Question 33: What solutions do you have for extending cycle length in distillate hydrotreating units limited by product color?

Muthu Srinivasa (Criterion Catalysts & Technologies)

Color chemistry is very complex and strongly influenced by the feed molecules and the unit operating conditions. Dehydrogenation of saturated aromatics (condensation) and/or insufficient removal of nitrogen containing molecules can both result in off spec product color issues. Dehydrogenation or condensation reactions are favored by low H2pp and high temperatures.

The diesel fuel color pipeline standard is <2.5 (ASTM-D-1500). Feed properties which influence color of the finished product are the type of feed stock (such as Straight run or cracked), crude origin (such as conventional or synthetic crude), nitrogen content and end point.

Operating conditions such as low H2pp, high feed vaporization at EOR high temperatures and poor distribution leading to localized peak bed temperatures also influence product color. Only a small quantity of "color bodies" is required to result in off-spec product. Generally, at EOR conditions of high temperature, aromatics saturation starts declining rapidly and can lead to product color issues.

When these issues arise, Criterion works with our customer to evaluate the potential options.

Brian Watkins and **Charles Olsen** (ART)

It is well known that the color of distillate products is affected by the reaction conditions in the hydrotreater, especially temperature and hydrogen partial pressure. As (outlet) temperature increasesand/or hydrogen partial pressure decreases, the product color degrades. It is also generally accepted that the species responsible for color formation in distillates are polynuclear aromatic (PNA) molecules some of which cause color issues even at low concentrations. Certain nitrogen (and other polar) compounds have also been implicated as problems for distillate product color and product instability. These species can polymerize to form condensed aromatic structures, which tend to be green to yellow/brown in color and can also form sediment via oxidation and free radical reactions.

PNA's such as these are readily saturated to one and two ringed aromatics under typical diesel hydrotreating conditions at start of run (SOR), but as the temperature of the reactor increases towards EOR, an equilibrium constraint may be reached whereby the reverse dehydrogenation reaction becomes more favorable. At some combination of low hydrogen partial pressure and high temperature the dehydrogenation reaction predominates and PNA's begin to form resulting in a degradation of the color of the diesel product. Other work (Takatuka et al, 1991 NPRA Annual Meeting, Paper AM-91-39)showed that the color bodies responsible for diesel product color degradation ware concentrated in thehigher boiling points in the diesel (>480F). This suggests that color can be improved by adjusting the diesel endpoint. To learn more about color degradation in ULSD see Advanced Refining Technologies

Catalagram #105.

One approach that may be applied for extending cycle length is to increase quench to the bottom bed of the hydrotreater. This accomplishes two things which are important to maintaining a good environment for hydrogenation of PNA’s. It reduces the outlet temperature and helps to increase the outlet hydrogen partial pressure relative to no or lower amounts of quench.

This, of course, requires that the upper beds of the hydrotreater be run at higher WABT’s in order to maintain the required HDS conversion. This means that the furnace must have sufficient capacity to achieve the higher inlet temperatures. Operating in this manner offers the potential to add an additional 10-20°F on to the cycle length depending on the unit capabilities (furnace, quench capacity).

Another approach, which may be implemented with the one just discussed, involves adjusting the feed to the unit. FCC LCO is known to have a significant impact on diesel product color. Reducing (or eliminating) the amount of LCO in the feed will help to suppress product color degradation as the unit approaches EOR. There is also data showing that the color bodies that cause problems for ULSD tend to be concentrated at the higher boiling points of the distillation on the feed/product. Reducing the endpoint of the LCO reduces the concentration of these species which will help maintain acceptable product color as the unit moves towards EOR.

Paul Zimmerman (UOP)

Color bodies have often been thought to be related to polynuclear aromatics (PNA) and/or heterocyclic nitrogen compounds. The PNA's could either exist in the feed (generally in higher concentrations for high end-point feeds, and cracked stocks like FCC LCO, coker stocks, etc.), or could be formed in the reactor from aromatic condensation reactions which are favored by high temperature, low H2 partial pressure, localized high residence time due to channeling, etc. The level of PNA’s can potentially increase towards the end of the run, when temperatures are increased to maintain the product sulfur target, H2 partial pressure may be reduced due to feed vaporization, and catalyst activity is lower due to aging of the catalyst (coking, etc.).

Feed nitrogen compounds are generally concentrated in the heaviest feed fractions and are often higher in concentration in cracked stocks. Some refiners have correlated color stability with the nitrogen content of the product. In storage, basic nitrogen compounds in the product could react with oxidation products to form color bodies.

For the design of a new diesel hydrotreating unit, design operating conditions can be set to obtain good product color. For an existing diesel hydrotreating operation, one or more of the following steps may be required to improve diesel product color at end of run:

•Reduce the endpoint of the feed (especially of any cracked stocks) to reduce feed PNA and nitrogen levels.

•Reduce the number of cracked stocks in the feed.

•Install a more active catalyst which can operate at lower reactor temperatures.

•Switch to NiMo type catalyst for better nitrogen conversion and PNA saturation.

•Increase H_2 partial pressure either by increasing total pressure if possible, increasing makeup gas H_2 purity, installing a recycle gas H_2S scrubber (if none exists), etc.

•Reduce LHSV (either by reducing throughput or adding catalyst volume) and lower reactor temperatures.

•Increase the H_2 / Oil ratio.

•Blanket the diesel storage tanks to eliminate exposure to air.

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