Boosting profitability in a maximum propylene FCC

Refiner and supplier collaborated to evaluate, prepare, and execute the revamp of an FCC and an LPG olefins additive trial

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The CEPSA La Rábida refinery operates a maximum propylene fluid catalytic cracking (FCC) unit. This FCC is highly integrated with the rest of the refinery, which mainly produces fuels, asphalts, and petrochemical products. The FCC unit often runs a mixture of unconverted oil (UCO) and vacuum gasoil (VGO).

The revamp project

The La Rábida refinery and BASF Refining Catalysts have a long history of collaboration and continuous improvement. In a previous effort, the refinery and BASF jointly evaluated the then-new Zip additive for the La Rábida application. The result was a successful implementation of the Maximum Propylene Solution (MPS) catalyst technology and its long-term use at the refinery.[1] MPS allowed the refinery to achieve high levels of propylene, up to the handling limits of the unit. The FCC was often constrained downstream with the refinery's liquified petroleum gas (LPG) processing capacity. For this reason, the La Rábida refinery decided to investigate the potential profitability of a revamp to increase its LPG handling capacity.

In addition to utilising its own technical workforce, CEPSA regularly works with the BASF technical service team to ensure that their assets run in the most profitable manner. In order to evaluate the revamp potential, both CEPSA and BASF conducted extensive simulations to forecast future scenarios in order to find an optimum between minimum investment and maximum profitability. It was determined that a revamp to increase the LPG handling capacity could be profitable for the refinery and a formal project was started.

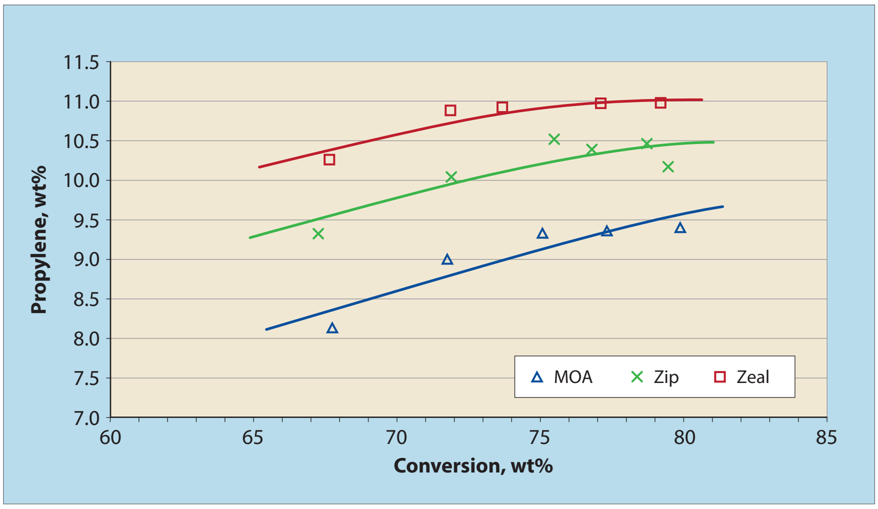

Figure 1 The evolution of BASF ZSM-5 additives, with Zeal delivering 10% higher propylene than Zip. Included for historical context is the previous generation additive, Maximum Olefin Additive (MOA)

The turnaround ended up being more challenging and complex than expected. In order to alleviate some of the unexpected difficulties, BASF designed a customised on-site training course dedicated to emergency shutdown procedures, work preparation processes, and new project start-ups. Later, during the turnaround itself, BASF provided on-site advice and jointly discussed the inspection reports to ensure a successful, safe, and on-time project completion. Finally, in order to meet the gap of the then-current and the to-be scenarios, in which additional propylene could be handled, BASF offered a new technology to achieve the expected results from the La Rábida FCC.

High activity additive

BASF introduced CEPSA to its latest offering: the Zeal LPG olefins additive. Compared to the Zip additive that CEPSA was using at the time, Zeal was expected to generate 10% higher propylene at the same additive dosage, coming from the higher inherent activity of the additive. **Figure 1** shows that Zeal is able to deliver higher propylene than the Zip LPG olefins additive at the same dosage rate.

Zeal is the result of R&D work focusing on a higher activity additive. It brings the benefits of Zip by following a similar manufacturing process to ensure additive activity and integrity, while boosting activity even higher. Higher activity is ideal for refiners and operators of FCCs, especially those in the maximum propylene segment and those with a high degree of integration into chemical plants, to find an optimal balance between additive loading and catalyst activity. Zeal is particularly advantageous when a

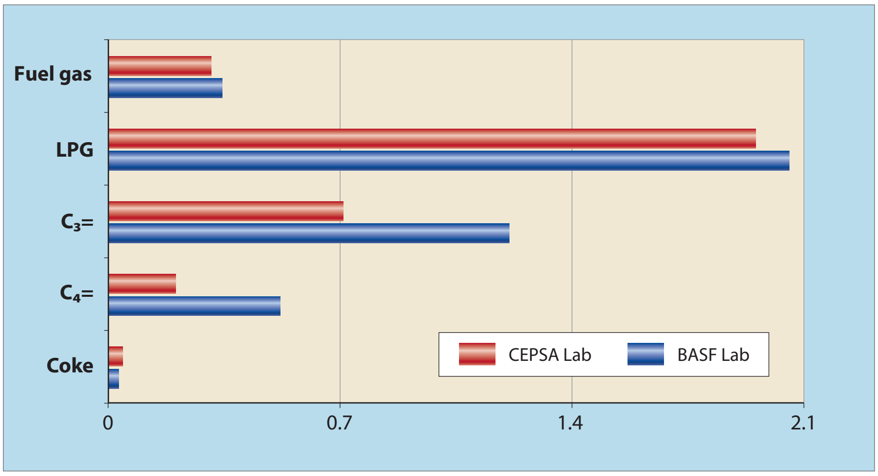

Figure 2 Comparison of CEPSA (red) and BASF (blue) lab results of Zeal testing performed at same additive content

refinery is adding the olefins additive from a hopper separate from the catalyst's. In some FCCs, when an LPG olefins additive is supplied from a separate hopper, it becomes a diluent to the fresh catalyst, which is providing both LPG and gasoline precursors that are further converted with ZSM-5, and lowers the overall activity of the catalyst circulating in the inventory. Therefore, some refineries reach a limit in the amount of olefins additive they can add to the FCC in order to avoid the dilution effect of the base catalyst. Refineries that are operating close to the limit of the maximum additive concentration in the inventory can adopt Zeal. The new additive can be added at equivalent loading versus any incumbent additive or, in the extreme case where the refinery is already limited by the dilution effect, it can be added at a lower dosage rate while still achieving the same LPG yields. This can represent an important debottleneck to some refineries.

In addition, the *in-situ* manufacturing nature of BASF catalysts allows the MPS catalyst to be formulated in such a way that prevents the loss of activity when combined with olefins additives like Zip or Zeal. This was the case for the CEPSA La Rábida refinery, in which it is critically important to maintain catalyst activity at a high level. Therefore, the MPS catalyst not only includes a high activity LPG olefins additive, but delivers high catalytic cracking ability for the feed as well.

Additive testing and validation

Prior to commencing any new product trial, CEPSA R&D plans and executes a thorough and detailed laboratory evaluation.[2] In a previous collaboration between CEPSA and BASF, the refiner fine-tuned the deactivation conditions needed for an FCC focused on maximum propylene.[2] In a previous joint publication, CEPSA described that 1) longer deactivation times for ZSM-5 additives and 2) steam deactivation instead of deactivation involving metals were the most suitable for mimicking conditions for its refinery and equilibrium catalyst. Instead of trying to match the physical properties of equilibrium catalyst, the CEPSA laboratory aims to mimic equilibrium catalyst performance, including yield selectivities and octane response. In taking this approach, CEPSA ensures that data generated in the laboratory are the most representative of what will happen in the FCC unit.

In this recent example, BASF supplied the CEPSA laboratory with a Zeal sample. The laboratory deactivated the sample under the conditions described previously and tested it with the base MPS catalyst against the Zip additive at constant additive loading. In this evaluation, the Zeal additive gave 6% higher propylene on a relative basis, with results from CEPSA closely matching the results from BASF (see **Figure 2**).

The predictions showed that CEPSA's revamp expectations and ability to handle more propylene could be fulfilled with the new technology by delivering higher LPG olefins and in particular higher propylene. After carefully evaluating the laboratory results alongside the revamp expectations, the refinery decided to trial the new product. The targets to secure a successful trial were clearly defined by CEPSA: at the same additive loading (Zip versus Zeal) and similar conversion levels, the Zeal product was expected to deliver 6-10% higher propylene yields while keeping other variables constant. A trial plan was jointly prepared and executed.

FCC refinery trial

The trial started at the end of 2019. During the trial, the feed quality changed significantly. As a result, the equilibrium catalyst became severely contaminated with sodium coming in with the feed. Sodium is a well-known poison for the active zeolite in an FCC catalyst, particularly USY zeolite, and has an irreversible effect. Therefore, with the change in feed quality, conversion in the unit also suffered and was lowered significantly. In addition to the increase in sodium, the furfural extracts stream was eliminated from the feed diet. In order to close the heat balance due to this change, slurry recycle was introduced. In summary, the feed diet was significantly changed during the trial, making monitoring of the trial

Summary of operating changes between the base case and trial period

Parameter	Zip base case	Zeal trial period	Deltas
ROT, °C	540	520	-20
UCO, %	25	52	+27
Slurry recycle, T/d	0	133	+133
Ecat Na, ppm	2359	5905	+3235

Table 1

much more complex. A summary of the main operating changes is shown in **Table 1**.

In order to continue to monitor the trial, an advanced multivariate statistical model was developed, considering the extreme change in sodium levels coming in with the feed and the change in feed bulk characteristics, among other variables. This type of model is an added service available to monitor complex trials, especially when trial period conditions are different from the base case conditions. The model was based on various operating parameters, including ROT and LCO yield as a proxy for the unit conversion. The model matched the base case very well (predicted yields matched actual yields) and it was determined to be the most suitable method to monitor the Zeal trial's progression. As the trial advanced, the model was populated with the new operating data and feed conditions to produce an expected yield profile. Then the expected versus actual yields during the trial were compared. The data showed that during the trial period, when normalising for the significant changes in feed quality and conversion, the propylene yield from the FCC unit increased by 1.8-2.0 wt%, representing a significant increase in propylene selectivity over the base case (see **Figure 3**) when operating at the same additive level. The trial confirmed that profitability was realisable with the higher activity olefins additive Zeal.

Technical evaluation of Zeal was the last point to finalise the revamp project. Both the laboratory data and the plant operating data confirmed that Zeal delivers higher LPG olefins at the same additive content. With the change in unit configuration, LPG handling limits, and the new additive in the unit, the revamp project is considered a success as having added significant profitability to the CEPSA refinery. By allowing the FCC to handle more LPG products, in particular propylene, and by changing to a more active LPG olefins additive, the refinery was able to increase its propylene output and overall FCC profitability.

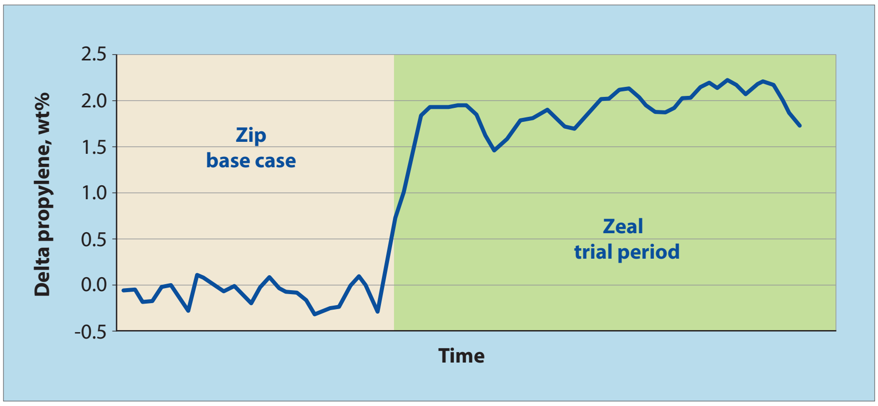

Figure 3 An increase in propylene yields was observed during the Zeal trial period over the Zip base case

Conclusion

Collaboration between CEPSA R&D, CEPSA plant managers and operators, and BASF Refining Catalysts allowed for a safe and successful revamp and catalyst trial at the La Rábida refinery in Spain. In addition, an optimal deactivation procedure has been identified that is suitable for maximum propylene FCC units. Clear definition at the start of the revamp project made it possible to focus on increased FCC profitability in which competing resources (capital and time for instance) were balanced. The clear need from CEPSA for increased propylene selectivity was met with the latest generation LPG olefins additive from BASF Refining Catalysts, Zeal. The safety of all teams involved was paramount in this project, in which benchmarking and safety training were critical points of success. Most importantly, the refiner has continued to innovate over the last decade through their technical teams and the support of the BASF technical services and R&D teams.

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