Catalytic hydrodeoxygenation of Bio-Oils: evaluation of operating conditions in a batch reactor and in a continuous trickle-bed reactor

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Objectives and novelty

Fast pyrolysis of lignocellulosic biomass is a promising route for producing renewable liquid intermediates. However, raw bio-oils contain large amounts of oxygenated compounds and water, which results in low heating value, high acidity and viscosity, poor stability and limited miscibility with conventional fuels. Catalytic hydrodeoxygenation (HDO) is therefore a key upgrading step to obtain more stable liquid fuels and/or valuable chemical intermediates.

Conventional HDO catalysts based on noble metals or sulfided transition metals still present important drawbacks, such as high cost, sulfur contamination of the products or deactivation under severe hydroprocessing conditions. In this context, transition-metal carbides, especially molybdenum carbide supported on carbon nanofibers (Mo_2C/NFC), represent an attractive sulfur-free alternative because of their noble-metal-like catalytic properties, lower cost and high stability.

The main objective of this PhD thesis was to evaluate the performance of a Mo_2C/NFC catalyst in the HDO of lignocellulosic bio-oils, moving from batch experiments to a continuous trickle-bed reactor. The work builds on previous studies with model compounds and extends the approach to real biomass-derived feeds, addressing process optimization, catalyst stability and operation under more realistic continuous conditions.

Results

IThe first part of the thesis focused on the HDO of a lignocellulosic bio-oil in a batch reactor. Temperature, initial H_2 pressure, reaction time and catalyst-to-bio-oil ratio strongly affected both the conversion of the feed and the product distribution into upgraded bio-oil, aqueous phase, gas and solid residue. The upgraded liquid was mainly composed of phenols, cyclic ketones, carboxylic acids, esters and aromatic compounds. Under optimized conditions (350 °C, 40 bar H_2, 0.19 g catalyst per g bio-oil and 1 h), 65% of the organic fraction was converted into a liquid product with a higher heating value of 30 MJ kg^{-1}, approximately twice that of the original feed, with a deoxygenation degree of 70% and an energy efficiency of 62%. Milder conditions (250 °C, 20 bar H_2 and 0.14 g catalyst per g bio-oil for 0.5 h) favored the production of a phenol-rich liquid fraction.

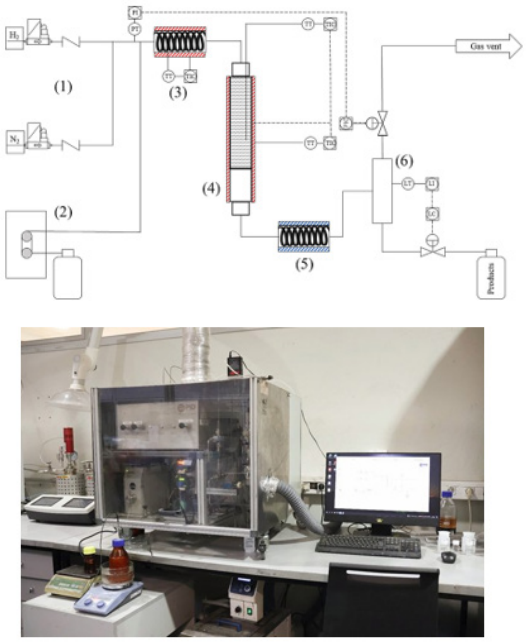

Figure 1. Schematic representation and laboratory set-up of the continuous trickle-bed reactor used for HDO experiments.

In the second part, guaiacol was used as a representative model compound for lignin-derived phenolics in the continuous reactor shown in Figure 1. The effect of H_2 pressure, temperature and weight hourly space velocity on benzene production was evaluated. At 75 bar H_2 and 350 °C, guaiacol conversion reached 90-98%, with benzene/cyclohexane contents in the liquid product as high as 81%. Reducing the space velocity from 10 to 4 g_{org} $gcat^{-1}$ h^{-1} improved deoxygenation and catalytic stability. A 30 h stability test showed stable conversion and no significant catalyst deactivation, while post-reaction characterization confirmed the preservation of the carbide phase.

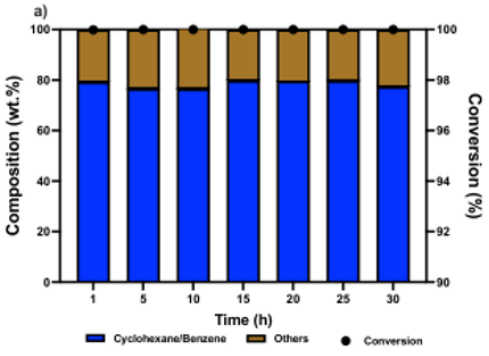

Figure 2. Stability tests in guaiacol HDO at 350 °C, 75 bar H_2 and 4 $gorg \cdot g^{-1} \cdot cat \cdot h^{-1}$.

Finally, the continuous reactor was applied to the HDO of a real lignin-derived bio-oil fraction. When methanol was used as solvent and hydrogen donor, excessively high temperatures promoted gasification, whereas lower temperatures led to insufficient activity and selectivity. Intermediate conditions, particularly 400 °C, favored the formation of phenols and alkanes and improved the energy properties of the upgraded liquid. Lower space velocities enhanced deoxygenation due to the longer contact time between feed and catalyst. Among methanol, ethanol and propanol, propanol was the most effective hydrogen donor, decreasing the oxygen content and promoting the formation of phenolic and cyclic compounds. Under the selected conditions (propanol, 400 °C and 4 mL $gcat^{-1}$ h^{-1}), Mo_2C/NFC exhibited stable performance during 10 h of continuous operation.

Conclusions

This thesis demonstrates that molybdenum carbide supported on carbon nanofibers is an efficient, stable and sulfur-free catalyst for the hydrodeoxygenation of biomass-derived bio-oils. In batch operation, the catalyst enabled the conversion of lignocellulosic bio-oil into upgraded liquids with higher heating value and lower oxygen content. In continuous operation, it showed high activity and stability for guaiacol HDO, with remarkable selectivity towards deoxygenated products and no significant deactivation during long-term experiments.

The use of real bio-oil feeds in a continuous trickle-bed reactor represents an important step towards more realistic process conditions. The results highlight the importance of controlling temperature, space velocity and hydrogen-donor solvent to balance deoxygenation, liquid yield and selectivity. Overall, Mo_2C/NFC is validated as a promising catalytic system for producing renewable fuels and value-added chemicals from lignocellulosic bio-oils.

References

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