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.

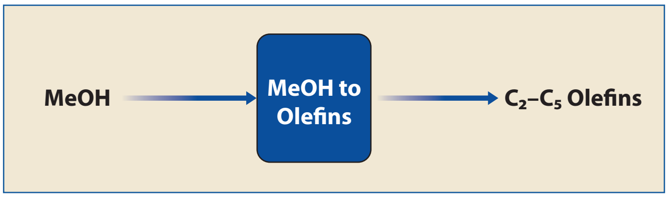

Figure 1 Converting methanol to olefins is a proven technology with many licence providers

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.

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

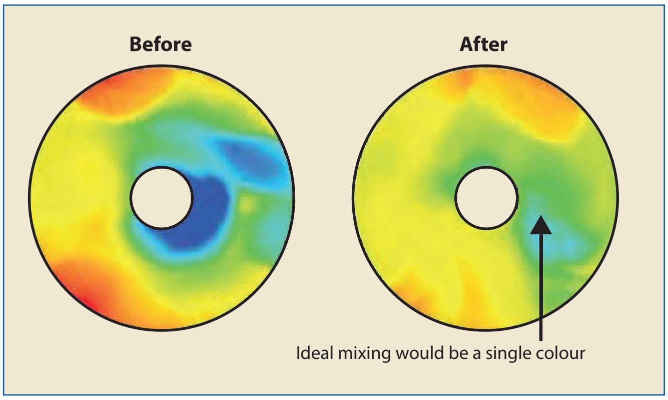

Figure 1 CFD analysis can improve distribution and mixing in radial and vertical directions in reactors

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.

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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.