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HP Special Report

Petrochemical Developments

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New catalyst increases FCC olefin yields

Spanish Petroleum Co. (CEPSA) has three refineries in Spain (Tenerife, La Rábida in Huelva and Gibraltar–San Roque) that produce transport fuels and petrochemical feedstock. The La Rábida refinery started operations in 1967, and the refinery configuration and port facilities allow the refinery to produce, store and distribute a wide range of products for industry and consumers. The fluid catalytic cracking unit (FCCU) was designed with the goal to enable processing flexibility for a wide variety of feeds.[a]

In recent years, the profitability of European refineries has been negatively affected by a number of large-scale trends. Two particular trends are the reduced appetite for gasoline imports from Europe to the East Coast of the US and the movement toward dieselization. However, adaptable refineries are able to improve product mix to meet changing societal needs and maintain profitable margins. In particular, refineries able to produce high-quality petrochemicals feedstock (like propylene), make the right amount of gasoline and increase conversion of low-value feeds, have improved margins.

Around 80% of propylene is generated as a byproduct of ethylene via steam cracking and gasoline by the FCCU. However, recent shifts to using lighter feedstocks in steam crackers have resulted in a decrease in propylene production.[1] There is potential to fill this gap with FCCU propylene. Analysis of FCCU equilibrium catalyst (ECat) data shows increased propylene make from all regions between 2002 and 2012. This trend is expected to continue.[2] At the La Rábida refinery, making propylene is an attractive proposition, since the refinery and petrochemical sites are closely integrated.

CEPSA's La Rábida refinery has been producing high propylene yields for almost 25 years. Nonetheless, the refinery wished to challenge the status quo and investigate if even better performance was possible. The base case catalyst was a high propylene yield catalyst.[3] To see if the new catalyst would outperform this, laboratory testing and a commercial trial were undertaken.

Trial objectives. The refinery defined four objectives for the new catalyst. They were:

1. Increase propylene and isobutylene yields
2. Maintain similar light cracked naphtha at higher propylene yield
3. Increase bottoms upgrading and conversion
4. Improve the capability and flexibility to process

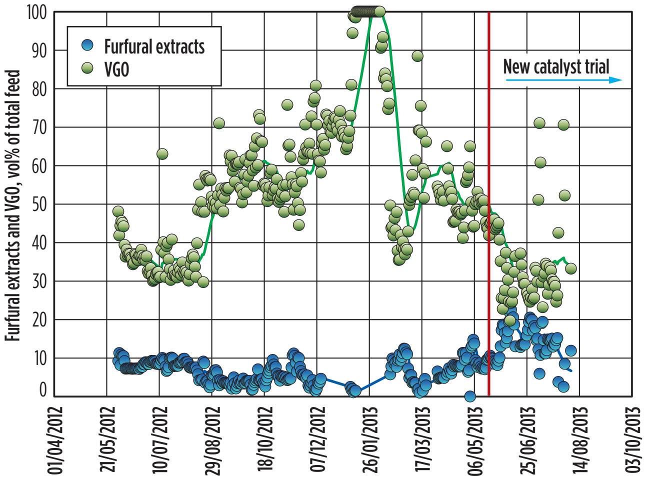

FIG. 1. FCCU feed composition.

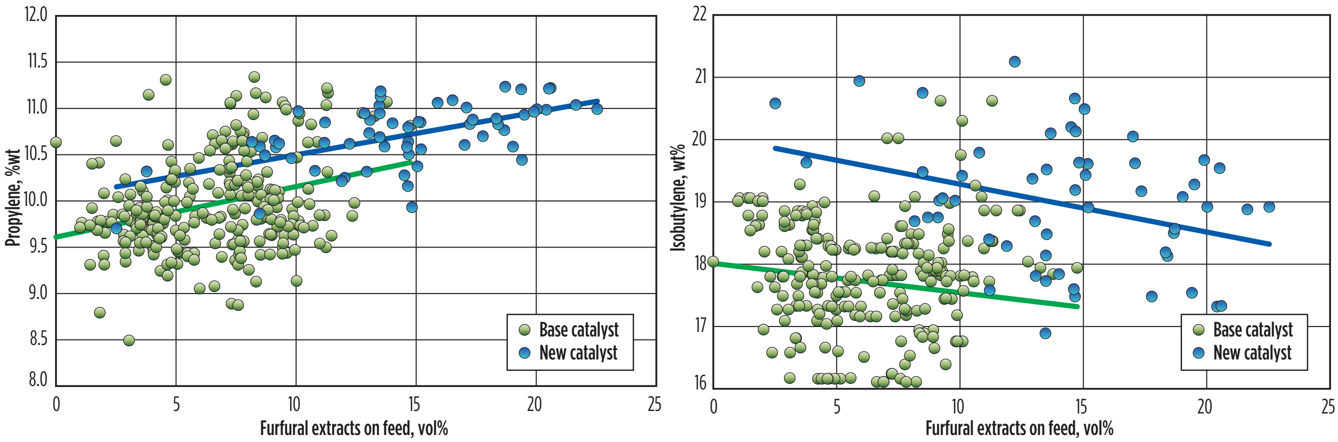

FIG. 2. Propylene (left) and isobutylene (right) yields vs. proportion of FE in feed.

unconverted oil (UCO) from the hydrocracker and other nonconventional feeds in the FCC.

Laboratory testing. Prior to the commercial trial, CEPSA R&D performed a catalyst evaluation in its laboratory, comparing catalysts from the incumbent and new catalyst suppliers.[b] Fresh catalyst samples from each supplier were steam deactivated to simulate commercial ECat and then tested in a Davison circulating riser pilot plant unit. Based on the results of this evaluation, the new catalyst was selected for a commercial unit trial.[b]

In general, FCCUs typically produce around 4 wt% to 6 wt% propylene, depending on feed type, operating conditions and the FCC catalyst. By optimizing all these factors, propylene production can be increased up to 12 wt%.[2,4]

To generate higher propylene yield, ZSM-5 additive is typically added on top of the base catalyst, which can result in dilution of the base catalyst activity. As a rule of thumb, every 5% of non-FCC cracking material in the unit inventory reduces the FCC conversion by 1%. This is not a concern at low ZSM-5 additive levels, but at the high levels required to truly maximize propylene, it can become an issue. This can require higher fresh catalyst addition rates to compensate for this activity dilution.

The catalyst under evaluation does not suffer activity dilution because the ZSM-5 functionality is present in the base catalyst formulation. The presence of the ZSM-5 zeolite also allows for maximized liquefied petroleum gas (LPG) olefins.[5, 6] This particular catalyst allows for the production of highly olefinic naphtha by providing enhanced diffusion of feed molecules to pre-cracking sites located on the external, exposed surface of highly dispersed zeolite crystals. This results in higher bottoms conversion with high yields of olefinic naphtha. The gasoline range olefins are then selectively converted to LPG olefins by the ZSM-5 functionality.[8]

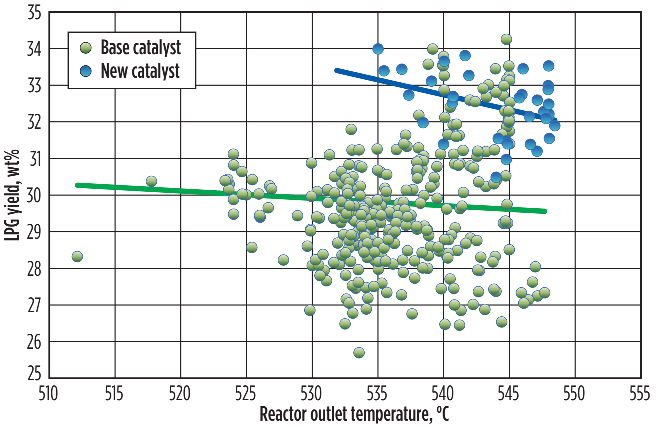

FIG. 3. Total LPG production vs. reactor outlet temperature.

Technical support service. While the catalyst was being tested, technical support services were provided to the refinery. The package included site visits and logistical support, process and laboratory sample analysis and FCCU optimization using a number of proprietary tools.

Trial results. The La Rábida FCCU feed is a mixture of vacuum gasoil (VGO) and nonconventional feed components, such as UCO from the hydrocracker, Furfural extract (FE) from lubes processing and other low-value components. It is desirable to process all the UCO in the FCCU because recycling this in the hydrocracker tends to shorten catalyst cycle length.

As the proportion of UCO in FCCU feed is increased, the proportion of FE must also be increased to improve slurry viscosity and heat balance in the FCCU. However, FE contains about 80% hydrocarbons with aromatic rings, and with the previously supplied catalyst in the base case operation, it was difficult to convert this material in the FCCU. In addition, the refractory FE contributed to increased slurry yields. Historically at La Rábida, the maximum amount of FE that could be processed in the FCCU was constrained by the maximum slurry disposal to fuel oil.

The new catalyst delivered improved bottoms cracking performance, allowing more of the FE aromatic side chains to be converted. As a result, it was possible to significantly increase the proportion of FE in feed. The FE limit with the base catalyst was around 10%, while, with the new catalyst, the FCCU is now able to operate with up to 20% FE in feed. The flexibility to increase the proportion of FE in the FCCU feed enabled all the UCO production from the hydrocracker to be sent to the FCCU for the first time. Increasing the FE and UCO in FCCU feed has enabled the refinery to significantly reduce the amount of VGO sent to the FCCU. VGO is a good quality FCC feed, but it is also significantly more expensive than FE and UCO. Further, it is preferred to send VGO to the hydrocracker where it is more valuable to the refinery. The net results were:

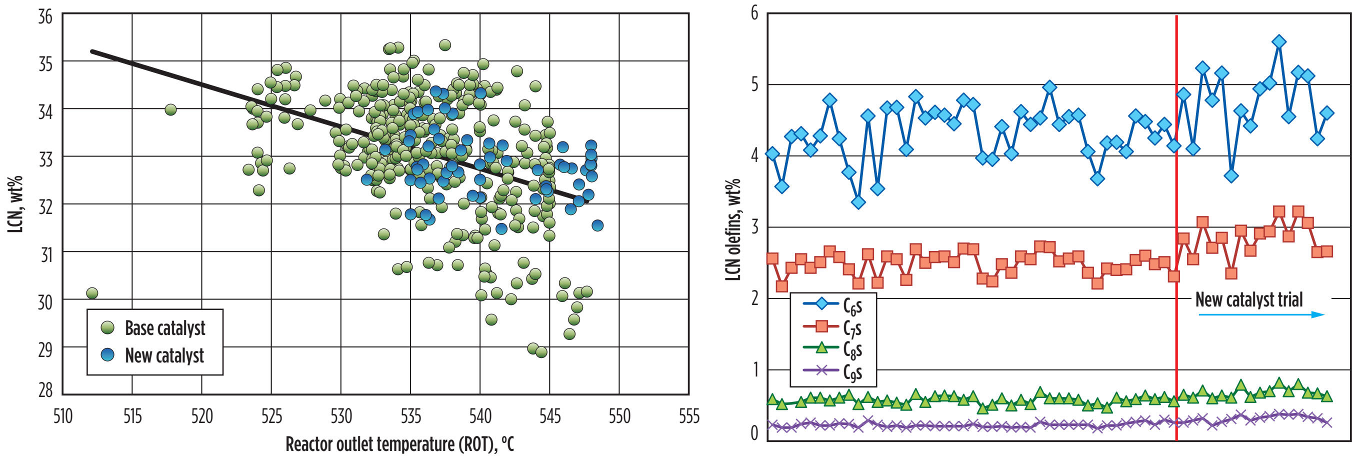

FIG. 4. Light-cracked naphtha (LCN) yield vs. ROT (left) and CEPSA R&D LCN olefins wt% for the La Rábida feed (right).

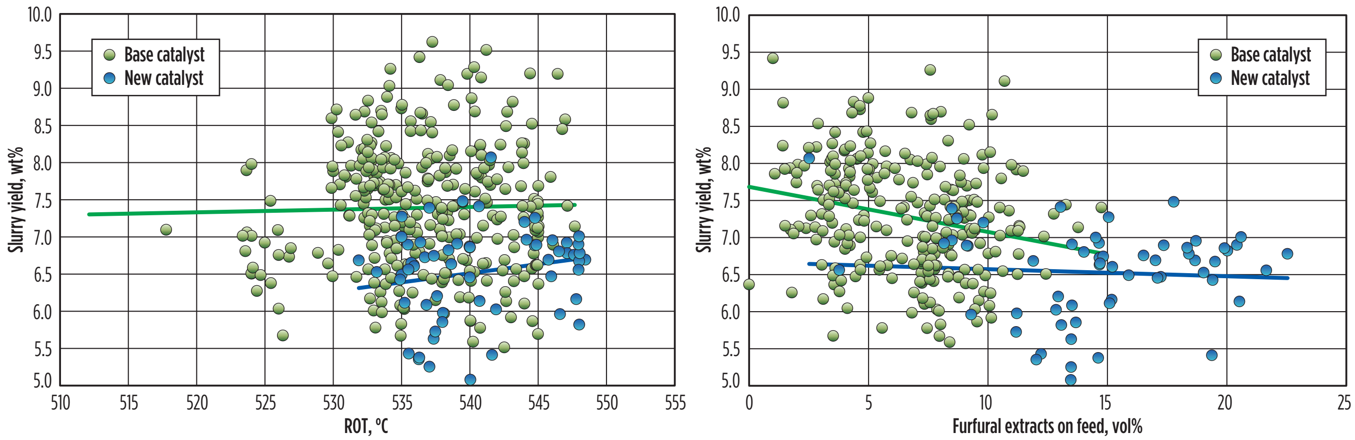

FIG. 5. Slurry yield vs. ROT (left) and proportion of FE in feed (right).

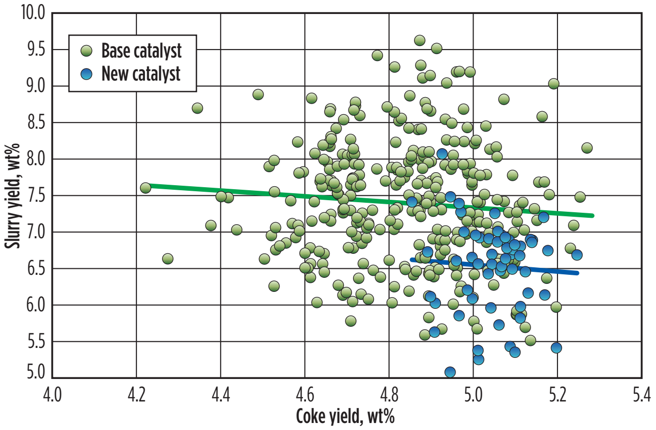

FIG. 6. Slurry yield vs. coke yield.

TABLE 1. Yield improvements and feed changes provided increased profitability

	Base catalyst	New catalyst
FE in feed, wt%	Up to around 10	Up to 20
UCO in feed	Part of production	All production
Propylene yield, wt%	Base	+0.81
Isobutylene yield, wt%	Base	+0.92
Total LPG, wt%	Base	+2.14
Total naphtha yield, wt%	Base	–0.81
Light cycle oil yield, wt%	Base	–1.26
Coke yield, wt%	Base	+0.2
Slurry yield, wt%	Base	–0.89
Conversion, wt%	Base	+2.12
Raw FCCU profitability	Base	+2.5 $/B of feed

1. Reduced FCCU feed cost
2. Improved integration of the FCCU and hydrocracker
3. Expanded FCCU and refinery operating window.

The changes in FCCU feed composition are shown in **FIG. 1.**

Increased yields. The new catalyst met the main trial objective by significantly increasing both propylene and isobutylene yields for all feed compositions (**FIG. 2**). At the same time, the total LPG production (C_3s and C_4s) was significantly increased, even at lower riser outlet temperatures (ROTs), as shown in **FIG. 3.**

Fine-tuning the catalyst formulation enabled the light-cracked naphtha (LCN) yield to be maintained over a range of ROTs, consistent with defined objectives (**FIG. 4**). Increases in propylene and isobutylene yields (**FIG. 2**), and total LPG production (**FIG. 3**), came from improved bottoms upgrading (**FIGS. 5** and **6**). Plus, the CEPSA R&D analysis of the LCN suggests a slight increase in remaining C_6–C_9 olefins (**FIG. 4**) achieved by the new catalyst even though LPG olefins have increased. This indicates that there is potential to further increase the propylene yield by optimizing the ZSM-5 functionality of the catalyst.

Upgrading. Bottoms upgrading (**FIGS. 5** and **6**) and conversion (**FIG. 7**) improved. This was achieved despite the significant increase in the proportions of highly aromatic FE and UCO in the feed. Since the catalyst under consideration has a unique pore architecture and optimized porosity for heavy feed molecule diffusion, the zeolite-based cracking provides the capability for deep-bottoms conversion with good coke selectivity. **FIG. 5** shows much lower slurry yield over a range of ROTs. The right side of **FIG. 5** illustrates that, even for the new operating window (with a significantly higher proportion of FE in feed), the slurry yield is still lower than that achieved by the base case catalyst.

All the objectives set by the refinery for the new catalyst were met. This resulted in an improvement in FCCU profitability, as summarized in **TABLE 1.**

Benchmarking. Based on an ECat benchmark database, 20 to 30 FCCUs worldwide are targeting maximum propylene production (**FIG. 8**). As the figure shows, the catalyst tested at La Rábida refinery is used by the three units with the highest propylene yield vs. conversion and highest LPG olefins yield vs. conversion.

The new catalyst, combined with technical support service from the catalyst supplier, enabled the CEPSA La Rábida refinery to maximize propylene and isobutylene yields, expand total LPG production, maintain LCN yield, improve bottoms upgrading and expand the FCCU operating window. These changes led to an increase in the FCCU's potential to improve refinery profitability (+2.5 $/bbl of feed). Improved FCCU integration with other parts of the refinery was also achieved.

Plus, processing all the UCO in the FCCU helps improve catalyst cycle length at the hydrocracker. The increased propylene yield supports CEPSA's activity in the petrochemicals area, while the increased C_4 olefins yield minimizes the need for ethyl tertiary butyl ether unit feed imports. The improved conversion of low-value components, otherwise destined for fuel oil production, improves the efficiency and profitability of the overall refinery.

By challenging the status quo, CEPSA has improved the refinery's sustainability and economic performance. HP

NOTES

[a] Designed by Exxon Mobil
[b] BASF

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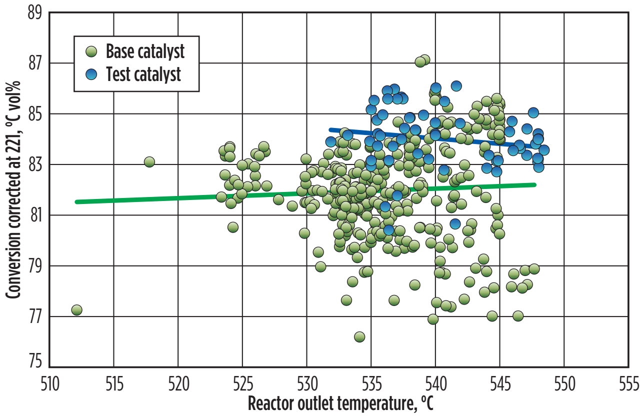

FIG. 7. Conversion corrected at 221°C vs. reactor outlet temperature.

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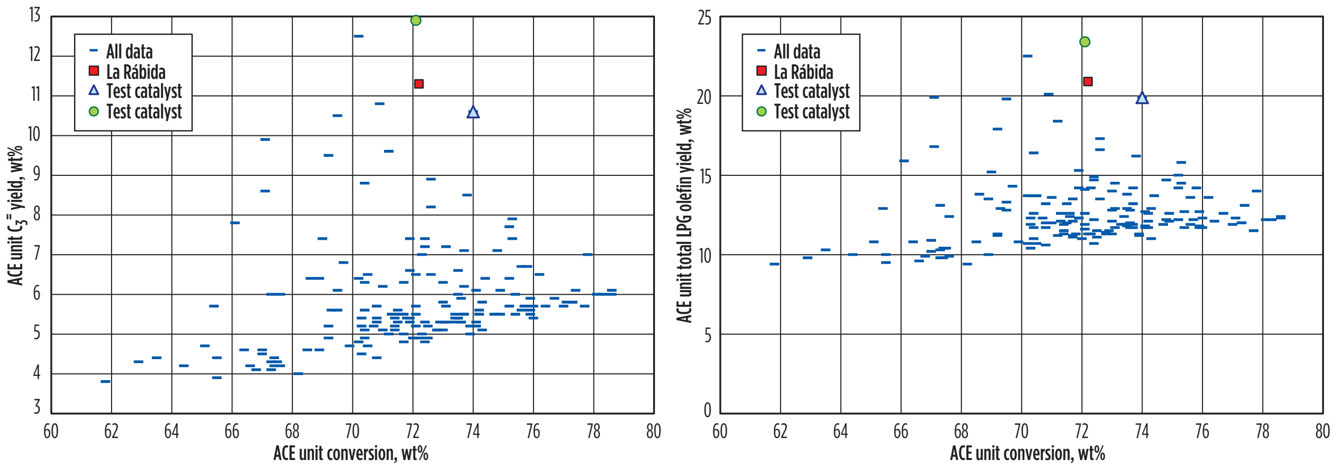

FIG. 8. Equilibrium catalyst benchmarking.