## Question 22: Which is the impact of feed asphaltenes content on hydrocracker cycle length?

**Shankar Vaidyanathan** (Flour)

The asphaltenes are high boiling, high molecular weight and hydrogen deficient materials that are the least reactive in a hydrocracking environment. Heavy vacuum gas oil may be contaminated by asphaltene entrainment with resid due to inadequate fractionation, inefficient wash or an operational upset in the upstream vacuum unit. Controlling the HVGO distillation end point to limit metals, CCR and asphaltene entrainment may be a better operational strategy while feeding a hydrocracker, than just focusing on VGO yield in the vacuum unit without improving HVGO back-end distillation. Vacuum gas oil is a poor solvent for asphaltenes. Hydrotreated VGO is poorer, so the asphaltene may tend to precipitate out in the lower catalyst beds.

Commercial recommendation is to limit the asphaltenes in feed blend to 0.05 wt.% nC7 insoluble; the licensor or catalyst supplier may have a lower specification by their proprietary analytical test method. High asphaltene content in feed leads to increased catalyst deactivation. The catalyst fouling rate is quite steep; for e.g., doubling the feed asphaltene content may double the catalyst fouling rate from a baseline of 2-3 deg F/month to 4-6 deg F/month, significantly reducing hydrocracker cycle length. Asphaltenes may also precipitate on equipment surfaces leading to fouling and pressure drop issues. Much of the knowledge and catalyst technology for handling asphaltenes in hydrocrackers come from the experience with resid hydrotreaters. Better activity demetallation catalyst or size shaped activity grading may be necessary. Depending on the crude source, additional processing considerations may be needed if the asphaltenes are further compounded with clay type complex to avoid premature pressure drop and plugging of the catalyst beds.

**Minh Dimas** (CITGO)

We do not check for asphaltenes. We test for Con Carbon (CC) and we try to limit it to 0.05 wt.%. The impact of feed CC in a hydrocracker depends on the H2 partial pressure and the operating temperature of the reactor: high H2 partial pressure and low temperature will saturate coke precursors, but high temperatures and low H2 partial pressure will thermally degrade these precursors to form coke – causing maldistribution, higher pressure drop, and requiring more temperature to achieve a target conversion.

For us, since we limit the HCO 95% to 795 deg F, the deactivation rate slows down.

**Raj Patel** (Haldor Topsoe, Inc.) Asphaltenes are very complex molecular structures containing metals, nitrogen, aromatics, heteroatomics and aliphatics. The asphaltenes are found in the heavy end of the

VGO feed. A poor separation of VGO and vacuum tower bottom in the vacuum column often leads to a heavy tail in the VGO with large amounts of asphaltenes. Such a tail can be very detrimental for the hydrocracker catalysts, leading to rapid deactivation and change in selectivity.

A typical hydrocracker is loaded with a catalyst grading including a demet catalyst to trap most of the feed contaminants such as Ni and V, followed by the hydrocracker pretreatment catalysts removing most of the organic sulfur, nitrogen and polyaromatics and followed by relatively more costly hydrocracking catalyst. The Asphaltenes are very large molecules and require a specialized demet catalyst for effective removal. Topsoe offers demet catalysts especially designed for Hydrocrackers and VGO units designated TK-700 series.

The cocktail of feed metals (Fe, Ni and V), known as permanent catalyst poisons, large amounts of coke precursors such as polyaromatics and organic nitrogen and the very refractive sulfur and nitrogen species in such heavy ends can lead to a fast deactivation of all the catalysts found in the hydrocracker. In most hydrocrackers, the hydrogen pressure is rather high, which reduces the deactivation caused by coke formation.

It is difficult to give a quantitative measure for the direct impact of feed asphaltenes. The amount of asphaltenes correlates with feed metals, amount of PNAs, feed endpoint, organic nitrogen and reactivity of sulfur and nitrogen species to be converted. The amount of asphaltenes is a tool to describe the “toughness” of the feed. Increase in feed asphaltenes content from e.g., 20-30 ppm to around 1000 ppm asphaltenes, which is the case for a heavy tail containing atmospheric residue, can cause the catalyst deactivation to increase from e.g., 1 deg F/month to up to 5-10 deg F/month.

Moreover, a hydrocracker that is operated at high conversion (recycle operation) and runs with high asphaltenes feeds will result in higher HPNA formation. This will also dramatically reduce the cycle length and might cause fouling in downstream equipment.

Processing heavy VGOs and dealing with asphaltenes in particular call for very robust catalyst systems. Besides high performance grading and HDM catalysts, robust bulk catalysts are also of key importance. Due to the unique pore structure of Topsøe’s BRIM™ technology catalysts; these catalysts have a high poisons tolerance. BRIM™ catalysts are able to withstand a contamination level of more than 8-10% Ni+V while still providing activity for removing sulfur and nitrogen.

Optimal protection of the hydrocracker catalyst is of paramount importance, as small amounts of coke precursors and feed metals will change the performance of the hydrocracker catalyst with high deactivation rate and change in selectivity.



Tags

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Catalysts

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