Question 31: With heavy gas oil hydrotreating and mild hydrocracking units producing diesel product with 30 to 50 ppm sulfur, what options do you employ to recover maximum volume of ULSD? Are there other diesel quality concerns, and how are they resolved? How does the yield and quality change over the cycle?

PATRICK GRIPKA (Criterion Catalysts & Technologies)

We have many customer examples of FCCPT units and mild hydrocracking (MHC) units directly producing on-spec ULSD with Criterion catalyst systems. Many refiners who are making 30 to 50 ppm sulfur diesel from hydrotreating and/or mild hydrocracking unitsare able to blend this into the diesel pool and still have the whole pool meet the less than 15 ppm diesel sulfur specification. In these cases, there is typically overtreating in another hydroprocessing unit.

Assuming unit pressure and recycle gas, rates are maximized, in order to reduce the sulfur to the ULSD level, the immediate options a refinery has are feed rate, feed composition, and feed cutpoint. All are essentially managing the overall feed difficulty and processing requirement in the hydrotreater. Depending on refinery flexibility, it may be feasible to move a portion of the most difficult feed stream to another hydrotreating unit so the subsequent easier feed will produce a lower sulfur diesel. Another solution is to lower the feed endpoint and send the hardest to treat molecules to another hydroprocessing unit. However, these options are less than ideal as there are often economic penalties due to non-optimal operation across these multiple units. The Best Practice is to improve the catalyst technology in the heavy gas oil hydrotreater or mild hydrocracker and produce ULSD directly.

I have two examples that demonstrate how catalyst technology has been used to increase overall ULSD make within an FCCPT unit. In both examples, the refiner chose the option of reducing feed cutpoint in previous cycles to meet the desired diesel properties so on-spec ULSD was being produced. However, use of improved catalyst technology has allowed the cutpoint to be increased in subsequent cycles.

<u>Example 1: Potential to Significantly Increase the Endpoint and Increase the Amount of ULSD Make</u>

The graph below shows product sulfur level and the endpoint of the diesel product from an FCCPT unit. Two cycles from an FCCPT unit are represented, and the catalyst was upgraded to a CENTERA™ catalyst system in Cycle 2. Both cycles were consistently producing diesel in the 1-to 30 ppm range; however, the big difference is that the diesel T90 in Cycle 1 was limited to the 525 to 575°F range, which is a very light diesel (almost a kerosene), but the diesel T90 in Cycle 2 is in the 625 to 670°F range, which represents a 100°F increase in diesel T90. Feed qualities and operating conditions are similar between the two cycles. The improved catalyst performance has resulted in an overall increase in recoverable diesel. As noted above, one of the biggest levers to maximize cutpoint is proper catalyst selection.

Example 2: Potential to Continue Producing Higher Amounts of ULSD as the Cycle Progresses

The graph below shows percent diesel yield versus days onstream; the red dots represent the previous cycle; and the blue dots represent the subsequent cycle with an improved catalyst system. Here the FCCPT unit processes all the coker gas oil –heavy and light –in the refinery. The yield of ULSD removed in the fractionator is very important to the economics of the refinery. The improved CENTERA™ catalyst system resulted in a more stable ULSD yield profile as the previous cycles exhibited a drop-offin ULSD production at the end of the cycle due to the unit’s inability to maintain product sulfur at the higher endpoint. Over the cycle with the improved CENTERA™ catalyst system, the average yield of diesel was 5% higher, with an average 10°F higher diesel fraction T-95compared to the previous cycle.

In terms of diesel quality, the diesel produced from the FCCPT or MHC unit routinely meets U.S. specs. As shown below, the diesel cetane for this unit meets/exceeds U.S. specifications and was similar for both cycles and exhibited stable quality over the cycle.

DAVID VANNAUKER (Haldor Topsoe, Inc.)

Diesel sulfur has a profile with the sulfur concentration increasing as the boiling point increases. A simple option is to produce a wider-cut jet stream that can be used as a blend stock with ULSD. Another option is to change the next catalyst load to increase the HDS functionality, which has been proven to enable the full wide-cut ULSD. When units increase the EP, there is a potential for higher pour/cloud point. Employing dewaxing or isomerization catalysts can resolve this issue.

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