Question 22: What sets the endpoint limit for feed to an Ultra-Low Sulfur Diesel unit? Should 90%, 95%, 98% or Final Boiling Point be monitored and what is an acceptable tail for amount of feed greater than the cutpoint spec? Is the answer different for straight-run diesel vs coker diesel vs Light Cycle Oil feed components?

AMIT KELKAR (Shell Catalysts & Technologies)
There is limited boiling point shift from feed to product in a typical diesel hydrotreater. The boiling point shift correlates strongly with H2 consumption which is dependent on feed properties and unit conditions. In our experience, boiling point shift varies from 5 – 10 oF for mostly straight run feed to 30 oF plus for highly aromatic feeds such as LCO and LCGO. The ASTM D975 specification for Ultra Low Sulfur Diesel is a maximum D86 T90 of 338 oC (640 oF). In most units the feed cut point is set so that it meets the final product distillation specification. Raising the cutpoint worsens the cold flow properties particularly for paraffinic straight run streams. Cut point for straight run streams is set to ensure product meets the cold flow specification.
In addition to worsening cold flow properties, raising the cut point brings in streams with more refractory sulfur species. Substituted dibenzothiophene is a classic example of this type of molecule wherein the sulfur atom is sterically hindered by the alkyl groups resulting in very low reaction rate. These types of species are more common in cracked feeds such as LCO and LCGO. Increasing the cut point for such feeds is likely going to require higher delta WABT compared to a similar change for straight run feeds.
T90 or T95 is best suited for unit monitoring. FBPs tend to have a lot of variability compared to T90 and T95 and are unsuited for use as a controlled variable. Repeatability and Reproducibility of T90 or T95 is much better compared to FBP for D2887.

SERGIO ROBLEDO (Haldor Topsoe, Inc.)
Both 90% BP and FBP should be monitored in an Ultra Low Sulfur Diesel unit. ASTM D-975 establishes the maximum 90% BP at 640 °F, based on ASTM D-86 distillation method. Therefore, the feed component(s) 90% BP should be controlled, such that based on their volume percentage, the blended feed meets ASTM D-975 specification. A diesel hydrotreater is not ideal to correct 90% BP. An increase in WABT of roughly 50 °F is required to drop the 90% BP by only 5 °F, and this is mainly via thermal cracking.

It should be noted, that the use of one of Haldor Topsoe’s very selective dewaxing catalysts can shift the T90 significantly. This will enable the refiner to increase the endpoint of the feed while still meeting the T90 spec, resulting in more diesel barrels.

With respect to FBP, ASTM D-86 is a poor method to truly capture how big of a tail and as such, how much coke precursors are sent to the diesel hydrotreater. ASTM D-2887 (SimDist) is a much better method to understand how high the tail is to the hydrotreater. Typical off-set between both methods is usually 75 – 100 °F, but we have seen discrepancies as high as 600 °F in the most extreme cases. Needless to say, the amount of coke precursors, and as a result deactivation rate and cycle length were very different than expected from D-86 method. Therefore, before drawing harder from a specific stream,

it is recommended to analyze the stream via D-2887 to have a baseline sample to compare to.

As for what level is acceptable for the tail, it depends somewhat on hydrogen partial pressure. A higher-pressure unit will suffer less coking than a lower pressure unit. The higher amount of poly-aromatics present, the higher the propensity for coking. For each changing aromatic ring class, the effect can be an additional 10-25% increase in deactivation. The actual increase will depend on the hydrogen partial pressure and ring-class type.

MICHAEL PEDERSEN and VERNON MALLETT (Honeywell UOP)
Foremost, feedstock boiling range must be selected to permit satisfying product specifications such as cold flow properties, gravity and distillation limits. The most useful indicator of acceptable boiling range will depend on operating experience and the constraining specifications at each site. For example, there may be more flexibility defining feedstock if the controlling specification is ASTM D-86 T90 than if the limit is true boiling end point. Some boiling range reduction can be expected in a ULSD hydrotreater.

The more aromatic the feed and the higher the unit operating pressure, the more significant the impact. As indicated in the question, boiling range limits are dependent on feed type. Product cold flow properties often constrain maximum cut point for straight run streams. Particularly for cracked stocks, sulfur and nitrogen content as well as amount of polyaromatics compounds increase rapidly with boiling point. As an example, Light Cycle Oil polyaromatics content could increase from approximately 4 weight percent at a Final Boiling Point of 690°F, to 16 weight percent at a Final Boiling Point of 730°F. With increasing end point the complexity of sulfur compounds also increases, including more dibenzothiophenes. This will result in higher operating temperatures to achieve product ULSD. Hydrogen consumption will increase accordingly.

Processing Coker Diesel material in a diesel hydrotreating unit also brings processing complexity and severity. A mild hydrocracking operation is a possible option to allow processing higher distillation boiling range feeds. ULSD product quality can be achieved with minimal yield selectivity shift. There are several examples in which a straightforward revamp of a diesel hydrotreating unit enabled mild hydrocracking operation, as long as there is ample unit design pressure and hydrogen supply. A revamp does require attention to a few critical details.

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