Rejuvenated catalysts optimise refinery margins in high severity ULSD applications

Rejuvenated catalysts compare well with fresh catalysts for performance in high pressure ULSD applications with added cost savings

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Across the world, slowed growth in fuel demand, weak profit margins, strict environmental regulations on CO_2 emissions, and legislation on renewable fuels are significantly impacting the refining industry. As a result, there is a greater need to optimise refining costs and maximise profitability.

The cost of replacing a catalyst at the end of its life is substantial, so it is important to choose an appropriate catalyst. Evonik's Excel rejuvenated hydrotreating catalyst for ultra-low sulphur diesel (ULSD) applications can help refiners reduce operating costs and maximise profitability while remaining environmentally conscious with their hydrotreating applications.[1] In this article, we compare the performance of this catalyst with its fresh counterpart in a parallel test at hte.

What are rejuvenated catalysts?

In a diesel hydrotreatment reactor (ULSD application), catalysts are typically replaced every two to four years, depending on the severity of the unit. ULSD catalysts deactivate mainly due to coke deposition over their lifetime. To recover the activity of the catalyst, coke is removed by carefully burning it under mild oxidative conditions. Referred to as regeneration, the active sites over the catalyst may sinter or agglomerate due to exotherms during this process. Rejuvenation allows for the selective removal of metal contaminant deposits, restoring the spent catalyst's activity to near fresh.[1-2] Excel rejuvenation enables the redispersion of agglomerates on the regenerated catalyst to restore its activity to fresh by utilising a proprietary chemical treatment.

Evonik's hydroprocessing solutions can achieve the following benefits:

- Reduction of the catalyst refill cost by about 50% compared to fresh catalyst
- Faster catalyst supply compared to long lead times for fresh catalyst
- Better environmental footprint, since these hydroprocessing solutions decrease CO_2 emissions, preserve natural resources, and avoid catalyst waste being sent to landfill
- Similar performance compared to fresh catalyst in terms of activity and, more importantly, in terms of stability

Using Excel rejuvenated catalysts, compared with fresh catalyst production, CO_2 emissions are reduced by approximately 6000kg CO_2 per ton of fresh catalyst replaced, thereby significantly contributing to the circular economy. Over the last five years, Evonik has successfully supplied more than 8000 tons of Excel rejuvenated catalyst to refineries worldwide, resulting in 48 000 tons of CO_2 not being emitted to the atmosphere.

To demonstrate the robustness of these rejuvenated catalysts, independent catalyst testing and comparison was performed at hte, the high throughput experimentation company. In this study, different Excel rejuvenated NiMo catalyst configurations were compared with their parent fresh material. The commercial NiMo catalyst is a well-proven, high activity catalyst for producing ULSD at moderate to high pressure when sufficient hydrogen is available to maximise its hydrogenation activity. It is designed to maximise nitrogen and sulphur removal with increased hydrogenation for polyaromatic conversion and volume gain. In addition, the same Excel rejuvenated NiMo catalyst was loaded as a standalone in a commercial ULSD unit. This article also presents commercial data comparing Excel rejuvenated NiMo with a fresh alternative NiMo catalyst to illustrate the stability of the Excel catalysts.

Experimental

The test was performed in an X4500 trickle-bed high throughput test unit at hte's laboratories in Heidelberg. This state-of-the-art reactor system has consistently proven to be an excellent tool for comparing different catalyst systems head-to-head under identical conditions. In addition, the test unit was equipped with individually heated reactors, allowing for the simultaneous testing of different reactor temperatures.[3] Catalyst testing was performed at multiple temperatures while having the same pressure, hydrogen-to-oil ratio, liquid hourly space velocity (LHSV), and hydrogen purity.

The performance of Excel rejuvenated NiMo was compared with its parent fresh catalyst by loading the rejuvenated NiMo catalyst as a standalone or as stacked beds, with either fresh NiMo or Excel rejuvenated CoMo catalyst, as per the loadings shown in **Figure 1** and **Table 1**.

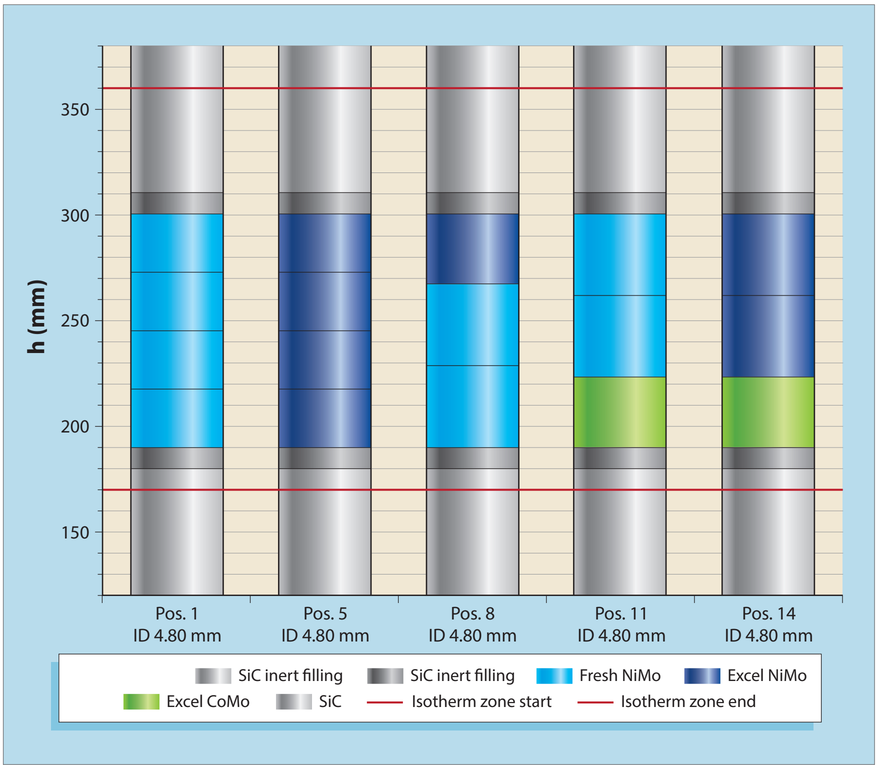

Figure 1 Loading configurations of fresh and rejuvenated catalysts

Loading configurations of fresh and rejuvenated catalysts		
Positions	**Catalyst type**	**Loading configuration**
Pos. 1	Fresh NiMo	100%
Pos. 5	Excel NiMo	100%
Pos. 8	Excel NiMo/Fresh NiMo	30%/70%
Pos. 11	Fresh NiMo/Excel CoMo	70%/30%
Pos. 14	Excel NiMo/Excel CoMo	70%/30%

Table 1

The catalyst volume employed was 2 mL per reactor, with catalyst stacks as small as 0.6 mL used for reactors loaded with 30% rejuvenated and 70% fresh catalyst. The catalysts were tested as full-bodied extrudates, which were sorted by length to select only those with a length shorter than 4mm. The inner diameter of the reactors was 4.8mm.

The feed, a blend of SRGO (50 wt%), LCO (25 wt%), and CGO (25 wt%) from a European refinery diesel hydrotreater, was used to carry out catalyst testing (see **Table 2**). The experiments were conducted at a hydrogen partial pressure of 75 barg, LHSV = 1.00 h^{-1} and H_2/oil = 609 Nm^3/m^3 using four different temperatures (see **Table 3**).

After a dry-out step at 115°C for four hours, a common wetting and sulphiding procedure was implemented, where dimethyl disulphide (DMDS) was added (2.5 wt%) to straight-run gasoil for catalyst activation. This 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 10 to 50 ppmwt. The feed for this test was chosen to test the catalysts with 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 no more than 30% of the hydrogen introduced was consumed. This precaution was taken to mitigate the concerns of catalyst deactivation due to operating in a hydrogen starved regime.

Operating conditions used to perform catalyst testing				
Conditions	**pH_2, barg**	**LHSV, h^{-1}**	**H_2/oil, Nm^3/m^3**	**Temperature, °C**
6	75.0	1.00	609	358
7				361
8				363
9				365

Table 3

Feed to diesel hydrotreater used to perform catalyst testing	
Analysis	**Feed to diesel hydrotreater (50% SRGO/50% cracked feeds)**
Density 15°C, kg/m³	903.5
Sulphur, wt%	1.2587
Nitrogen, ppmwt	965.9
Bromine Number, gBr/100 g	6.4
Total aromatics, wt%	47.7
Mono-aromatics, wt%	19.1
Di-aromatics, wt%	23.9
Tri-aromatics, wt%	4.7
Poly-aromatics, wt%	28.6
Simulated distillation (SimDist)	
10%, °C	237
95%, °C	417
FBP, °C	454

Table 2

Excel rejuvenation enables the recovery of equivalent activity to fresh. To detect activity differences of less than 10% in a laboratory test, every aspect of the test – from reactor loading, temperature control, equal feed distribution between reactors to product sample preparation and analyses – has to be carried out with utmost care to minimise all possible errors. For accuracy, it is crucial when comparing catalyst activities to have a good mass balance throughout the experiments. In this case, mass balances for all catalysts compared were in the range of 99.5 ± 1%.

Results and discussion

The fresh and rejuvenated catalysts were tested in parallel at various process conditions while focusing on the parameters below after the hydrotreating reaction:

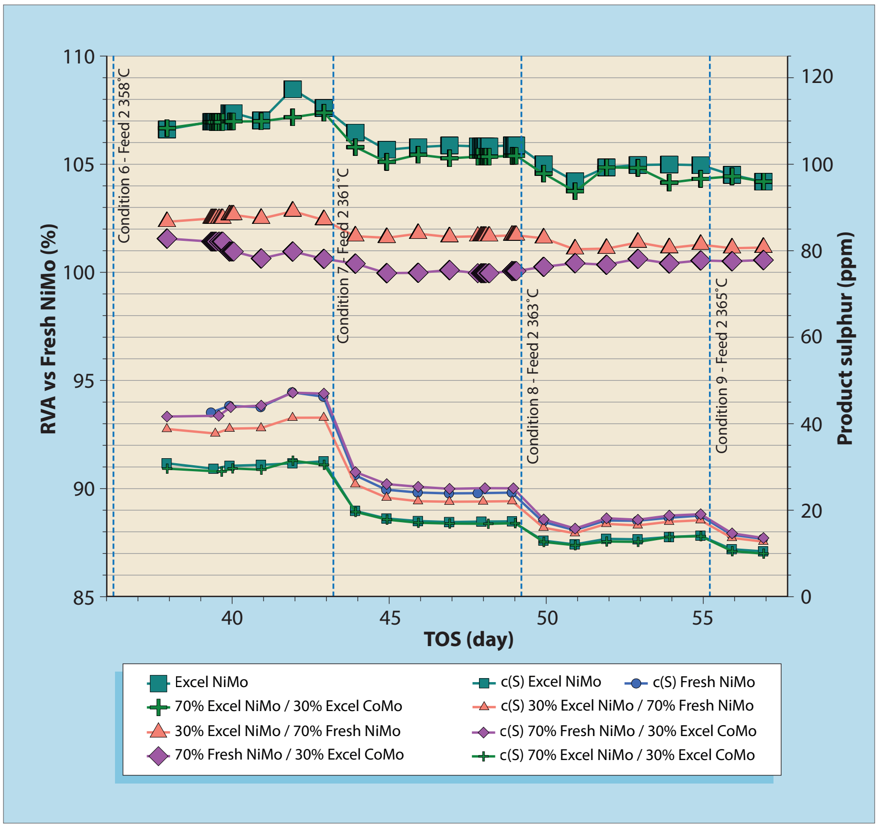

Figure 2 HDS-RVA of Excel rejuvenated configurations vs fresh NiMo catalyst activity

- Hydrodesulphurisation (HDS) activity
- Hydrodenitrogenation (HDN) activity
- Aromatic saturation and volume swell
- Hydrogen consumption
- C_5+ yield

Hydrodesulphurisation activity

Figure 2 shows ULSD pilot plant testing and compares the fresh hydrodesulphurisation (HDS) activity with its Excel or stacked bed configurations. We can observe the Excel rejuvenated catalyst's enhanced behaviour as a standalone or stacked bed configuration compared to its parent fresh. This results in a HDS relative volumetric activity (RVA) between 100% and 104% for all the rejuvenated configurations compared to fresh, while achieving the 10 ppmwt product sulphur range.

Hydrodenitrogenation activity

Figure 3 shows ULSD pilot plant testing and compares the fresh hydrodenitrogenation (HDN) activity with its Excel or stacked bed configurations. We can observe that a full load of rejuvenated catalyst or combined with fresh catalyst in a stacked bed configuration (30% Excel NiMo and 70% fresh catalyst) exhibited an equally high activity as a full load of fresh catalyst. We find HDN-RVA between 100% and 105% for the 10 ppmwt product sulphur range compared to fresh. Using some Excel rejuvenated CoMo catalyst (30%) at the bottom of the loading with fresh or Excel NiMo catalyst at the top, both stacked configurations show slightly lower HDN activity between 90% and 94% vs fresh while reaching the 10 ppmwt product sulphur range. This is expected since NiMo has higher HDN and aromatic saturation versus CoMo in high-pressure applications, especially when processing cracked feedstocks with high levels of nitrogen and aromatics.

Hydrodearomatisation activity

In **Figure 4**, the aromatics content is represented for the feed and products specific to all the catalyst configurations tested at 358°C (condition 6), whereas aromatics for feed and products at 365°C (condition 9) are represented in **Figure 5**. In **Figure 5**, condition 9 allows for the highest volume swell, resulting in higher aromatic saturation than condition 6. This can be explained by the higher reactor temperature used, namely 365°C, reaching the

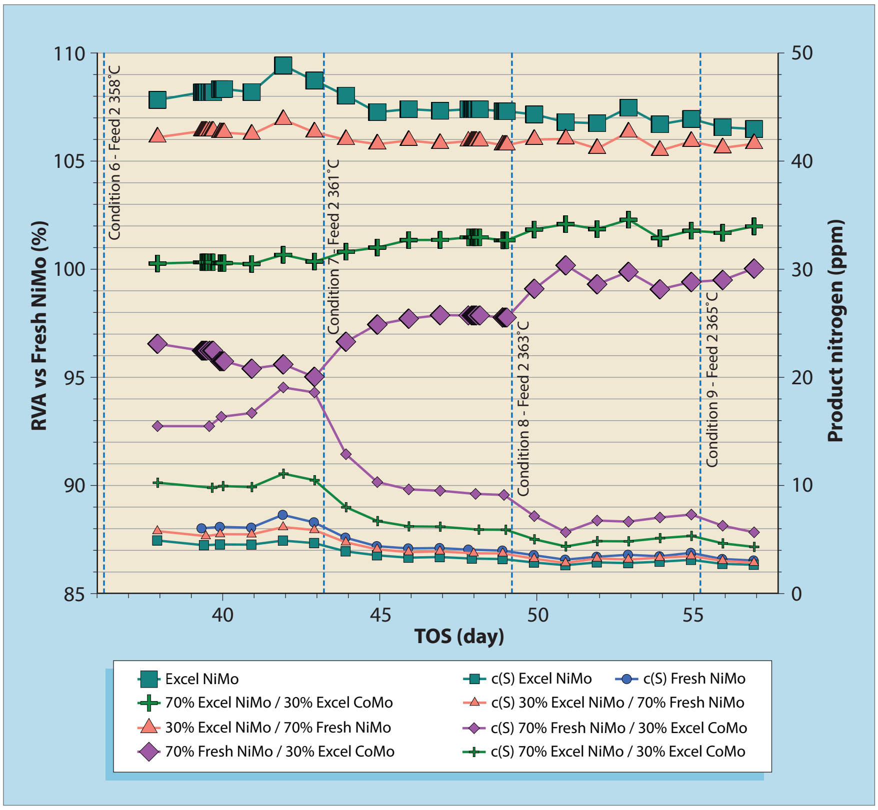

Figure 3 HDN-RVA of Excel rejuvenated configurations vs fresh NiMo catalyst activity

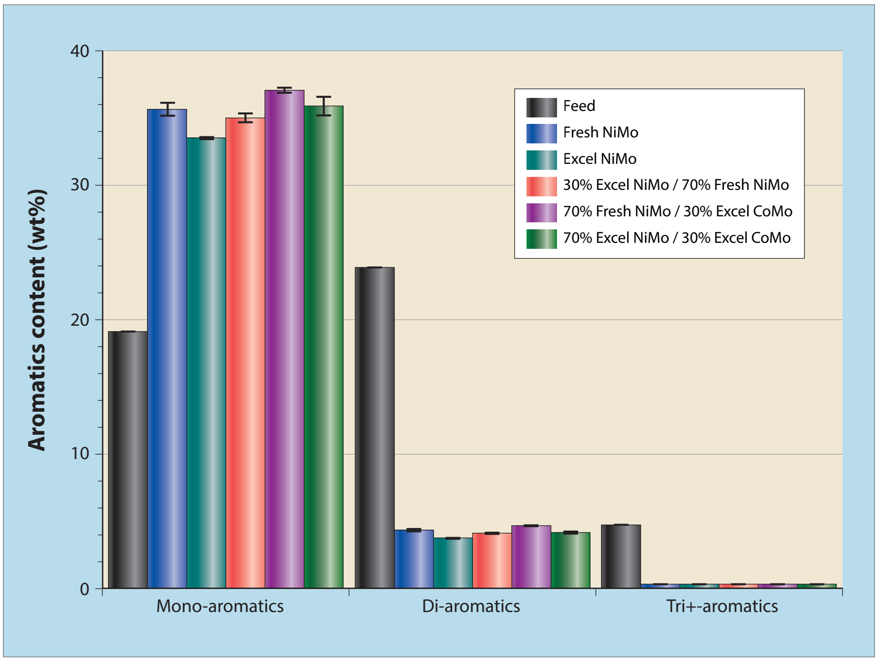

Figure 4 Aromatics content in feed and products for condition 6

10 ppmwt product sulphur range. For condition 9, mono-aromatics are saturated the most, resulting in more volume swell and lower residual content of mono-aromatics. Excel rejuvenated catalyst as a standalone has even showed enhanced performance in terms of aromatic saturation in comparison with its parent fresh, since it exhibited 30 wt% as mono-aromatics compared to 31.9 wt%. It can be noticed that the stacked bed versions loading with Excel NiMo and fresh catalysts exhibited similar mono-aromatics content compared to fresh as a standalone and, therefore, a similar volume swell. Both stacked bed Excel CoMo versions loaded with either Excel NiMo or fresh resulted in slightly lower mono-aromatics content. This can be explained by the fact that CoMo catalysts provided lower HDN and aromatic saturation compared to NiMo catalysts.

Figure 6 shows volume swell efficiencies and compares Excel or stacked configurations to fresh catalyst. Excel rejuvenated catalyst as a standalone is able to achieve 104.9% of volume swell compared to 104.6% for its fresh while reaching the 10 ppmwt product sulphur range. The stacked bed configuration loaded with 70% fresh NiMo and 30% Excel CoMo exhibits the lower volume swell, namely 104.1% for the 10 ppmwt product sulphur range. This can be easily explained by the fact that CoMo catalysts are typically less active for HDN and aromatic saturation than NiMo catalysts.

The term volume swell refers to the increase of liquid volume when the product density and boiling range are lowered by hydrotreating. This is induced by different reactions, such as HDS and HDN, but, more importantly, the saturation of poly-aromatics and mono-aromatics. In **Figure 6**, the volume swell has been quantified by comparing the liquid product density with the feed density. As per **Figure 7**, Excel rejuvenated catalyst and its stacked options exhibited a similar C_5+ yield compared to fresh for the 10 ppmwt product sulphur range.

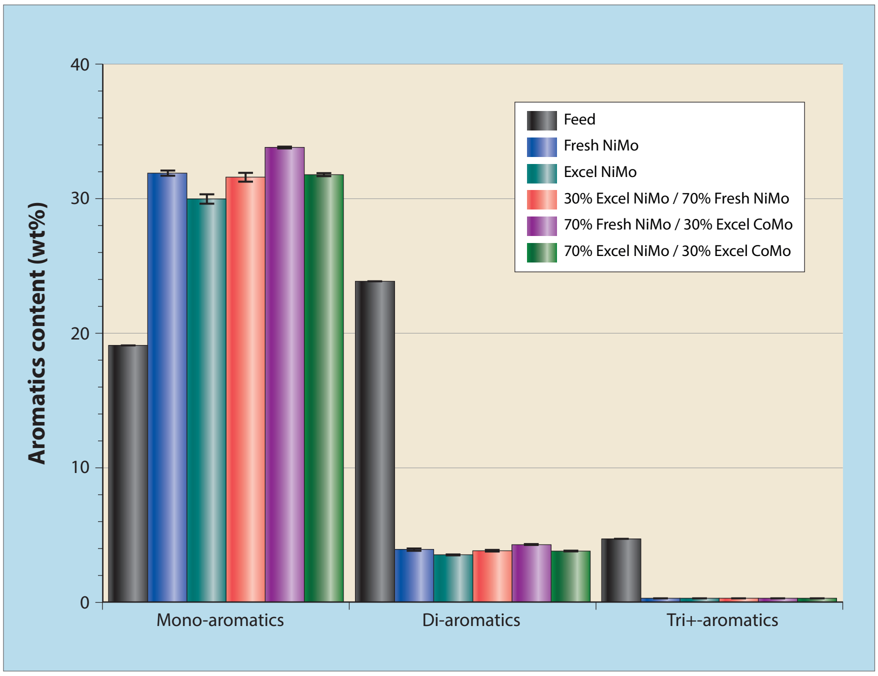

Figure 5 Aromatics content in feed and products for condition 9

Hydrogen consumption

Figure 8 shows hydrogen consumption and compares Excel or stacked configurations with fresh. Excel rejuvenated NiMo as a standalone exhibited better hydrogenation activities (HDS, HDN, and HDA activities) than its parent fresh, leading to a slightly higher hydrogen consumption. Excel rejuvenated NiMo catalyst as a standalone achieved about 1000 scf/bbl (or 178 Nm^3/m^3), whereas its parent fresh consumed about 900 scf/bbl (or 160 Nm^3/m^3), corresponding to an increase of 10.1% in terms of hydrogen consumption. Experience has shown that stacked beds containing both CoMo and NiMo catalysts can be designed to provide high HDS performance while minimising hydrogen consumption. For instance, the stacked bed configuration, including 70% rejuvenated NiMo and 30% rejuvenated CoMo, is able to reduce hydrogen consumption by 50 scf/bbl (or 9 Nm^3/m^3) while maintaining equal product sulphur concentration compared with 100% rejuvenated catalyst.

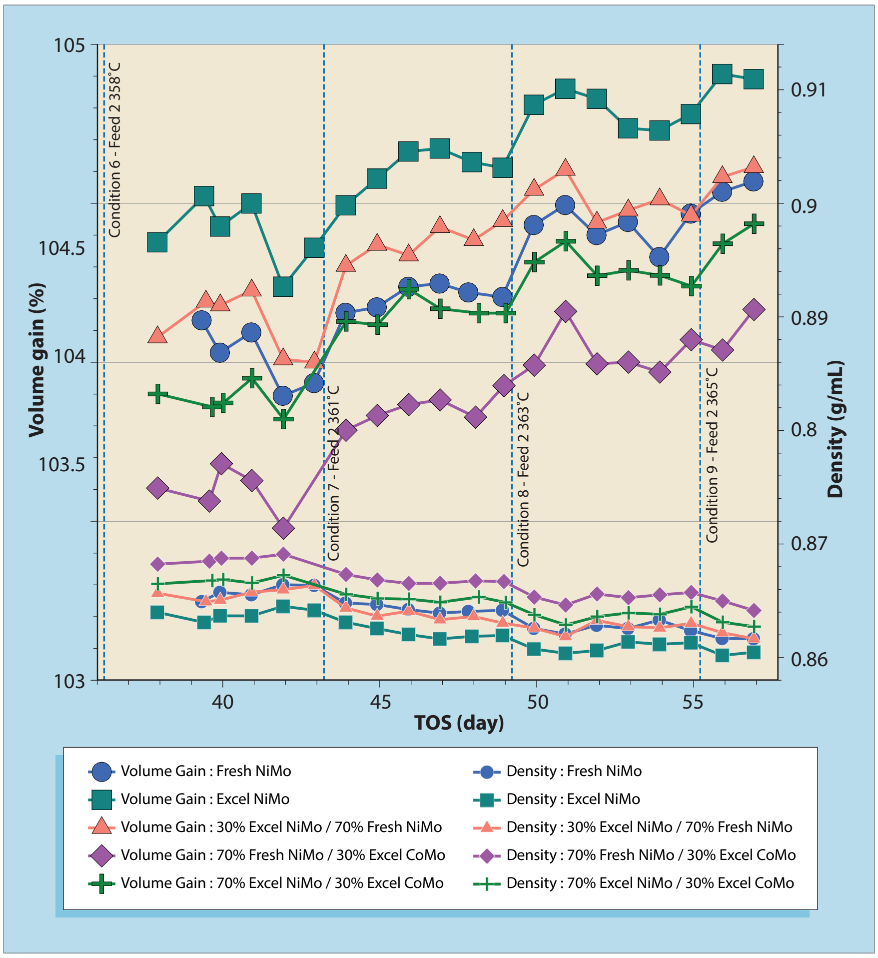

Figure 6 Volume swell for all catalyst configurations

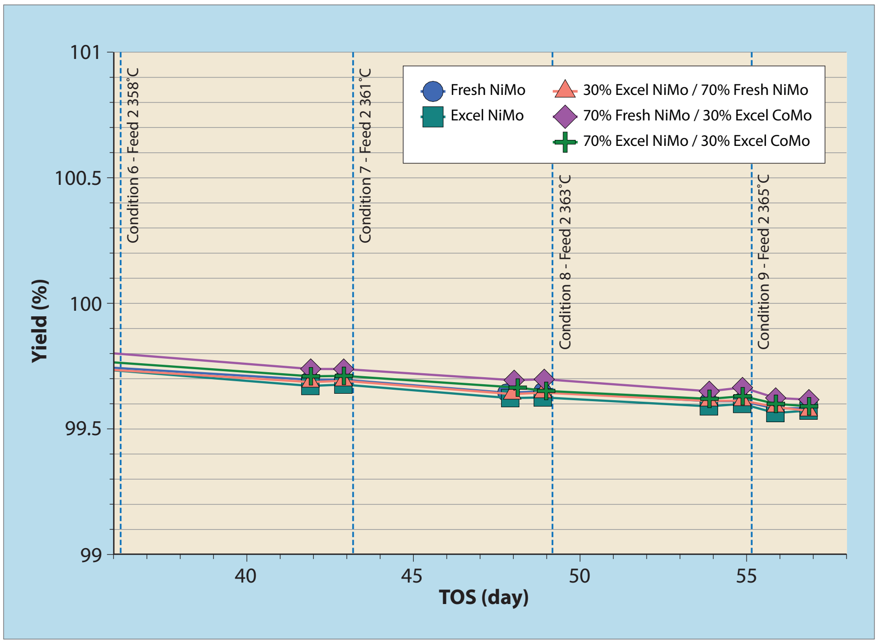

Figure 7 C_5+ yield for all catalyst configurations

Example of a commercial run

Evonik provided the same Excel rejuvenated NiMo catalyst to help the refinery extend its hydroprocessing unit cycle until the next turnaround.[4] The catalyst was proposed to maximise HDS/HDN activities and poly-aromatics hydrogenation. The feed and operating conditions were carefully evaluated to optimise catalyst system design and simultaneously meet multiple unit objectives. Throughout the technical evaluation, there was a commitment to ensure high catalyst quality to maximise performance and reliability. The European refiner operated the DHT unit in two modes:

1 ULSD mode by processing a blend of light gasoil (75 wt%), heavy gasoil (3 wt%), vacuum gasoil (2 wt%), and cracked gasoil (20 wt%).

2 Heating oil mode by processing a blend of light gasoil (20 wt%), heavy gasoil (45 wt%), vacuum gasoil (15 wt%), and cracked gasoil (20 wt%).

As a result, the unit was able to process a blend of light and vacuum gasoil with coker distillate to produce two grades of final product. The unit achieved the projected cycle length while reducing catalyst expense. A summary of the feed and operating conditions is shown in **Table 4**.

The rejuvenated NiMo catalyst provided high HDN activity combined with deep HDS levels to handle the high nitrogen concentration in the feed blends. The primary objectives of the hydrotreater were:

- To produce ULSD, targeting a product sulphur of 11 ppmw
- To produce heating oil, targeting a product sulphur of 55 ppmw

The rejuvenated catalyst gave this European refiner the expected performance while enabling substantial cost savings versus loading fresh catalyst. This unit successfully produced on-specification product for both modes throughout the cycle, with Excel NiMo on par with the previous cycle loaded with fresh alternative NiMo catalyst. The normalised weighed average bed temperature (WABT) for both cycles is shown in **Figure 9**.

Conclusions

Excel rejuvenated NiMo catalyst, as a standalone, demonstrated slightly better hydrogenation activities (HDS, HDN, and HDA) than its parent fresh under high severity ULSD conditions operating with 50% of cracked feed. Rejuvenated catalyst can offer a good alternative to fresh catalyst by loading it as a full reactor or as stacked beds with fresh and reducing the fill cost without affecting the unit's performance. Rejuvenated catalyst demonstrated similar activity and stability performances with respect to fresh catalyst for ULSD commercial applications. Substantial cost savings are achieved with the use of rejuvenated compared to loading fresh catalyst. The high throughput reactor system proved to be an excellent tool for a refiner to ensure the catalyst will exhibit the best performance for meeting their unit objectives prior to buying it.

References

1 *Handbook of Spent Hydroprocessing Catalysts* 2010, Ch 7, 191, Elsevier ISBN 978-0-444-53556-6.

2 Optimising refinery margins with rejuvenated catalysts, *PTQ*, Q4 2021, 47-49.

3 I-T Trotus, J-C Adelbrecht, F Huber, N Pongboot, T Upienpong, *PTQ*, Q4 2019, 79-83.

4 Rejuvenated catalyst cuts changeout costs, *PTQ*, Q4 2019, 114-115.

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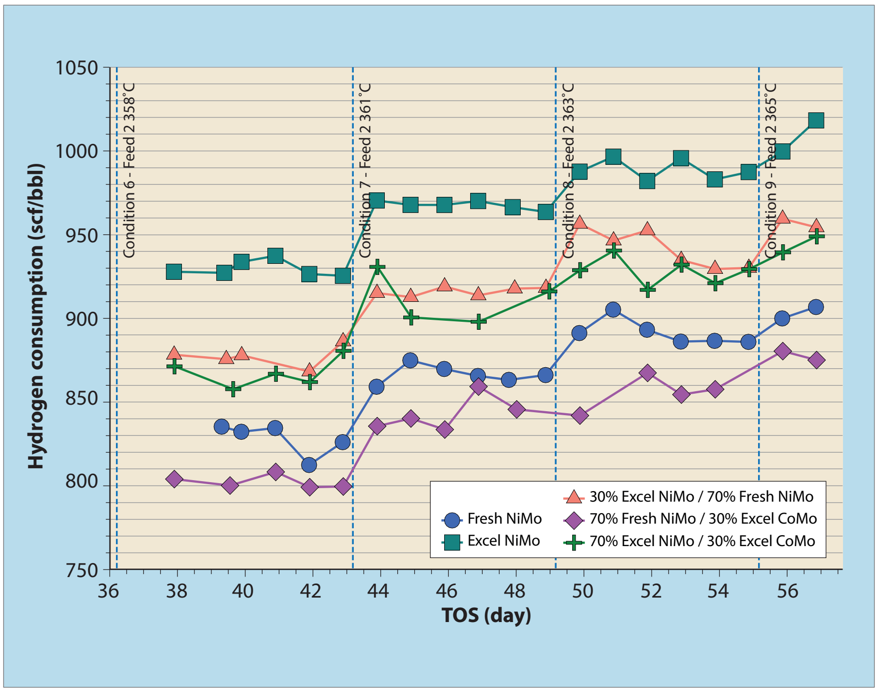

Figure 8 Hydrogen consumption for all catalyst configurations

Feed and operating conditions of the European refiner

Parameter	ULSD mode	Heating oil mode
Feed sulphur, wt%	0.29	0.44
Feed nitrogen, ppmw	250-350	400-500
Density, kg/m³	850	867
D-86 (FBP), °C	360	381
Operating pressure, barg	71	71
LHSV, h^{-1}	3.1	2.6

Table 4

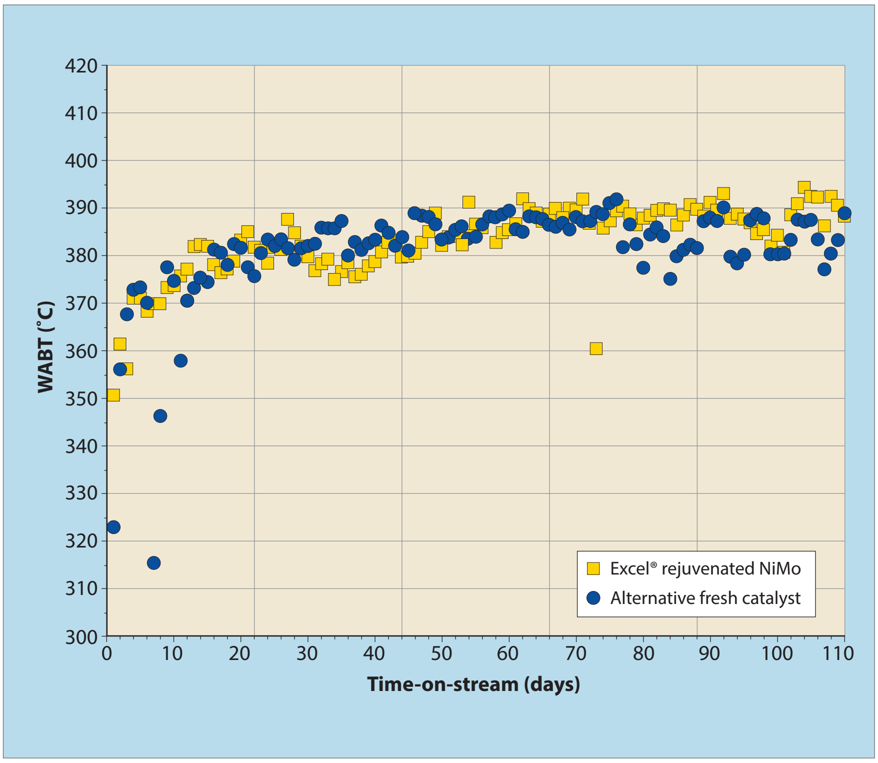

Figure 9 Comparison of rejuvenation with conventional fresh catalyst