Unlocking the Potential of Animal and Vegetable Oils for Renewable Fuels via Hydrotreating

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Highlights

- The bimetallic catalyst outperforms the monometallic one in HDO activity on renewable feedstocks.
- The presence of species as phosphorus and nitrogen reduces the HDO activity.
- The acidity in low-acid feedstocks as vegetable oils increases with oxygen conversion.

1. Introduction

Climate neutrality in transportation sectors necessitates large quantities of renewable fuels, especially for energy-intensive industries and long-distance transportation. As a readily available raw material, biomass can be utilized for fuel production and established technologies, such as hydrotreating of vegetable and animal oils, have the capability to convert biomass into fuel. The demand for biofuels has been consistently rising over the years, with a total production of 171 million m^3/year in 2022 [1], driven by new renewable fuel policies. While nowadays the 90% of biofuels are still produced from first-generation feedstocks (vegetable oils), the remaining 10% comes from second-generation feedstocks (used cooking oil, animal fats, distillers corn oil and crude tall oil) with an expected growth in the foreseeable future [2]. However, a significant variation exists in the physicochemical properties (fatty acid composition, free fatty acid content, nitrogen concentration and contaminants) when comparing waste oils and fats to virgin oils and even within the same category. These properties significantly influence the hydrotreating process, which involves the removal of heteroatoms (S, N, O) and the saturation of olefins and aromatics. It is evident that the selection and development of hydrotreating catalysts capable of both hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN), is crucial for these new feedstocks and the key to optimize the selectivity and yields of the product. Topsoe A/S has been advancing and refining the HydroFlex™ technology and hydrotreating catalysts since 2004, enabling the conversion of a wide range of feedstocks into drop-in renewable diesel (RD) and synthetic aviation fuel (SAF).

2. Methods

In this study, the aim was to compare the HDO/HDN activity and selectivity of two hydrotreating catalysts on real feedstocks with diverse properties at different experimental conditions. Experiments were carried out in Topsoe's hydrotreating pilot plant facilities and conducted in a once-through, fixed-bed, high-pressure setup, loaded with either TK-MM (monometallic) or TK-BM (bimetallic) catalyst, specifically designed and commercially available for hydrotreatment of renewable feedstocks. The temperature was varied in a 120°C range, the pressure applied was between 25 and 75 barg and LHSV between 0.5 and 1.75 h^{-1}. At each condition, gas and liquid samples were drawn and analyzed after reaching line-out and utilized to close mass balance calculations together with oxygen conversion (from D5266 modified for oxygen analysis) and selectivity towards HDO/DCX route. The feed and liquid products were also additionally analyzed to determine properties such as fatty acid distribution, simulated distillation, density and acid number.

3. Results and discussion

This study shows a higher HDO activity with soybean oil for TK-BM compared to the same feedstock tested with TK-MM (Figure 1), as the incorporation of the second metal enhances the triglycerides reactivity towards alkanes formation [3]. TK-BM shows also an improved oxygen removal with distillers corn oil compared to TK-MM, even though the higher fatty acid content of the feedstock (acid value=32 mgKOH/g), phosphorous (7.3 wt ppm) and nitrogen (84 wt ppm) might decrease the overall hydrotreating reactivity. A separate test with soybean oil doped with model FFA has proven that the effect of FFA in the feedstocks is negligible and the penalty in HDO activity could be attributed to phosphorus and nitrogen species.

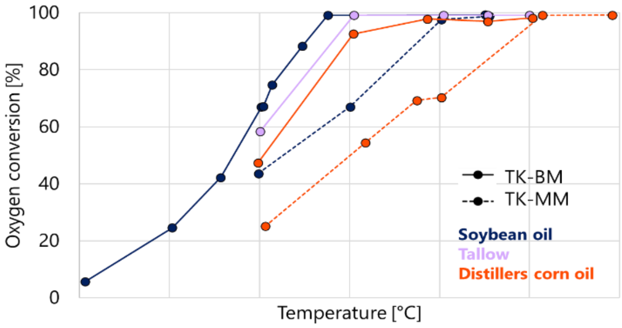

Figure 1. Oxygen conversion towards temperature for TK-MM and TK-BM tested with different feedstocks.

The presence of fatty acids in the feedstock or reaction intermediates is also a critical aspect in the upscaling of the hydroprocessing technology as it strongly affects both process design and material selection. The utilization of low-acid feedstocks, such as vegetable oils, might appear as the safest and cheapest option as both the feedstock and hydrotreated vegetable oil (HVO) have an acid number <0.1 mgKOH/g. However, results in Figure 2 show that the acidity (TAN) increases along with the oxygen conversion as an indication of the reaction mechanism. In the HDO pathway, the triglycerides are converted into saturated triglycerides, consequently into free fatty acids (FFA) and alkanes as main product.

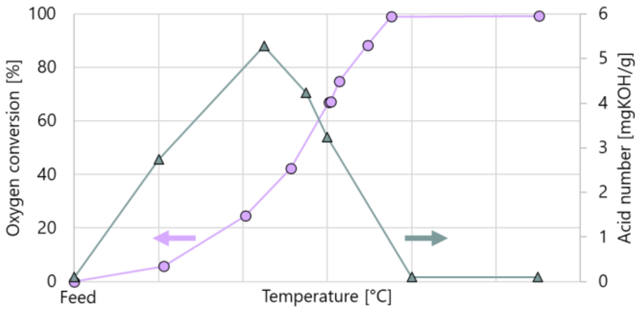

Figure 2. Oxygen conversion (left) and acid number (right) towards temperature on TK-BM on soybean oil.

These reaction steps can be retrieved from Figure 2: the TAN profile shows a peak at an intermediate temperature where the oxygen conversion is ~ 30% and by decreasing the temperature also the oxygen conversion decreases as well as the TAN number. As the temperature increases, the oxygen conversion increases, i.e. the triglycerides are converted into FFA, while the alkane formation is the limiting step and thus TAN is still >0. At complete oxygen conversion (higher temperatures) triglycerides are converted into FFA, which in turn are converted into alkanes giving a TAN=0. This indicates that within refinery sections where partial oxygen conversion ranges between 5-90%, the acidity exerts a significant impact on both the design and efficient functioning of the unit.

4. Conclusions

The study demonstrates that the choice of catalyst significantly impacts HDO activity with different feedstocks. Despite the presence of fatty acids and other impurities, improved oxygen removal is achievable. The acidity of the feedstock, which increases with oxygen conversion, plays a crucial role in the design and operation of the hydroprocessing unit.

References

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Keywords
hydrotreating; renewables; hydrodeoxygenation; hydrodenitrogenation