

Optimal catalyst selection

FCC pretreat: Choosing between CoMo and NiMo catalysts

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The choice of catalyst for the world's FCC pretreaters and mild hydrocrackers has traditionally always ended up with a nickel molybdenum based catalyst. The background for this trend needs to be found in the past with respect to product requirements and metal costs. 15-20 years ago, the incentive to desulphurise the FCC feed was not pronounced, since the legislation for sulphur in the finished products was not nearly as strict as it is today. Instead, focus was on removing VGO nitrogen to protect the downstream acidic FCC catalyst. Along with that, the price on nickel was much lower than the price of cobalt, so one would need a very good reason for choosing a cobalt-containing catalyst.

Today, the situation is completely different. In most FCC pretreaters the requirements for product sulphur are the main constraint and dictate how most units are run. Regardless of the unit pressure the catalysts today need to deliver as much hydrodesulphurisation (HDS) activity as possible while at the same time removing as much nitrogen as possible. The current high demand for diesel fuel makes the obtainable VGO conversion lucrative to many refiners, and this catalyst ability is prioritised when selecting catalyst systems today. On top of all this, the CoMo based catalysts are no longer significantly more expensive than NiMo based.

Haldor Topsøe has developed and improved both CoMo and NiMo catalysts for more than 30 years. As part of this continuous work, the BRIM™ Technology was developed eight years ago. One of the key benefits of the BRIM™ CoMo catalysts used in FCC pretreat service is

their remarkably high HDS and HDN functions in low-to-medium pressure applications. As illustrated below, their activities outperform the traditional NiMo based catalysts. Only in the rare case where the NiMo catalyst is allowed to reduce product nitrogen to extremely low levels will they have an advantage over the CoMo catalyst – this only takes place with very low nitrogen feeds and/or true high pressure units approaching hydrocracker conditions. Also shown below is the lack of difference in conversion activity between CoMo and NiMo type catalysts in FCC pretreat and mild hydrocracking services caused by thermodynamic equilibrium constraints within this regime.

The high operating stability of the BRIM™ CoMo catalysts is another benefit, however not discussed in this note.

Despite the change of industry requirements and the fact that the BRIM™ CoMo catalysts in many applications are way superior to conventional NiMo catalysts, there is still some reluctance left in the industry leaning towards selecting the “known but old” NiMo solution. To illuminate this problem and to promote the optimal technical solution, we are presenting recent industrial feedback and pilot plant work from the BRIM™ catalysts used in FCC pretreat and mild hydrocracking services.

The BRIM™ catalyst portfolio for FCC pretreat applications consisted initially of the catalysts TK-558 BRIM™ (CoMo) and TK-559 BRIM™ (NiMo). These products have recently been replaced by an entire new generation of further optimised catalysts: TK-560 BRIM™ (CoMo), TK-562 BRIM™ (CoMo) and TK-561 BRIM™ (NiMo).

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Pilot plant work

Three different pilot plant studies are presented below. They all focus on showing the difference in performance of the BRIM™ VGO catalysts at different reactor conditions such as pressure and temperature. The drawn conclusions from these experiments are as follows:

HDS

The highest activity CoMo catalyst (TK-562 BRIM™) is significantly better at removing sulphur than the NiMo catalyst at all the test conditions. It is 10-50% better in HDS dependent on the pressure. The same trend is observed for the less active CoMo catalyst TK-560 BRIM™, however with a smaller margin.

HDN

The difference in HDN activity is marginal between the CoMo and NiMo catalysts – within 10%. It is worth noticing that the highest activity CoMo catalyst (TK-562 BRIM™) appears slightly more HDN active than the NiMo catalyst at low-to-medium pressure.

VGO conversion

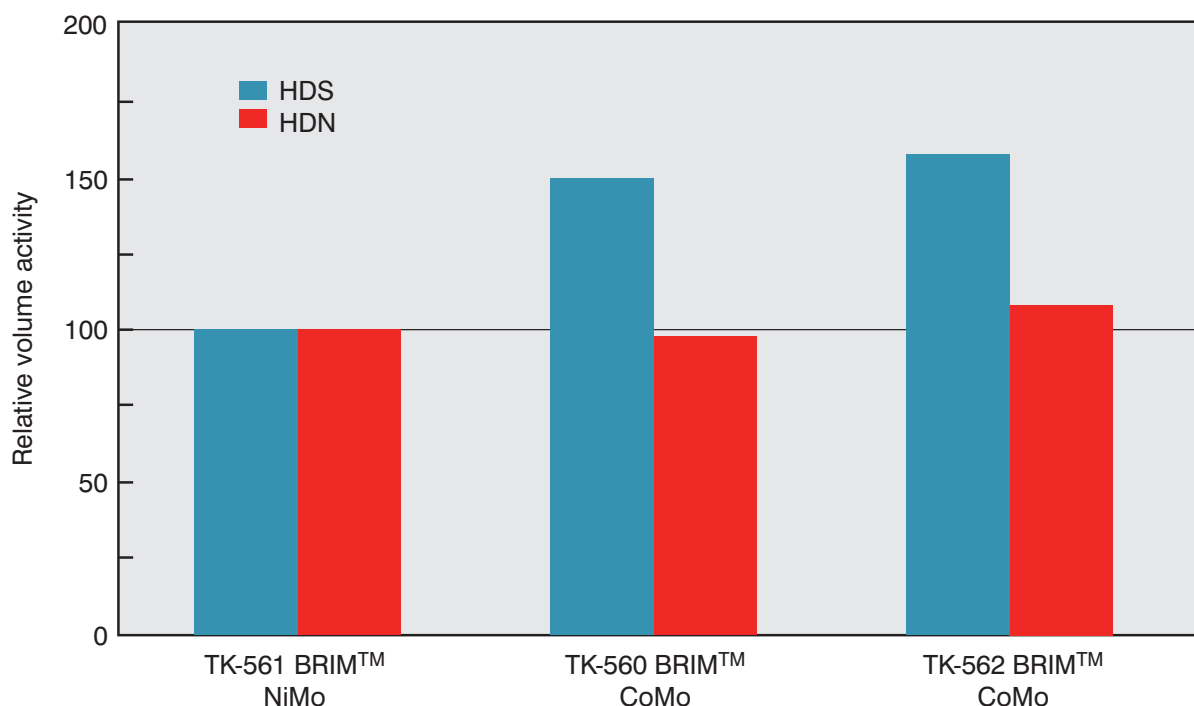
There is no observed difference in VGO net conversion between the BRIM™ VGO catalysts, when the hydrogen partial pressure is below 90 barg, i.e. the CoMo catalysts deliver the same conversion activity as the NiMo catalyst.

Hydrogen partial pressures below 90 barg will typically provide conversions in the range of 5-30 wt %, and this conversion is mainly related to HDS, HDN and particularly HDA. HDA is linked to the nitrogen removal and thermodynamic equilibrium.

From this work it is evident that, at these conditions and with these types of feed, the choice of a BRIM™ CoMo catalyst will return most value. Their high sulphur removing activity, along with the fact that they provide the same nitrogen removing and conversion activity as a NiMo catalyst, makes it difficult to justify a NiMo solution at low-to-medium pressure.

Low pressure FCC PT test

VGO from Russian export crude, 340°C and 45 BARG H₂ partial pressure



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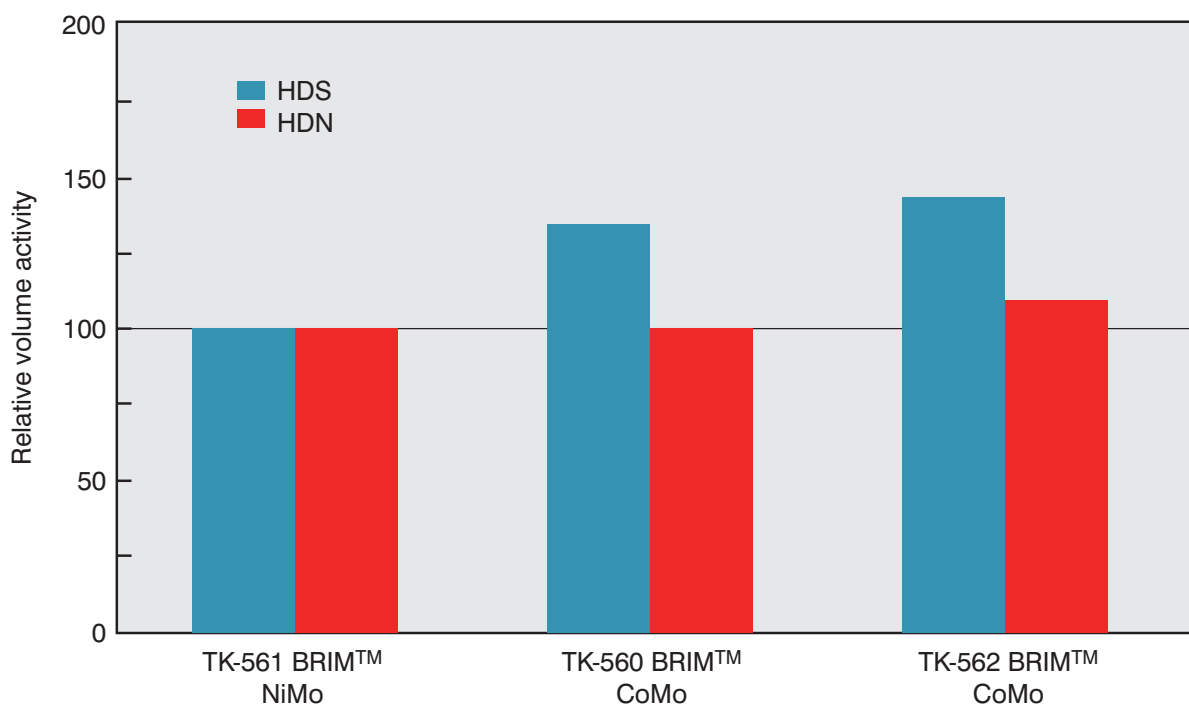
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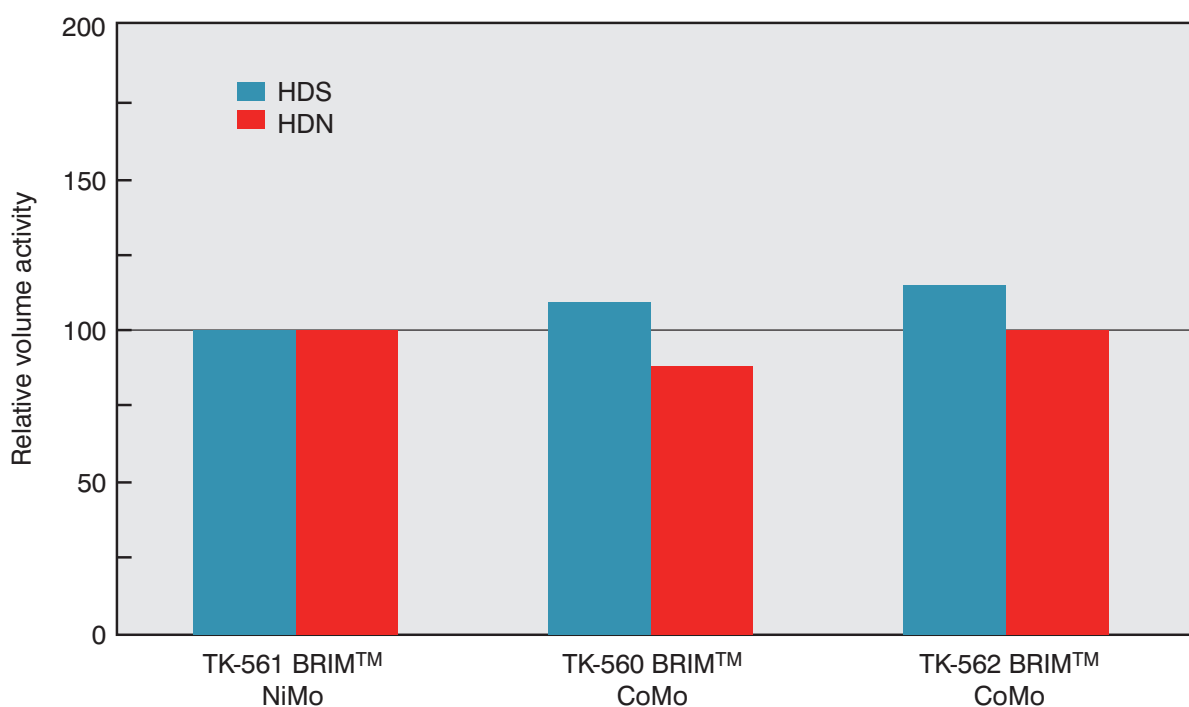
Medium pressure FCC PT test

VGO and HCGO from Middle East crude, 350°C and 70 BARG H₂ partial pressure



High pressure MHC test

VGO from Russian export crude, 360°C and 90 BARG H₂ partial pressure

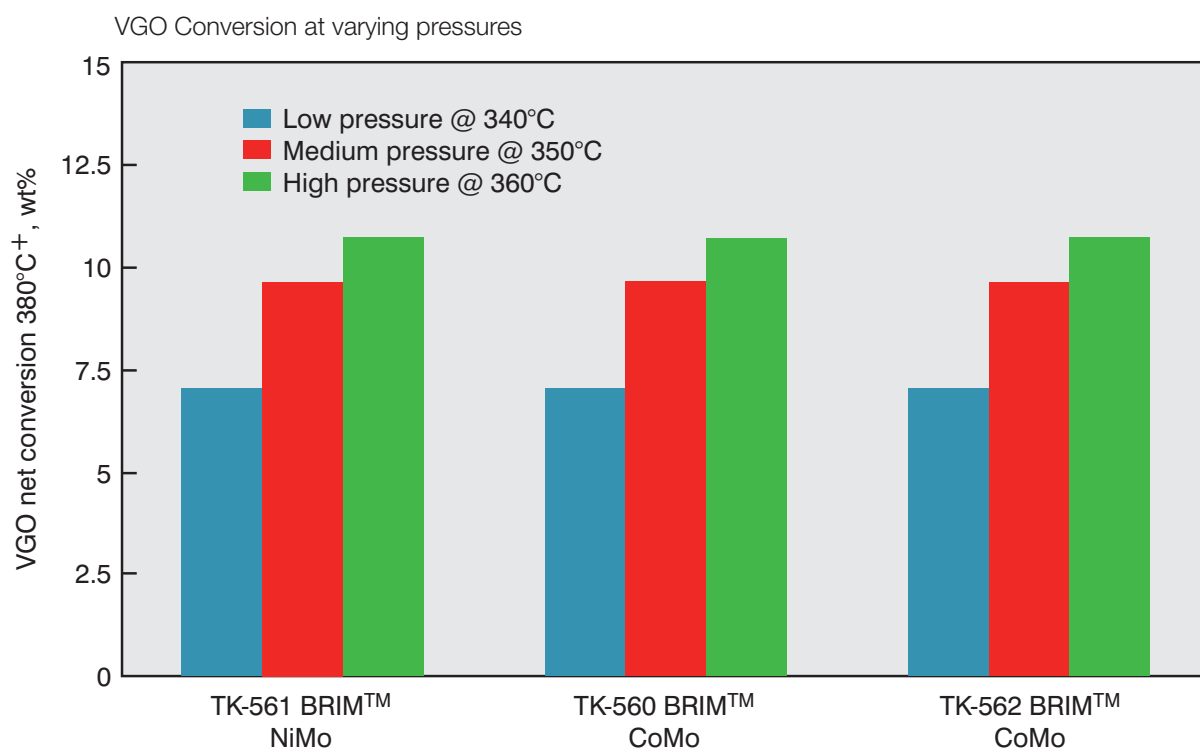


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Industrial performance

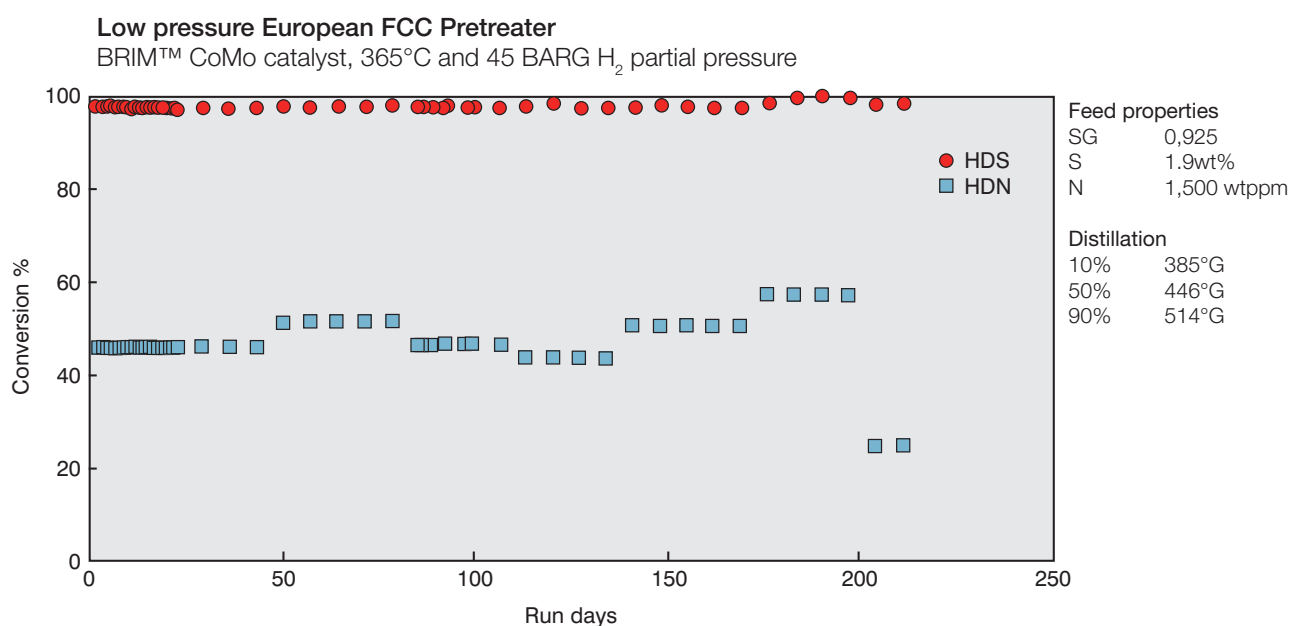
From units running with the BRIM™ VGO catalysts, it is possible to look at the general trend on achievable HDN and corresponding HDS levels in different operating regimes such as pressure and temperature.

The below plots are depicting actual catalyst performance in four different industrial units equipped with either BRIM™ CoMo or NiMo catalysts. All units are running in high severity mode with a product VGO sulphur content of 200-400 wt ppm that enables production of ULSG (< 10 wt ppm sulphur in the gasoline pool).

One observation is that the HDN conversion, with more or less constant HDS conversion, is going up with increasing pressure and temperature, which is exactly what the general theory is dictating. However, from looking at

the plots one cannot see the catalyst type effect on the HDN conversion, i.e. we do not observe higher HDN conversions from the NiMo catalyst data. This observation is in line with the pilot plant data discussed in the previous section: The difference in HDN activity between a CoMo and a NiMo catalyst in FCC pretreat service is marginal.

The large and significant difference lies in the HDS activity. However, these cannot be compared in the three plots below, as the sulphur conversion is > 90% for all cases.

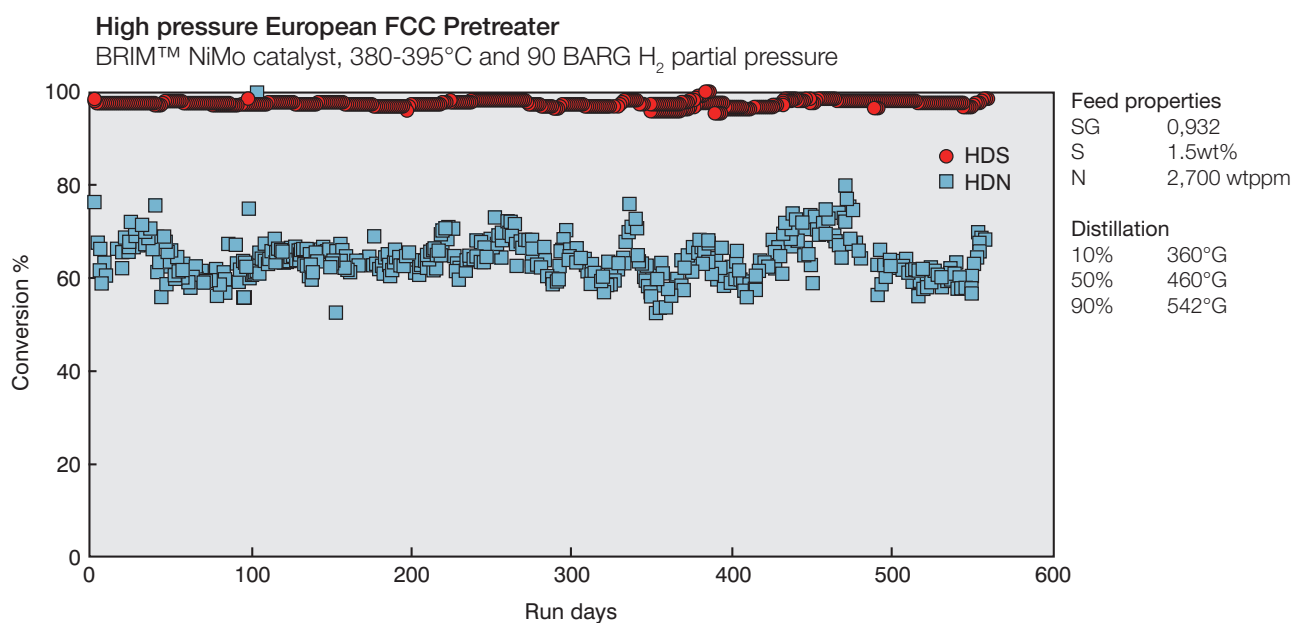
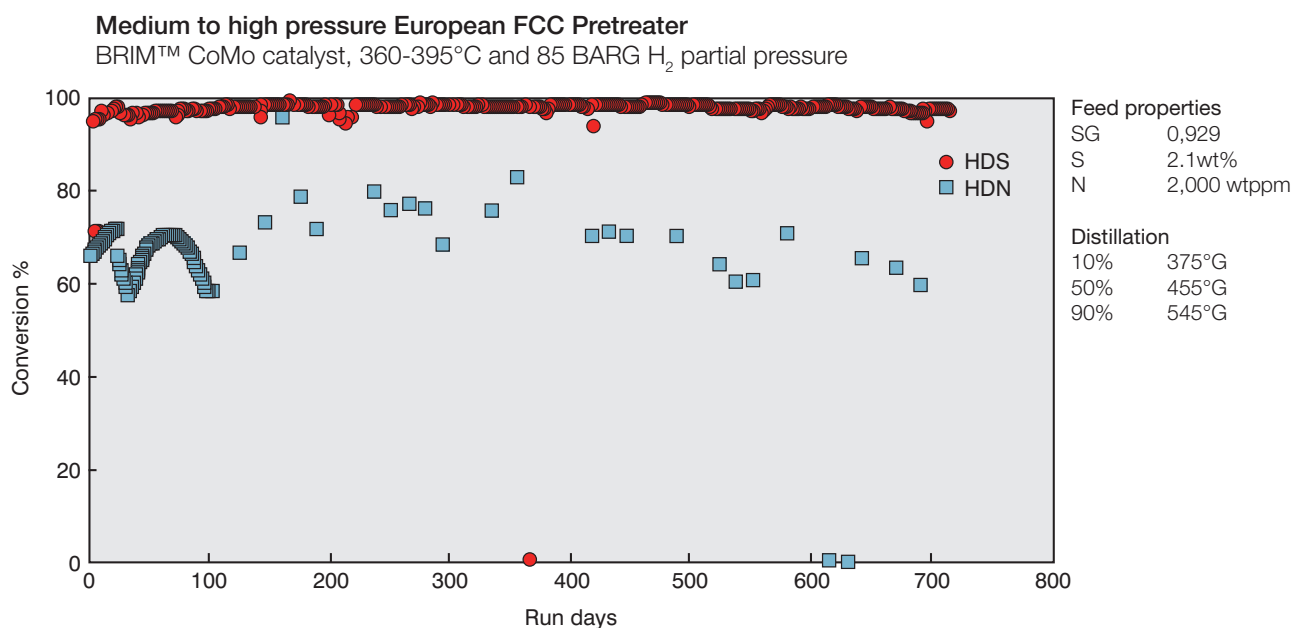


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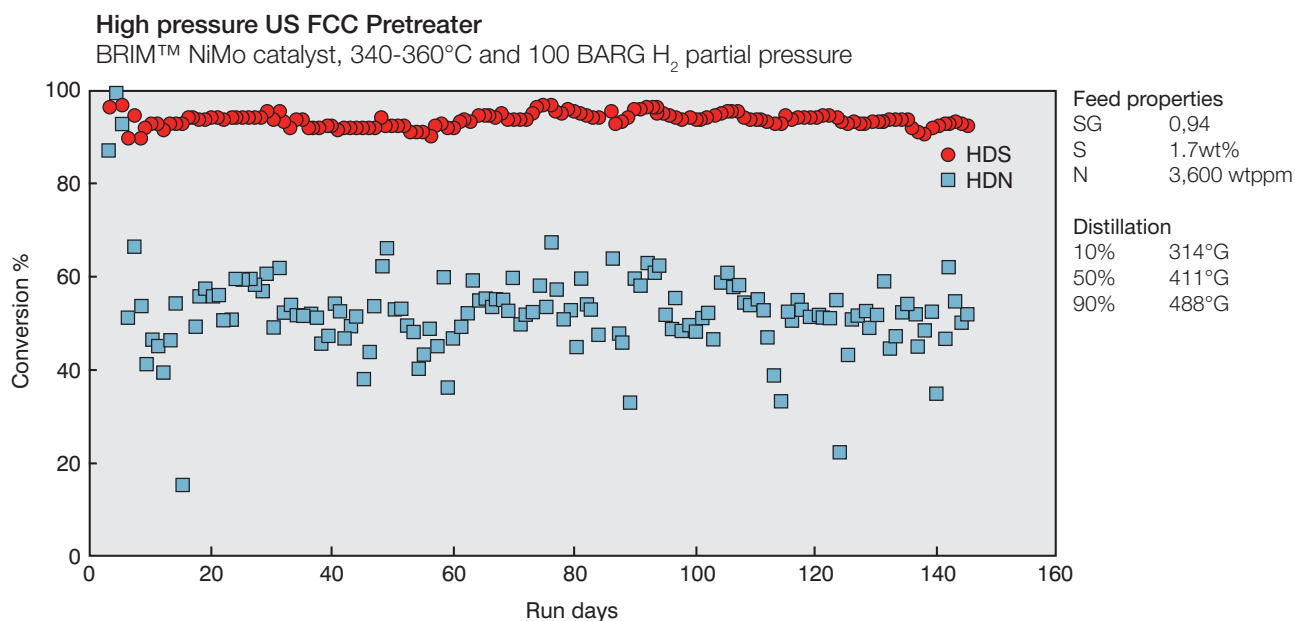


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From a large European FCC pretreater operating at 85 barg hydrogen partial pressure, it has been possible to normalise and compare operating data from the current cycle with a BRIM™ CoMo catalyst and the previous cycle with a conventional NiMo catalyst. This is a very unique opportunity, since it rarely is possible to side-by-side compare two different catalyst types in the same industrial unit. It should be mentioned that the cycle with BRIM™ CoMo catalyst was done with new compact reactor internals, giving a somewhat larger catalyst volume. The difference in volume is accounted for by the normalisation, so the HDS temperature plot below can be used directly to compare the performance and stability of the two types of catalyst. (see next page)

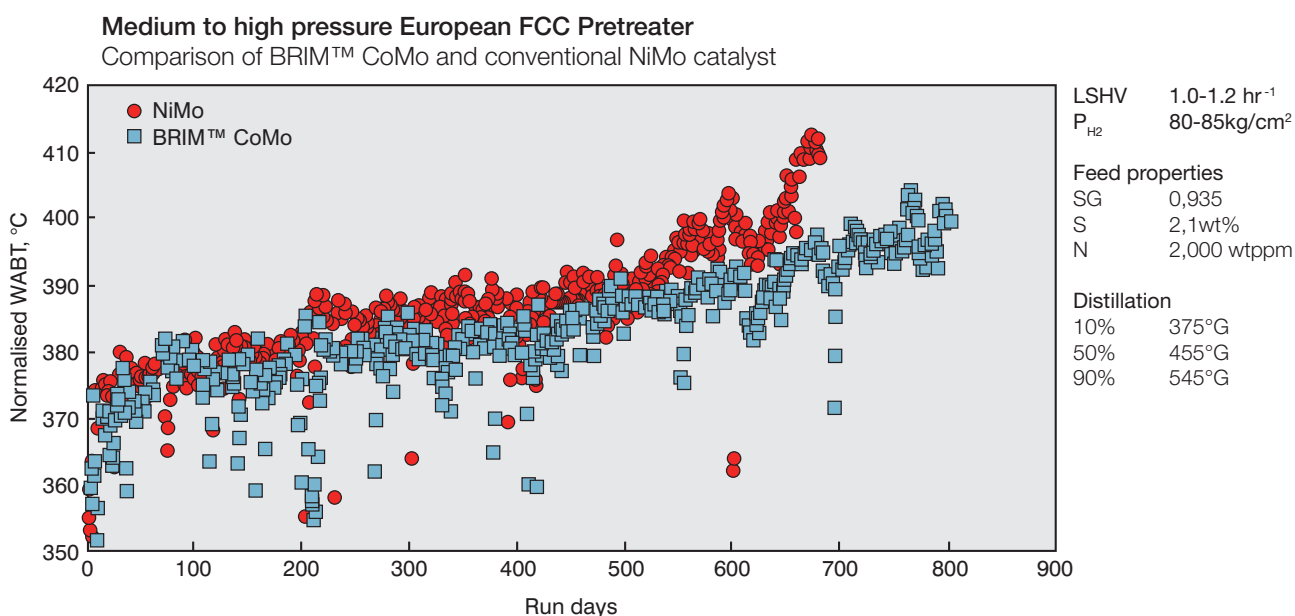
Due to data scattering it is not possible to establish the exact difference in start-of-run activity between the two catalysts, but it appears that the BRIM™ CoMo catalyst initially had a higher activity, corresponding to at least a few degrees lower temperature. More importantly though, it is evident that the BRIM™ CoMo catalyst is more stable in operation and at high temperature has a significantly lower deactivation rate compared with the NiMo catalyst. This behavior is absolutely in line with the pilot plant data presented earlier. The difference in stability is also well known and is mainly due to the faster deactivation of hydrogenation sites on NiMo catalysts, but also due to the nature of the BRIM™ catalyst's pore structure giving them very high robustness in particularly VGO service.

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Conclusion

In FCC pretreaters and mild hydrocrackers operating at low-to-medium pressure, the best technical approach is to use a cobalt molybdenum based catalyst instead of a nickel molybdenum based catalyst. The BRIM™ CoMo solution will provide a clear and significant benefit in the sulphur removing capabilities, while the nitrogen removing activity is often slightly better or at least as good as the NiMo solution.

At high pressure, the difference between BRIM™ CoMo and BRIM™ NiMo is narrowed down to approximately 10%, and

the two types of catalyst behave in a more or less similar manner. The trend at high pressure is that the BRIM™ CoMo is slightly more HDS active and the BRIM™ NiMo is slightly more HDN active.

At partial pressures of hydrogen not exceeding 90 barg, there is no difference in achieved VGO conversion into lighter products between the BRIM™ CoMo and NiMo catalysts.