Predicting hydrotreater performance while co-processing vegetable oil

Catalyst performance prediction model based on test data assesses the impact of co-processing renewable feedstocks for optimal hydrotreater operations

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Many refineries rely on pilot plant test data for selecting catalysts, as this provides direct insight into their performance, facilitating selection of the best catalyst for increasing margins. Against this backdrop, processing renewable feedstocks can be a complex process due to the wide range and quality of feedstocks available. Therefore, Avantium developed a 16-reactor unit that can effectively test the impact of co-processing vegetable oil on the overall performance of catalysts. The selection of the right catalyst is crucial, given the diversity of feedstocks.

In parallel, Catalyst Intelligence developed a catalyst performance prediction model (HydroScope) that translates pilot plant test data into commercial performance, enabling assessment of the impact of catalyst quality on overall profitability. Avantium partnered with Catalyst Intelligence to use its performance prediction model to optimise hydrotreating unit performance employing pilot plant test data and to enhance its catalyst testing services.

The pilot plant test allows for the calculation of hydrodesulphurisation (HDS) activity, product selectivity, and inhibition factors. The HydroScope model allows for assessing the impact of co-processing renewable feedstocks on cycle length, hydrogen consumption, and product yields. It is therefore recommended that test results be further simulated in this hydroprocessing model. By doing so, an assessment of the most optimal unit conditions and their impact on cycle length can be made.

While processing soybean oil, a portion of the oil is converted through the decarbonylation route, resulting in the formation of carbon monoxide (CO), which inhibits the HDS reaction. The CO can be removed by purging recycle gas, but this comes at the cost of valuable hydrogen. The impact of purging on cycle length can be calculated for each catalyst system, resulting in the selection of the most economical solution.

High-throughput catalyst testing

Accurate catalyst evaluation is important in catalyst selection, and increased product yields, energy efficiency, and overall product quality. High-throughput catalyst testing and small-scale reactors offer several advantages compared to larger reactor systems.[1] Using reactors of smaller scale to evaluate catalysts with renewable feedstocks presents a clear advantage; smaller volumes reduce the amount of feed required, avoiding the typical issues associated with obtaining large quantities such as handling, shipping, and storage (also for longer-term availability of reference feed material). Overall, small-scale parallel reactor systems like

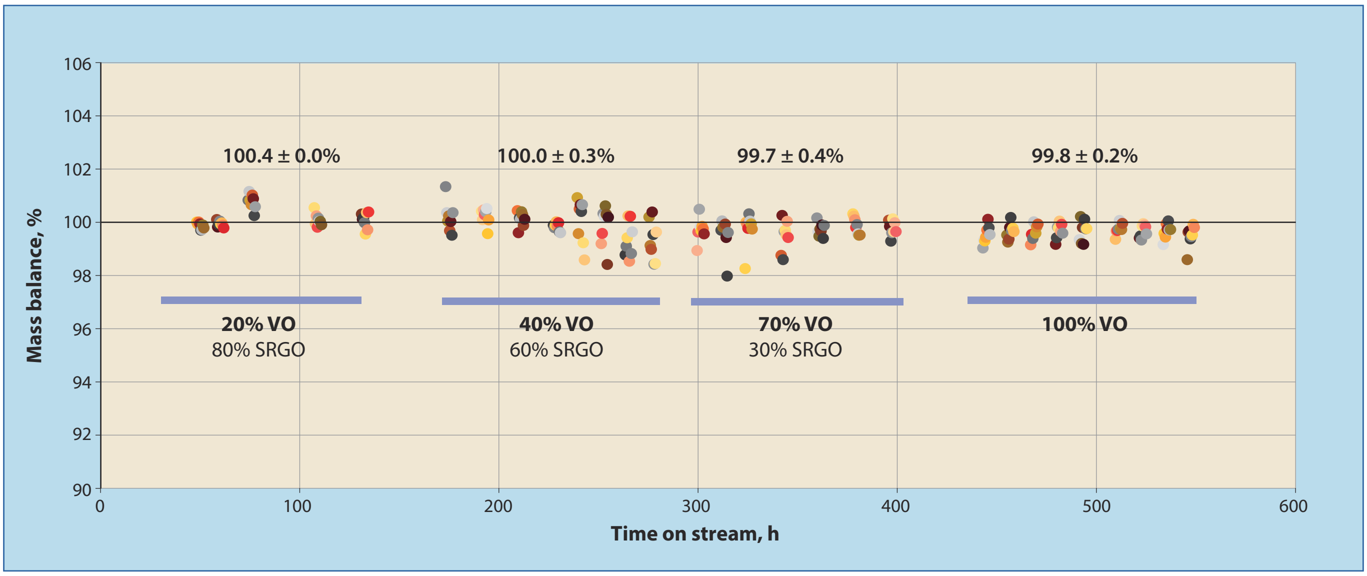

Figure 1 Mass balance for all feedstocks tested (colours varied by reactor) including water in gas measured in online GC

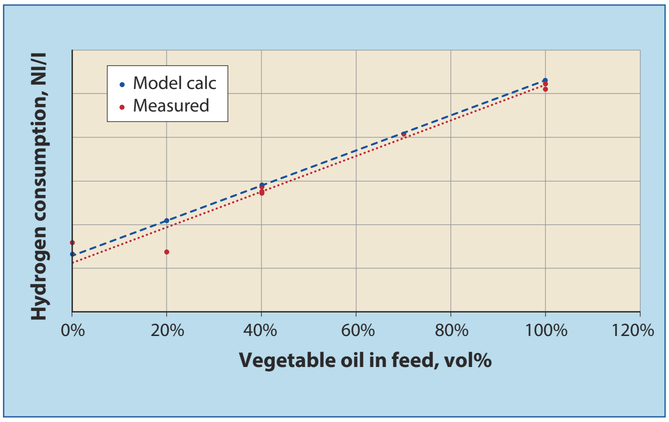

Figure 2 Total H_2 consumption

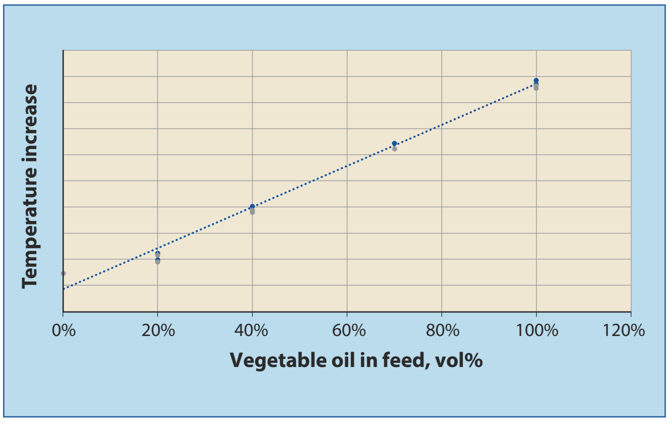

Figure 3 Expected exotherm

the unit used for this test[2] are more cost-effective than large-scale reactors.

Avantium performed a test with 0-100% soybean oil, achieving close to 100% mass balance without having pressure drop issues (see **Figure 1**). The results were published,[2] the main conclusion being that the Flowrence 16-microreactor test unit proved reliable and consistent for predicting start-of-run performance, simulating the impact of co-processing renewable feedstocks on cycle length, hydrogen consumption and product yields, and predicting the impact in the commercial unit.

Vegetable oils decompose according to various reaction routes, such as hydrodeoxygenation, decarboxylation, and decarbonylation, producing water, CO_2 and CO, respectively:

Hydrodeoxygenation:
$C_3H_5(C_{17}H_{33}COO)_3 + 15\ H_2 \rightarrow C_3H_8 + 6\ H_2O + 3\ C_{18}H_{38}$

Decarboxylation:
$C_3H_5(C_{17}H_{33}COO)_3 + 6\ H_2 \rightarrow C_3H_8 + 3\ CO_2 + 3\ C_{17}H_{36}$

Decarbonylation:
$C_3H_5(C_{17}H_{33}COO)_3 + 9\ H_2 \rightarrow C_3H_8 + 3\ CO + 3\ H_2O + 3\ C_{17}H_{36}$

Using the product yields from the test, the importance of each reaction route can be calculated, allowing the refiner to make a good assessment of the yields originating from fossil feed and vegetable oil.

H_2S partial pressure affects the degree of hydrodeoxygenation (HDO) vs decarboxylation.[3] CO is known to inhibit desulphurisation activity.[4] A significantly higher temperature is usually required to achieve the same HDS performance, reducing cycle length. CO does not dissolve in oil products and is mostly removed by purging some recycle gas. Increasing the gas purging can lower the CO partial pressure, but this inevitably comes with a cost. Evaluating the effects of purge gas rates and cycle duration can assist the refiner in optimising the unit with minimal expenses.

Catalyst suppliers have developed catalysts with reduced susceptibility to inhibition. Several catalyst characteristics, such as metal composition, affect the sensitivity to CO and the reaction mechanisms. According to Bezergianni,[5] the HDS effectiveness of the NiMo catalyst remains unaffected by the addition of waste cooking oil, while the CoMo catalyst is significantly impacted. This can pose a problem for low-pressure units that require the most active and stable performance of CoMo catalysts. Ni is said to exclusively promote the decarboxylation of fatty acids, while Mo promotes HDO.[6] HDO is preferred over decarboxylation as the yields are higher and less CO is formed, thereby reducing the need for purging gas. Catalyst suppliers have developed various catalyst systems to provide the best catalyst performance.

Refiners should conduct tests on different catalyst systems to determine the impact on unit operation and profitability. However, this approach is not straightforward as the impact of conditions on CO formation and purge gas rates must be assessed, which varies for each catalyst system due to its sensitivity to CO being dependent on catalyst quality. The HydroScope prediction model translates pilot plant test data into commercial performance for all hydrotreating applications, including optimising units to process vegetable oil. Proper assessment of the optimal catalyst system requires quantifying CO formation and its effect on catalyst inhibition and gas purge.

Simulation of pilot plant test results

The soybean oil test was conducted at various temperatures, sufficiently high to ensure full conversion of the soybean oil and enable production with sulphur below 10 ppm (<10 ppm S). To avoid H_2 starvation, the H_2/oil was increased from 400 to 1,400 Nl/l, ensuring that H_2 consumption remained below 25% of the H_2 supply. The H_2 consumption measured closely matched the expected value (see **Figure 2**). Converting vegetable oils generates a significant amount of heat, and based on the reactions that occur, the resulting exotherm can be calculated as depicted in **Figure 3**. At levels of 20% vegetable oil or higher, the exotherm exceeds 100°C, making it unrealistic to process 40% or more vegetable oil without special temperature control measures.

Increasing the H_2/oil did not result in a significant increase in CO partial pressure during the test, and the HDS performance was hardly affected by the presence of soybean oil in the feed. The percentage of HDO vs decarboxylation was calculated using the CO_2, CO, and water yields. Based on these data, product yields can be calculated, including

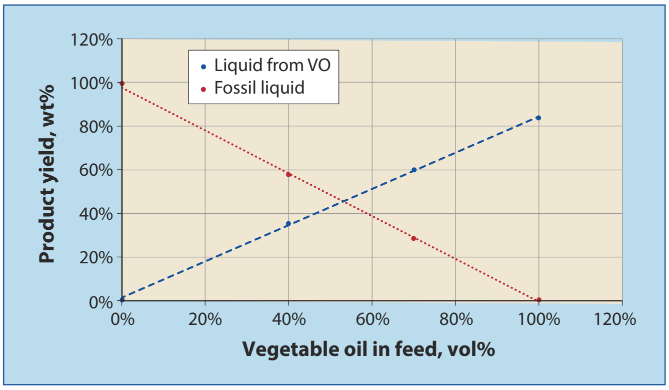

Figure 4 Product yields (liquid from VO and fossil liquid)

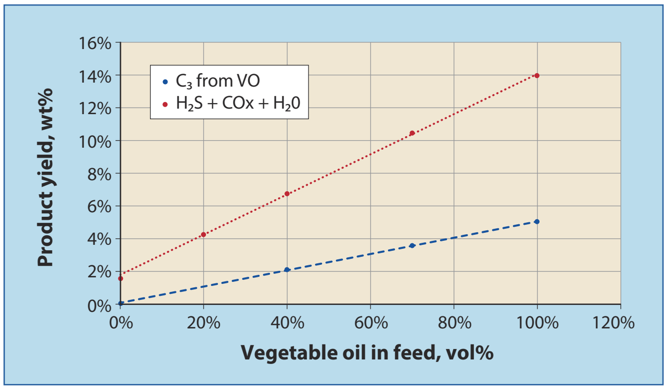

Figure 5 Product yields (C_3 from VO and $H_2S + COx + H_2O$)

those originating from vegetable oil, as illustrated in **Figures 4** and **5. Figure 6** indicates that the predicted percentage of HDO calculated with the model closely matched the experimental results.

By calibrating the model, commercial performance can be predicted, which has been done for the case with the 20% soybean oil.

Case study with 20% soybean oil

Based on the properties shown in **Table 1**, 100% straight-run gas oil (SRGO) is considered the base case. Given the quality of the SRGO and the test conditions selected, we anticipate a cycle length of at least four years can be obtained.

For predicting the performance of 20% soybean oil, the catalyst activities from the test were taken and a catalyst deactivation rate, assuming a four-year cycle length for the base case. Production of ULSD with 8 ppm S was simulated. For the 20% soybean oil case, we estimated the start-of-run (SOR) weighted average bed temperature (SOR WABT), exotherm and end-of-run (EOR) conditions. Additionally, we calculated the percentage HDO, which was found to be higher than in the test, as shown in **Figure 6**. This is related to the fact that commercial units are adiabatic and operate at a lower reactor inlet temperature, the temperature at which the soybean oil is converted.

The estimated cycle length for the 20% soybean oil test conditions appeared longer than the base case. This is because the 20% soybean oil blended feed sulphur content is lower, and the CO formed creates a low CO partial pressure because of the increased H_2/oil ratio. However, we expect the CO partial pressure in commercial units to be much higher because a significant part of the CO formed will be recycled. A longer cycle length is only achievable when all the treat gas going to the hydrotreater is fresh make-up gas without CO. In almost all cases, the treat gas consists, for a major part, of recycle gas containing some CO. The CO in treat gas needs to be controlled by purging some of the recycle gas. **Figure 6** shows that a higher purge gas rate results in a lower CO in treat gas, reducing the required operating temperature and increasing cycle length. Still, the hydrogen loss comes at a cost. Consequently, the question must be raised: "What is the most optimal purge gas rate?".

Different feedstock properties

Feed type	SRGO	Soybean oil	20% blend
Density @ 15°C	0.8569	0.9255	0.8716
S, ppm	14,848		11,003
N, ppm	267		213
SimDist, °C			
5%	221	553	229
95%	403	614	606

Table 1 Comparing performance of different feedstocks

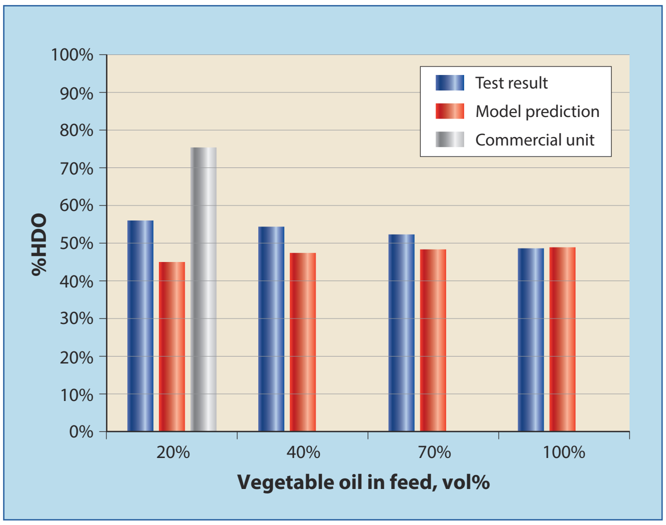

Figure 6 %HDO vs vol% soybean oil in feed

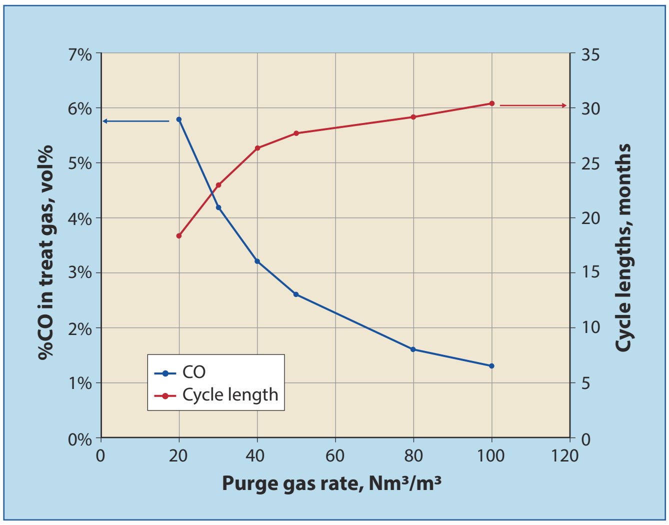

Figure 7 Impact purge rate on CO in treat gas and cycle length (20% soybean)

For the 20% soybean case, the correlation between purge gas and cycle length was estimated. Simulating the effect of purge rate (also impacting clean make-up gas rate) on the percentage of CO (%CO) in the treat gas and cycle length reveals that, for this particular operation, the cycle length substantially increases up to a purge gas rate of 40 Nm^3/m^3, as shown in **Figure 7**.

Conclusions

Co-processing vegetable oils in commercial units results in high reactor exotherms and reduced HDS activity. The extent to which this happens depends on the performance of the installed catalyst, especially with respect to CO formation and CO inhibition. Therefore, it makes sense to test the various catalyst systems side by side to measure the various activities, selectivities, and CO inhibition factors prior to choosing a catalyst for this service. The impact of co-processing (vegetable oils) on cycle length in commercial units can be calculated, and the costs of purge gas can be considered. In turn, this economic information can be used to select the best catalyst for the commercial hydrotreater unit.

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References

1 Ortega C, *Can. J. of Chem. Eng.*, 2021, 99, 1288-1306.

2 Vilela T, Quickly screen catalysts for hydrotreating of vegetable oil using high-throughput micro-pilot plants, *Hydrocarbon Processing*, May 2022.

3 Coumans, A E, Catalytic hydrodeoxygenation of biomass to sustainable fuels,nhttps://pure.tue.nl/ws/files/67124689/20170601_Coumans.pdf

4 Bezergianni S, Dagonikou V, Sklari S, The suspending role of H_2O and CO on catalytic hydrotreatment of gasoil: Myth or reality? *Fuel Processing Technology*, 144, Apr 2016, 20-26.

5 Bezergianni S, Effectiveness of CoMo and NiMo catalysts on co-hydroprocessing of heavy atmospheric gas oil-waste cooking oil mixtures, *Fuel*, Jun 2014, 125, 129-136.

6 Douvartzides S L, Green Diesel: Biomass Feedstocks, Production Technologies, Catalytic Research, Fuel Properties and Performance in Compression Ignition Internal Combustion Engines, https://res.mdpi.com/d_attachment/energies/energies-12-00809/article_deploy/energies-12-00809.pdf

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