Rejuvenate profits and support sustainability with reused catalysts

Rejuvenated catalysts can optimise refinery margins for cat feed hydrotreating (CFH) applications

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Across the world, uneven refining margins despite a recovery in fuel demand, renewable fuel legislation, and strict environmental regulations on CO_2 emissions strongly impact the refining industry, placing the onus on refiners' need to optimise costs and maximise profitability. End-of-life reactor catalyst changeout is a significant and inevitable refining facility expenditure. It is also a good opportunity to make a better choice for the future by selecting the optimum catalyst to lower these costs and optimise profit. In today's business climate, there are more cost-effective and environmentally responsible solutions than simply replacing like-for-like.

Evonik's Excel rejuvenated cat feed hydrotreating (CFH) catalyst can help global refiners reduce operating costs and maximise profitability while remaining environmentally conscious with their hydrotreating applications, including FCC pretreating (via CFH).[1]

The performance of these rejuvenated catalysts was compared to their fresh counterparts in a parallel catalyst test trial conducted at hte GmbH under CFH operating conditions, using one of its high throughput units.

What are rejuvenated catalysts?

In a CFH unit, pretreating catalysts are typically replaced every one to three years, depending on unit severity. When the main bed catalyst is protected from contamination due mainly to nickel (Ni) and vanadium (V), then the CFH catalyst deactivation (over its lifetime) will mainly be due to coke deposition.

To recover or regenerate catalyst activity, coke is ex-situ removed by carefully burning it under mild oxidative conditions. This process is referred to as regeneration. During regeneration, the active sites over the catalyst may sinter or agglomerate due to exotherms, leading to a less than optimal catalyst performance. Restoration to the near-to-fresh activity of regenerated catalyst is achieved by rejuvenation.[1,2,3,4] Excel rejuvenation enables catalyst metal agglomerates to be redispersed on the regenerated catalyst, restoring its activity to fresh conditions by utilising a proprietary chemical treatment.

The optimum catalyst for the CFH unit depends on feed properties, operating conditions, and product targets. Evonik offers different Excel rejuvenated catalysts systems: (1) CoMo, (2) NiMo, and (3) NiCoMo providing high activity and stable performance during the life cycle. Other sought-after benefits include:

- 50% reduction in catalyst refill cost as compared to fresh catalyst
- Faster catalyst supply compared to long lead times for fresh catalysts
- Better environmental footprint as seen with Evonik's hydroprocessing solutions for decreasing CO_2 emissions and preserving natural resources while avoiding having to transport catalyst waste to landfills
- Similar-to-equivalent performance compared to fresh catalyst in terms of activity, product yield distribution and stability.

Using Excel rejuvenated catalysts reduces CO_2 emissions by approximately 6,000 kg CO_2 per ton of fresh catalyst replaced (i.e., compared with fresh catalyst production), thereby significantly contributing to the circular economy.

Over the past five years, Evonik has successfully supplied over 8,500 tons of Excel rejuvenated catalyst to refineries worldwide, resulting in a saving of 51,000 tons of CO_2, which would otherwise have been emitted into the atmosphere.

Independent testing

To demonstrate the robustness of Excel rejuvenated catalysts, an independent catalyst test and comparison was performed at hte GmbH – the high throughput experimentation company. In this study, different Excel rejuvenated catalyst configurations (NiMo, CoMo and NiCoMo) were compared with their parent fresh material.

These commercial catalysts are well proven for CFH applications where aromatics saturation is of key importance, as these compounds cannot be further cracked under FCC conditions. Sulphur and nitrogen removal are also important as these will ease the further steps required to upgrade the FCC gasoline and light cycle oil products up to current fuel specifications.

The test was performed in a classical X4500 trickle-bed high throughput test unit, a product line designed in-house to address the challenges of hydroprocessing applications at hte's laboratories in Heidelberg, Germany. This state-of-the-art reactor system has consistently proven to be an outstanding tool for comparing different catalyst systems (as full-bodied extrudates) head-to-head at the same time under identical and industrial conditions.

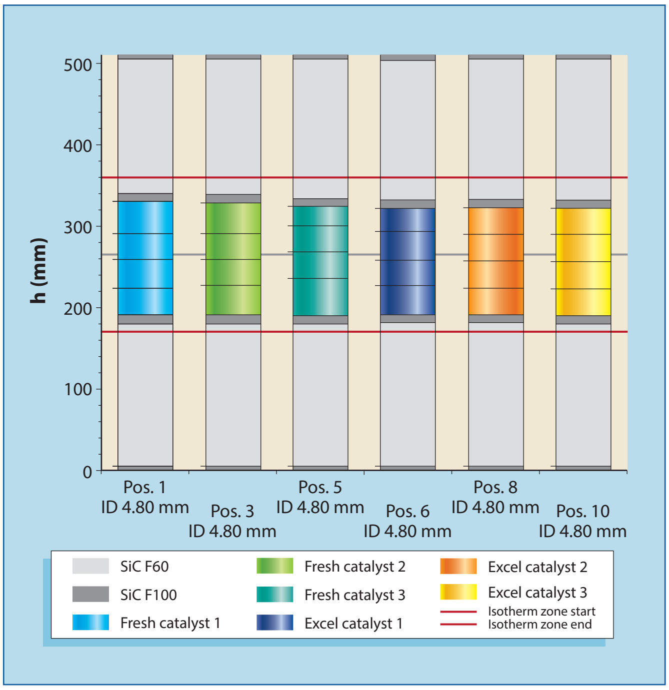

Figure 1 Loading configurations of fresh and Excel rejuvenated configurations

In addition, the test unit was equipped with individually heated reactors, allowing for the testing of different reactor temperatures at the same time.[5] The catalyst testing was performed at multiple temperatures with the same pressure, hydrogen-to-oil ratio, liquid hourly space velocity (LHSV), and hydrogen purity.

The performance of Excel rejuvenated catalysts has been compared with their parent fresh catalysts by loading Excel rejuvenated catalysts as standalone, as per the loadings shown in **Figure 1** and **Table 1**.

The catalyst volume employed was 2 mL per reactor. The catalysts were tested as full-bodied extrudates, which were sorted by length to select only extrudates with a length shorter than 4 mm. The inner diameter of the reactors was 4.8 mm.

The feed, a blend of vacuum gas oil (VGO) (90 wt%) and heavy coker gas oil (HCGO) (10 wt%) from a European refinery, was used to perform catalyst testing (see **Table 2**). The experiments were conducted at a hydrogen partial pressure of 80-120 barg, LHSV = 1.00 h^{-1} and H_2/Oil = 400 Nm^3/m^3 using three different temperatures (see **Table 3**).

After a dry-out step at 115°C for four hours, a common wetting and sulphiding procedure was carried out, where dimethyl disulphide (DMDS) was added (2.5 wt%) to straight-run gas oil for the catalyst activation.

The catalyst activation was followed by a line-out period and start-of-run (SOR) temperature conditions. The experiments were designed in such a way that sulphur effluents at different conditions ranged from 100 to 1000 ppmwt.

The feed for this test was carefully chosen in order to test the catalysts at very high concentrations of nitrogen and aromatics. For this reason, the gas-to-oil ratio (GTO) was kept at a relatively high level to ensure that no more than 30% of the hydrogen introduced would be consumed. This precaution was taken as a mitigation measure to alleviate the concerns of catalyst deactivation resulting from a hydrogen-starved regime.

Excel rejuvenation yielded an equivalent activity to its

Positions	Catalyst name	Catalyst state
Pos. 1	NiMo: Catalyst 1	100% Fresh
Pos. 3	NiCoMo: Catalyst 2	100% Fresh
Pos. 5	CoMo: Catalyst 3	100% Fresh
Pos. 6	NiMo: Catalyst 1	100% Excel Rejuvenated
Pos. 8	NiCoMo: Catalyst 2	100% Excel Rejuvenated
Pos. 10	CoMo: Catalyst 3	100% Excel Rejuvenated

Table 1 Loading configurations of fresh and Excel rejuvenated catalysts

Analysis	Feed to CFH unit (90% VGO/10% HCGO)
Density 15°C, kg/m³	930.5
Sulphur, wt%	2.0283
Nitrogen, ppmwt	2132.94
Bromine Number, gBr/100 g	11.8
Total aromatics, wt%	51.2
Mono-aromatics, wt%	26.2
Di-aromatics, wt%	11.1
Tri-aromatics, wt%	6.3
Tetra-aromatics, wt%	7.7
Poly-aromatics, wt%	25.1
Simulated distillation (SimDist)	
10%, °C	369
95%, °C	565
FBP, °C	614

Table 2 Feed to cat feed hydrotreating unit used to perform catalyst testing

Conditions	ppH_2 (barg)	LHSV (h^{-1})	H_2/Oil (Nm^3/m^3)	Temperature (°C)
3	80			360
4	80			370
5	80	1.00	400	375
7	120			360
8	120			370
9	120			375

Table 3 Operating conditions used to perform catalyst testing

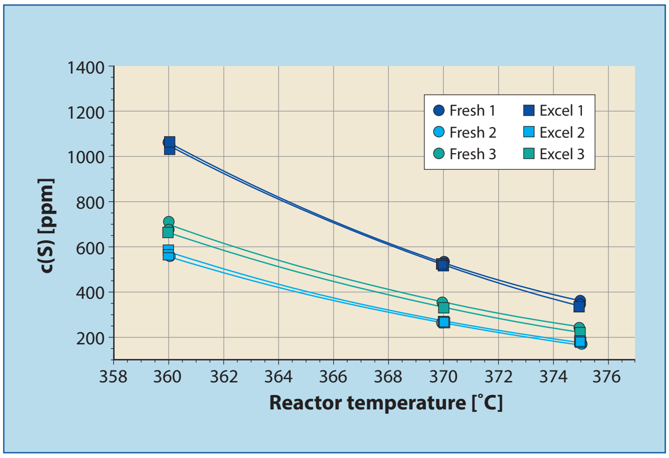

Figure 2 Product sulphur vs temperature for catalyst configurations tested at 80 barg

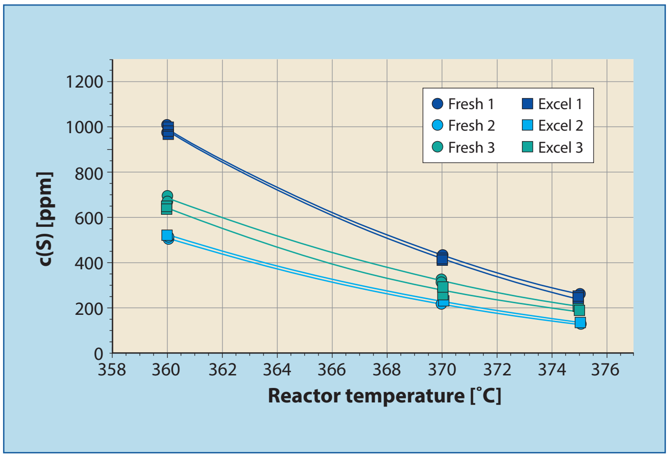

Figure 3 Product sulphur vs temperature for catalyst configurations tested at 120 barg

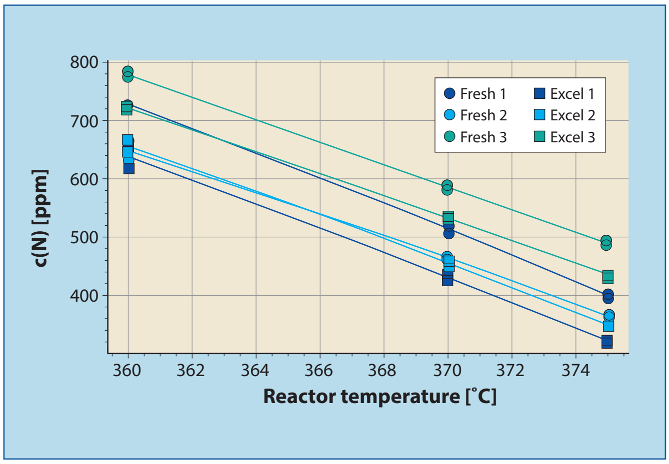

Figure 4 Product nitrogen vs temperature for catalyst configurations tested at 80 barg

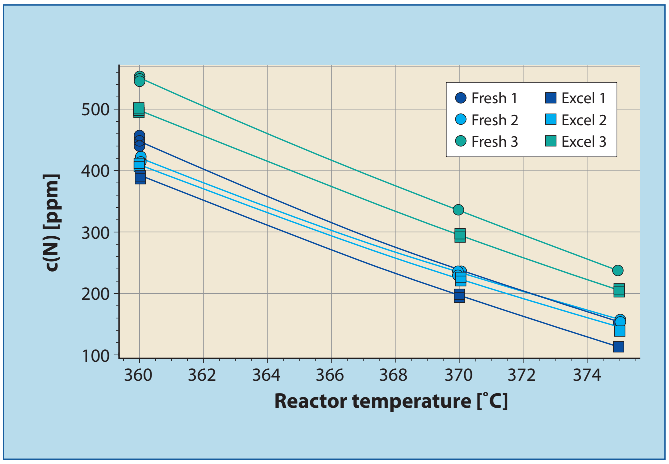

Figure 5 Product nitrogen vs temperature for catalyst configurations tested at 120 barg

fresh counterpart/parent. To detect activity differences of less than 10% in a laboratory test, every aspect of the test – from reactor loading, temperature control, and equal feed distribution between reactors to product sample preparation and analyses – needs to be carried out with utmost care to minimise all possible errors. One crucial factor requiring accuracy for comparing catalyst activities is to ensure a good mass balance throughout all the experiments being compared. In this case, mass balances for all catalysts compared were in the range of 99.5 ± 1%.

Results and discussion

The fresh and Excel rejuvenated catalysts were tested in parallel at various process conditions, focusing on the following parameters after the hydrotreating reaction: hydrodesulphurisation (HDS) activity, hydrodenitrogenation (HDN) activity, aromatic saturation and volume swell, hydrogen consumption, and C_5+ yield.

Hydrodesulphurisation (HDS) activity

Figures 2 and **3** show the CFH pilot plant testing and compare, side-by-side, the fresh HDS activities with its Excel rejuvenated state. The main outcomes were:

• Excel rejuvenated catalysts perform equivalent to their parent fresh catalyst for both pressures tested

• HDS activity has not been significantly impacted by the partial pressure of hydrogen for both CoMo and NiCoMo catalysts

• HDS activity has been significantly impacted by the increase in partial pressure of hydrogen for NiMo catalyst. The product sulphur was reduced by about 100 ppmwt when the ppH2 (inlet) increased from 80 to 120 barg

• Excel rejuvenated catalysts will allow low product sulphur levels to be maintained with high HDS compared to fresh in CFH applications to meet environmental regulations on gasoline, LCO sulphur content, and FCC unit sulphur oxides (SOx) emissions.

Hydrodenitrogenation (HDN) activity

Figures 4 and **5** show the CFH pilot plant testing and compare, side-by-side, the fresh HDN activities with their Excel rejuvenated state. The main outcomes were as follows:

• Excel rejuvenated catalysts perform equivalent or better compared to their parent fresh catalyst for both pressures tested in terms of HDN activity

• Excel rejuvenated NiMo (Catalyst 1) and CoMo (Catalyst 3) perform better than their parent fresh catalyst in terms of HDN activity for both pressures tested

• HDN activity has been significantly impacted by the increase in hydrogen partial pressure for all catalysts tested

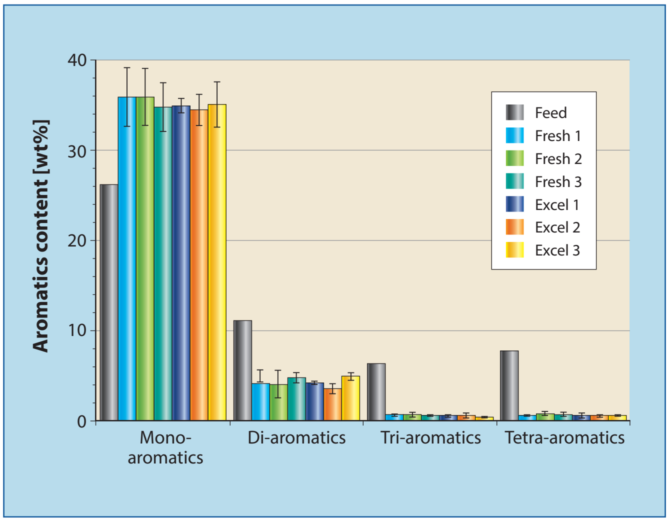

Figure 6 Aromatics content for catalyst configurations tested at 80 barg and 370°C

- Effect of H_2 partial pressure on HDN is more significant than HDS. It can be explained by the fact that hydrogenation of an N-containing ring occurs prior to C-N bond scission over conventional catalysts
- The HDN rate can be affected by the equilibrium of N-ring hydrogenation because N-ring hydrogenation occurs before nitrogen removal (hydrogenolysis). In marked contrast, HDS does not always require hydrogenation. HDS can proceed via two possible mechanisms: (1) ring hydrogenation followed by hydrogenolysis or (2) direct hydrogenolysis. That is the reason why HDN reactions have been enhanced when pressure increased from 80 to 120 barg
- Excel rejuvenated NiMo catalyst exhibited higher HDN activity compared to its fresh (and other fresh) or Excel rejuvenated CoMo/NiCoMo catalysts: 120 ppmwt nitrogen for Excel vs 160 ppmwt for fresh at 120 barg and 375°C
- The rejuvenated catalyst will protect FCC zeolite catalyst active sites from nitrogen to meet the refiner's FCC unit product yields, selectivity, and operations.

Hydrodearomatisation (HDA) activity

The aromatics content in **Figure 6** is represented for both the feed and the products specific to all the catalyst configurations tested at 370°C/80 barg (condition 4). Excel rejuvenated catalysts as standalone have exhibited equal performance in terms of aromatic saturation in comparison to their parent fresh, reaching about 35 wt% as mono aromatics for all catalyst configurations.

Aromatic compounds are not easily cracked in an FCC unit, and the limited amount of cracking achieved can produce a large amount of coke, deactivating the active site of the FCC zeolite catalyst. Excel rejuvenated catalysts exhibit a high degree of poly-nuclear aromatic (PNA) saturation to promote conversion in the FCC into more valuable products compared with fresh.

Figures 7 and **8** show volume swell efficiencies and compare, side-by-side, Excel and fresh catalyst at two different pressures. The term 'volume swell' refers to liquid volume increase when the product density and boiling range are lowered as a result of the hydrotreating process. This is induced by different reactions, such as HDS and HDN, but more importantly, the saturation of poly-aromatics and mono-aromatics.

Figures 7 and 8 quantify the volume swell by comparing the liquid product density with the feed density. Both Excel rejuvenated catalysts and fresh catalysts enable about 102.4% of volume swell to be achieved at 80 barg/375°C, whereas the volume swell enables 102.8% to be achieved at the same temperature but at a higher pressure (120 barg). This slightly higher volume swell can be explained by the fact that HDN and, more importantly, aromatic saturation (ASAT) are enhanced at a higher partial pressure of H_2.

In **Figures 9** and **10**, Excel rejuvenated catalyst exhibited a similar C_5+ yield compared to their parent fresh, namely

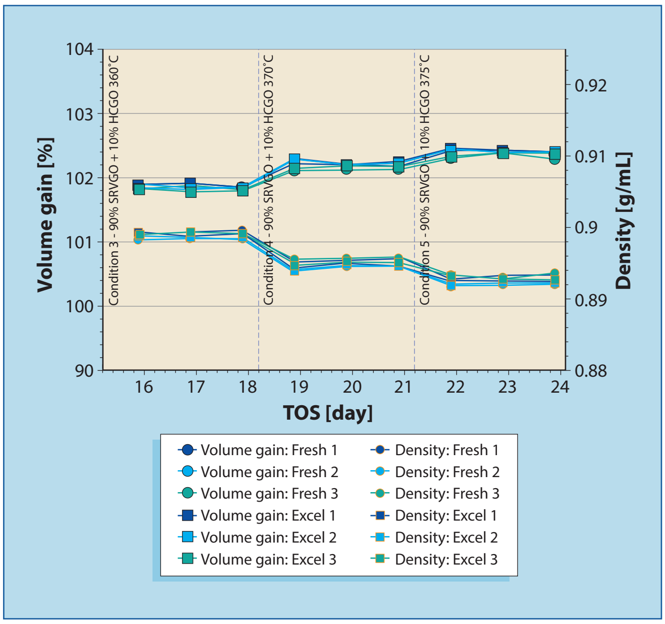

Figure 7 Volume gain for catalyst configurations tested at 80 barg

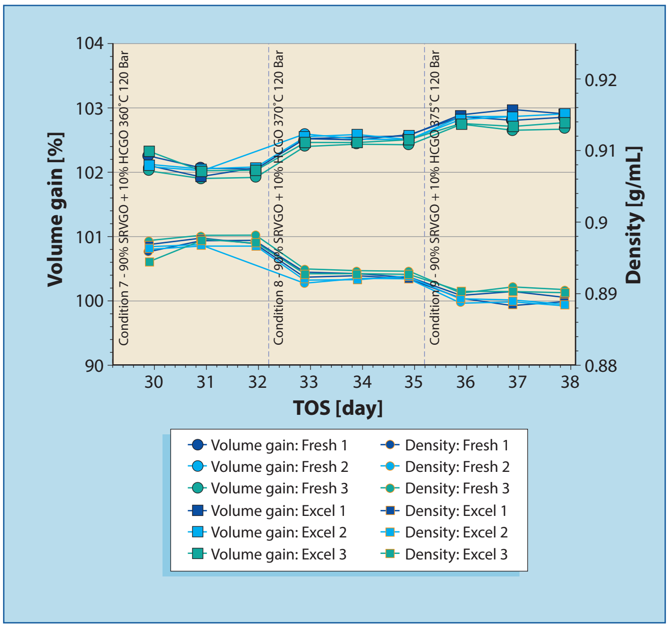

Figure 8 Volume gain for catalyst configurations tested at 120 barg

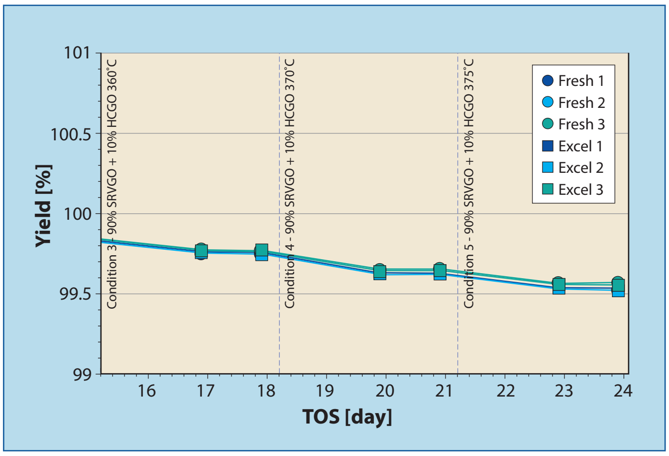

Figure 9 C_5+ yield for catalyst configurations tested at 80 barg

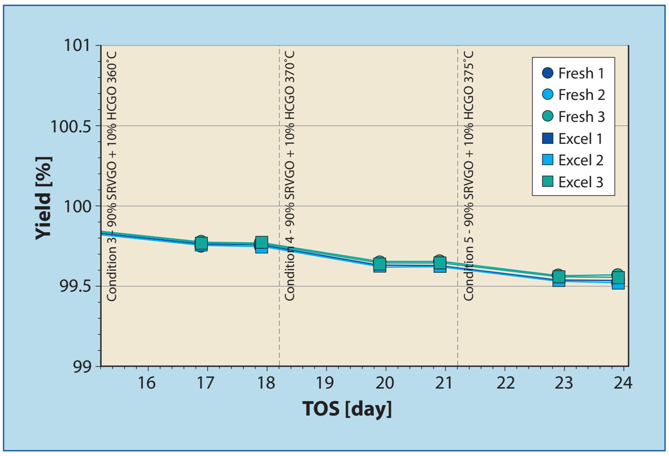

Figure 10 C_5+ yield for catalyst configurations tested at 120 barg

between 99.5% and 99.6% for both pressures tested at 375°C.

Differences in hydrogen consumption

Hydrogen consumption did not exhibit large differences when comparing the Excel rejuvenated material side-by-side against their fresh parent. The hydrogen consumption for both fresh and Excel rejuvenated did increase when the pressure increased from 80 to 120 barg: between 560-600 scf/bbl at 80 barg/375°C and 640-700 scf/bbl at 120 barg/375°C. This can be explained mainly by the higher ASAT and HDN activities for all catalyst configurations when there is a higher partial pressure of H_2.

Conclusions

Excel rejuvenated catalysts demonstrated equivalent hydrogenation activities (HDS, HDN, and HDA) compared to their parent fresh catalysts under high severity CFH conditions operating with 90% VGO and 10% HCGO (against a backdrop where typical CFH unit operating conditions involve H_2 partial pressure of 40-100 barg, LHSV at 0.5-2.0 h^{-1} and a H_2/oil ratio of 200-500 Nm^3/m^3).

This study strongly demonstrates that Excel rejuvenated catalysts can offer a valuable alternative to fresh catalysts by loading them as a full reactor or as stacked beds with fresh, thus effectively reducing the fill costs without impairing the performance of the unit.

Excel rejuvenated catalysts demonstrated similar activity and stability performances with respect to fresh catalyst for CFH commercial applications. Substantial cost savings during changeout operations may be achieved using Excel instead of fresh catalyst.

The hte high throughput reactor unit proves to be an invaluable tool for refiners. It allows the selection of the catalyst exhibiting the best performance for a given unit operation, hence minimising the risk involved in the purchase of a catalyst. Excel rejuvenated catalysts behaved similarly to their parent fresh catalysts in CFH applications, leading to:

- Maximal HDS activity to reduce the sulphur level in LCO and gasoline streams as well as meet FCC SOx emissions
- Maximal HDN activity to reduce the nitrogen level prior to the FCC unit to avoid inhibition of the FCC zeolite-based catalyst
- Maximal ASAT to avoid coking of the FCC catalyst
- Increase conversion of heavy feeds (VGO and HCGO) into more valuable products.

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