FCC catalyst for maximum propylene

A case study for boosting unit profitability through FCC catalyst selection for propylene maximisation

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CEPSA's (Compañía Española de Petróleos SAU) Gibraltar-San Roque refinery operates as a fully integrated refining and petrochemical site. The refinery, originally started up in 1967, is designed to produce a wide range of transportation fuels and petrochemical feedstocks and is strategically located next to the Straits of Gibraltar, supplying local and export markets with a wide range of products. The Gibraltar-San Roque refinery is the largest refinery in the Iberian Peninsula, with a daily crude oil processing capacity of 240 000 b/d.

The fluid catalytic cracking (FCC) unit is the primary hydrocarbon conversion unit in the modern petroleum refinery. It uses heat and catalyst to convert a variety of high molecular weight feeds (for instance, gas oils, cracked gas oils, deasphalted gas oils, and atmospheric/vacuum resids) into lighter, more valuable products such as gasoline, light fuel oil, and petrochemical feedstocks such as propylene and butylenes.[1] Rapid growth in demand for propylene in China and the shift to shale gas based ethane cracking in North America have created an acute supply shortage in propylene.[2] Several propylene producers have announced capacity expansions utilising new on-purpose technologies such as propane dehydrogenation (PDH). The majority of the capacity expansion will be in the US, China, and the Middle East, increasing the propylene imbalance in Europe. Refiners, particularly those integrated with petrochemical complexes, have the opportunity to increase propylene yield on the FCC and help reduce the supply gap and realise higher FCC product margins.

The FCC unit at CEPSA's Gibraltar-San Roque refinery is a UOP High Efficiency design with a throughput of approximately 5200-5500 t/d. The FCC unit is a key process unit of the refining complex, upgrading low value feedstock, primarily blends of gas oils – straight run vacuum gas oils (SRVGO) and hydrotreated vacuum gas oils (HTVGO) – with FCC slurry recycle, but also atmospheric residue, furfural extracts and visbreaker naphtha, to deliver higher value alkylate, gasoline and diesel for blending in the refinery fuels pool and to provide aromatic rich feedstock and propylene to the petrochemical site.

After almost 20 years of partnership between Grace and the Gibraltar-San Roque refinery, during which time numerous new catalyst technologies were introduced that delivered successive improvements in FCC unit operating profitability, CEPSA challenged the status quo and implemented back-to-back FCC catalyst trials with Grace and an alternative FCC catalyst supplier.

As will be subsequently discussed, the performance of Grace's ProgREss-26 FCC catalyst compared to the previous Grace catalyst yielded a considerable improvement in operating profitability for the FCC unit and refinery.

FCC catalyst trial objectives and operating constraints

The refinery defined three primary objectives for the FCC unit to increase the operating

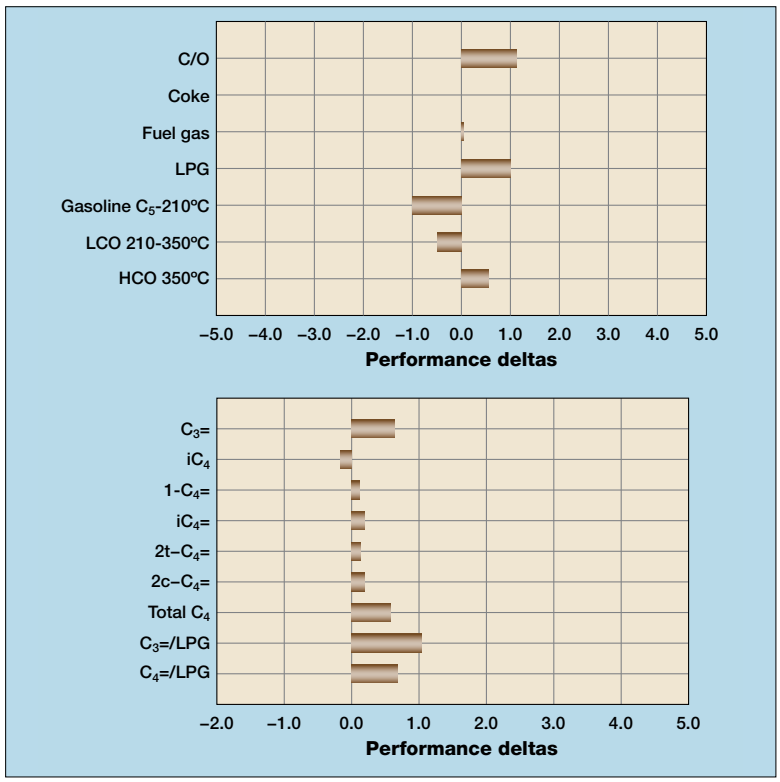

Figure 1 Improved performance with Grace's ProgREss-26 demonstrated by CEPSA's pilot plant test results

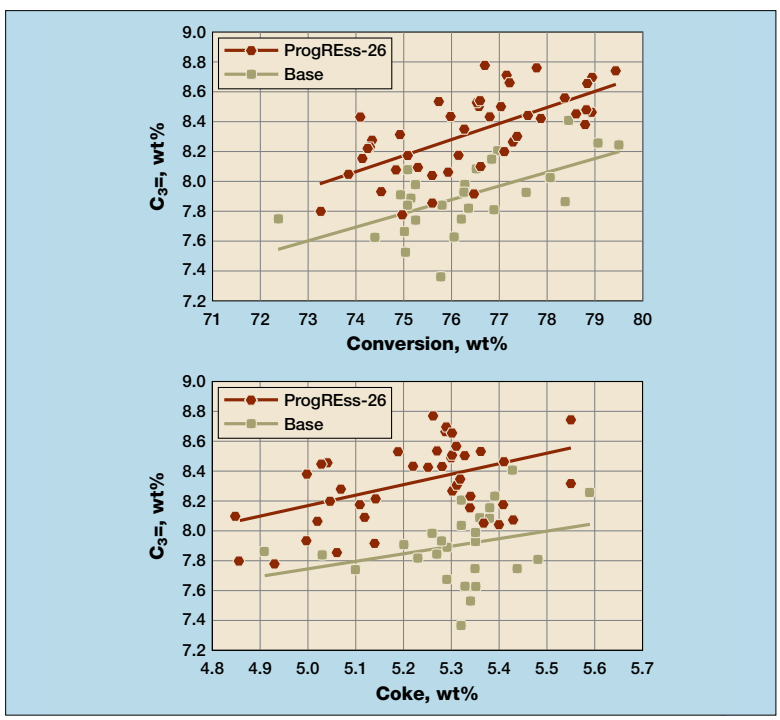

Figure 2 ProgREss-26 improves FCC unit propylene yields at (a) constant conversion and (b) constant coke

profitability of the unit and refinery, as part of CEPSA's selection of the catalyst technology in unit back-to-back trials:

1. Maximise propylene production
2. Maximise LPG at constant gasoline production
3. Minimise bottoms.

Gibraltar-San Roque refinery's main FCC unit operating constraints are typically:

1. Wet gas compressor (WGC) capacity
2. Regenerator temperature
3. Regenerator air blower capacity.

ProgREss FCC catalyst technology

The ProgREss FCC catalyst is part of Grace's propylene maximisation technology for both hydrotreated and non-hydrotreated feed applications. It was initially developed during the period of hyperinflation in rare earth prices, and is a member of a low or no rare earth FCC portfolio, the RepLaCeR catalysts. RepLaCeR catalysts deliver optimum performance at lower rare earth concentrations, minimising refinery exposure to hyperinflated prices. ProgREss FCC catalysts are an extension of the ProtAgon catalyst family and are manufactured using Grace's EnhanceR technology, the leading manufacturing platform in EMEA. Grace has an extensive catalyst and additive portfolio for increasing propylene yields.

ProgREss-26, designed with an optimised zeolite to matrix ratio and finely tuned rare earth content, provides:

- Low hydrogen transfer activity for enhanced olefins production

- High ZSM-5 activity to selectively crack gasoline range olefins into LPG olefins
- Best in class delta coke and dry gas, allowing the expansion of the FCC unit operating window within the unit operating constraints
- Premium bottoms upgrading with best bottoms to coke selectivity
- Targeted catalytic activity without any increase in catalyst additions.

To maximise propylene in an FCC unit, high ZSM-5 activity and stability are required in the circulating catalyst inventory. The activity of the ZSM-5 must be balanced with sufficient Y-zeolite based FCC technology, to boost LPG olefins production. The ProtAgon family of technologies delivers both of these attributes in a single particle system.

Catalyst retention is critical to the FCC unit's operation and Grace's ProgREss-26 catalyst technology provided considerably better attrition resistance compared to the alternative technology trialled. With improved physical properties, Grace helped Gibraltar-San Roque refinery to further minimise catalyst losses (reduce particulate emissions) and hence also improve the reliability of the expander operation.

Laboratory testing

Prior to the FCC catalyst trials, pilot plant testing in CEPSA's R&D laboratory was conducted to compare FCC catalyst performance for each supplier. The FCC catalysts were steam deactivated to mimic the Ecat properties in the commercial unit, and tested in the DCR circulating riser pilot plant. The

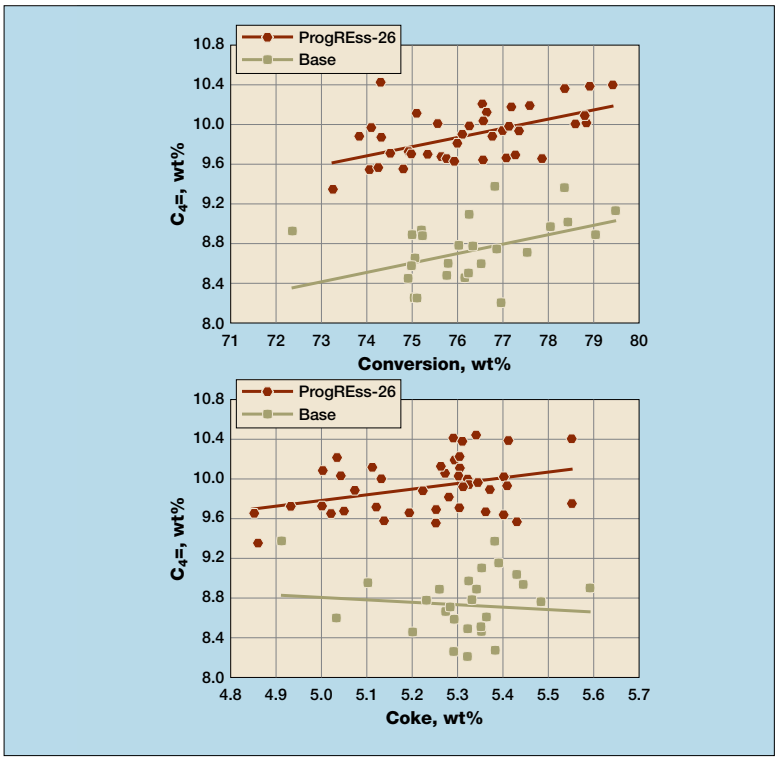

Figure 3 ProgREss-26 improves FCC unit butylenes yields at (a) constant conversion and (b) constant coke

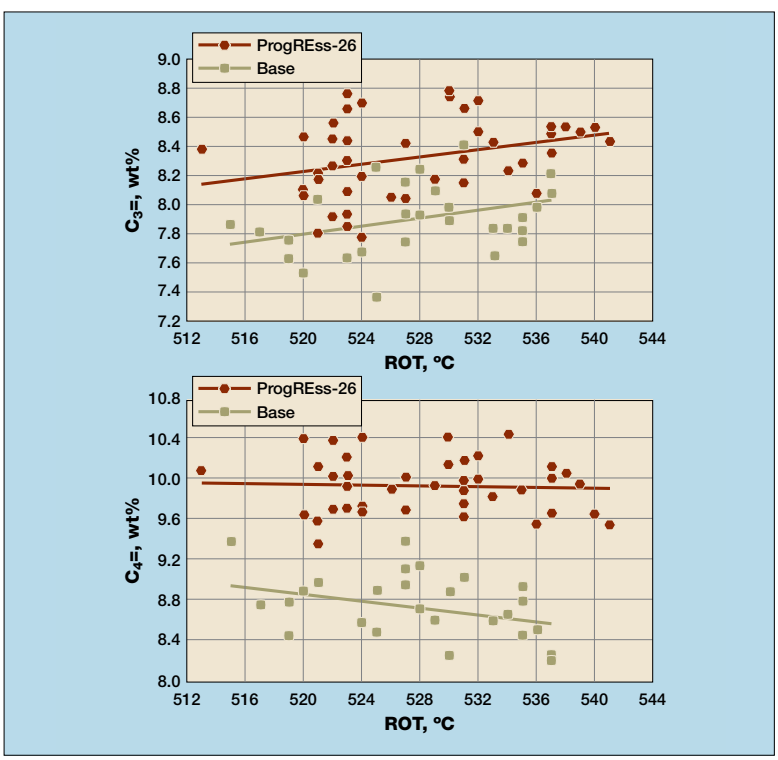

Figure 4 ProgREss-26 maximises FCC unit LPG olefins yields over a range of reactor severities (riser outlet temperature)

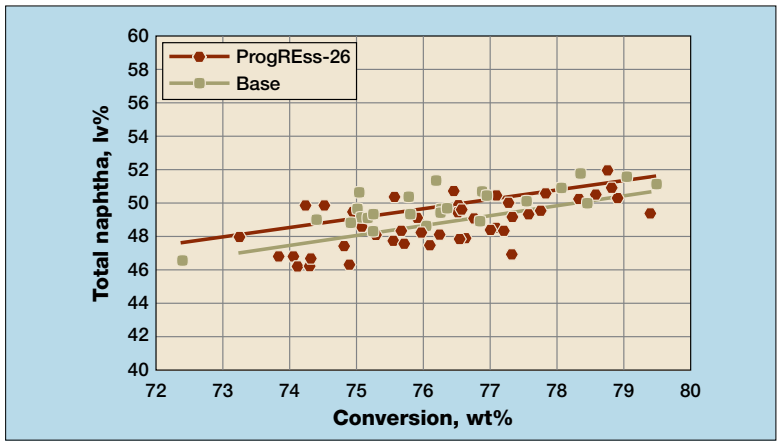

Figure 5 FCC naphtha yield was maintained with ProgREss-26

Grace's ProgREss-26 catalyst delivered improved performance in the commercial FCC unit

Performance	Base catalyst	ProgREss-26
Conversion, wt%	Base	+1.0
$C_3^=$, wt%	Base	+0.6
$C_4^=$, wt%	Base	+0.9
LPG, wt%	Base	+2.1
LPG olefins, vol%	Base	+2.2
Total naphtha, wt%	Base	-0.46
LCO, wt%	Base	+0.44
Bottoms, wt%	Base	-1.55
Coke, wt%	Base	-0.10
Unit profitability, M€/yr	Base	+ 4.0

Table 1

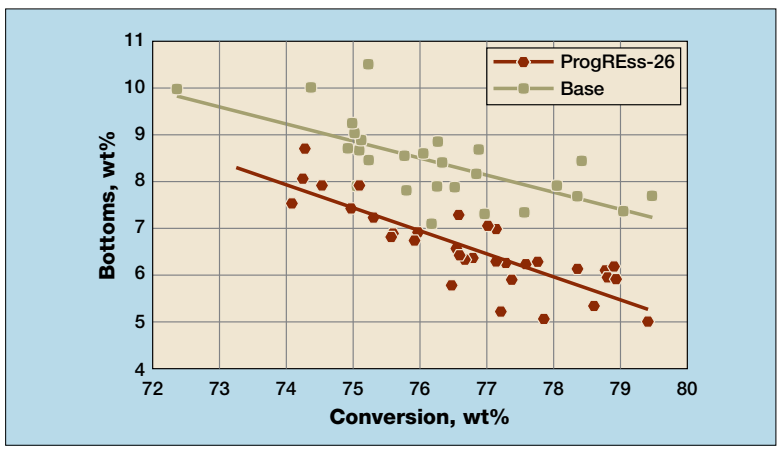

Figure 6 Superior bottoms upgrading was observed with ProgREss-26 catalyst

testing highlighted the improved performance of Grace's ProgREss-26 catalyst compared to the alternative catalyst technology trialled in terms of LPG olefins make, the primary objective of the unit for maximum FCC profitability (see **Figure 1**). Regarding bottoms upgrading capability, the improvements with ProgREss-26 are described in **Figure 6**, with commercial unit data.

FCC catalyst trial results

As shown in **Figures 2** and **3**, when comparing Grace's ProgREss-26 and the incumbent base Grace technology (ProgREss-518), propylene and butylenes yields were boosted significantly at both constant conversion and constant coke yield.

The improvement in LPG olefins make was exhibited over a broad range of operating severity and feedstock quality (see **Figure 4**). Significant gains in LPG olefins yields, both with propylene and butylenes, were obtained with ProgREss-26 with increasing riser outlet temperature (ROT). This is explained by the optimised, lower hydrogen transfer of the ProgREss-26 catalyst that results in enhanced selectivity and yields of gasoline range olefins, the precursors to LPG olefins.

An important objective for CEPSA's FCC unit was to maintain gasoline yields. In general, an increase in the ZSM-5 content in a catalyst formulation results in a notable decline in gasoline yield, due to the cracking of gasoline range olefins. However, ProgREss-26 catalyst demonstrated a superior activity to crack the heaviest feedstock fractions into gasoline, thereby off-setting the enhanced cracking of gasoline into LPG range products, and hence minimising gasoline loss (see **Figure 5**). The gasoline octane remained similar (RON) or slightly better (MON) with the reformulated ProgREss-26 as compared to the base catalyst.

The improved bottoms cracking demonstrated by ProgREss-26 catalyst in the commercial unit is shown in **Figure 6**.

Gas make

One of the major constraints of Gibraltrar-San Roque refinery is the volumetric flow rate of its wet gas compressor. As **Figure 7** shows, ProgREss-26

catalyst demonstrated very low gas make and the lowest hydrogen yield. The gas selectivity is due to the inclusion of premium metals trapping functionality and its tailored hydrogen transfer activity. Lower gas make allowed the refinery's operations team to widen the operating window compared to the alternative technologies and alternative catalyst. and other supplier. Improved selectivity also minimises the risk of losses in profitability arising from constrained operation during the warmer summer months, due to excessive dry gas make constraining the wet gas compressor. Industry benchmarking of Ecat hydrogen yields reveals that ProgREss-26 catalyst has the lowest hydrogen yield at a given metals level (see **Figure 11**).

Catalyst delta coke

ProgREss-26 includes tailored and enhanced metals trapping technology to yield very low delta coke. Improving delta coke enabled the FCC operations team at Gibraltar-San Roque refinery to expand the FCC unit operating window and to maximise LPG without breaching regenerator temperature constraints. The alternative technology trialled exhibited higher delta coke and poorer bottoms to coke selectivity (see **Figure 8**). As a result, regenerator temperature increased by as much as 25°C dense phase at similar propylene levels (see **Figure 9**). When compared to global benchmarks, the coke selectivity of ProgREss-26 as measured in Ecat ACE testing is considered "best in class" (see **Figure 12**).

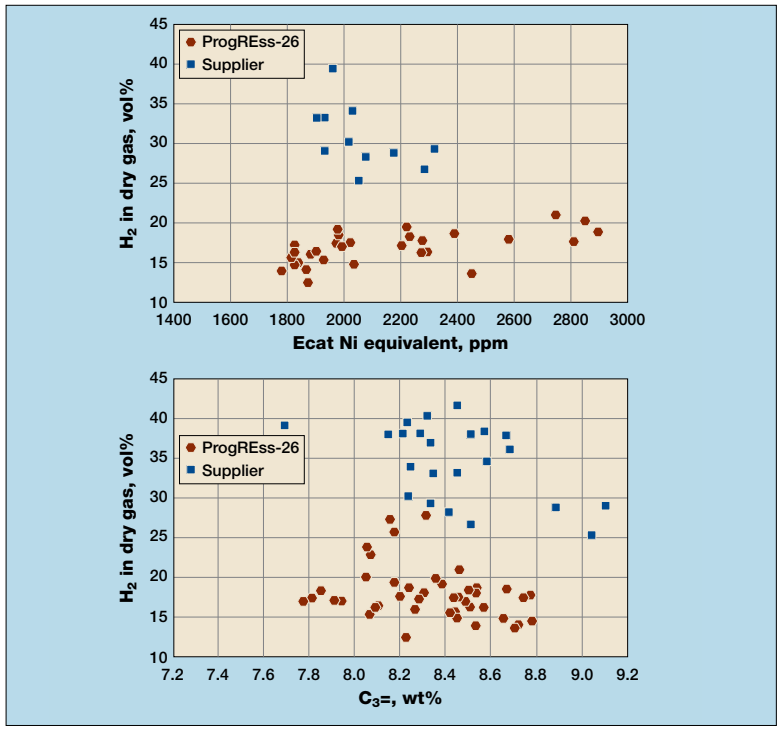

Figure 7 ProgREss-26 reduced hydrogen in dry gas, here as a function of (a) Ecat Ni and (b) propylene yield (commercial data)

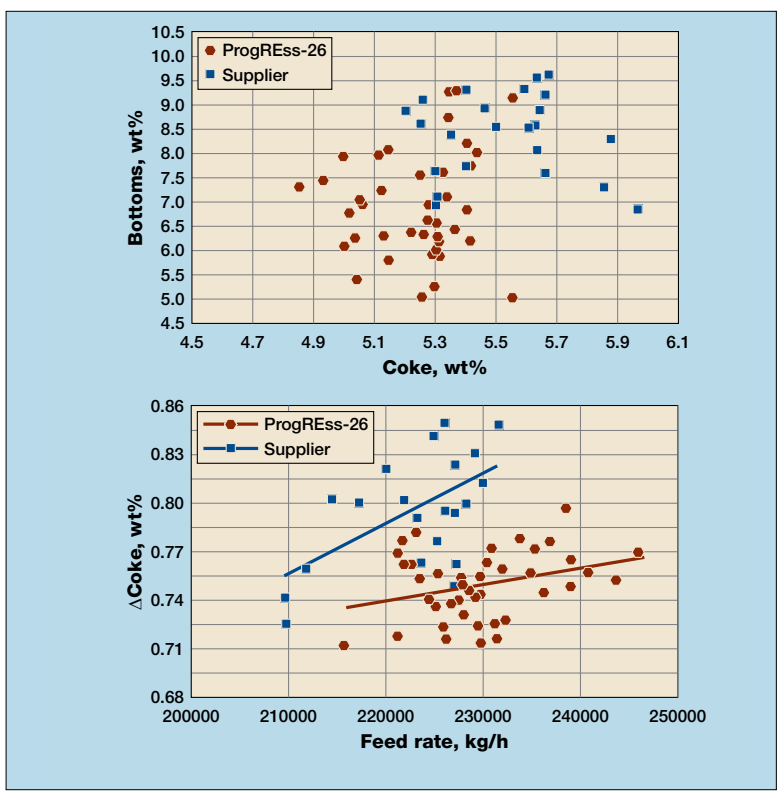

Figure 8 ProgREss-26 lowered bottoms yield and improved delta coke relative to the alternate supplier

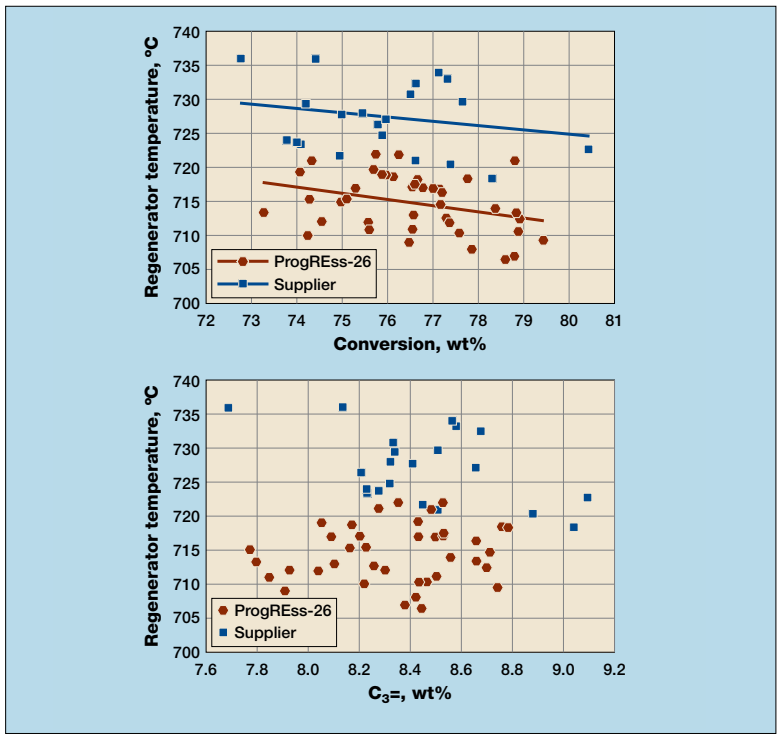

Figure 9 The coke selectivity advantage of ProgREss-26 lowered regenerator dense phase temperature

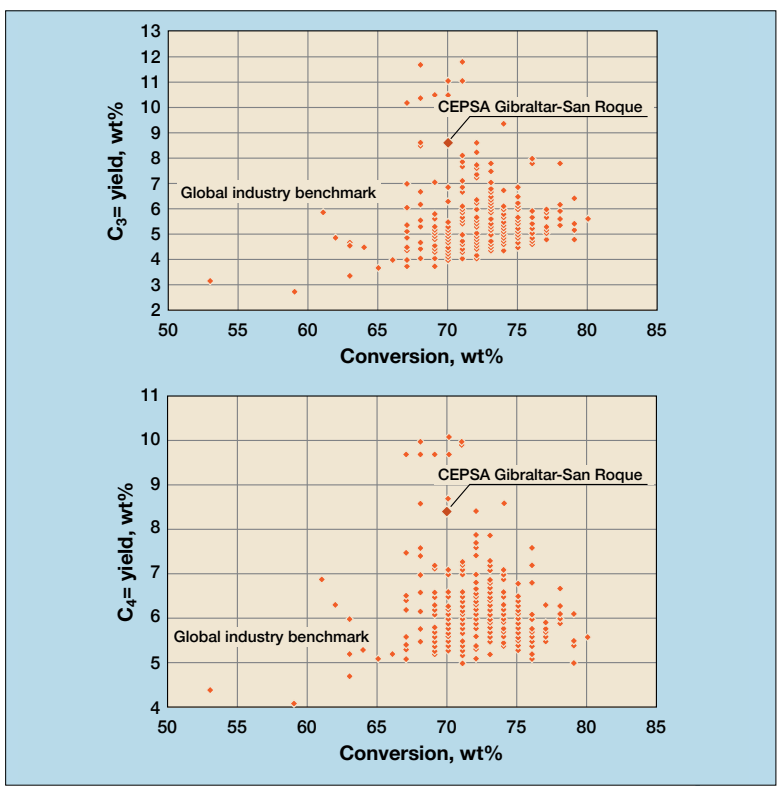

Figure 10 ProgREss-26 exhibits leading propylene and LPG selectivity (Ecat ACE global benchmark)

Benchmarking

A benchmarking study performed on a global basis (see **Figure 10**) allowed for a comparison of Grace's ProgREss-26 at Gibraltar-San Roque refinery with the FCC units worldwide that target maximum propylene production. Based on Grace's global Ecat benchmarking by ACE testing, the catalyst used at Gibraltar-San Roque refinery demonstrates amongst the highest yields of best in class propylene and LPG olefins in the industry.

The outstanding LPG olefins performance was achieved whilst maintaining industry leading coke and gas selectivity, as exhibited by Ecat ACE benchmarking (see **Figures 11** and **12**, respectively). The hydrogen yield and coke selectivity obtained with ProgREss-26 is among the best on a worldwide basis.

Conclusion

CEPSA conducted a rigorous FCC catalyst selection process that comprised lab testing at its R&D facility and back-to-back unit trials at Gibraltar-San Roque refinery. The goals of the selection process were to evaluate catalyst performance and increase overall FCC unit profitability. Maximising LPG olefins and improving bottoms upgrading at the lowest bottoms to coke were the main objectives of the catalyst selection. ProgREss-26 FCC catalyst, together with a dedicated technical support, enabled the refinery to maximise propylene and isobutylene yields, enhance total LPG production, maintain gasoline yield,

improve bottoms upgrading and expand the FCC unit operating window to allow the refinery to process heavier feed. The increased propylene yield supports CEPSA's activities in the petrochemicals area, while the increased C_4 olefins yield minimises the need to import feed for the ethyl tertiary butyl ether (ETBE) unit. The improved upgrading of low value components, otherwise destined for fuel oil production, improved the efficiency and profitability of the overall refinery operation. In addition, the reliability and sustainability of the FCC unit operation were improved with the best attrition resistance of ProgREss-26. Lower catalyst losses meant that the refinery's legislative constraints on environmental emissions were not exceeded (stack emissions). The economic and reliability benefits of moving to ProgREss-26 have been confirmed by the refinery.

With ProgREss-26, the refinery can choose to take advantage of a wider FCC unit operating window by increasing reaction severity and/or introducing lower cost feedstock such as atmospheric residue.

In this case study, Grace confirmed its capability and flexibility to reformulate and optimise FCC and add value to its refinery partners.

Grace's team would like to thank CEPSA's Gibraltar-San Roque refinery technical team and R&D group for their contributions and fruitful discussions.

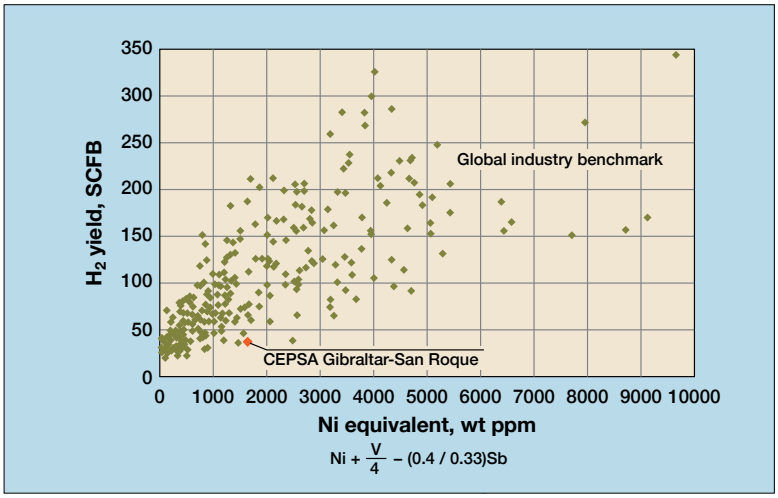

Figure 11 The H_2 yield of ProgREss-26 is amongst the lowest in the industry (Ecat ACE testing industry benchmark)

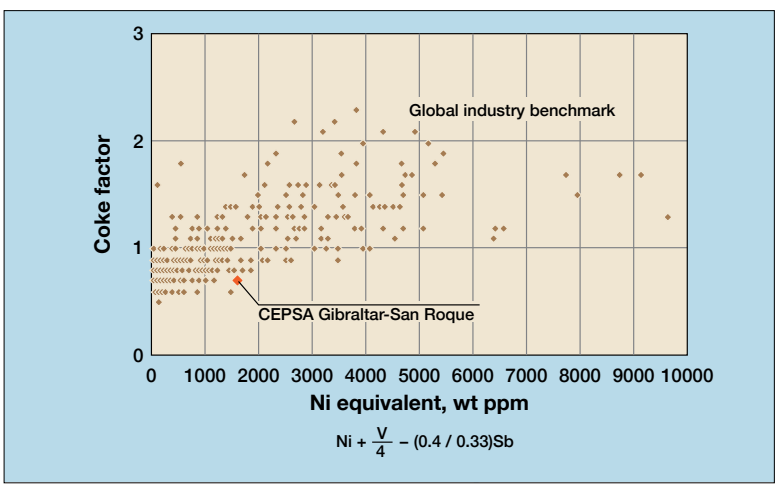

Figure 12 The coke selectivity of ProgREss-26 is amongst the best in the industry (lowest Ecat coke factor by ACE testing benchmark)

References

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