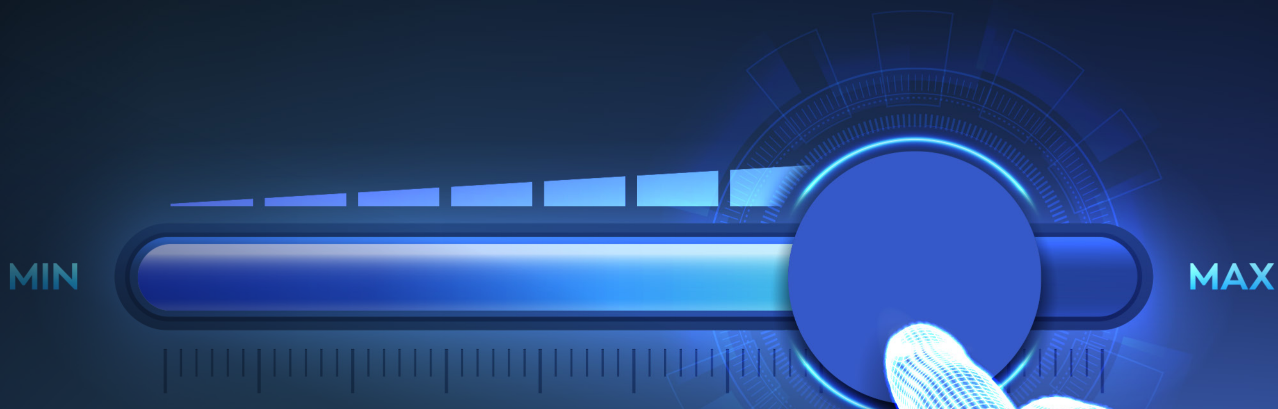
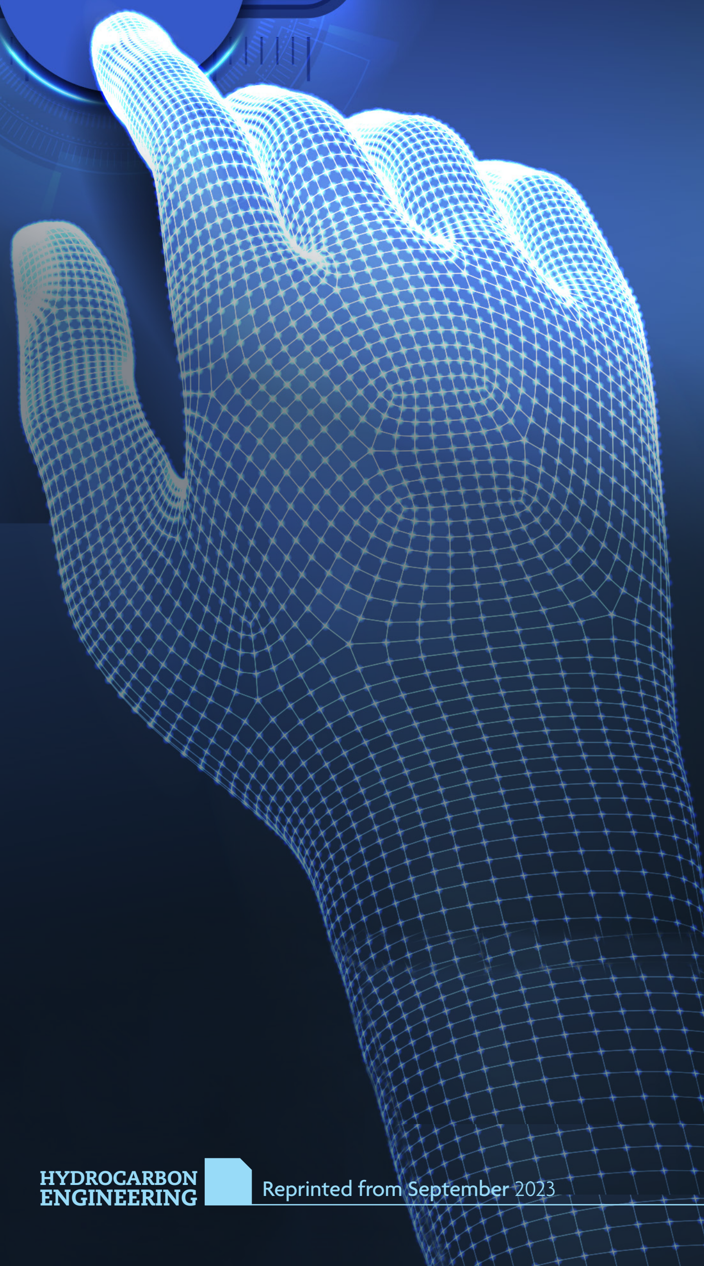
MAXIMISING POTENTIAL





Modesto Miranda Lopez, Hernando Salgado, Aaron Liew, Emmanouil Smaragdis and Corbett Senter, BASF, outline the challenges of maximising butylenes from residual feeds, and the importance of novel catalyst technology.

Fluidised catalytic cracking units (FCCUs) are a major source of global butylenes production, and global butylene consumption is expected to continue growing over the course of the coming years. Alkylate produced from butylenes offers a high value gasoline blending stock, as well as a raw material to produce petrochemicals. BASF reviewed the objectives of hundreds of global FCCU operations between 2018 and 2021, and observed that 40% of FCCUs identified increased LPG olefin yields in their objectives.[1] FCCUs in North America clearly displayed the highest preference for butylenes over other LPG components. As the demand for butylenes has grown, new FCCU catalyst technologies have been developed to address this challenge and increase butylenes yields from FCCUs.

This article will describe the challenges associated with the maximisation of butylenes yields in FCCUs which process resid feeds. These challenges include: elevated levels of nickel and vanadium in the feed; the need to balance high yields of olefins with the maintenance of catalyst activity; and the difficulty of upgrading heavy FCCU feed molecules. Various types of FCCU catalyst functionalities designed to help overcome these challenges, developed through collaboration with key refinery partners, will be discussed. Finally, a case study of a commercial refinery trial of the BASF Fourtitude catalyst will be presented. This is the third catalyst that has been introduced to the market using BASF's Multiple Framework Topology (MFT) technology. The catalyst trial demonstrates how various catalyst functionalities can be combined to maximise yields and selectivity of butylenes from residual feedstocks.

Challenges of maximising butylenes from residual feeds

Designing a catalyst for butylenes maximisation in an FCCU that processes high levels of metals in its feed has a number of challenges associated with it. First, there should be a balancing act between the catalyst stability and the olefin selectivity. For example, rare earth oxides play a key role in catalyst stability. Increasing the rare earth content on zeolite in the catalyst will increase catalyst stability. However, increasing rare earth content on zeolite also increases the rate of hydride transfer reactions in the FCCU riser. This leads to a decrease in the yields of olefins from the FCCU, including butylenes.

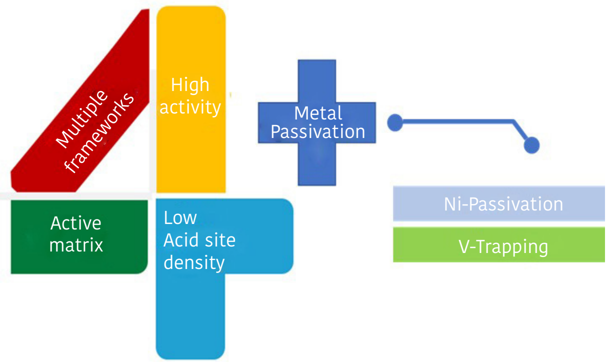


Figure 1. Technology functions contributing to MFT technology.

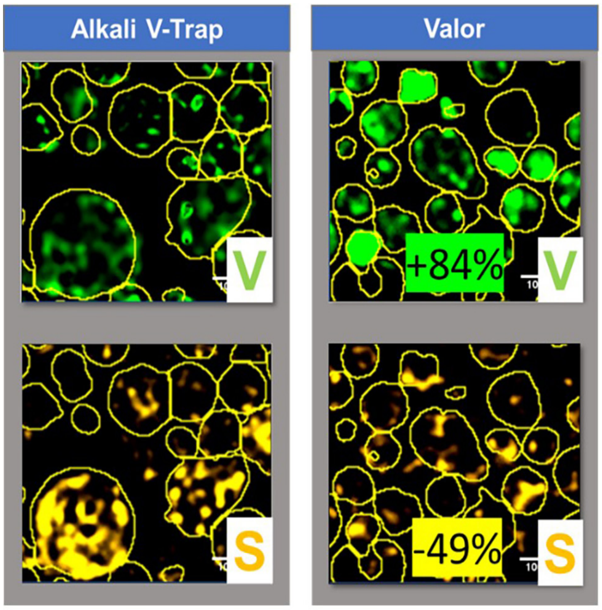


Figure 2. Scanning electron microscope images of vanadium and sulfur concentration of two different vanadium traps, following metalated deactivation. Amount quantified using ImageJ.

The second challenge is effectively dealing with elevated levels of metals present in the FCCU. The two most common contaminants are nickel, which increases hydrogen and coke yields, and vanadium, which primarily reduces catalyst activity through zeolite destruction. Using effective metals passivation technologies is crucial to effectively dealing with these contaminants. However, this is not always a straight-forward task, as nickel exists in different states, is immobile, and can be reactivated by Cl contaminant.[2,3] On the other hand, vanadium is highly mobile in the FCCU environment and never truly deactivates as a contaminant.[4] Therefore, careful consideration should be made regarding the strength and type of metal passivation technology. Finally, the appropriate amount of zeolite and matrix phases should be chosen so that bottoms upgrading and butylenes production can be maximised.

Catalyst development and solution

Fourtitude is a recent innovation that combines MFT with metal passivation technologies to offer advanced products for butylenes maximisation in FCCUs which process metals-containing, resid feed. The balance of all of these factors can be seen in Figure 1. The appropriate combination of MFT technology with metals passivation technologies comes from knowledge gained through laboratory experimental studies, in-unit catalyst trials, and collaboration with refiners.

As mentioned previously, vanadium and nickel are two of the most ubiquitous contaminant metals in FCCU feeds. Significant research has been carried out to understand the behaviour of nickel in an FCCU. Key findings include the fact that nickel exists in a variety of different oxidation states within an FCCU, is not mobile, and is less active when fully oxidised. The presence of chlorides in an FCCU can also reactivate oxidised nickel.[2,3] A combination of boron-based technology (BBT) and specialty alumina is the most effective in passivating nickel. Boron and alumina are highly reactive towards nickel, and boron adds the functionality of being mobile. Consequently, their combination provides a versatile and robust method for dealing with the complexity of nickel contamination. In addition, the in-situ manufacturing method limits the amount of chlorides entering the FCCU with the catalyst and is another key design consideration which plays a role in reducing the impact of nickel.

Vanadium, unlike nickel, is highly mobile and works in combination with sodium to destroy zeolite framework and lower catalyst activity.[4] Traditionally, alkali-based technologies, including MgO and CaO were used to passivate vanadium in FCC. However, the presence of sulfur presents challenges in using these alkali-based technologies. MgO and CaO are both highly reactive with sulfur in an FCCU environment, which limits their ability to passivate vanadium.

In response, BASF developed Valor, a rare earth-based vanadium passivation technology which shows much stronger tolerance to sulfur and is more effective in mitigating the impacts of vanadium. This improvement can be seen in Figure 2, as Valor shows significantly less sulfur uptake and, consequently, higher vanadium uptake, in a study where two vanadium passivation technologies, Valor and an alkali-based technology, were deactivated in the presence of sulfur and vanadium. The use of a secondary zeolitic framework is a strategy that can be used to maximise butylenes selectivity. In the Fourtitude catalyst development process, several potential zeolitic frameworks were screened using rapid laboratory testing to identify candidates that demonstrate improved butylenes selectivity. The best candidates were then further optimised by modifying the chemical and physical properties to further enhance butylenes yield. As a result, prototype testing developed specialty zeolites which could be used to increase butylenes selectivity over propylene while lowering saturates. Additionally, the zeolitic frameworks improved isomerisation of products, increasing gasoline octane values. These frameworks achieved the desired selectivity improvements, without sacrificing catalyst activity, nor generating more hydrogen and coke.

Finally, with identification of the appropriate metal passivation technologies and zeolitic frameworks, significant effort went into combining all of these features into a single catalyst to maximise butylenes yield and selectivity, limit yield of coke and hydrogen, maximise cracking of heavier feed molecules, and maintain catalyst activity. Fourtitude's improved performance can be seen in pilot-scale testing against a previously developed MFT catalyst, Fortune, which was designed to maximise butylenes in a non-resid environment (Figure 3). Test results clearly show that Fourtitude is able to maintain, and even slightly improve, butylenes selectivity compared to Fourtune and significantly lower coke and hydrogen yields.

Commercial trial

While robust performance in testing is a key step in the development of catalyst technology, catalytic performance must ultimately be demonstrated in commercial operation. An early trial of this catalyst occurred in a Europe, the Middle East, and Africa (EMEA) unit highly integrated with petrochemicals production. They had the objective of maximising butylenes yield, and improving bottoms upgrading, without sacrificing propylene production, and the unit processes a feed with high levels of metals (>3000 ppm NI and > 4000 ppm V on ECAT). The results of the trial can be seen in Figures 4 and 5.

Figure 4 shows FCCU butylenes yields as a function of riser outlet temperature (ROT) and in comparison to propylene yields. The results of the trial indicate that, even at lower ROT, the FCCU was able to achieve approximately 1 wt.% higher yields of butylenes. This data also highlights the improved selectivity to butylenes, as the amount of butylenes produced compared to propylene also increased.

A post-audit of the Fourtitude catalyst trial was performed and the rest of the yield shifts at constant operating conditions can be seen in Figure 5. Once again, a clear increase in butylenes yield and selectivity was seen during the catalyst trial. Both LPG olefins increased as desired by the refinery, but the total LPG did not increase significantly, meaning that invaluable LPG saturate molecules (propane and butanes) decreased during this trial. This is a significant aspect of improving refinery profitability. Naphtha yields also increased as a result of increased conversion due

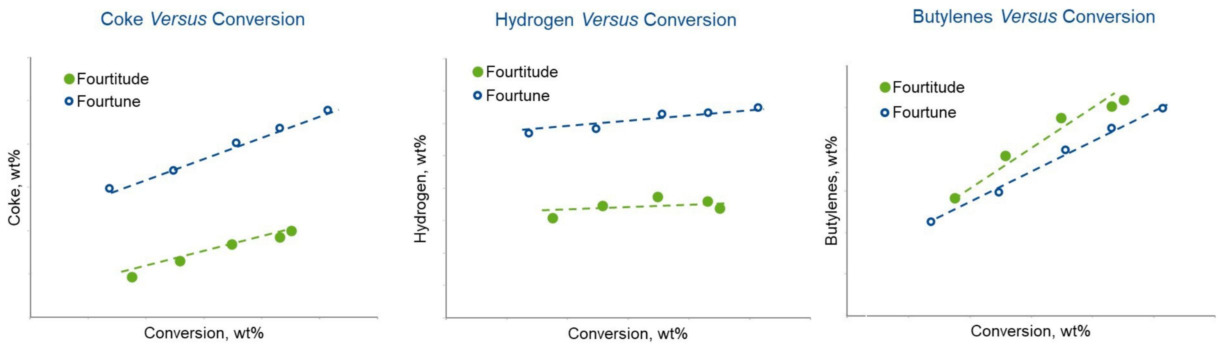


Figure 3. Pilot-scale testing of Fourtitude vs. Fourtune catalysts.

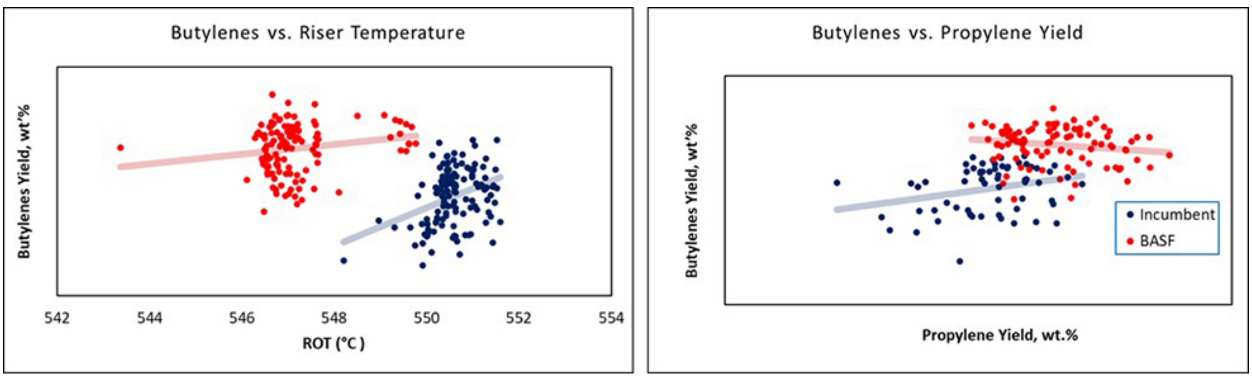


Figure 4. Commercial trial results of Fourtitude vs incumbent catalyst.

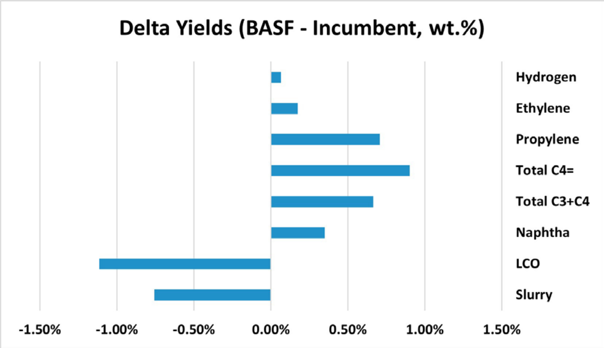


Figure 5. Summary of yield deltas of Fourtitude compared to incumbent catalyst.

to improved activity and activity maintenance provided by the enhanced vanadium tolerance of the catalyst.

Furthermore, there was a significant decrease in slurry yields as a result of improved bottoms upgrading. This was proof of both improved matrix functionality and preservation of zeolite from the improved vanadium tolerance, which is important for pre-cracking of heavy feed molecules. All of these changes occurred with a minimal increase in hydrogen yield, a testament to the ability of the catalyst to effectively passivate nickel. Hydrogen yields are also a function of product olefinicity and, in this case, an increase in hydrogen was expected, despite the improved metals passivation. This was due to the significant increase in olefins and decrease in saturates. It was determined that the new Fourtitude catalyst provided an improvement of more than US$0.75/bbl when compared to the incumbent catalyst.

Conclusions

Many FCCUs have a strong incentive to maximise their production and selectivity of butylenes. This incentive is only expected to increase in the future as tighter vehicle standards increase demand for high-octane fuels, and the global demand for petrochemicals increases. As a result, there is a continued need to improve the ways in which butylenes yield and selectivity can be maximised from FCCUs which process residual feed. To achieve this improvement, several challenges must be faced, including overcoming contaminant metals, identifying appropriate zeolite frameworks, and balancing catalyst activity with selectivity. Many years of research and development, alongside collaboration with refiners, has enabled BASF to develop an FCCU catalyst solution which meets these challenges.

References

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