Deactivation behaviour

Loss of activity in FCC pretreating

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When selecting hydroprocessing catalysts for FCC pretreaters, the main focus is on the catalyst's start-of-run (SOR) activity, i.e. the ability to desulphurise and denitrogenate the FCC feed at the beginning of the cycle. Obviously, this is a very important parameter, and a lot of research and development work is put into optimising the start-of-run activity of new catalysts. However, something which actually is more important than initial activity that does not receive the same amount of attention is the deactivation behavior of a certain catalyst, i.e. the parameters causing catalyst deactivation and the different catalysts' ability to defy the loss of activity during the cycle.

The importance of the deactivation rate can be illuminated by the small example below, where the difference in activity is compared with the difference in deactivation rate:

	High stability catalyst Deactivation 1.5°C/month	**Low stability catalyst** Deactivation 2.0°C/month
Low activity catalyst SOR temperature: 360°C EOR temperature: 400°C	27 months cycle	20 months cycle
High activity catalyst (+20%) SOR temperature: 355°C EOR temperature: 400°C	30 months cycle	23 months cycle

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As can be seen, the gain by choosing a high activity catalyst is three months, whereas the gain by operating a catalyst with low deactivation is seven months.

Loss in catalytic activity in VGO services is caused either by carbon lay-down on the catalyst surface (coking) or by contamination by poisons in the catalyst pores and surface.

The parameters recognised to influence the permanent loss in catalytic activity are the partial pressure of hydrogen, the hydrogen availability, the reactor operating temperature and certain feedstock characteristics. These characteristics comprise content of coke precursors (nitrogen and polyaromatics) but also contaminants acting as catalyst poisons (Ni, V, Fe, As etc.).

Since the above deactivation parameters are mainly unit specific and dictated by design and refinery requirements, they can be optimised, but they are difficult to change significantly. Therefore it is a major task for the catalyst developers to come up with catalyst formulations that will help prolonging the cycle length of the unit.

One of the unique features of the Topsøe BRIM™ VGO catalysts is their open and robust pore structure, giving a very high poison tolerance and low affinity for coking reactions. This has resulted in a generation of catalysts that deactivates significantly slower than older conventional catalysts, thereby providing longer cycles than previously possible. On the next pages, we present industrial examples of the deactivation behaviour of BRIM™ VGO catalysts in very different operating regimes such as severe contamination, low pressure coking, low pressure combined with high temperature coking etc.

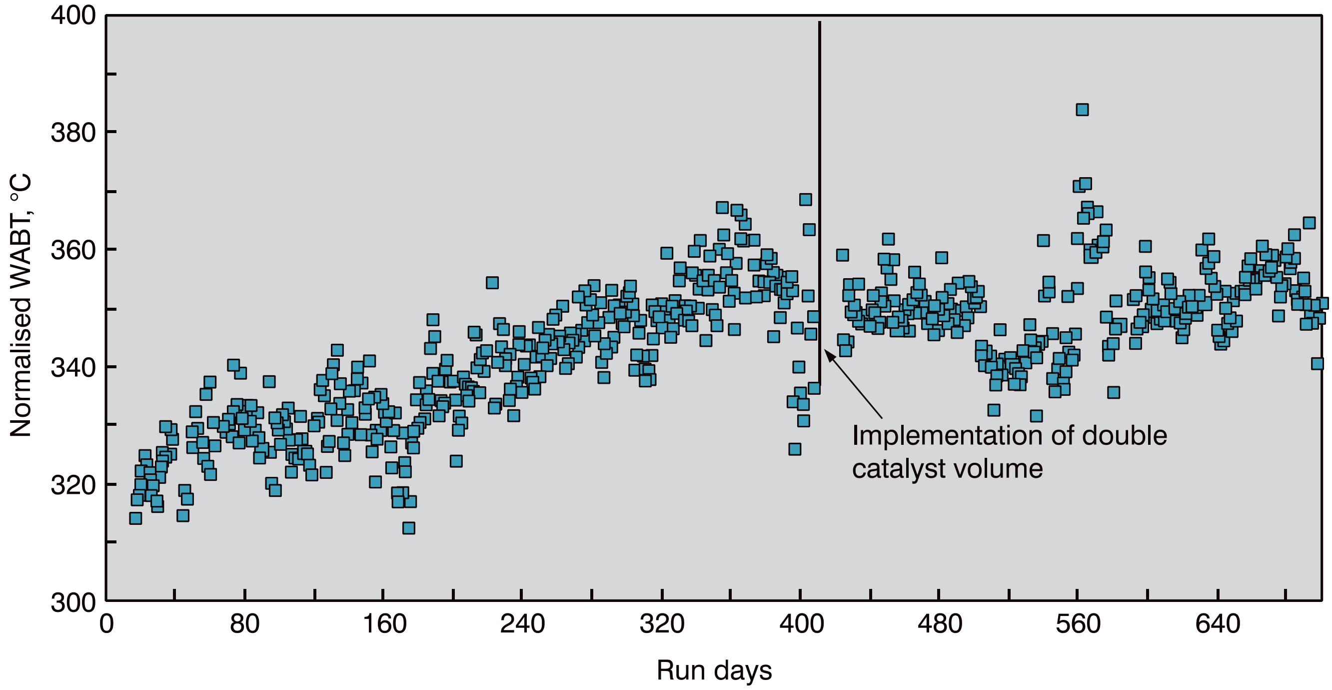
Industrial deactivation

Metal tolerance

The first example on deactivation is from a unit operated at low temperature (310-330°C) and also low pressure. In this unit, the catalyst is not deactivated due to coke lay-down but mainly due to heavy metal contamination.

The average deactivation is 4°C/month. This is obviously a fast rate, but it is regarded as low when considering the type of feed being processed. The catalyst is continuously being exposed to a feedstock containing extremely high levels of nickel and vanadium. From sample analyses of spent BRIM™ VGO catalyst from other units it has been demonstrated that the catalyst is able to withstand a contamination level of more than 8-10 wt % Ni+V, while still providing activity for removing sulphur and nitrogen. A conventional HDS catalyst with a traditional pore system would not be able to maintain its HDS function while being subjected to such level of contaminants.

Normalised HDS temperature, Low pressure Russian FCC pretreater
47 barg H_2 partial pressure, Ni+V: 4+14 wttpm in feed



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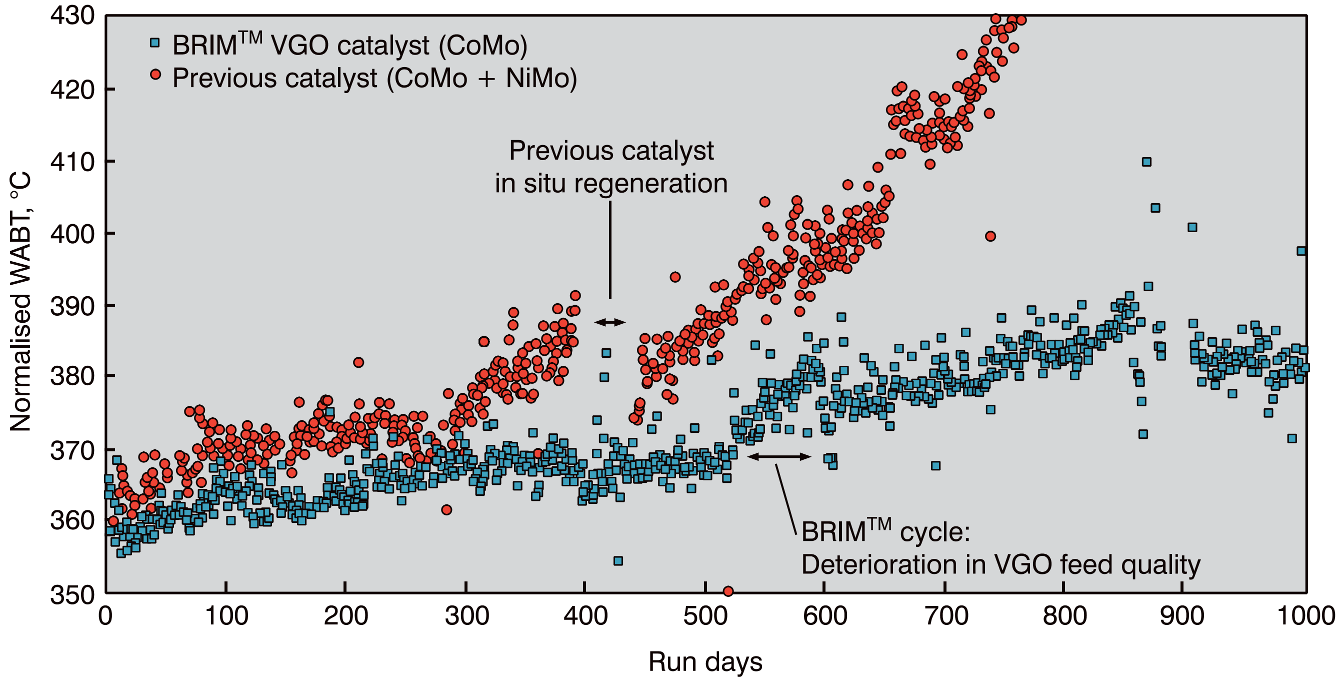
Low partial pressure of H_2
The plot is an illustrative example of how a critical low H_2 partial pressure is handled by a BRIM™ CoMo VGO catalyst and by a more traditional CoMo/NiMo stacked bed solution. The deactivation seen here is a classic example of catalyst coking.

The cycle with the BRIM™ catalyst actually lasted more than three years, which was a record for this unit, and the operating stability was remarkable.

When looking into the data more closely, it can be seen that in periods with lower than average P_{H2} (< 40 barg), the deactivation rate was clearly higher for both catalysts, whereas the deactivation slope flattened when the refiner was able to increase P_{H2} to above 45 barg. The BRIM™ catalyst was simply more capable of handling both regimes and never experienced accelerated coking as the other catalyst did.

Normalised HDS temperature, Low pressure European FCC pretreater
45 barg H_2 partial pressure



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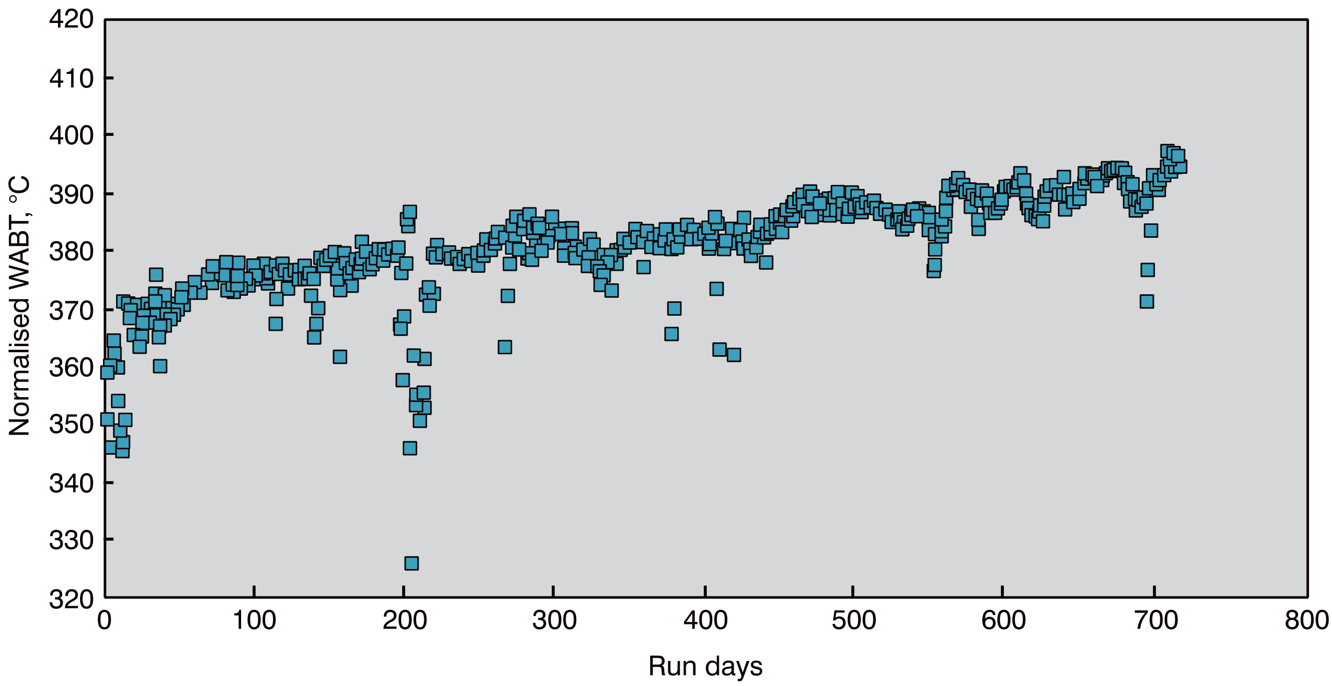
High partial pressure of H_2
In this case, a BRIM™ VGO catalyst of the CoMo type is working in a high severity unit operated at a somewhat higher pressure (P_{H2} 83 barg). The average reactor temperature for the cycle has been >385°C, which implies that accelerated coking normally is at risk.

Instead of accelerated deactivation, which is very difficult to deal with, the BRIM™ catalyst has shown a steady and predictable behaviour with a deactivation rate of 1°C/month.

The overall performance of the BRIM™ catalyst has outperformed the previous experiences with NiMo catalysts in the same unit.

Normalised HDS temperature, Semi-high pressure European FCC pretreater
83 barg H_2 partial pressure



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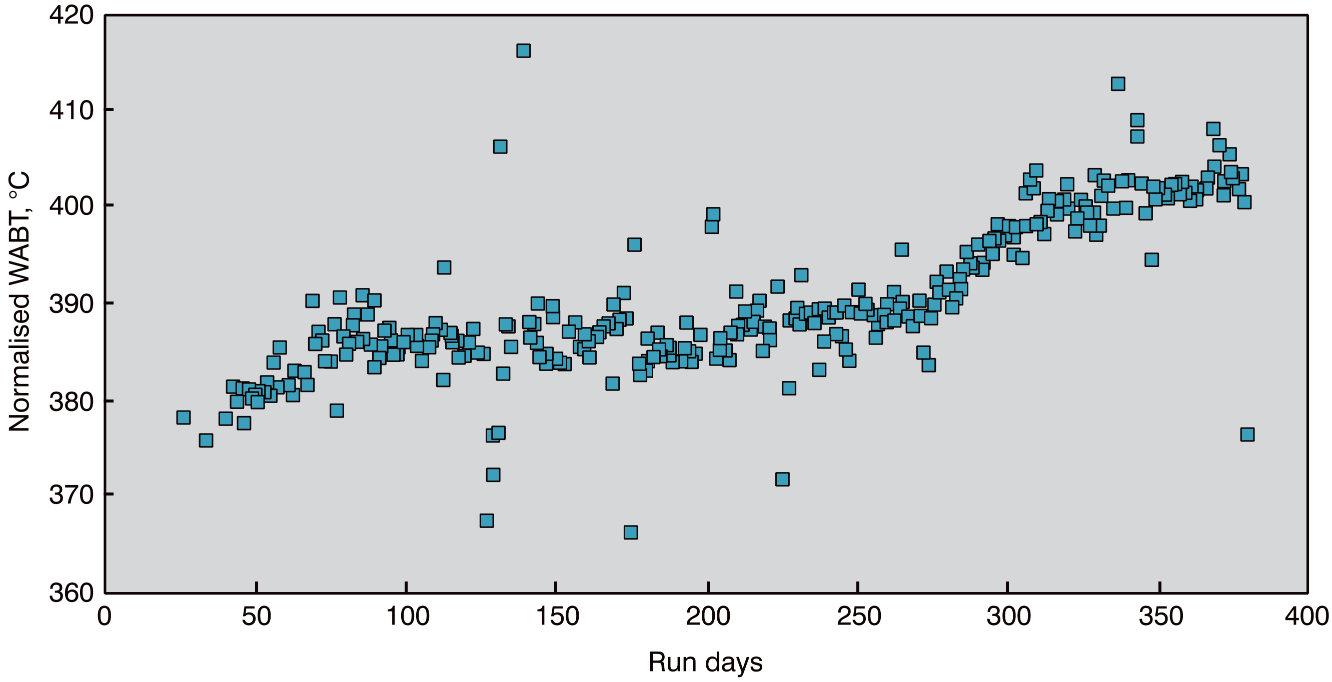
Low partial pressure of H_2 combined with high temperature
From a FCC pretreat catalyst point of view, one of the worst scenarios is one with low H_2 partial pressure and a high temperature. This is likely to give a very fast deactivation, since the coking reactions are favoured in all possible ways.

The below graph is from such unit (low pressure), operating in mild hydrocracking mode (MHC) to achieve as much VGO conversion into gas oil as possible. The average deactivation rate in the MHC mode has been kept at 2°C/month with a BRIM™ VGO catalyst based on cobalt and molybdenum. This performance is significantly better (more VGO conversion) and more stable than with the previous catalyst which was based on cobalt, molybdenum and phosphorous.

Normalised HDS temperature, Low pressure European FCC pretreater
43 barg H_2 partial pressure and 380-405^{0}C operating temperature



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Conclusion

Hydroprocessing catalyst deactivation is caused by carbon lay-down (coking) and/or by contamination of the catalyst with contaminents/poisons such as Ni, V, Fe, As etc.

Compared to conventional catalysts, the family of BRIM™ VGO catalysts is designed to withstand the typical deactivation in a highly improved manner due to the nature of the catalysts' structure.

The catalyst coking rate is observed to be much lower when utilising the BRIM™ technology and their tolerance towards metal contamination and resistance to coking are clearly exceptionally high.

In different operating regimes, the BRIM™ VGO catalysts have shown very high operating stability, while dealing with low pressure, high temperature and feedstock contaminants.

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Haldor Topsøe A/S - Nymøllevej 55 - 2800 Kgs. Lyngby - Denmark
Tel. +45 4527 2000 - Fax. +45 4527 2999 - www.topsoe.com

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