Question 19: With limited hydrogen availability for desulfurization of diesel, what criteria influence the optimization of hydrogen consumption between the FCC Pretreat and ULSD units? What catalytic options exist to achieve the desired balance of consumption?

Martin Gonzalez (BP)

Hydrogen supply and compression constraints are becoming more common for refineries in the US as more and more bitumen-based crude is brought in from Canada. These crudes are hydrogen-deficient and their processing commonly leads to a greater volume of coker products, which will also have high hydrogen uptake in a hydrotreater. For this reason, a refiner may be forced to sacrifice hydrogen uptake in FCC feed for the sake of producing ULSD, or vice versa, and refiners are increasingly looking for handles that will enable them to make this trade-off.

Where hydrogen supply in a refinery is constraining, H2 consumption in diesel and gas oil hydrotreaters can be manipulated by varying feed rate, feed composition, reactor temperature, and/or reactor pressure. Lowering pressure and temperature in a hydrotreater will generally raise product sulfur and reduce hydrogen consumption. In FCC pre-treat service, lowering reactor temperature and/or pressure to free up hydrogen will result in a lower yield of FCC naphtha, and such naphtha will have a higher sulfur content. In ULSD service, reducing hydrogen consumption will worsen product cetane and sulfur.

Thus, the key factor in deciding whether to utilize hydrogen for FCC pre-treat vs. ULSD relates to the economics of gasoline production in comparison to diesel. When a gasoline blend is constrained on octane or sulfur, FCC pretreating feed may be favored. Likewise, a cetane or sulfur constraint in a ULSD product may make it attractive to divert more hydrogen into diesel treating service. Finding the optimum balance usually requires a refinery linear program that is tuned for hydrogen consumption and sulfur removal. In high pressure units, NiMo catalysts will generally promote a higher hydrogen uptake, while CoMo can promote sulfur removal at a lower hydrogen uptake.

Tim Lewer (Shell)

The criteria are set by balancing the product specifications and positive economics from volume gain and/or FCC conversion with H2 availability. A minimum amount of H2 consumption is required to achieve the ULSD sulfur and Cetane specs and to maintain the FCC feedstock sulfur for low sulfur gasoline production. The volume gain by enhancing the hydrogenation activity of the ULSD catalyst system or improved product quality through dewaxing must be compared to the improvement in FCC conversion, reduction in LCO production, and reduced gasoline post treatment severity by enhancing the hydrogenation and hydro denitrification of the FCC Pretreat catalyst system or the addition of conversion through Mild hydrocracking.

In the ULSD unit, stacked bed catalyst loadings with CoMo and NiMo catalysts enable a tailoring of the performance and H2 consumption to meet the determined economic drivers. Selective placement of the NiMo catalyst is critical to meeting the optimized H2 consumption. The inclusion of Dewaxing catalyst may alter the stacked or sandwich loading to accommodate ULSD production with less hydrotreating catalyst while properly preparing the feed for dewaxing.

In the FCC Pretreat unit, stacked bed loading of CoMo and NiMo catalysts should be combined with reactor temperature profiles that promote the desired extent of hydrogenation. The addition of mild hydrocracking catalyst requires a shift to additional NiMo catalyst for increased HDN performance.

Kaspar Vogt (Albemarle)

The minimum hydrogen consumption is set by the mandatory ULSD specifications in diesel hydrotreaters and in FCC pretreat (FCC-PT) typically by the FCC naphtha sulfur. Any additional hydrogen can be added to the product and can be financially beneficial to the refinery. In diesel additional H2 can be used to process worse feeds and/or produce higher Cetane lower density product. In FCC-PT additional hydrogen can improve the feed to the FCC unit resulting in better yields, improved product properties and less FCC catalyst usage. Per refinery the optimum usage of H2 needs to be calculated.

Unsurprisingly, no single catalyst formulation is able to deliver optimum performance across the wide variety of feeds and process conditions used in ULSD and CFHT service. By necessity, a series of catalysts, each having its optimal application window, is able to deliver the best balance of superior activity and stable operation. Proper catalyst selection balances the objectives of the unit (desulfurization, denitrogenation, cetane uplift, aromatic saturation) with the capabilities of the unit (hydrogen partial pressure, hydrogen availability) to maintain stable performance throughout the cycle. NiMo vs. CoMo catalyst at the same product sulfur can consume around 10% more hydrogen. By applying multiple catalysts in STAX® configurations, the hydrogen consumption can be minimized while still capturing the activity benefit.

Greg Rosinski (ART)

For any given feed, hydrogen consumption is a function of hydrogen partial pressure, LHSV, H2/Oil and catalyst. For the most part, the first three variables are fixed for a given unit, since throughput reduction is not an economical choice. Thus, catalyst selection is one of the few constraints which refiners are willing consider.

CoMo catalysts have lower hydrogen consumption than NiMo catalysts due to lower aromatic saturation activity. At equivalent product sulfur, using all CoMo catalyst in the FCC Pretreater will lower the hydrogen consumption with a longer cycle in terms of HDS activity, but at the cost of lower conversion in the FCC and higher LCO yields. Using all NiMo catalyst in the FCC Pretreater will result in higher FCC gasoline yields and lower LCO yields due to higher PNA saturation, but a shorter cycle life in terms of HDS activity.

With regards to the ULSD units, if the unit is high pressure, using a NiMo catalyst will result in higher aromatic and PNA saturation. This may be beneficial if cetane upgrade is desired; however, there may be a diminishing return on hydrogen for the incremental cetane upgrade over a CoMo catalyst.

ART can help optimize both FCC Pretreater and ULSD performance based upon the refiners needs, including hydrogen consumption, cetane uplift and cold flow properties. ART provides the ApART and SmART staged catalyst systems for FCC Pretreat and ULSD applications, respectively. ART has helped many refiners manage hydrogen consumption in both units by using staged catalyst systems utilizing NiMo, CoMo and NiCoMo catalysts optimized to enhance HDS, HDN or HDPNA activity for a given feedstock. Furthermore, ART's relationship with Grace Davison can further enhance the unit optimization to include the FCC unit as well as the FCC pretreater and the ULSD unit. Utilizing the technical resources of both ART and Grace Davison, the refiner can gain a more comprehensive understanding of the interactions and dependence of these units on each other in terms of hydrogen consumption and product property enhancement.

Raj Patel (Haldor Topsoe, Inc.)

With a limited supply of hydrogen, the refiner will always look for ways to optimize the consumption in the different hydrotreating units. In this context "optimization" frequently means minimization, but the value-adding effect of hydrotreating through volume-swell, improved product properties and improved performance of downstream units (e.g. better conversion and product distribution in the FCC when the feed has been pre-treated) should also be taken into account. Generally, in all units there will be a minimum hydrogen consumption, given the constraint that the product must meet certain specifications. This hydrogen is mainly consumed by HDS and hydrodearomatization (HDA) reactions and to lesser degree by saturation of olefins, HDN reactions and hydrocracking. However, due to the above mentioned positive effects of hydrogen addition as well as unit configuration and feed properties, one will often have a certain operating window within which it is possible to reach production targets. Even so, the hydrogen consumption often decreases from SOR to EOR, and as product specifications must be met even at EOR there is typically a give-away at SOR. In other words, the hydrogen consumption is higher than actually required at SOR. Topsøe markets the Reverse Shift process to alleviate this problem. By this process hydrogen consumption is more or less constant throughout the cycle and thus a substantial saving at SOR is achieved.

The most important knobs that one can turn to change hydrogen consumption are unit pressure, feed properties, catalyst selection, product specifications and operating strategy. An overall economic evaluation of both the ULSD and the FCC complex should be made to closely determine optimal usage of hydrogen before these knobs are turned and a thorough understanding of consequences is needed to determine optimal configuration. A higher partial pressure of hydrogen will increase hydrogen consumption through higher aromatic saturation but also increase catalyst lifetime. Feed properties are usually fixed, but in some cases feed tailoring can significantly reduce hydrogen consumption without compromising overall economics. The catalyst selection is critical to achieving profitable operation, as considerable changes can be made from e.g. changing from CoMo to NiMo type catalysts. Generally, the CoMo type catalysts (such as TK-578 BRIMTM) use less hydrogen than NiMo type catalysts (such as TK-607 BRIMTM), but the feed reactivity (content of sterically hindered sulfur species and nitrogen inhibitors) may force the use of either CoMo or NiMo if the required HDS conversion must be met. The exact impact on hydrogen consumption for different catalyst, feedstock, process conditions and operating strategy requires detailed model of the chemical reactions occurring in the reactor. Both kinetic and equilibrium limitations must be properly described and Haldor Topsøe has developed models from fundamental knowledge of catalyst reactivity and reaction modeling that allow for optimizing the unit economy.

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