Question 10: What are refiners' experience with respect to unit availability, catalyst performance and product quality when co-processing "renewable" feedstocks in a ULSD unit? Is there a big variation in operability with different sources of renewable feedstocks?

Brian Moyse (Haldor Topsoe)

The co-processing of renewable feedstocks in a ULSD unit means introduction of feed components that are completely foreign to a diesel hydrotreater. These oxygenates will react quite readily with hydrogen to form normal paraffins in the diesel range but in doing so consume high amounts of hydrogen and cause high heat release. In a coprocessing mode these reactions will often occur in the topmost layers of active catalyst. This region will be subjected to low hydrogen partial pressures and high temperature and therefore be prone to increased dP build-up.

Adding to the problem is the existence of numerous contaminants in most ‘renewable’ feeds that will deposit on the grading catalyst layers. This has also been the experience of several refiners that have introduced even small amounts (roughly 5%) of renewable feeds. This actually limited the cycle length as the dP was continuing to increase in co- processing mode. The solution to these challenges are connected to both catalyst and process design. Topsoe has developed a series of biofuels catalysts that have been tailored to ensure gradual conversion of the bio-components and exhibit excellent stability by being able to tolerate higher levels of coke. In one instance, a skimming with subsequent installation of Topsoe tailored grading and biofuels catalysts has eliminated the high dP buildup rate and brought it down to normal “fossil”-operation levels.

Catalyst performance is also closely related to the chemistry of the oxygenate conversion reactions. These produce oxygen containing gases (CO,CO2, and H2O) that may severely inhibit the HDS and HDN activity of certain catalyst types. Even ppm-levels of CO thus decrease the HDS activity of CoMo catalysts by several degrees F, whilst NiMo catalysts are almost unaffected. Gas formation and hydrogen consumption is also related to whether reactions occur by a hydrodeoxygenation or a decarboxylation pathway. The relative usage of these two pathways depends on catalyst type and process conditions.

The main influence on product properties stems from the poor cold flow properties of the normal paraffins produced from the ‘renewable feed’. This will result in higher cloud and pour unless a dewaxing step is introduced. Topsoe markets TK-928 and TK-932, which are sulfidic catalysts that are installed in the bottom of the reactor, in order to improve the cold flow properties with minimum yield loss.

The major component of most tallow and renewable oils is almost always of the triclyeride structure, but may vary in chain length and degree of unsaturation. These differences have implications for product properties and hydrogen consumption.However, it is very important to pay attention to the amount and type of contaminants in these alternative feedstocks because they may severely limit cycle length due to

plugging and poisoning of the grading and active catalyst. An effective scheme to remove contaminants is by proper grading design and/or by feed pretreatment to ensure stable operation.

Topsoe has spent a lot of effort in understanding the reaction chemistry and developing catalyst and process technology to handle the challenges of co-processing. Based on this knowledge, the introduction of renewable feeds can in most cases be carried out with no cycle length penalty. This is provided that the proper changes in catalyst loading are made and a moderate unit revamp is carried out. This is especially true for cases where large amounts of coprocessing must be handled. Topsoe has been able to validate the performance of our biofuels catalysts and process design features in industrial operations. We continue to learn from a growing number of references using Topsoe renewable fuels catalyst and technology.

Vern Mallett (UOP)

UOP does not have any direct commercial experience with UOP Licensees co-processing vegetable oils in hydroprocessing units. We have done pilot plant studies co-processing various amounts of vegetable oils with diesel and found that there is significant suppression of HDS reaction rates due to the presence of CO and H2O.

There are several other issues to keep in mind when considering the co-processing of “renewable” feedstocks in an ULSD unit:

1. The olefin and oxygen contents of these feeds are relatively high. This results in increased hydrogen consumption and higher heat release in the reactor.

2. These feeds typically contain free fatty acids, so plant metallurgy must be evaluated to see if it is appropriate.

3. Simple hydrotreating of “renewable” feeds will typically result in an increase in the diesel pour point and cloud point.

4. “Renewable” feed stocks may contain impurities not normally seen in petroleum feed stocks, including phosphorous, sodium, potassium, calcium, magnesium and other impurities. These impurities vary greatly depending on the feedstock source and pretreatment the feed has received. These impurities can have an adverse impact on the hydrotreating catalyst life.

This question was previously addressed at the 2009 NPRA Question and Answer session, question number 70. UOP provided along with other panelists detailed answers to this question.

Praveen Gunaseelan (Vantage Point Energy Consulting)

The reason for co-processing renewable feedstocks such as vegetable and animal fats and oils in refinery ULSD units is to produce diesel that contains a portion of biodiesel, in contrast to blending biodiesel in a subsequent step. Co-processing can have significant impacts on ULSD operation, as outlined below:

· **Unit availability:**

· Can be impacted if the feed poisons or impairs the activity of the catalyst

· Catalyst:

· Can be rapidly fouled or deactivated

· Produced water can destabilize the catalyst

· Product quality:

· Normal paraffins produced from renewable feeds can impair cold flow properties. An isomerization reactor may be required downstream of the ULSD unit to address this.

· Off-spec product can be generated (because the renewable feed can introduce competing reactions that interfere with the traditional desulfurization and denitrification reactions)

· **Impact of feedstock type:**

· Can have a variable effect on the life of catalyst, volume of side products, etc.

· Additional pre-processing or post-processing may be required depending on the feedstock contaminants or side products.

Brian Watkins (ART)

ART has conducted testing on various petroleum blends containing between 10-80% renewable sources of feedstock. The catalysts most active for this type of processing are AT580 and NDXi, both premium high activity NiMo catalysts used widely in ULSD and hydrocracking pretreat service. The data show that simple bio-based oils such as soybean, rapeseed & palm oils, when co-processed in a diesel feedstock require essentially the same temperature for 10 ppm product sulfur as the diesel feed alone.Comparing the feeds at ultra low sulfur levels suggests that the co-processing of the renewable oils has a small effect on the performance of the hydrotreater with the variability being about 10°F for <10 ppm product sulfur.

Due to the nature of the renewable sources, a boost in the product cetane index is also observed due to the increase in n-paraffin content in the diesel product. These n- paraffin’s, however, raise concerns about the diesel product cloud point. Normal paraffin’s have a significantly higher cloud point than other hydrocarbons of similar carbon number. Since hydrotreating converts the fatty acid chains into long chained n- paraffin’s, the cloud point of the hydrotreated product will increase compared to the product using a SR base feed only. At lower blending concentrations the effect is minimal, but it needs to be considered depending on the target market for the product.

Based on these results, the use of ART’s high activity hydroprocessing catalysts can enable refiners to co-process renewable oils through conventional refining equipment. Co-processing can be incorporated into a refiner’s operating strategy with minimal detriment to catalyst stability or yields, but the effect on an individual operation willdepend on the base feed and conditions requiring ART to evaluate the optwho wish to consider incorporating co-processing biofeeds into their operation, but want to understand the

optimum configuration to maximize their profitability.

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