature shift catalyst is typically a Cu-Zn-Al oxide formulation.

The FT process dates back to 1925 and, therefore, has a century of catalyst development and reactor technology improvements to tailor product selectivity and accommodate the highly exothermic FT reactions. For SAF purposes,

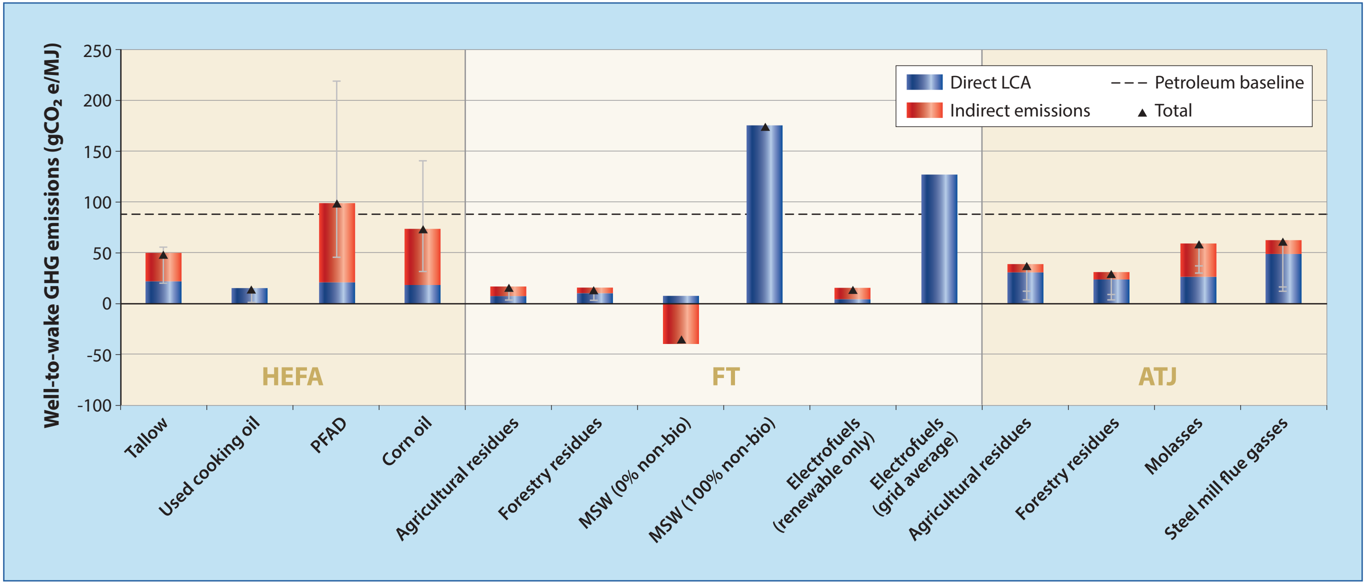

Figure 2 Well-to-wake GHG emissions for SAFs made from non-crop feedstocks relative to petroleum jet fuel baseline.[4] The error bars on this figure reflect the range of possible displacement emissions considering the low and high ends of the ranges estimated from literature

supported Co catalysts operating in the low-temperature FT regime (200-250°C) are preferred since they have a good selectivity to long-chain paraffins, low selectivity to oxygenates and olefins, and are resistant to deactivation. However, the FT Schulz-Flory product distribution results in higher carbon number waxy molecules that must be hydrocracked and hydroisomerised to maximise SAF product with the appropriate cold flow properties.

With some 420,000 bbl/day of FT commercial capacity used for gas-to-liquids (GTL) production from natural gas ranging from 2,500 to 140,000 bbl/day units, technology providers offer large scalable options based upon several reactor design schemes. These include the following:

- Slurry bed reactors – Sasol, Axens.
- Shell and tube reactors – Shell Global Solutions.
- Short path radial flow reactors – Johnson Matthey (JM)/bp CANS reactors.

Considering the gasification, syngas purification, WGS-FT, and hydrocracking/hydroisomerisation infrastructure needed for FT-SPK processes, the capital is significant. Some potential to mitigate Capex is possible if integration into existing refining or petrochemical complexes is possible.

Fulcrum BioEnergy licensed technology and built a facility near Reno, Nevada to process some 175,000 tons/year of MSW to 42 million litres/year (11 million gal/year or 725 bbl/day) of fuel that was sent to Marathon Refining for final processing. The JM/bp FT CANS technology was employed. Early in 2024, DG Fuels announced a $4 billion FT-SPK project in Louisiana to produce 600,000 metric tons of SAF (200 million gal/year or 13,000 bbl/day) from 1.0 million tons per year of bagasse, sugar cane pulp, and MSW.

The FT technology employed is JM/bp FT CANS and NextChem MyRechemical NX Circular for biomass gasification and purification. This would be the largest FT SAF plant announced as of mid-2024. Production is targeted to begin in 2028. Offtake agreements have been secured with Delta Airlines and Air France-KLM. DG Fuels has also announced a 193 million gal/year (730 million litres/year or 13,000 bbl/day) biomass-to-SAF project in Nebraska. No technology selections have been announced.

Carbon intensity and regulatory complexity

In the final analysis, it is expected that the lowest carbon intensity SAFs – those exhibiting the lowest life cycle analysis (LCA) for emissions (also referred to as well-to-wake or WtW emissions) – will be subject to the lowest tax penalties or highest incentives for use. It is appropriate that reported LCA value ranges for the processes described be reviewed:

- Base case petroleum jet fuel: 89g CO_2 e/MJ (US RFS, ICAO), 87g CO_2 e/MJ (California LCFS).
- HEFA processes: 13.9-60.0g CO_2 e/MJ.
- ATJ processes: 23.8-65.7g CO_2 e/MJ.
- FT-SPK processes: 7.7-12.2g CO_2 e/MJ.

FT-SPK processes are noticeably favoured, but the economics of greenfield or brownfield investments compared to HEFA synergies with existing refining assets are a clear inhibition in the near term.[3,4]

Feedstock sources play a key role in GHG emissions savings in SAF processes. **Figure 2** provides a succinct example for the processes discussed here. For HEFA processes, used cooking oil (UCO) is clearly advantageous. For reference, both US soybean and EU rapeseed feeds yield about 70g CO_2 e/MJ LCA values. FT-SPK processes benefit greatly from non-biological MSW feeds.[4]

Regulatory requirements and incentives are regionally specific. In the EU, ReFuelEU Aviation promotes the increased use of SAF as the single most powerful tool to decrease aviation CO_2 emissions. The measure is part of the Fit for 55 package to meet the emissions reduction target of 55% by 2030. It sets requirements for aviation fuel suppliers to gradually increase the share of SAF blended into the conventional aviation fuel supplied at EU airports to a 2%

share of SAF in EU airports from 2025 and a 70% share of SAF in all EU airports from 2050.

The landscape in the US is complex and subject to change with the new administration and US Congress. A brief case study demonstrates the US complexity. A SAF producer in California is faced with US Renewable Identification Number (RIN) values 94% of that of RD and California Low Carbon Fuel Standard (LCFS) credits 90% of RD credits, and subject to spot prices for jet typically some 5-6% lower than diesel. While the US Inflation Reduction Act (IRA) helps even the unbalance, its future is uncertain.[5]

Conclusion

The production of SAF may indeed offer a better opportunity for viability in renewable fuels production in the near future. However, there is a large dependence on not only localised regulations and incentives but also the capital outlays involved and to be subsequently recovered. The speculative look at the economics of SAF production vs RD production is not within the scope of this article. Published case studies specific to the US and California in particular are available.[5,6]

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Value of pre-activated catalyst in HEFA units

Hydroprocessing units designed for fossil feedstocks cannot easily switch to HEFA feedstock processing without a solution that addresses the significant challenges

Steve Mayo
Eurecat

The rapid increase in processing capacity for hydrotreated esters and fatty acids (HEFA) to produce renewable diesel (RD) and sustainable aviation fuel (SAF) has been nothing short of phenomenal. Starting from less than 50 KBPD capacity 10 years ago, global capacity is now approaching 500 KBPD. Despite recent setbacks in unit profitability, strong growth in HEFA processing capacity is expected to continue through 2030, with a projected doubling of current capacity. To date, North America has seen the largest increase in HEFA processing capacity, driven by strong incentives and subsidies for RD. By 2030, HEFA processing capacity is projected to shift from RD in favour of SAF, with all regions expected to show substantial capacity gains compared to the present level (see **Figure 1**).

While similar in some respects to the hydroprocessing of fossil feedstocks in which refiners are well versed, hydrotreating HEFA introduces significant challenges:

- The feedstock is sulphur-free.
- High olefin and oxygen content make the feedstock very reactive.
- Very high hydrogen consumption.
- Large reaction exotherms.
- Copious quantities of reaction byproducts (C_3H_8, H_2O, CO, CO_2).
- Phospholipids may cause catalyst activity loss and pressure drop build-up.
- Feedstock corrosivity may increase.
- Long-chain n-paraffins require catalytic dewaxing and/or hydrocracking to meet cloud point (RD) or freeze point (SAF) specifications.
- Undesired conversion to lighter products (gas, naphtha) significantly reduces unit profitability.

Grassroot units licensed from technology providers address all these challenges with bespoke process design and catalysts. Hydroprocessing units designed for fossil feedstocks are usually incapable of directly switching from fossil to HEFA feedstock processing. Even small amounts of a renewable feedstock (<10%) processed together with fossil feedstock in an existing unit will see compromised operation and cycle length.

However, those same units can often be revamped to process 100% renewable feedstocks. Technology providers can reuse much of an existing unit's hardware along with a new catalyst system to switch the unit from fossil to HEFA service. This is particularly true of hydrocracking units, which already have the robust hardware needed to accommodate the HEFA feedstock's high reactivity and hydrogen consumption as well as improve the resulting cold flow properties.

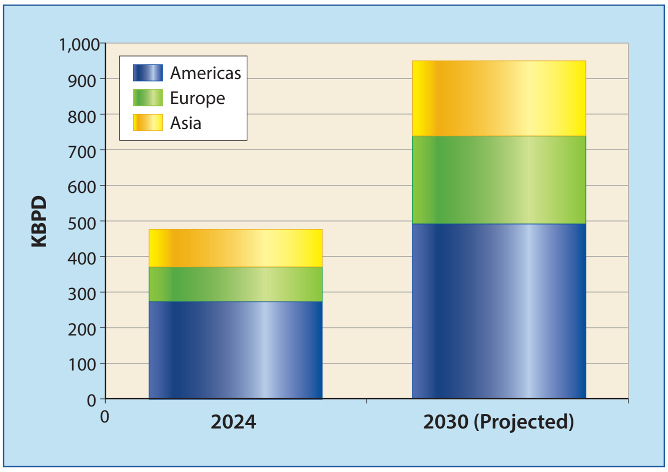

Figure 1 Current and projected HEFA processing capacity to RD and SAF *Sources: EIA/USDOE, IEA, S&P Global, Argus*

Figure 2 shows the five general reactions that take place in a HEFA unit:

❶ Phosphate removal from phospholipids.
❷ Saturation of olefins in fatty acids.
❸ Propane removal from the glycerol backbone of the triglyceride.
❹ Deoxygenation of free fatty acids.
❺ Cracking and/or isomerisation of normal paraffins.

Reaction one depends on the feedstock origin as well as pretreatment steps completed ahead of the HEFA unit. Reactions two to four are common among most HEFA units and are often referred to as hydrodeoxygenation (HDO) or hydrotreated vegetable oil (HVO) reactions. The objectives of Reaction five depend upon the desired product split between RD and SAF.

Ex-situ catalyst activation

The sulphur-free HEFA feedstock initially seems like a positive aspect of HEFA processing compared to processing fossil feeds. No sulphur and no hydrogen sulphide (H_2S)

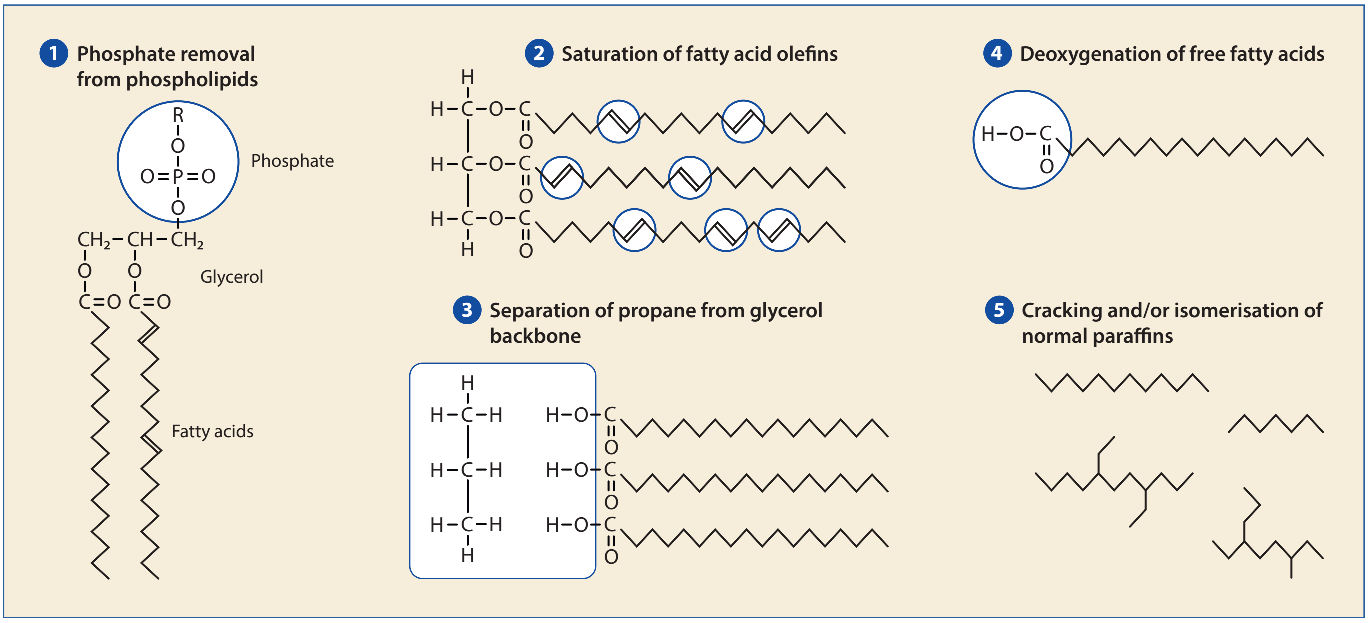

Figure 2 HEFA unit reactions

greatly simplifies gas and water treatment processes, if not eliminating the need entirely. However, since HEFA units utilise supported metal sulphide catalysts, the lack of sulphur in the feedstock introduces a new challenge not found in fossil feed processing: retaining catalytic metals in their sulphidic state while operating in a reducing environment.

Although metal sulphides reduction under HEFA processing conditions is slow, continuous operation in a sulphur-free atmosphere will eventually lead to sulphur and activity losses. Small H_2S amounts in the process gas are sufficient to counterbalance reduction reactions and mitigate catalyst sulphur loss. Continuous injection of a small amount of a readily decomposable sulphur compound, such as dimethyl disulphide (DMDS), with the HEFA feed ensures the catalysts remain fully sulphided.

Like all metal sulphide catalysts, catalysts for HEFA processing units are manufactured as metal oxides and must be activated (sulphided) prior to use. In-situ activation of the oxidic HEFA catalysts is an option, but there are several issues which make in-situ activation problematic. In-situ activation requires copious amounts of H_2S, including a finishing step with more than 1 vol% in the recycle gas.

This H_2S has to be removed from the gas stream, but unlike fossil units, which have an amine scrubber to remove H_2S, HEFA units have no need for one. Purging the H_2S- rich recycle gas to flare may be the only option to remove it, but that runs the risk of exceeding permit limits. Another issue with in-situ activation of HEFA catalysts is input heat limitations.

Considering the high heats of reaction, HEFA units are usually highly heat integrated and may only have a small furnace. The unit's normal heat of reaction cannot be accessed to supplement the furnace heating capacity because the catalyst has no activity yet. In addition, in-situ sulphiding should not be performed with the reactive HEFA feedstock because it could lead to a less-than-optimal activation. This combination of factors makes in-situ activation of HEFA catalysts very challenging. Considering the infrequency of catalyst activation, correcting the issues with added hardware or even maintaining existing hardware is not justified. Ex-situ activated catalyst provides a more cost-effective solution to these problems.

Advantages

The previously described limitations are generally sufficient to justify the modest cost premium of ex-situ activation over in-situ activation for HEFA unit catalysts. However, additional benefits may also make ex-situ activation an economically advantageous choice. The biggest economic advantage of ex-situ activated catalyst is the short time needed to return the unit to normal operation. Depending on the unit's operating margin, the time savings from ex-situ activated catalyst can be substantial.

The margin from the increased production is usually much more than the cost difference for ex-situ activation. Ex-situ catalyst activation can also be considered a type of insurance since it mitigates risk from unforeseen start-up events.

Mechanical breakdowns and turnaround delays do not affect the cost of activation or the resulting catalyst activity. Finally, the very simple start-up procedure requires no additional staffing or expertise. Eurecat's proprietary Totsucat ex-situ activation applications in both fossil and HEFA units have been well documented.

A well-activated catalyst is not the last step in a HEFA unit's start-up procedure. Freshly activated catalyst has pristine active and support phases, free of adsorbed species, which would moderate its catalytic behaviour. This condition is often referred to as hyperactivity, referring to the period before the catalyst reaches equilibrium with adsorbed reaction inhibitors. During this period, catalyst activity may exceed the ability of the unit to deliver a stable environment for the catalyst to operate.

It is standard practice to break in catalysts by operating under mild conditions with a feedstock free of high reactivity components until hyperactivity is reduced. During the break-in period, catalyst activity is tempered by slow reaction inhibitor accumulation (coke precursors, organic nitrogen) on its surface. These adsorbed species serve to moderate catalyst activity when reactive feedstock components are added to the unit. Following catalyst break-in precautions helps ensure the catalyst stays on a path to stable performance and deactivation rate.

As shown in **Figure 3**, catalyst deactivation by coke in a hydroprocessing unit is a path function. The path is initiated when a reactive feedstock (containing hydrogen deficient and/or other reactive components) is combined with a hyperactive catalyst (free from adsorbed reaction inhibitors). When both elements are present, high reaction rates can cause hydrogen consumption at such a high rate that replacement of the consumed hydrogen is too slow to keep up with reaction requirements.

The resulting hydrogen shortage causes ppH_2 to fall and falling ppH_2, in turn, causes hydrogen dissolution into the feedstock and hydrogen diffusion into catalyst pores to fall as well. The result is hydrogen depletion at the active site where it is needed to support reactions. Exothermic hydrogenation reactions simultaneously cause reactor temperature to increase, driving reaction rates higher and adding even more hydrogen demand to the already limited supply. Low ppH_2 and high temperature favour dehydrogenation, oligomerisation, and condensation reactions instead of the desired hydrogenation reactions.

Those reactions can generate coke precursors, which strongly adsorb on catalytic surfaces. Since the adsorption of coke precursors inhibits catalyst activity, equilibrium conditions will eventually be restored. However, substantial activity will be lost in the meantime, which is virtually impossible to recover. It is best to avoid starting conditions that lead down the coke deactivation pathway.

Formation pathways

While not a cracked feedstock per se, the hydrogen-deficient bonds and reactive oxygen heteroatoms in HEFA feedstock cause it to behave strikingly similar to cracked feedstock processed in a fossil hydrotreater. Both feedstocks consume high amounts of hydrogen and generate high heats of reaction. Both are prone to coke precursor generation when reaction rates are too high.

A main difference compared to cracked feeds is that HEFA feedstocks are generally free of aromatics. Polyaromatic condensation is a main cause of coke precursor formation with cracked feedstocks. Coke precursor formation with HEFA feeds more commonly proceeds via a paraffinic olefin oligomerisation pathway. It is worth noting that there are renewable unit feedstocks rich in aromatics, such as tall oil. Units processing this type of feedstock follow a coke precursor formation pathway similar to units that process cracked fossil oil feedstock.

HEFA units face most of the same constraints as fossil oil hydrotreaters regarding the introduction and processing of reactive feedstocks. Similar precautions apply to protect the catalyst by breaking it in prior to exposure to a reactive feed, but there are differences in how break-in is executed in HEFA units. Since all HEFA feedstock has high reactivity,

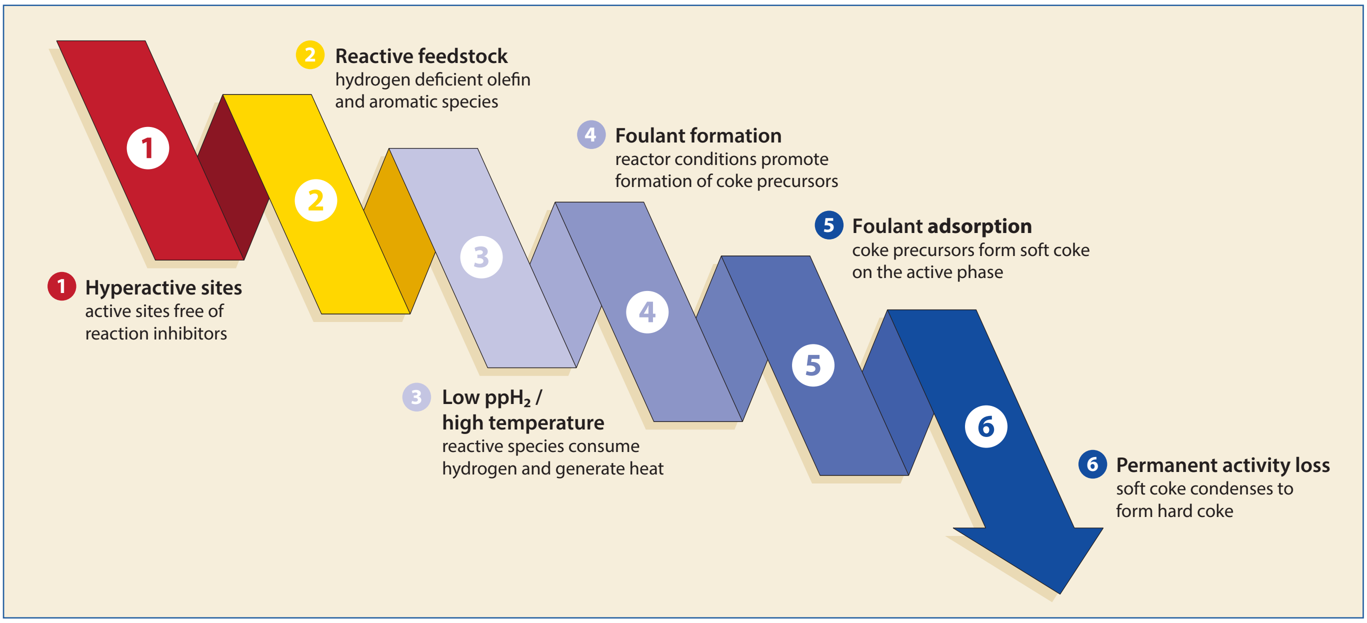

Figure 3 Reactive feedstock coke deactivation pathway

stored products from the HEFA unit itself are the most readily available feedstock with low activity.

However, HEFA product is unsuitable for catalyst break-in since it has no ability to generate the species needed to temper catalyst hyperactivity. In addition, no hydrogen consumption or heat of reaction is generated from processing HEFA product as feedstock. Some amount of reactive HEFA feedstock has to be added to HEFA product to make it suitable for catalyst break-in. This is easier in principle than in practice, but with careful control of HEFA feedstock addition rate, a good outcome is possible.

Protecting biofeedstock

What if the catalyst break-in period could be avoided altogether? If catalyst could be delivered already activated and pre-conditioned to mitigate hyperactivity, reactive feedstocks could be added immediately upon start-up. Eurecat's proprietary pre-activated catalyst conditioning treatment for HEFA units, Totsucat BFP, eliminates the challenges associated with properly breaking in HEFA catalyst.

The proprietary BFP stands for Bio Feedstock Protection, a conditioning treatment applied to Totsucat catalyst such that the catalyst's hyperactivity is tempered by pre-carbonisation. Both catalyst hyperactivity and reactive feedstocks are necessary to initiate the rapid formation of coke precursors. BFP removes a catalyst's hyperactivity so that reactive HEFA feedstocks can be introduced immediately without fear of promoting accelerated catalyst deactivation.

Totsucat eliminates the problems of H_2S and heat input common to in-situ sulphiding of HEFA unit catalysts. BFP eliminates the necessity for catalyst break-in before reactive feedstock introduction. HEFA feedstock can be added immediately upon unit start-up. Since the catalyst is already active, the heat of reaction will be available to supplement the furnace in raising the reactor to normal operating temperature.

Restoring RD and SAF capacity

The net result of using Totsucat BFP is full restoration of RD and/or SAF production capacity much more quickly than is possible with in-situ catalyst activation. The carbon source for BFP's pre-carbonisation treatment is a bio-oil, suitable for use as a HEFA feedstock. That makes BFP fully compatible with all HEFA unit operational and regulatory requirements.

The case for using pre-activated catalyst in the HDO section of HEFA units is compelling, but what about pre-activation of downstream dewaxing and/or cracking catalysts? Hydroisomersation dewaxing catalysts are used to improve the cold flow properties of RD while minimising yield loss to less valuable products. After the HDO section of the HEFA unit, where oxygen and olefins are removed, the resulting product stream consists of pure normal paraffins 16-18 carbon atoms in length.

The material boils in the correct range to be suitable for use as diesel fuel, but the cloud point is far too high at 45-50°C. Cold flow properties must be improved to meet diesel fuel specifications. To reduce cloud point without excessive RD yield loss, catalysts with both cracking and isomerisation functionality are used. The normal paraffins are first catalytically cracked, followed by isomerisation of the fragment(s). Paraffin isomerisation greatly reduces the cloud point of the original n-paraffin without significantly changing the boiling point. Ideally, the isomerised paraffin would retain a similar carbon number to the original n-paraffin.

Dewaxing unit designs

RD technology licensors offer single-stage and two-stage dewaxing unit designs. Since single-stage designs have small H_2S amounts in the gas, a base metal (NiW) is used for the catalyst's hydrogenation functionality. Two-stage designs have a 'sweet' second stage and typically use noble metal (Pt and/or Pd) for the catalyst's hydrogenation functionality.

Acidity for the cracking functionality of the catalysts used in both single- and two-stage unit designs comes from a shape-selective zeolite (MFI/ZSM-5) or an amorphous silica-alumina (ASA) incorporated into the support.

Single-stage catalysts are activated by sulphidation, and two-stage catalysts are activated by reduction.

Pre-activation of base metal catalysts on shape-selective zeolite supports is currently not possible. Users report a lower yield to RD for ex-situ activated catalyst compared to the same catalyst activated in-situ. The reason for this shift in selectivity is unclear, but until a suitable method of pre-activation for these grades is identified, process licensors recommend in-situ activation. Despite the necessity to activate the single-stage dewaxing catalyst in-situ, it is still worthwhile to ex-situ activate catalysts used in the HDO section.

The advantages of reduced H_2S gas and faster heat-up time previously described remain. In addition, Totsucat BFP speeds up in-situ activation of base metal dewaxing catalyst. BFP allows HEFA feedstock to be added at start-up and eliminates the need for catalyst break-in. Not only does this allow in-situ activation of the dewax catalyst to proceed immediately, rather than waiting for the HDO catalyst to break-in, it also allows the unit to more easily reach the elevated temperatures required to fully activate NiW catalyst.

SAF production from the n-paraffins exiting the HDO section requires the average boiling point of the stream to be reduced by catalytic cracking. The catalysts used for this are similar to base metal (NiW) zeolitic cracking catalysts used in jet-selective fossil oil hydrocrackers. Unlike RD units, where no boiling point reduction is necessary, increasing yields to SAF in a HEFA unit causes greater yield loss to lighter, less valuable products.

> **Since SAF production in HEFA units carries a yield loss penalty, the positive economics of higher SAF production has to be balanced against reduced yields to RD and increased yields to lighter products**

Since SAF production in HEFA units carries a yield loss penalty, the positive economics of higher SAF production has to be balanced against reduced yields to RD and increased yields to lighter products. The cracking catalysts used to produce SAF in HEFA units are activated by sulphidation. Totsucat is suitable to activate the catalysts used to produce SAF in HEFA units and has numerous references.

Ex-situ pre-activation of the catalysts in HEFA units is justified both technically and economically. Eurecat's Totsucat BFP provides a robust solution to the unique feedstock characteristics and process limitations that make in-situ activation of HEFA unit catalysts so challenging.

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Can pyrolysis oil unlock greater plastic circularity?

Combining pyrolysis and vapour-phase catalytic upgrading offers lower temperature and energy requirements, higher yields, and optimised product distribution and selectivity

Markus Hartung
Evonik Catalysts

Much of our society is dependent on plastics, with the first synthetic plastics manufactured more than 150 years ago. Plastics made the development of computers, cell phones, and advances in modern medicine possible. Food production, transport, and power rely on plastic for efficiency and safety, while our possessions are cheaper, lighter, stronger and safer.

It is no wonder that plastic production is increasing exponentially. Between 1950 and 2018, consumption grew about 180 times, from two million tons to 368 million tons. The UN Environment Programme (UNEP) states that 430 million tons of plastic are produced each year; production is expected to double yet again by 2050. However, the reputation of plastics has suffered in recent decades due to environmental and public health concerns.

Looking at start-of-life, approximately 98% of single-use plastic produced today comes from fossil fuels. About 4% of global oil and gas production is being used as feedstock for plastics, while 3-4% is used to provide energy for the manufacture of plastics. A 2021 report found none of the 100 largest plastic producers procure more than 2% of their feedstock from recycling sources, presenting a window for opportunity.

Criticism of plastics has largely been directed towards end-of-life management. A third of plastics are single-use; if we look specifically at the plastic used in packaging, about 95% of its material value is lost after a short first-use cycle, representing an $80-120 billion missed opportunity. The amount of plastics that end up in landfill, incinerated, or leaked into the environment stands at 72%, and the rate of successful plastic recycling sits at a reported 9%. Emissions from plastic production and disposal are expected to double in the next 35 years.

A more circular economy is needed to improve the current state of these bespoke statistics. Chemical recycling has been touted as part of the solution, with one particular method, pyrolysis, gaining interest internationally and offering a route to de-fossilising raw material streams into refineries. Organic material, including biomass, waste, tyres, and especially plastics, is transformed into pyrolysis (pyrolytic) oil or gas, which can be repurposed and utilised as reusable crude oils.

Plastic recycling status

There is no single reason behind low recycling rates; they stem from multiple factors. One significant challenge is the make-up of many individual plastic products using materials such as flexible films, multilayer materials, and coloured plastics, which cannot be recycled with conventional mechanical recycling or are entirely non-recyclable. Despite this, industries and legislators face growing public pressure to increase the collection, recycling, and reuse of all plastics. However, varied international management of the problems also presents a barrier to this.

In European Organisation for Economic Co-operation and Development (OECD) countries, the annual plastic waste generated per person is 114 kg. In the US, annual plastic waste generation is 221 kg per person, while Australia generates 148 kg per person. In the UK, figure for 2021 was reported at 99 kg per person. The Asian continent is the largest plastic waste producer, and individual Asian countries can vary widely in plastic waste rates. Developing countries in South and Southeast Asia are major destinations for waste exports, particularly from the EU and US.

There is no dedicated international instrument in place for plastics recycling today. Some countries are taking action to reduce plastic consumption or increase recycling through campaigns and awareness-raising measures. Other countries have specific laws in place, obliging businesses to minimise waste, adopt recycling targets, and phase out single-use plastics. The EU aims to ban single-use plastics by 2030 and cut the amount of plastic packaging by 15% by 2040. Australia mandated that 100% of plastic be recycled or reused by 2040. However, the country's largest soft-plastics recycling scheme collapsed in 2022.

Collection of waste differs between developed economies, where recyclable waste is typically collected by waste management companies and sorted and cleaned with equipment, and developing countries, which often rely on human waste pickers. The US faces difficulty because its systems for collection and management of plastics waste are organised at state and regional levels, but they are highly variable. In many Asia Pacific countries, the main drivers of plastic pollution are inadequate waste collection and processing infrastructures.

The primary existing method of plastic recycling, an industry standard, is mechanical recycling. Established on an international scale and around for decades, mechanical recycling sees plastic waste processed into secondary raw materials or products without chemically disrupting polymer chains in the process. An energy-efficient process, mechanical recycling boasts a low-carbon footprint, minimal environmental impact, and helps reduce landfill disposal. In cases of mixed and/or contaminated plastic streams, these must be sorted and cleaned thoroughly to make a product of good quality – a process that ends up being both time-intensive and costly.

However, mechanical recycling is feedstock specific, only accepting polyethylene terephthalate (PET), high-density polyethylene (HDPE), polypropylene (PP), or low-density polyethylene (LDPE) in most cases. Its impact is also limited on a global scale, as it cannot be utilised for hard-to-recycle plastics, which is where chemical recycling comes in.

Chemical recycling

Also known as advanced recycling, chemical recycling is the process of converting polymeric waste by altering its chemical structure and returning it to substances that can be used as raw materials. While introduced to industry decades ago, interest in these recycling technologies and the possibilities they present has been renewed in recent years.

Complementing existing plastic recycling methods, chemical recycling can better deal with mixed plastic waste streams, like films and laminates, that would otherwise result in incineration or landfill. Examples of these methods include gasification, depolymerisation, hydrocracking, and pyrolysis.

> **Pyrolysis has the potential to convert used plastic waste streams unsuitable for mechanical recycling into high-quality feedstock for even the most sensitive petrochemical industry applications**

A transformative chemical recycling technology, pyrolysis has the potential to convert used plastic waste streams unsuitable for mechanical recycling into high-quality feedstock for even the most sensitive petrochemical industry applications.

The process sees plastics collected at the end of their product life cycle and heated to high temperatures (300-900ºC) in an inert atmosphere without oxygen. Thermal degradation causes these plastic materials to break down into smaller molecules, in turn, transforming plastic waste into pyrolysis (pyrolytic) oil or gas, which can be repurposed and utilised in the form of reusable crude oils.

Suitable for multiple applications, pyrolysis oil can reduce dependence on fossil fuels, presenting a lower carbon solution for hard-to-abate sectors and diversifying energy materials. In petroleum refineries, it can be used as a more sustainable and high-quality feedstock alternative to fossil naphtha, including ethylene and propylene production, which are core monomer building blocks of most plastics.

Pyrolysis oil can also be used as a fuel to power vehicles and machinery (once refined and blended with conventional fuels), which is particularly beneficial for industries that still rely heavily on crude oil and natural gas, such as shipping, construction, and manufacturing. It can even replace diesel with regard to engine performance and energy output in certain instances. Primary drivers of increasing pyrolysis capacity are oil and gas corporates, which are expected to utilise most pyrolysis oil as a fuel replacement.

Global interest in pyrolysis as a means of managing plastic waste can be seen in the development of significant commercial pyrolysis technologies for the processing of plastic waste. In the US, the American Chemistry Council advocates for state and federal policies that support these technologies for recycling and has emerged as a prominent research area in Europe.

Large chemical companies are starting to invest in pyrolysis oil production. Initial commercial plants vary between 10 and 50 kta; as of 2023, at least nine 10 kta capacity pyrolysis or hydrothermal chemical recycling units were scheduled to come online in Europe. Of those, however, only two are known to have achieved production by the end of the same year.

Since 2021, the global input capacity for pyrolysis plants has increased by more than 60%. Even so, the true potential of pyrolysis is still predominantly untapped. Approximately five million tons of plastic waste is currently mechanically recycled in Europe, compared to the 50,000 tons of plastic waste that is chemically recycled. There is clearly a significant opportunity to increase these rates, provided certain challenges can be overcome.

Meeting specifications

Pyrolysis oil contamination is one such hurdle, affecting purity and composition. Mixed waste plastics are often a complex combination of polymers. The final composition of such products can differ due to regional and country-specific factors. Plastics such as PET and polyvinyl chloride (PVC) can yield oxygenated and chlorinated compounds. These chlorides and their complexity pose an additional issue.

Tending to exist in roughly equal concentrations throughout the boiling point range of pyrolytic oil, they attach to hydrocarbons of varying chain lengths and have differing levels of steric hindrance. This can cause corrosion issues in steam cracking furnaces in petrochemical plants and result in plant and equipment breakdown.

Steam crackers feature very tight specifications that need to be satisfied if the oil is added as a feedstock. As such, these impurities need to be removed in an economical and sustainable way. Currently, the amount of plastic pyrolysis oil that can be fed into a steam cracker is less than 10%. Therefore, it is not possible to use the oil in steam crackers on any commercially significant scale.

Additionally, the products formed from pyrolysis are heavily dependent on both the composition of the feedstock and the process conditions. Impacts include type of reactor, heat transfer, residence time, heating rate, and temperature. When looking specifically at commercial catalytic pyrolysis, a major challenge is improving selectivity, promoting deoxygenation reactions, and reducing catalyst degradation through coke formation.

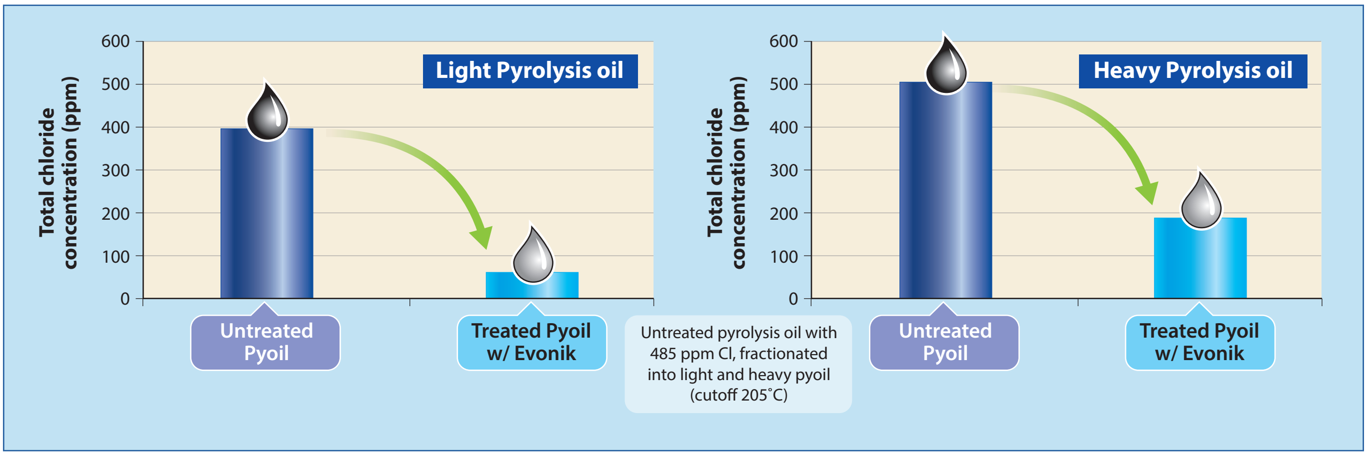

Figure 1 Treating light and heavy pyrolysis oil with Evonik's specialised adsorbent resulted in significant reduction of chlorides

Catalyst solution

Recent technological advancements, notably new and improved catalysts, have increased pyrolysis efficiency and output quality. Catalysts play a key role in both the quality and quantity of recycled plastic waste processing. Part of this movement includes catalytic pyrolysis, a process that combines pyrolysis and vapour-phase catalytic upgrading, offering lower temperature and energy requirements, higher yields, and optimised product distribution and selectivity.

For PVC, pyrolysis produces toxic, corrosive organochlorine compounds and hydrogen chloride (HCl). However, the right catalysts can be used to dechlorinate and condense these gases. To minimise HCl emissions, adsorbents or additives introduced in close contact with the plastic vapour in the reactor can assist with dichlorination through adsorption, a technique also known as in situ upgrading.

Evonik's chloride and fluoride adsorbents and hydroprocessing catalysts allow for the separation of impurities and the reduction of contamination during production. Researchers are taking industrially proven processes and adsorbents used elsewhere in the industry and applying and adapting them to plastic waste recycling processes to introduce new brands of products for purification.

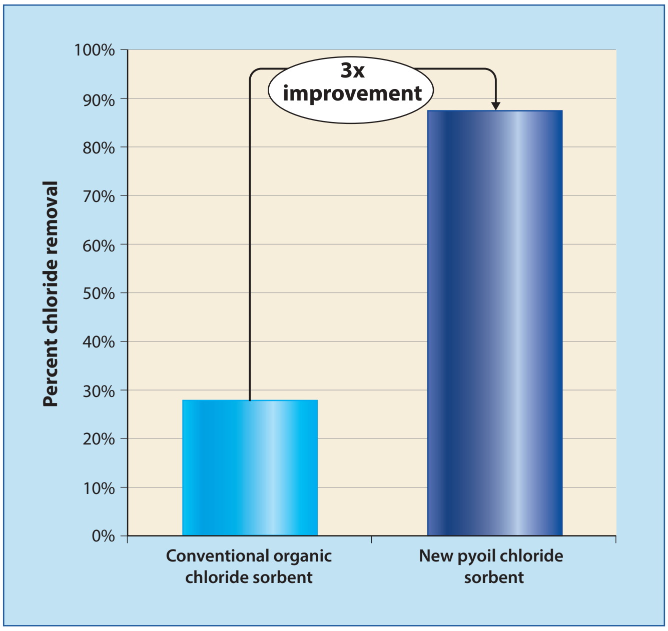

Figure 2 Evonik's specialised adsorbent demonstrates significant improvements over existing sorbents

Hydroprocessing catalysts are an important tool for contributing to refineries' sustainability goals because they can be regenerated and reused. As well as catching unwanted elements and removing contaminants, hydroprocessing also reduces olefins and aromatics, decreasing heater fouling in steam crackers, increasing yields, and helping make pyrolysis oil suitable for steam cracking.

Case study

The recent development of a new specialised adsorbent for removing organic chlorides from plastic pyrolysis oil is shown in **Figure 1**, demonstrating significant chloride reduction across the treatment of both light and heavy pyrolysis oil.

In this case study, industrially produced pyrolysis oil was distilled into a naphtha (light) and residual (heavy) fraction with a cut-off point of 400°F (200°C). Chloride concentration decreased by 300 parts per million (ppm) across both oils, with removal efficiency higher for the naphtha fraction. These specialised adsorbents have also demonstrated three times higher chloride removal than conventional organic chloride sorbents (see **Figure 2**).

The brand's alkoxide catalysts and process technologies also enable the recycling of PET and coloured PET plastics, which are not suitable for mechanical recycling, at the end of their lifecycle.

Partnership and circular economy success

The management of plastic waste is clearly siloed, with mandates of usage and recycling differing between regions and countries. Businesses and industries are also having to adhere to stricter, although not uniform, emission rules, creating more confusion. Simultaneously, downstream brands and retailers are finding themselves increasingly subject to consumer pressure for more sustainable products; eco-friendly producers are growing more rapidly in the marketplace than other incumbents.

Part of the reason the management of this problem is so varied internationally is due to the high economic cost of plastic waste and the complexity that collecting, sorting, and cleaning said waste presents. According to McKinsey, $50 billion may be needed by 2030 to support the scale-up of plastic recycling investments. One-third will be dedicated to feedstock sourcing and preparation, while the remainder will go towards building out mechanical and advanced recycling capacity. To achieve 20-30% recycling content for plastic packaging globally, the estimated figure is $100 billion, spanning collection, sorting, and mechanical and advanced recycling technology.[1]

As such, more collaboration is vital from catalyst providers, refineries, plastic manufacturers, recycling facilities, and government and regulatory bodies. Such partnerships are important tools to de-risk the journey and could include buy-sell agreements for intermediates (including pyrolysis oil), new ventures to sort feedstock (plastics recovery facilities), and upstream investment by waste management companies. Additionally, government intervention and incentives can help reshape the industry, similar to what originally sustained the growth of fossil fuel feedstocks.

Positive momentum is already being seen. Upstream firms are investing in supplementary infrastructure for pyrolysis, a confirmation of their confidence. In February 2024, it was reported that 16 10 kta pyrolysis units were scheduled to come online in Europe in 2024 and 2025.

Conclusion

The urgency to find a solution for plastic waste increases alongside rising plastic consumption. The research supports shifting to a circular economy, suggesting that doing so could reduce the volume of plastics entering oceans by 80% by 2040, and greenhouse gas emissions by 25%. From an economic standpoint, a circular economy could save governments $70 billion by 2040, create 700,000 additional jobs, and represent a revenue opportunity of more than $1 trillion in Europe alone in 2050.

As an innovative and forward-looking solution, pyrolysis holds significant promise, and a greater adoption rate will benefit from economies of scale. It is estimated that by 2040, chemical recycling technologies will experience an average cost reduction of 37.5%, and by 2033, pyrolysis could reach positive net earnings. The costs for virgin plastics production are expected to increase substantially, by up to 71%. This estimate is driven in part by increased fossil fuel prices, making a method like pyrolysis a necessity.

By integrating knowledge across the entire value chain, the supply of pyrolysis oil feedstock and the demand for recycled materials can expand, diversifying and de-fossilising the pool of raw materials available to refineries. The important role that chemical recycling, particularly pyrolysis, plays in delivering a circular plastics economy cannot be denied.

Reference

1 McKinsey & Company, August 16, 2023, A unique moment in time: Scaling plastics circularity. www.mckinsey.com/industries/chemicals/our-insights/a-unique-moment-in-time-scaling-plastics-circularity

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Control points during the lifecycle of precious metal catalysts

Key contractual factors can greatly influence metal value returns for precious metals spent catalysts

Brad Cook
Sabin Metal Corporation

More and more petroleum and petrochemical operations around the world are using catalysts that include precious metals (PM), which commonly include platinum, palladium, ruthenium, rhodium, gold, and rhenium. When these catalysts have reached the end of their operational lifespan, they must be replaced during a plant or unit turnaround so plant function can be restored to optimal process efficiency and optimum reaction rates.

However, when the spent catalysts are forwarded to a PM refiner, many owners miss opportunities to enhance recovered monetary value, not realising best practices to safeguard profitability. The following discussion aims to provide an overview of control points throughout the lifecycle of PM catalysts and bring some clarity to strategies that maximise financial returns and minimise losses. These control points include:

- Procurement
- Operational considerations
- Reclamation
- Documentation.

Procurement

Strong catalyst lifecycle management demands careful attention to every stage involving the handling of PM catalysts, all the way through to the final evaluation of their PM content. A crucial first step is accurately assessing the amount of PM in the fresh catalyst. Companies that conduct thorough sampling and testing at this stage show foresight. Due to variations in PM loading during catalyst production, each catalyst bead, and therefore each drum of catalyst, can differ slightly.

Manufacturers of PM-containing products aim to keep these levels at or above agreed-upon minimums. Statistically, about half of all catalyst drums produced will have less than the average amount of PM, while the other half will have more. Since catalyst manufacturers often produce reformer catalysts in large batches weighing millions of kilograms, pinpointing the exact drums received can be a complex task.

Another key factor to consider is the moisture content of the catalyst at the time of purchase. The average water content should be clearly specified on the certificate that comes with the catalyst, as this data plays a crucial role in assessing the value of PM in spent catalysts during reactor changeouts. Proper tracking of PM quantities requires thorough record-keeping throughout the catalyst's entire lifecycle, ensuring detailed oversight from start to finish.

Operational considerations

Tiny dust particles, often referred to as 'fines' in the industry, are constantly being generated throughout the lifecycle of these catalysts. When fresh catalysts are loaded into reactors, it is essential to avoid high wind conditions to prevent the loss of this dust. Many catalysts, particularly those based on alumina and coated with PM, can have fines with much higher concentrations of PM by weight when compared to the original catalyst beads.

For example, if a catalyst is loaded with 0.25% platinum, losing one kilo of fresh catalyst beads could result in the loss of 2.5 grams of platinum, worth about €75 at current market prices. In contrast, losing a kilogram of fines during the catalyst's lifecycle could result in the loss of 20 grams or more of platinum, equating to €600 or more per kilogram lost.

During processing, catalysts collect various impurities like coke, carbon, moisture, trace solvents, or additives designed to extend their lifespan. These impurities can have a significant effect on the final recovery at the PM refiner. When the catalysts arrive at the refiner, tests are conducted to evaluate impurity levels, moisture content, benzene concentrations, and other factors.

This information helps determine whether thermal reduction is needed to remove the impurities before accurate sampling can take place. Experienced process engineers use this impurity data to gain insights into past operations. For example, a high carbon content in spent catalysts from a reformer unit could indicate issues such as channelling, offering valuable feedback to improve reactor operation.

Reclamation

Proper spent catalysts packaging, weighing, and correct classification for international shipment can be complex, especially for those without experience in the process. While many downstream companies choose to fully outsource the changeout procedure, internal oversight remains essential to ensure the complete collection of all PM-bearing materials, secure cargo handling, and accurate hazardous classification. Any losses or liabilities incurred will ultimately affect the company's bottom line, not the contractor's.

Managing the shipment of hundreds of metric tons of spent catalysts, which contain significant values in platinum, palladium, and other PM, is best handled by specialists. Sabin International Logistics Corporation (SILC) has previously discussed the intricate web of domestic and international regulations, permits, and logistical hurdles involved in shipping PM-bearing catalysts, elaborating on the process of organising transportation from any global location to Sabin's recovery and refining facilities.

The reliability of the chosen PM refiner is crucial for receiving quality service. Ethical compliance in the PM industry is essential to avoid financial and legal risks. Catalyst owners should be diligent in selecting a PM recycler, as unethical practices, such as misrepresenting metal content or other deceptive behaviours, have been prevalent in the industry. Consulting regulatory bodies and media sources are recommended to ensure a comprehensive investigation and verification of the recycler's financial standing, safety, environmental compliance, and other certifications.

The vendors in the world of PM refining can be classified as brokers, secondary refiners, and primary refiners:

Brokers: Not an actual PM refiner, but a middleman who must, in turn, have the PM recovered by a secondary or primary refiner, which will be discussed in further detail. If the catalyst owner finds themselves in need of fast cash for their PM content, a reputable broker may be a good option. The trade-off will be sacrificing a large percentage of the overall market value of the PM, sometimes as high as 50%.

Secondary refiners: These companies essentially serve the low-volume market, as they typically run small-capacity processing and sampling operations. The purpose of the secondary refining side is to collect various materials and combine them into larger parcels, possibly upgrading them somewhat along the way. They do not produce pure PM and must ship their ultimate output to a primary refiner, so they are also a form of middleman.

Primary refiners: Companies that produce 99.9%+ pure PMs for return to the market (fully accredited and accepted by the banks, jewellery makers, and catalyst manufacturers). All the legitimate, certified, fine PMs on Earth come through a primary refiner.

The need to protect human rights and the environment requires strict adherence to all aspects of responsible sourcing and risk awareness. This protects customers, PM refiners, and ultimately all their employees and the end consumer. The Good Delivery programme from the London Platinum and Palladium Market (LPPM) and the Responsible Sourcing programme from the London Bullion Metals Association (LBMA) provide owners of PM assets with lists of acceptable PM refiners.

These certifications are critical to risk management. There has been increasing scrutiny of the PM industry from the US Department of Treasury, the LPPM, and the LBMA over the last 10 or more years. Concerns about drug cartels, terrorist groups, and other criminals make it mandatory for refiners to actively participate in stringent due diligence and anti-money laundering (AML) programmes. The Good Delivery and Responsible Sourcing designations, therefore, not only accredit the technical aspect (the ability to refine gold, silver, platinum, and palladium to 99.9%+ levels), but also include passing the strict sourcing audits annually. It is expected that compliance requirements will continue to grow more complex in the future as efforts expand to further guarantee responsible sourcing.

Figure 1 Pyro-metallurgical processes are required to recover and refine every possible ounce of precious metals like rhenium (Re) from catalytic operations in refinery and petrochemical facilities

Traditionally, recovery of platinum group metals and rhenium from petroleum and petrochemical catalyst is accomplished by dissolving the spent catalysts in strong caustics or acids. This hydrometallurgical recovery process is commonly referred to in the industry as 'digesting'. Except for aluminosilicates (or zeolites), digestion serves well in recovering the PM from spent process catalysts in most cases. Certain events and circumstances encountered over the life of the catalyst, however, can create many problems when trying to digest:

- Overheating during operation can harden substrates (gamma alumina converting to theta or alpha alumina), rendering them insoluble to even powerful solvents.
- Excessive fines or carbon content can prevent exposure of the catalyst surface area to the solvents.
- Metals present in the feed, or additives introduced to extend catalyst life, can create chemical imbalances and interfere with the desired chemical reaction.

Individually, each of these factors can reduce PM recovery, and in combination these effects can be great. In some cases, for example, as much as 20 or 30% of the rhenium contained can remain insoluble. Should these insoluble materials still hold PM, the hydrometallurgical refiners must send them out to a copper smelter to recover the platinum group metals, but the rhenium (Re) is lost.

A refiner that uses pyro-metallurgical technology such as Sabin's proprietary Pyro-Re process (see **Figure 1**) can

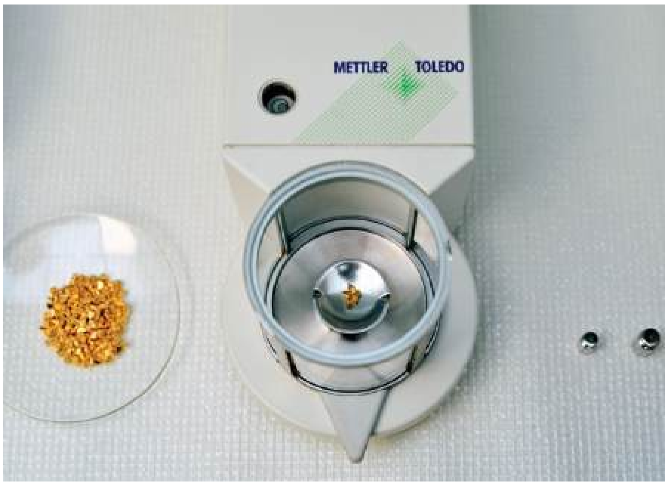

Figure 2 Precision and accuracy; most microbalances in precious metals labs are calibrated to one ten-thousandth of a gram

recover virtually all the Re from spent catalyst lots, maximising the return value because the catalyst owners are paid based on total PM content.

Wise customers will watch the PM refinery contract language very carefully: terms regarding the values being returned should be based on total PM contained and not on acid-soluble PM content. Settlement on acid-soluble values is almost always the equivalent of losing some PM assets.

Accurately weighing catalyst shipments, performing precise sampling, and following the highest industry standards for PM analysis are essential. Choosing a PM refiner based solely on the lowest bid can jeopardise sampling and assaying processes, potentially leading to inaccurate assessments and financial losses.

Achieving a precise evaluation of PM assets requires skilled personnel, properly calibrated equipment, and adequate time for thorough analysis – resources that demand training, maintenance, and other necessary investments (see **Figure 2**).

Once a pre-qualification audit has been completed and the capabilities of the chosen refiner are confirmed, catalyst owners should strongly consider overseeing the weighing and sampling processes in person. Alternatively, reputable third-party representation companies specialising in this field can serve as on-site monitors, ensuring accurate data collection, verifying the PM refiner's practices, and maintaining custody of samples throughout the analysis. This rigorous oversight ensures that all procedures are followed correctly and results are reliable.

Documentation

In recent years, the dynamics within the petroleum and chemical industries have resulted in frequent turnover of roles and responsibilities. With the typical lifespan of a PM catalyst ranging from two to five years, more purchasing agents, procurement managers, and process engineers are facing their first catalyst changeouts every year. This highlights the importance of establishing a formal, in-house programme to manage PM.

Using spreadsheets and databases to store historical data from each PM changeout and recovery can provide valuable insights into vendor performance and other key metrics. As previously mentioned, this data can also be helpful in evaluating reactor performance and tracking PM losses.

Unfortunately, the absence of formal, documented experience in PM recovery can leave companies lacking a thorough understanding of the technical complexities involved in PM recovery contracts, which often contain unique terms and conditions. Misunderstanding these details can lead to significant revenue losses.

Essential control points

It is essential to recognise that expenses related to transportation, PM refining services, and third-party representation are small compared to the inherent value of the PM. Failing to address contract specifics can end up being more costly than the catalyst reclamation process itself. The following are key contractual factors that can greatly influence metal value returns or increase costs:

Splitting limit: This defines the maximum acceptable discrepancy between buyer and seller analytical results. If results fall within this limit, the average is calculated for transaction purposes. Exceeding the limit necessitates a control sample sent to a third-party lab for resolution, known as the 'umpire.' Standard industry practice dictates a splitting limit of 1% relative, but less scrupulous refiners may attempt to raise this to 5% or even 10%, risking substantial financial compromise. A 1% limit mitigates risk and enhances analytical accuracy by demonstrating sample consistency and compelling labs to replicate each other's findings.

Lot size limitation: Implementing limits on the monetary value of individual assay lots supports control and risk management. Excessive monetary concentration in a single lot does not improve laboratory accuracy. It is advisable for PM refiners to create multiple smaller-value assay lots (for example, €500,000) rather than fewer larger-value lots to account for standard deviation and repeatability.

Penalties and hidden charges: Some PM reclaimers include penalties in fine print based on powder levels, carbon content, or minute quantities of other elements in spent catalyst shipments. These penalties can exceed €40,000 per instance if clients are unaware of these risks.

To sum up these bespoke control points for safeguarding your profits:

Contractual details: Understand the distinct terminology in PM reclaim contracts and meticulously review all provisions.

Third-party oversight: Consider engaging witnesses for reclamation and possibly representation for catalyst manufacturing processes and reactor loading/unloading.

Third-party laboratory: Comprehend assay exchanges and maintain thorough records to evaluate third-party lab performance. Ideally, less than 10% of exchanges should require umpire involvement. If the umpire process is necessary more than 10% of the time, and you find your company is consistently on the losing end, you may need to find a new lab vendor.

Shipping and hazardous classification: While outsourced handlers can aid, ensure experts internally and externally manage liabilities and transport expenses, especially for shipments classified as hazardous.

Spent catalyst condition: Share condition reports with your engineering team to uncover insights into process enhancements and equipment maintenance.

PM refiner selection: Conduct rigorous due diligence, ensuring adherence to regulatory, safety, and environmental standards through audits and documentation review. Knowing that your catalysts are going to a primary refiner with proper certifications means peace of mind and eliminates the middleman.

Documentation: Maintain comprehensive spreadsheets for each PM catalyst unit, tracking usage, historical recovery, vendor performance, and precise PM location.

Conclusion

It is estimated that more than 25% of all consumer products either contain PMs or are made using PMs. Now and for the foreseeable future, PMs will remain at the cutting edge of providing answers to some of humanity's most pressing needs, including:

- **Conservation**: Automotive catalysts and the industrial filtration units that reduce emissions.
- **Energy**: Fuel cells, gasoline production, jet fuels.
- **World health**: Treatments, devices, and pharmaceutical products that contain precious group metals (PGM) or are made using PGM; man-made gems in precision surgical lasers.

The metals called 'precious' were originally given that title based on their beauty. They are shiny, and people are attracted to things that are shiny. This made these metals highly sought after, which in turn made them valuable. They are still considered very valuable for their appearance, but the more we learn about these incredible elements, the more value they will continue to gain for even greater reasons.

PM are likely among the most recycled substances on planet Earth, as their value always seems to make it worth someone's time and effort to retrieve regardless of the form they make take. However, the industry needs to get better at recycling. It can be stated with confidence that the re-use of a PM ounce will mitigate energy use and lower emissions vs mining a new ounce. A beautiful aspect of PM sustainability is that they can be refined and re-used indefinitely. The goal should, therefore, be to gather them as thoroughly as possible after each of their incarnations and continue to maximise the number of refine/re-use cycles.

In conclusion, ensure that your vendor is following responsible recycling practices and conduct thorough due diligence to root out unethical behaviour and waste. Detailed knowledge of financial priorities, employee education, and establishment of the best internal practices for catalyst lifecycle management within your company are crucial, such as understanding the processes and verification of how materials are sampled and treated. Always strive to maintain a clear understanding of what is expected and seek transparency in these business relationships.

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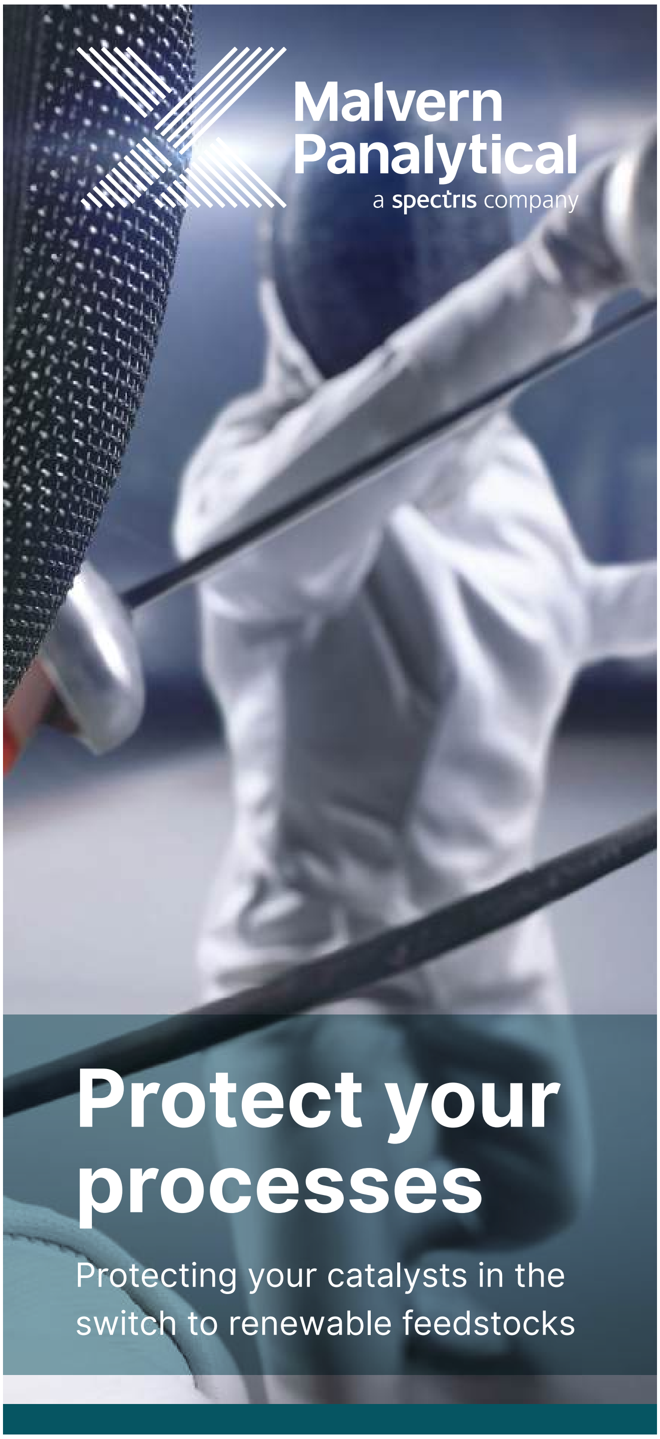


ACTIVITY
MAX

Maximising hydrocracker performance and middle distillate production

Combining high-quality materials and scalable low-cost catalyst manufacturing as a prerequisite to commercialise accessible USY zeolites

Danny Verboekend
Zeopore

Accessible (mesoporous) ultra-stable Y (USY) zeolites offer many benefits for refiners when applied as hydrocracking catalysts. However, their commercialisation appears complicated by the quality of the accessible USY zeolite and the scalability and cost of their manufacture. The enhancement of accessibility via the introduction of mesoporosity is typically associated with a reduction of intrinsic zeolitic properties, as illustrated in the case of acid strength. On the other hand, the inclusion of costly ingredients, such as organics and the to-be-treated parent USY zeolite itself, along with unscalable unit operations, is seemingly mandatory.

Selection of the optimal mesoporisation route provides a unique combination of preserved acid strength and accessibility. Moreover, advanced descriptors featuring mesoporosity and acid strength and type guide catalyst design maximise benefits in hydrocracking. Finally, the integration of dealumination and mesoporisation post-synthetic steps enables combining high-quality materials with scalable and low-cost manufacture.

Accessible USY zeolites

The catalytic potential of accessible mesoporous zeolites has attracted a lot of attention over the last decade. A 'relatively simple' post-synthetic treatment complements the intrinsic micropores existing in conventional USY with a network of complementary connected mesoporous. The mesopores in the resulting hierarchical micro-mesoporous USY zeolite lead to increased access to active acid sites in the zeolite crystals and, at the same time, aid the evacuation of already-cracked species.[1]

A variety of benefits have been reported, most importantly the increased yield to middle distillates at the expense of gas formation. Other benefits include higher activity, reduced hydrogen consumption, higher plant capacity, higher stability and longer cycle time, increased tolerance to more difficult feedstocks, higher quality of products, higher viscosity index, lower polycyclic aromatics, higher H-content, and an increased residue conversion.[2,3] However, despite this comprehensive list, the industrial adaptation of accessible USY zeolites has been underwhelming.

Conventional USY zeolites

USY zeolites have been used in hydrocracking for several decades. They are high-silica faujasites derived from high-alumina NaY zeolites, which are obtained through crystallisation in autoclaves. USY are obtained from NaY zeolites by application of an established post-synthetic dealumination protocol featuring ion exchanges, steam treatments, and acid leaching steps. As a result, the material is made more hydrothermally stable, giving rise to the term 'ultra-stable Y' or USY zeolites. Importantly, although only low-cost ingredients are used, the efforts and losses incurred during this dealumination routine increase the price of a USY by a factor of five to 10 compared to the relatively cheap starting NaY zeolite.

Mesoporous faujasites quality

In an ideal scenario, the desired zeolitic properties are maintained while introducing secondary porosity. However, the reality of mesoporous zeolites shows that upon the introduction of secondary porosity, the intrinsic zeolitic properties are reduced.[4] The latter is particularly true for USY zeolites, where the term 'ultra-stable' does not accurately reflect their behaviour upon mesoporisation. Compared to their relatively more stable ZSM-5 and beta zeolite counterparts, mesoporised USY zeolites typically feature significantly reduced micropore volumes, crystallinity, and acidity, which in turn can be related to the reduced activity of mesoporous USY zeolites.[5]

An important descriptor in the design of mesoporous USY zeolites is their strong acidity. This acidity typically relates to acid sites that are able to retain a basic probe molecule (such as ammonia or pyridine) at higher temperatures. The acidity of mesoporised USY zeolites has been assessed on a number of accounts, systematically showing a reduction in acid strength for the mesoporous zeolite (see **Figure 1**). Consequently, one of the challenges in the design of mesoporous zeolites is to ensure that, in addition to the quantity of mesoporosity, the quality of the zeolite is preserved or even enhanced.

Scalability and cost of manufacture

Likely, the most notorious aspect involved in the synthesis of mesoporous USY zeolites is the use of organic molecules, typically tetraalkylammonium cations such as cetyltrimethylammonium (CTA) or tetrapropylammonium (TPA).

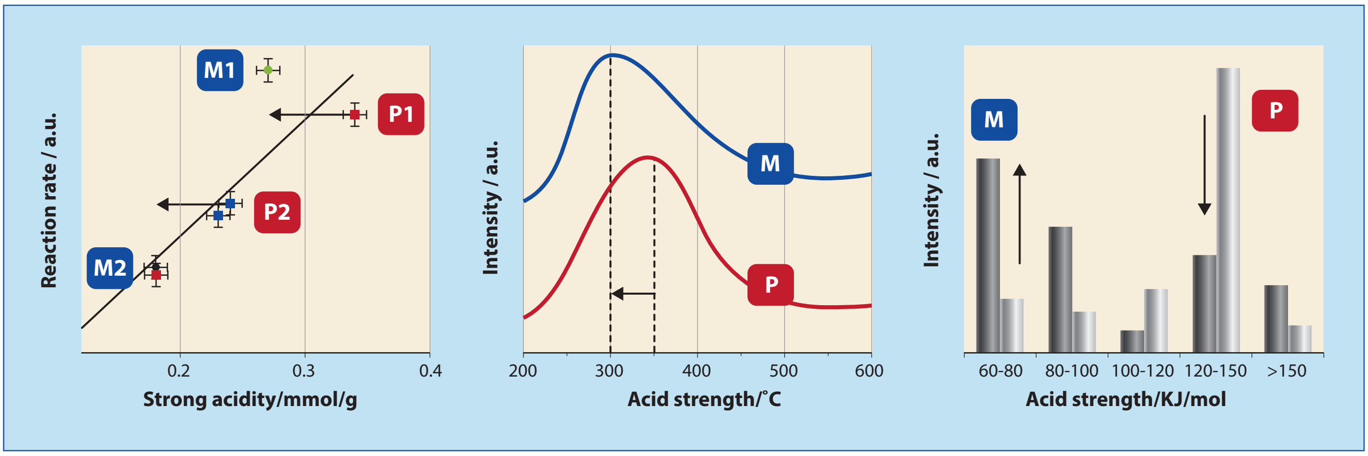

Figure 1 Academic works showing that mesoporous USY zeolites (Mx) display substantially reduced acid strength as compared to the parent zeolites (Px) they were derived from. *Reproduced with permission from the publishers. (Left) derived from [6], (middle) derived from [7], and (right) derived from [8]*

These species are used to scavenge dissolved silicon species, direct mesopore formation, and/or protect the fragile faujasite framework during the mesoporisation process (typically executed in alkaline media).[1] Illustratively, the state-of-the-art suggests that mesoporous USY zeolites of high crystallinity can only be made using organics (see Type D in **Figure 2**).

Such organic species are undesired as they not only complicate the wastewater treatment but also attach tightly to the zeolite. Accordingly, the removal of organics needs to be executed via combustion. This is a dangerous operation due to the release of explosive volatiles. It requires significant energy consumption and gives rise to carbon and nitrous oxide emissions.

Another undesired aspect is the unit operations associated with the manufacture of mesoporous zeolites. For example, the use of hydrothermal stages for extended periods is commonly reported. Moreover, using alkali cations to make alkaline media implies the need for complementary ion exchange treatments to restore the catalytically active protonic form. Furthermore, the use of organics carries the risk of foaming and separation difficulties. As a result, a 'relatively simple' mesoporisation treatment simply does not appear to exist.

Finally, it is crucial to highlight that one of the most overlooked expensive ingredients is the USY zeolite itself. As a precious zeolite, solid losses during mesoporisation should be minimised. The lack of coverage in the top right corner of Figure 2 is significant: not only will high-quality zeolites be unattainable without using organics, but achieving them also appears impossible without losing a sizable mass of the pristine parent USY zeolite. Thus, the underwhelming industrial adaptation may very well be attributed to the sub-optimal quality of the zeolite and a plethora of manufacturing challenges, complications, and costs (see **Figure 3**).

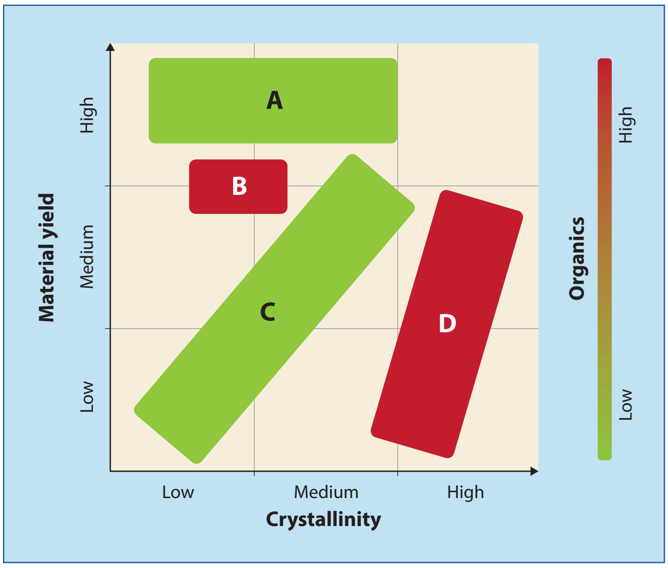

Figure 2 Overview of material yield (y-axis), crystallinity (x-axis), and the need for organics (colour) for four different types of mesoporisation approaches
Adapted from [1] with permission from the publisher

Limitations of conventional descriptors

In order to improve the understanding of mesoporous USY in hydrocracking, Zeopore has executed several hydrocracking campaigns. In each, industrial catalytic testing of a strategic variation of USY samples was applied. Zeolite powders were shaped into extrudates, impregnated with non-noble metals, and evaluated in the hydrocracking of vacuum gasoil in a fixed-bed reactor under both sweet and sour conditions.

In the quest for improved hydrocracking performance,

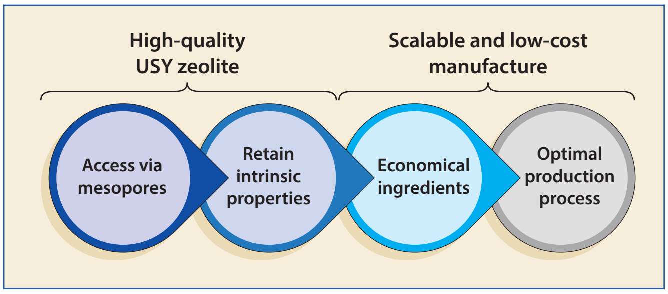

Figure 3 Challenges in the commercialisation of accessible USY zeolites range from attaining high-quality zeolites to ensuring a scalable and low-cost manufacture

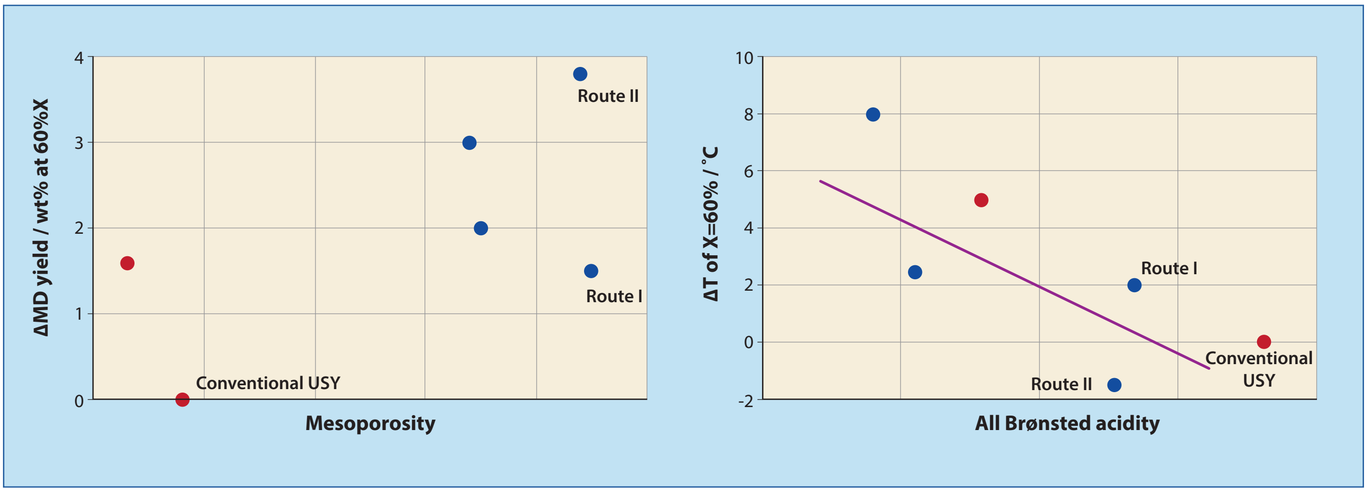

Figure 4 Middle distillate yield (MD, left) and delta of temperature of 60% conversion (right) as a function of common descriptors such as the mesoporosity (left) and overall Brønsted acidity (right)

the application of suitable descriptors to characterise the mesoporous USY zeolite is worthwhile. This becomes particularly relevant in cases where conventional descriptors fail. For example, take two seemingly similar mesoporous USY zeolites obtained via two different routes: 'Route I' and 'Route II'. Both materials feature a largely retained micropore volume and a roughly doubled mesopore volume (see **Figure 4, left**). Additionally, both samples have an overall acidity of about 80% as compared to the conventional USY zeolite (see **Figure 4, right**).

Taking the overall Brønsted acidity into account, one would expect both mesoporous zeolites to be substantially less active than the conventional USY. Moreover, using mesoporosity as a descriptor for selectivity, both mesoporous zeolites should yield a similar benefit in middle distillates make. The above hypotheses are obviously not in line with the remarkably different catalytic results in Figure 4. A broader evaluation of the samples within this study confirms the sub-optimal correlation of established descriptors with the performance of mesoporous zeolites.

Combining accessibility with acid strength

By closely evaluating the top-performing optimal samples, descriptors have been derived based on porosity and acidity, which correlate the set of materials to the hydrocracking selectivity and activity in a superior fashion.

A key ingredient in these descriptors proved the acid strength, expressed as the number of strong acid sites (probed at high temperatures) relative to the overall number of acid sites (probed at lower temperatures). Whereas Route I yielded a relative strength of about 40%, Route II yielded a relative strong acidity of 60%, similar to a conventional USY zeolite. The acidity of the mesoporous Route II sample represents a breakthrough: never before was a mesoporous USY zeolite with this level of mesoporosity prepared with the same acid strength as a conventional zeolite.

The acid strength was, therefore, included in advanced descriptors for selectivity and activity, giving rise to a selectivity and an activity number. The selectivity number refers to the relative number of strong acid sites compared to the total. The activity number is formed by correcting the strong Brønsted sites for undesired strong Lewis sites, both as measured with FT-IR spectroscopy of pyridine-probed zeolites.

It was hypothesised that the acid strength may account

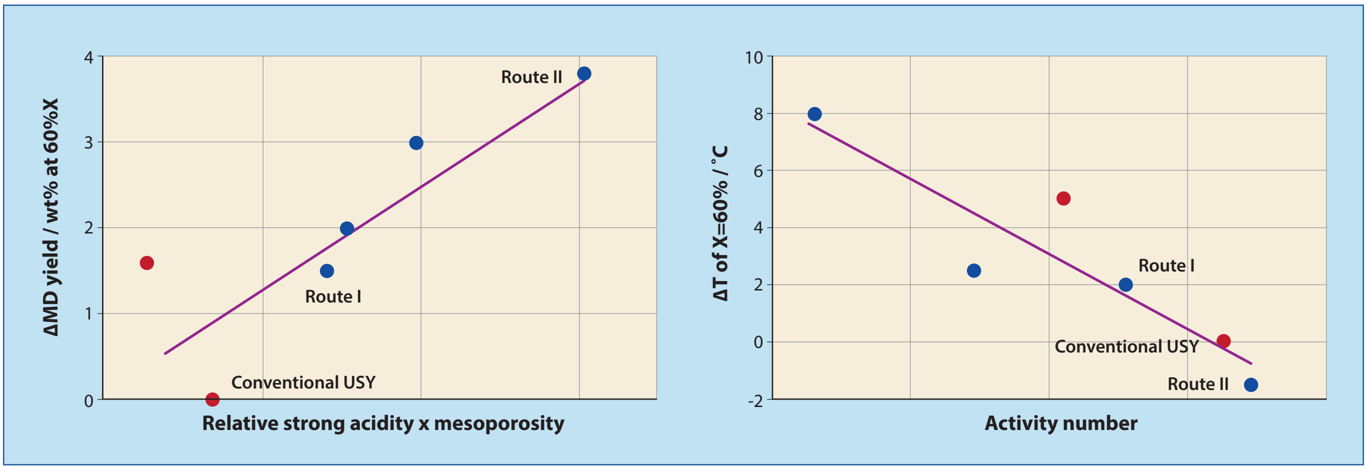

Figure 5 Middle distillate yield (MD, left) and delta of temperature of 60% conversion (right) as a function of advanced descriptors such as the mesoporosity multiplied with the relative strong acidity (left) and strong Brønsted acidity corrected with strong Lewis acidity (activity number, right).

Distinct routes for preparing mesoporous USY zeolites for hydrocracking

Aspect	Optimal mesoporous ←	NaY →	Conventional USY →	State-of-the-art mesoporous
Cost	Medium	Low	Medium	Very high
SiO_2/Al_2O_3 ratio	High	Low	High	High
Mesoporosity	High	Very low	Low	High

Table 1

for the doubled middle distillate yield compared to the other mesoporous sample, as well as the surprisingly increased activity compared to the conventional USY zeolite.

Multiplication of the relative strong acidity with the mesopore volume yields a much-improved relationship with the middle distillate yield (see **Figure 5, left**). Similarly, the activity number relates better to the activity of the catalysts (see **Figure 5, right**). These descriptors highlight the need to prioritise both mesopore quantity and quality in the synthesis of superior high-quality USY zeolites for hydrocracking.

Integrated dealumination and mesoporisation

Having a high-quality USY zeolite does not necessarily imply commercial relevance (Figure 3). For example, even if a high-quality mesoporous zeolite can be achieved without the need for costly organics, the dependency on a costly high-silica-alumina-ratio (SAR) starting USY complicates the business case.

Zeopore researchers have dedicated significant effort to stepping away from the state-of-the-art linear mesoporisation path (see **Table 1**), exploring the various routes present in the faujasite landscape to arrive at a mesoporous high-SAR USY. In doing so, the classical dealumination followed by the mesoporisation route is abandoned, opening up a wide variety of synthetic options within the two-dimensional faujasite landscape.

In this landscape, the researchers have managed to avoid the many pitfalls, overcome stubborn challenges, and exploit unexpected synergies. They have established a route that not only attains the required high-quality USY zeolite but does so using exclusively scalable and low-cost ingredients, including the parent zeolite.

Outlook

By understanding the complex material properties and exploiting synthetic potential, unique mesoporous USY zeolites and related means of manufacture have been created. This advancement creates a valuable position to bring the promising catalytic benefits of accessible USY zeolites to the refiner.

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Danny Verboekend is a founder and CSO of Zeopore Technologies. He is engaged in the strategic development of novel materials using strictly low-cost and scalable manufacturing routes, for established and novel (circular) catalytic applications.

Catalyst rejuvenation for greener hydroprocessing

The chemical industry enables so much of modern life, reaching 96% of all manufactured goods. However, its contribution to emissions cannot be denied, making sustainability an increasingly important part of a business's strategy.

Refiners face a balancing act to produce marketable products and maintain competitiveness in the face of increasingly stringent environmental regulations, external pressures, and surging energy costs.

The challenge is to find economically efficient and sustainable operation methods without compromising performance or safety. Here, catalyst rejuvenation presents a solution. Marrying performance and cost savings, this technology can help businesses minimise environmental impact and reduce waste.

Rejuvenation technology

Evonik's proprietary Excel rejuvenation technology focuses on reusing a catalyst after its lifecycle. A type of sustainable catalyst process, it recovers the full activity of spent hydrotreating catalysts, including the highly active Type II, to ensure their reuse in refining hydrotreating applications, with no loss to unit performance. The process involves the following steps:

- **Verification:** Only the highest quality catalysts are eligible for Excel rejuvenation in reuse applications. They must be free from contaminants, meeting strict chemical and physical specifications.
- **Regeneration:** A simple oxidation reaction that removes carbon and sulphur. Evonik's technology utilises a moving belt, minimising attrition, maximising yields, and maintaining physical properties to restore 65-85% of original activity (depending on the original catalyst type).
- **Rejuvenation:** The catalyst undergoes a treatment process to redisperse the active metals across the catalyst substrate, restoring active sites to the catalyst's original fresh activity.

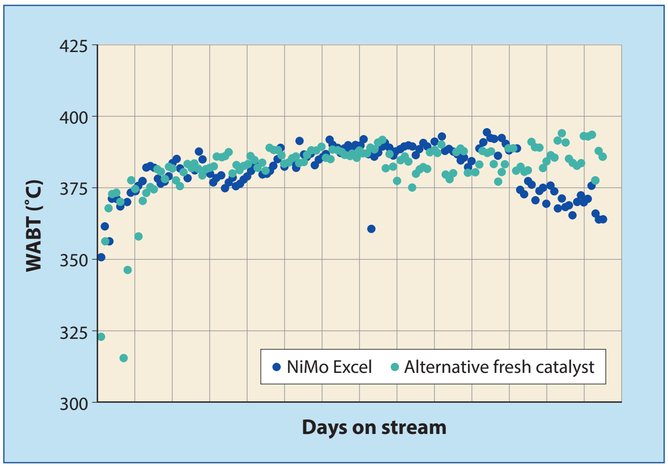

Figure 1 The Excel rejuvenated catalysts performed equivalently to the fresh catalyst from the previous cycle

The technology is relevant to both refining and re-refining and applicable to all manufacturers of both CoMo and NiMo catalysts. Potential applications include, but are not limited to, naphtha, kerosene, gasoline, ultra-low sulphur diesel (ULSD), gasoil, and hydrocracker pretreaters. Excel rejuvenation technology has been in commercial service since 2015 at numerous refineries internationally, consistently meeting or surpassing expectations.

Case study: High-pressure diesel hydrotreater

It can be seen in **Figure 1** how Excel rejuvenated catalysts brought significant sustainability, performance and, cost benefits when used in an ULSD unit in Europe.

The unit processes a blend of light gas oil (LGO), vacuum gas oil (VGO), and coker distillate at high pressure (72 barg) and severe liquid hourly space velocity (LHSV). Originally loaded with fresh catalysts, the business considered switching to rejuvenated catalysts for reduced lead times and lower fill costs.

> **Catalyst rejuvenation technology can support businesses in minimising waste and reducing emissions while maintaining stable and equivalent performance to fresh catalysts**

Evonik supplied an Excel rejuvenated high-activity NiMo catalyst from its inventory, accompanied by the proprietary CatGuard top bed grading and Durocel bed supports, providing a full reactor solution. The rejuvenated catalyst performed equivalently to the previous cycle and at reduced expense. Scope 3 emissions were reduced due to using these catalysts, proving that performance does not need to be compromised in the journey to reduce emissions.

Environmental impact and waste were further minimised by the fact that using rejuvenated catalysts, as opposed to fresh ones, reduces the number of catalysts that would typically end up in landfills.

Case study: Low-pressure distillate hydrotreater

Similar benefits were recorded at a low-pressure distillate hydrotreater in North America, spanning performance, cost, and environmental impact.

The hydrotreating unit processes a blend of distillate cuts at low pressure (35 barg) and high LHSV to produce ULSD and jet fuel. Sourced from Evonik's inventory, an Excel rejuvenated CoMo catalyst (KF-757) was used, with technical projections in line with the refinery's performance objectives. A full reactor solution was provided.

As **Figure 2** shows, Excel rejuvenated catalysts provided excellent stability and a low deactivation rate over the course of the cycle, meeting expectations with equivalent performance to the previous cycle. The refinery also benefited from lower Scope 3 emissions and reduced waste.

Conclusion

Performance does not have to be sacrificed in the pursuit of reduced emissions. Catalyst rejuvenation technology can support businesses in minimising waste and reducing emissions while maintaining stable and equivalent performance to fresh catalysts.

Additionally, externally certified Life Cycle Assessments provide avoided emissions calculations. In the instance of Excel rejuvenated catalysts, it has been found that their use results in a 60% reduction in CO_2eq/per kg of catalyst Global Warming Potential (GWP) emissions compared to fresh catalysts.

It is also crucial to note the cost savings Excel rejuvenation technology presents: between 30-50% savings when purchased directly from Evonik's inventory and up to 50-70% savings when refining organisations reuse catalysts within their own systems.

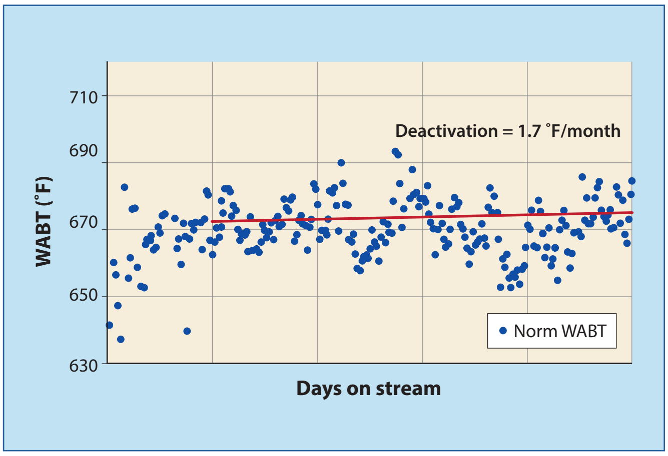

Figure 2 Demonstrated stable performance and low deactivation from the Excel rejuvenated catalyst

A comprehensive solution for companies aiming to optimise performance, Excel rejuvenation technology allows for a greener, more circular approach to catalyst management.

Excel, CatGuard, and Durocel are marks of Evonik.

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