Resid to propylene: the two-step approach

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

MELISSA CLOUGH MASTRY, HERNANDO SALGADO, BAHA EREN and WEI SHEUN GAN
BASF

The fluid catalytic cracker (FCC) remains one of the most important conversion units within a refinery for the generation of transportation fuels (i.e. gasoline and diesel precursors).[1] However, in certain markets, especially where integration between refineries and petrochemical plants is high, there is great incentive to maximise propylene over other products, including gasoline. In these regions, mainly in Asia and the Middle East, the financial incentive of propylene over gasoline and other liquid products is clear and is driving many of the new project builds. Furthermore, new hardware technologies are advancing, including new unit designs. For these reasons, catalyst technologies must also contribute to advancements in this field.

Catalyst technologies and performance are monitored on a weekly basis from most refineries in the world. The performance can be compiled over many years to demonstrate trends in FCC.[2] Historical equilibrium catalyst (Ecat) yields demonstrate an upward global trend in propylene, particularly in the Asia, EMEA, and Latin American regions (see **Figure 1**). This trend supports further utilisation of the FCC that will produce propylene from resid reliant regions and how important it is to design an optimal catalyst.

The FCC utilises a fluidised solid catalyst to crack oils into valuable products. The main contributor of catalyst activity is the zeolite Y, an important ingredient in all FCC catalysts. The zeolite Y is critical for generating a mix of products, including LPG olefins, naphtha (a gasoline precursor), and light cycle oil (a diesel precursor). Most FCC catalyst manufacturers employ ultra-
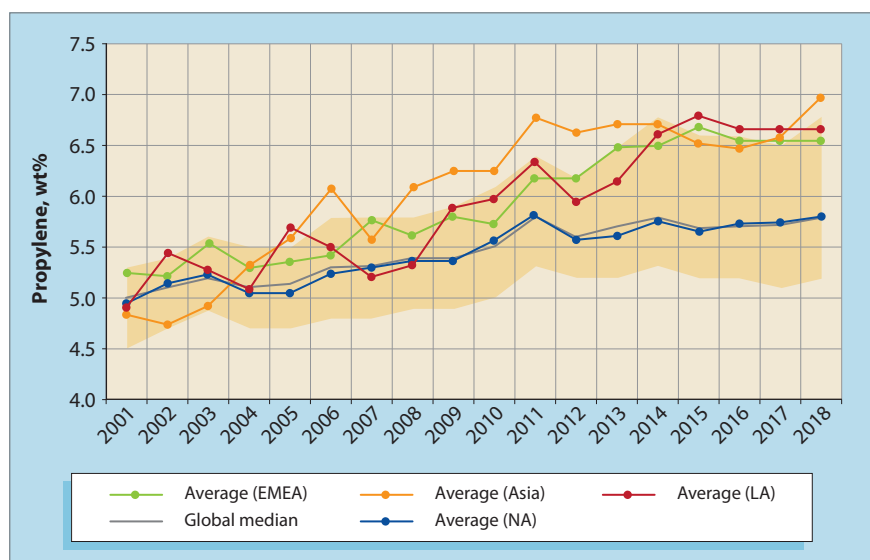

Figure 1 Historical Ecat propylene yield trend; EMEA: Europe, Middle East, and Africa; NA: North America; LA: Latin America

stable zeolite Y, or USY, an outcome of careful calcination in the manufacturing process.[3]

A second and important zeolite in the maximum propylene FCC is ZSM-5. ZSM-5 is a very shape selective zeolite, capable of cracking near-linear naphtha range olefins.[4] For this reason, ZSM-5 is very selective and cracks mainly C_5-C_9 linear or near-linear olefins. Without these temporary precursors in the FCC reaction, the ZSM-5 would contribute nothing to the FCC process. Therefore, the balance of high activity USY zeolite and ZSM-5 zeolite is critical. For example, with too much ZSM-5 in the FCC system, one might dilute the USY, penalising catalyst activity to an extent that there no longer remain C_5-C_9 linear or near-linear olefins for the ZSM-5 to crack.

Furthermore, for resid FCC applications there are additional challenges. For instance, resid feeds bring contaminant metals that can disrupt the FCC process, either cat-

alytically or through the generation of unwanted byproducts. The most critical contaminants that come in with resid feeds include vanadium (V), nickel (Ni), sodium (Na), and iron (Fe).

Vanadium is well known to destroy USY within an FCC catalyst, attacking the Si-O bonds and resulting in zeolite collapse. Ultimately, this leads to a loss in catalyst activity and thus will result in lower conversion, with all things constant.[5] Lower conversion means lower naphtha, lower feed for the ZSM-5 zeolite, and ultimately lower propylene. Nickel, on the other hand, operates with a very different mechanism.

Instead of destroying catalyst activity, nickel promotes dehydrogenation side reactions. Nickel is a very strong dehydrogenation agent, and thus will result in the generation of H_2 and coke, two byproducts that are unwanted in resid applications. Higher H_2 means higher loading on the wet gas compressor, which can often be a constraint for FCC units.

Higher coke generation means lower generation of other valuable products, including naphtha and LPG.

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

The last contaminant on the list is iron. Iron deposition occurs on the outside surface of the catalyst and in some cases can lead to pore blockage, acting as a physical barrier between feed and the important USY cracking sites.[6] This too will lead to a loss in conversion on the FCC unit, resulting in lower naphtha and ultimately lower propylene.

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

As a result of the very well understood mechanisms of USY cracking, ZSM-5 cracking, and metal contamination pathways, the science behind maximising propylene from an FCC unit, when confronted methodically, can identify an optimum solution for each maximum propylene unit. Since every FCC unit is different in terms of feed, contaminant metals, downstream processing constraints and product values, the answer to each maximum propylene resid unit will be unique, delivering in some cases up to $2.5/bbl or more in comparison with no optimised units.
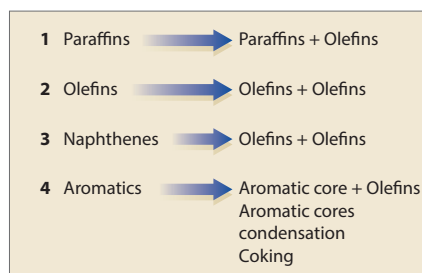

Figure 2 Main cracking reactions on Y-zeolite

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

Catalytic cracking mechanisms
First step: primary cracking using Y-zeolite

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

Other secondary reactions such as hydrogen transfer and isomerisation also take place, affecting the quality of the products in terms of paraffins, olefins, and aromatics

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

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

Second step: secondary cracking of naphtha to smaller molecules

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

The two steps are shown in **Figure 3**.[1] After introducing the two-step approach, with propylene being produced in both steps, it is clear that more light naphtha produced in the first step (feed cracking over Y-zeolite) leads to higher potential for more propylene in the second step (naphtha cracking over ZSM-5). Therefore, one of the key factors is how to maximise naphtha in the first step, which is more challenging when the feed contains residue streams such as demetalised oil, atmospheric residue, or vacuum residue.
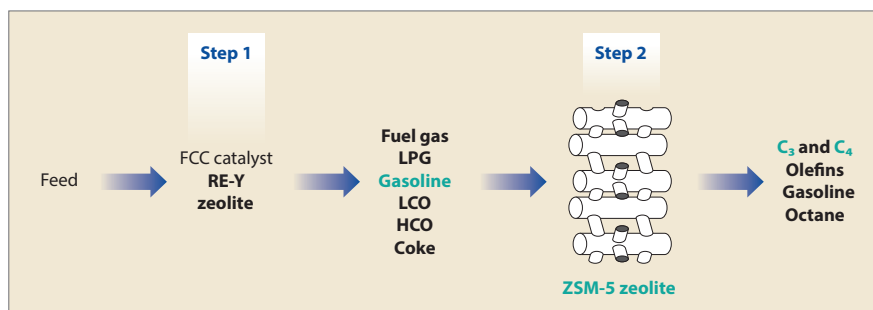

Figure 3 The two-step approach to produce light olefins in an FCC

Challenges of cracking residue feeds

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

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

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

Controlling the effects of nickel

Metals are present in the heaviest feed molecules, especially in asphaltene molecules or porphyrins. Ni is a hydrogenation catalyst widely used for hydrotreating applications, however under typical FCC conditions (low pressures and high temperatures) it behaves as a dehydrogenation agent, promoting hydrogen and coke formation (see **Figure 4**).[7]

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

Conventional Ni-trapping technologies are based on the use of specialty aluminas. The effectiveness of these technologies will depend on the alumina used and its dispersion characteristics, among other factors. A novel approach called Boron Based Technology (BBT) can also be employed. With BBT, a higher portion of contaminant Ni is kept in an electron-deficient state, inhibiting its reduction to a more detrimental
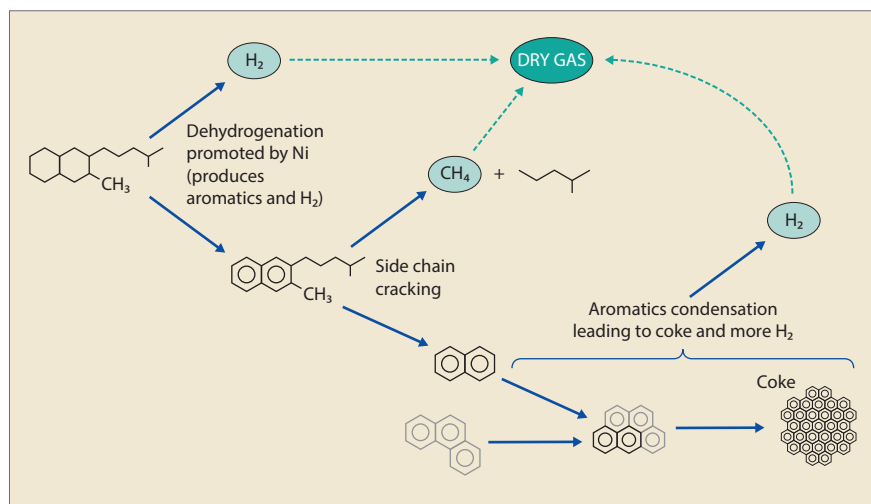

Figure 4 Hydrogen and coke-making reactions promoted by nickel

electron-rich state under FCC conditions, essentially providing a higher passivation efficiency and lowering unwanted dehydrogenation activity. In addition, boron does not induce NOx emissions as antimony injection (another common Ni-passivation strategy) does.

Controlling the effects of vanadium

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

over catalytic cracking, promoting coke making reactions.

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

Understanding the role of iron

Like Na, Fe can be present in fresh FCC catalyst since it is present in raw
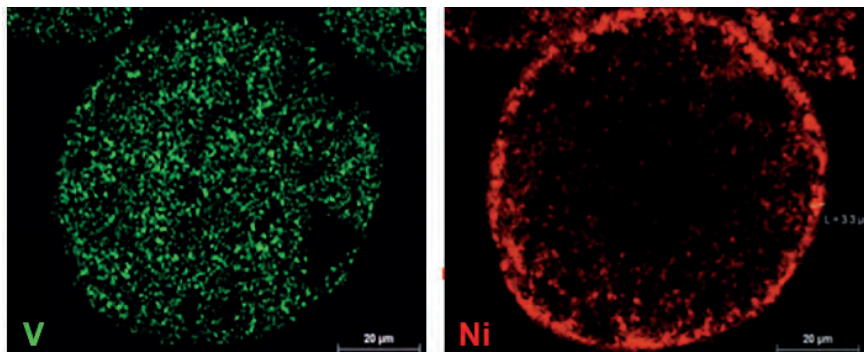

Figure 5 Comparison of mobile vanadium (left) and immobile nickel (right) on equilibrium catalyst

materials. Fresh catalyst can contain 0.25-0.75 wt% Fe. However, unlike Na, Fe already present in fresh catalyst is inactive and does not impact catalyst performance. Only added Fe from feed can affect FCC operation. The effect of added Fe on the catalyst surface can be observed in **Figure 6**.

Added Fe is calculated as the difference between Fe in the fresh catalyst and Fe in the equilibrium catalyst, according to the following equation:

$$Fe_{(Added)} = Fe_{(Ecat)} - Fe_{(Fresh)}$$

Added Fe deposits on the catalyst surface can result in lower surface area, therefore low conversion is sometimes seen under these circumstances with catalyst that has unoptimised surface porosity. With an engineered high surface porosity catalyst, the threshold for added Fe is much higher. A matrix with high porosity and engineered pore architecture is ideal to deal with added Fe to prevent pore blockage due to the different forms of Fe deposition. Other effects of Fe include: 1) changes in average bulk density (ABD), which can affect fluidisation and circulation; 2) mild dehydrogenation, leading to higher hydrogen and coke; and 3) increased SOx emissions, acting as an inverse SOx additive.

The full pathway from resid to propylene: the two-step approach

Summarising the proposed approach (see **Figure 7**) to convert residue feeds to propylene, from the catalytic point of view the first step is tolerance to metal contaminants, especially metals including Ni, V, Na, and Fe. Coke
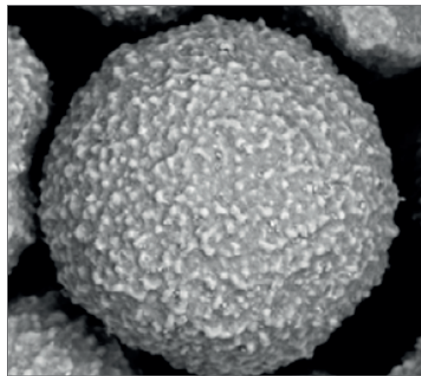

Figure 6 Ecat particle with 0.68 wt% added iron

selectivity characteristics are also important to minimise coke yields and therefore minimise heat balance effects.

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

In the second step, besides the catalytic properties of the ZSM-5 including high activity and stability, it is also important to consider mechanical properties such as resistance to attrition to keep the ZSM-5 material in the unit. Furthermore, reaction severity needs to be carefully defined since too high severity might increase thermal cracking and therefore over-cracking of naphtha to dry gas.

Case studies

Because the answer to each resid FCC unit's maximum propylene approach is different, case studies are provided to demonstrate the multitude of challenges and approaches.
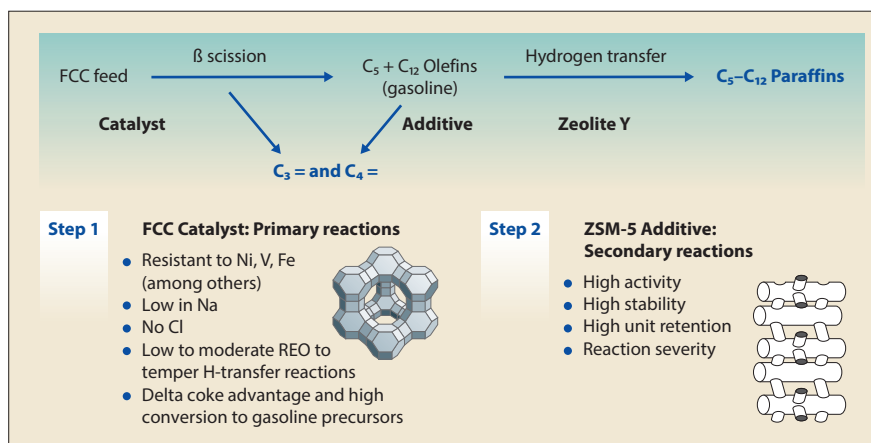
Case 1: resid FCC struggling with delta coke

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

Case 2: resid FCC defines turnaround objectives to increase CCR capacity

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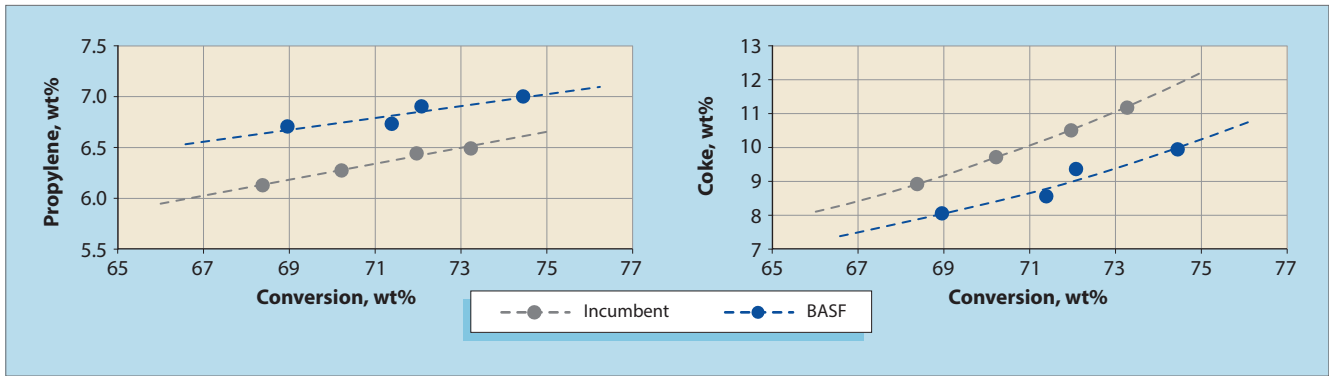

Figure 7 Main considerations in the two-step approach to maximising light olefins

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

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

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

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

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

Case 3: resid FCC looking to optimise catalyst solution

This refinery's main objective was to maximise propylene while processing heavier resid feeds. The FCC utilises BASF's MPS catalyst, which has high activity and high selectivity towards propylene. A combination of in situ manufacturing technology and the use of Valor vanadium passivation technology allowed the use of a lower rare earth catalyst to boost propylene selectivity. The FCC was processing feed CCR of around 2.8 wt%, which increased to 4 wt% during the trial. At the same time, the feed got much heavier and API decreased from 24.0 to 21.4. Feed vanadium more than doubled from 2.5 ppm to 5.4 ppm. Despite the heavier feed with higher CCR and metals, the catalyst addition rate per unit of feed was maintained. The unit was able to achieve record high conversion levels consistently and achieved a propylene yield of over 9.5 wt%, which was an increase of more than 1.8 wt% over the incumbent. The unit also observed a significant increase in C_4 olefins (+1.35 wt%), which enabled higher alkylate production downstream of the FCC. These results are demonstrated in **Table 2** and **Figure 10**. No external ZSM-5 was added before or during the trial.

Post- vs pre-turnaround conditions

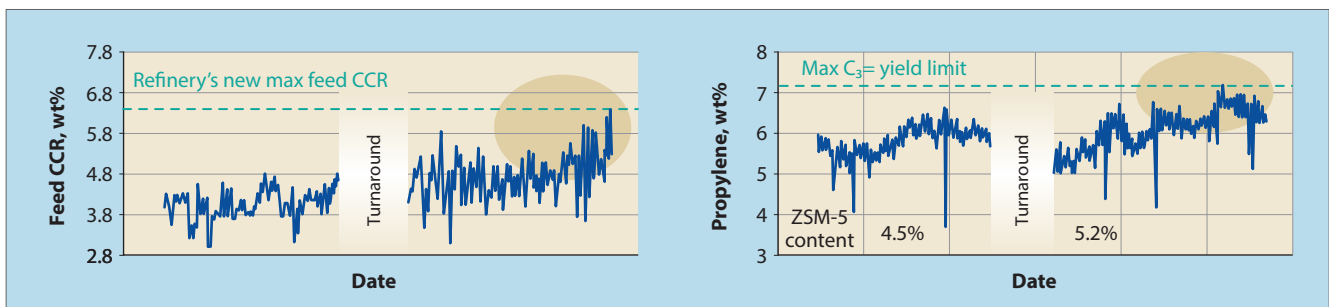|	Change, %
Feed rate, t/d	0.9
Feed basic N	11.6
Feed Ca	29.7
Feed density (15°C)	0.6
Feed di-aromatics	7.5
Feed Fe	168.1
Feed Ni	-14.9
Feed Na	43.7
CO, vol%	1.4
ROT, °C	0.0
Regen bed, °C	-0.1
Cat cooler duty, MW	-17.1

Table 1

Figure 9 Feed CCR and FCCU propylene yields before and after turnaround
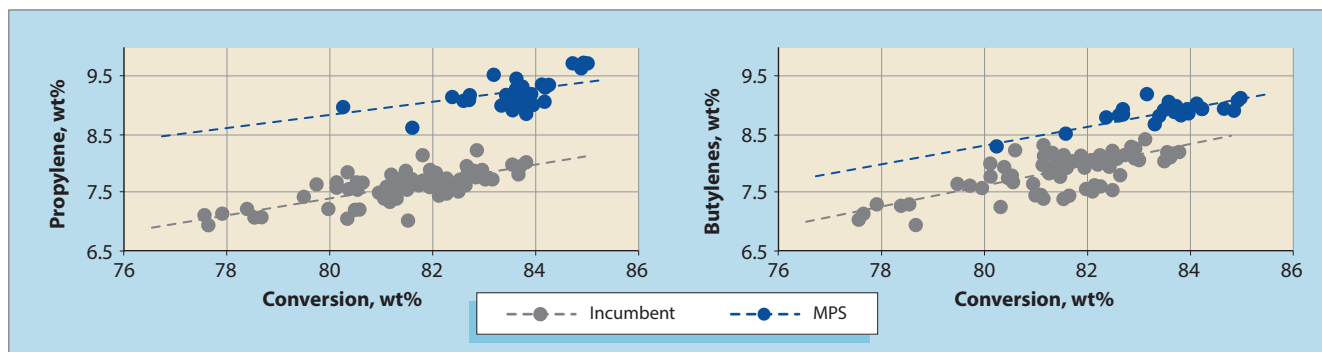
Figure 10 Propylene and butylenes selectivity before and after switching to MPS catalyst solution

Conclusions

Refiners who seek to reap the financial incentives of maximising their propylene yields from resid feeds are primarily located in Asia and the Middle East. These emerging markets and developing regions have created an environment for a high demand for propylene, where many of the refineries and petrochemical plants are integrated. While most propylene demand will be met by steam cracking, a significant portion of propylene demand can be fulfilled through optimising the FCC.

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

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

The catalyst must be metals tolerant in order to prevent activity and conversion loss due to the increased vanadium, iron, and sodium found in residual feeds. Maintaining and improving coke selectivity allows for more flexibility in the heat bal-

Increased conversion levels from heavier feed	
Start vs end of trial	**Change**
Feed rate, t/d	Base
Catalyst additions, t/d	Base
Feed API	-2.6
Feed CCR	+1.2 wt%
Feed Ni	Base
Feed V	+2.9 ppm
$C_3=$	+1.8 wt%
$C_4=$	+1.35 wt%
LPG+gasoline	+3.4 wt%

Table 2

ance around the unit and minimises impacts from feed effects. Protecting against dehydrogenation effects from nickel will give the flexibility needed in the downstream wet gas compressor and will give a more profitable yield structure.

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

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

variety of unique challenges and has shown improved annual profitability in one example of over $5 million.

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Hernando Salgado has more than 15 years of experience in the refining industry. He holds a degree in chemical engineering from the Industrial University of Santander in Colombia, and a Professional Doctorate in engineering (process design) from Delft University of Technology in the Netherlands.

Wei Sheun is the Business Development and Market Support Manager for BASF's refining catalyst business and is based in Singapore. He has more than 13 years of experience in the refining industry and holds a degree in chemical engineering from National University of Singapore and a MBA from Singapore Management University.

Melissa Clough Mastry is a Technology Manager for BASF's refining catalyst business and is based in Spain. She holds a BS in chemistry from the University of Florida, a PhD in chemistry from Texas A&M University, and an MBA with a focus on marketing from the University of North Carolina.

Baha Eren is a Technical Service Engineer for BASF's refining catalyst business and is based in Houston, Texas. He holds a BS in chemical engineering from the University of Texas.