Question 14: What is cycle life limiting factors in low pressure jet/kero hydrotreaters?

ROBERTSON (AFPM)

We have three questions coming up that the panel chose to answer only in the Answer Book to keep the question count down during the session. Question 14 is one of them. Kevin has a very detailed answer in the Answer Book, but we are not going to present the answer here. The panelists felt strongly about including these three questions in the Answer Book.

ANDREA BATTISTON (Albemarle Corporation)

Factors limiting cycle life in low pressure kero/jet hydrotreaters are mainly related to product quality specifications. In particular, specifications related to aromatic saturation such as smoke point and color.

Jet has very tight specifications for color and color precursors and is required to pass a specific test, the JFTOT (Jet Fuel Thermal Oxidation Test). The JFTOT measures color of oxidized deposits in a kero/air mixture at 527°F. Color detected by the JEFTOT is believed to be caused by precursors very similar to those responsible for color seen also with other color measurements, although the JFTOT can often reveal such species at lower concentrations [as low as 1 wppm.

The main constraints for kero hydrotreating operation are typically HDS and HDA activity. HDS is relevant, in particular, for ULSK production, for blending with on-road diesel (to improve cold diesel properties), city diesel (to lower soot formation) and sometimes with off-spec ULSD to reduce blended S content. HDA is mainly relevant for improving smoke point, but care must be taken in feedstock selection for low pressure kerosene units since the capability to saturate aromatics is limited.

In some instances, pressure build-up can be a limiting factor too, in particular when operation is easy and long cycles are achievable from a catalyst activity standpoint. A well-designed guard bed system with activity and catalyst shape grading for trapping of scale can help mitigate pressure drop issues.

Limitations in kero hydrotreating for both HDS and HDA become more severe when hydrogen pressure in the unit is low and when feed severity increases. In both cases SOR WABT is higher as a result, together with catalyst deactivation rate. As a consequence, a higher temperature is reached earlier in the cycle (as a rule of thumb, a 10°F increase of the feed T95 above 475°F corresponds to a 5°F SOR WABT rise due to the larger presence of refractory sulfur and nitrogen species, and of aromatics). Temperature becomes a serious problem in operation when feed becomes near fully vaporized. Heavier species left on the catalyst surface are more susceptible to dehydrogenation reactions. Traces of 2+ ring aromatics may cause color. In some cases, it may be desirable to raise temperatures sufficiently to fully vaporize the feed rather than operate near, but not quite, full vaporization.

Proper catalyst choice is important for achieving maximum cycle length in kero/jet low pressure operation while meeting product specifications. In general, CoMo catalysts with moderate hydrogenation activity, like Albemarle's KF 757, are preferred at low pressure when HDS is the main target because of their higher HDS activity and robustness with low hydrogen availability. A combination of CoMo/NiMo catalysts can also be applied to increase HDN and HDA activity, for instance, to promote smoke point improvement.

Units with small operating windows may benefit from even higher HDS activity, like Albemarle's KF 770. In low pressure commercial operation, KF 770 has demonstrated SOR WABT can be decreased by ~10°F compared to alternatives, leading to significant cycle length increase by delaying onset of temperature related color problems.

GREG ROSINSKI and **BRIAN WATKINS** (Advanced Refining Technologies)

For most jet and kerosene hydrotreaters, the end of run condition limitation is typically the product color or smoke point. Aromatics and poly-nuclear aromatic (PNA) compounds are a problem for both smoke point and color. Color bodies are PNAs that form as the reactor temperature is increased. Several of these types of molecules are green/blue and fluorescent in color, and the color is apparent at very low concentrations of these species. Certain nitrogen (and other polar) compounds have also been implicated as problems for distillate product color. These species can polymerize to form various color bodies and can also form sediment via oxidation and free radical reactions. At end of run conditions when the outlet temperatures are high enough, PNA saturation reactions become equilibrium limited, the formation of aromatic compounds is more favorable.

If the unit is having difficulties with color, several steps can be taken to extend the cycle length. Increasing the H2/oil ratio to the hydrotreater will increase the reactor outlet H2 partial pressure helping to slow down the reverse equilibrium reaction and can help in prolonging cycle life. Feeds such as light cycle oils and coker stocks typically have higher H2 consumption than straight run materials, which reduce the outlet H2 partial pressure. Increasing the available hydrogen to these units will help in maintaining the kinetic reaction. If unable to add additional hydrogen, minimizing cracked stocks will also help with color.

If the unit has enough quench available, operating with a descending temperature profile for the last bed can also assist with increasing cycle life. This also has the added benefit of improving the outlet hydrogen partial pressure which as mentioned above is beneficial to the PNA saturation reactions.

MUTHU SRINIVASA (Criterion Catalysts & Technologies)

The cycle limiting factors in low pressure ultra-low sulfur jet/kerosene (ULSK) operations are often tied to meeting color specification for jet fuel and limiting the vaporization fraction at reactor outlet to avoid dry point for ULSK (<10 ppm sulfur). ULSK EOR temperatures are generally higher than those of jet fuel production.

Factors that influence jet product color include both process conditions and feed composition.

Process Conditions:

- High outlet temperature
- Low H_2 partial pressure (pressure, % H_2, treat gas rate)
- Low LHSV
- Product sulfur (over treating well below 10 ppm)
- High reactor outlet vaporization reducing H_2 pp (partial pressure)
- Bad distribution (localized hot spots)

Generally, low H_2 partial pressure and less than 10 ppm product sulfur require reactor outlet temperatures beyond the aromatics equilibrium point resulting in both high concentration of diaromatics and poor color quality. Maximum reactor outlet temperatures allowable to control color vary and is a function of feed quality, H_2 partial pressure and LHSV. Some refiners operate the unit alternatively between jet mode and ULSK with limited tankage flexibility. This requires operating jet also to less than 10 ppm sulfur with a flexibility to blend with ULSK. This high severity operation can lead to color limited cycles.

Feed Composition:

- High aromatics (low API)
- Feed high T90/T95 distillation
- Feed source determines the feed relative processing difficulty. It has been observed that the feed color is much lower for Kerosene derived from high asphaltic or synthetic crudes as compared to sweet crude kerosene.
- High feed nitrogen (>50 ppm to 100 ppm) leads to higher product nitrogen beyond aromatics equilibrium temperature and results in bad color.

ULSK production is often blended to ULSD and hence color is not typically a major issue. EOR conditions for ULSK in low pressure hydrotreaters can be determined by maximum allowable temperature to avoid dry point in reactor. Low pressure and lower H_2 partial pressure requires higher reactor outlet temperature to meet less than 10 ppm which leads to higher vaporization. It is preferable to restrict reactor outlet vaporization to have better control on reaction kinetics

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