Question 26: What catalyst and metallurgy design considerations are important when evaluating the co-processing of highly acidic renewable distillates? What can be done to mitigate carbon monoxide formation?

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Acidity of renewable distillates can be intrinsic of the material (free acids of the vegetable oil) or generated during its conversion in the hydrotreating unit. Typically, free acids in vegetable oil amount to about 5%. This means that crude vegetable oil has a TAN number around 7, which requires special metallurgy for the pipelines to the feed drum. Once the vegetable oil (VO) is mixed with oil, acidity is reduced by dilution. For a typical co-processing operation, where VO intake ranges around 5% to 10%, standard metallurgy is, therefore, suitable for the connection between feed drum and reactor. At increasing intakes (i.e., above 10%), special metallurgy would be required.

An alternative is to directly resort to refined vegetable oil. In this case, VO is acid-free; therefore, no corrosion issues are expected in any part of the feed section. This solution also prevents fouling problems associated to VO impurities, such as sterols and phospholipids.

Acids are also formed during the conversion of VO to hydrocarbons. Indeed, triglycerides decompose to carboxylic acids (which then further react to yield paraffins). Since the triglycerides decomposition proceeds gradually along the reactor and the produced acids are readily converted, no local spots with acidic material are expected. Standard metallurgy of hydrotreating units is, therefore, suitable for these operations, except for those units with very poor metallurgy (often with very low design pressure).

As mentioned above, decomposition of triglycerides leads to carboxylic acid formation which, in turn, yields paraffins. This latter step can occur through different mechanisms: hydrodeoxygenation (HDO, yielding paraffins and water), decarboxylation (DCX, yielding paraffins and CO_2) and decarbonylation (DCN, yielding paraffins, CO and water). The latter two mechanisms are linked by the Water Gas Shift reaction. The straightforward way to decrease CO is to force the reaction to proceed through HDO, favored by high pressure and low temperature. Catalyst selection is important since the system requires high activity both for HDS (in order to reduce the operating temperature to reach the S target) and for hydrogenation (to enhance HDO). Another possibility is to catalyze the hydrogenation of CO to methane. This reaction, however, being highly exothermic, can cause local high ΔT, resulting in possible formation of hot spots. Additionally, the methanation reaction has high hydrogen consumption and, as such, is an inefficient way to use hydrogen. This should also be taken into account is considering downstream methanation, for example, in the high-pressure separator.

In general, CO generation from bio-feed co-processing can be managed. Driving the reaction of renewable material through DCN leads to a significant reduction in H_2 consumption compared to alternatives. Produced CO accumulates in the recycle gas and leads to strong inhibition of HDS reactions, but this effect can be kept under control with proper catalyst selection. Depending on the configuration of the refinery hydrogen network, CO containing gas can be either purified (for example, by PSA) or directed to other units where its inhibition effect is less severe.

Overall, operating strategy and catalyst selection for the co-processing of renewable material should be analyzed in great detail to find the optimal reaction path that provides the best compromise between H2 consumption, detrimental effects of CO and product yield structure.

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