

Transport fuels by H₂-free catalytic hydrodeoxygenation of waste cooking oil under hydrothermal conditions

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Highlights

- H₂-free catalytic hydrodeoxygenation of waste cooking oil
- Up to 42% waste cooking oil conversion using Ni/CNF catalyst under mild conditions
- High selectivities of 66-99% to diesel-range hydrocarbons

1. Introduction

Liquid biofuels are a promising alternative to reduce the dependence on fossil fuels and environmental impact [1]. However, they require an upgrading treatment to improve their low-quality physicochemical properties due to high oxygen content [2]. Catalytic hydrodeoxygenation (HDO) is a well-known method for removing the oxygen atoms from liquid fuels in the form of water, CO₂ and CO. It conventionally involves an H₂ atmosphere at 20-300 bar of pressure and 250-500 °C of temperature [3]. One of the disadvantages associated with the process is the high consumption of H₂. For this reason, H₂ donors have emerged as proposals to supply partially or fully the H₂ required in the HDO reaction. Among the substances reported are alcohols, formic acid and water. Water is a low-cost, available and non-toxic solvent. Moreover, in conditions near or above its critical point (374 °C and 220 bar), its properties change and become a better environment for acid-base reactions, in which, its dissociation into its ions H⁺ and OH⁻ can occur. In a previous work [4], the use of water as H₂ donor in the HDO of guaiacol for platform chemicals production (cresol, catechol and phenol) was analyzed. However, the challenges of this process are ascribed to the development of a catalyst able to present and maintain catalytic activity in hydrothermal conditions for long periods. In the present work, a preliminary study of the H₂-free HDO of waste cooking oil using water as H₂ donor in hydrothermal treatment conditions and using different carbon nanofibers-supported catalysts is presented.

2. Methods

The catalysts (Pd/CNF, Ru/CNF, Mo₂C/CNF and Ni/CNF) were prepared by incipient wetness impregnation of the CNF with the corresponding metal salt (PdCl₂, RuCl₃, (NH₄)₆Mo₇O₂ and Ni(NO₃)₂), to reach a final concentration of 1 wt.% of Pd and Ru, 20 wt.% of Mo and 10 wt.% of Ni. CNF synthesis can be found elsewhere [2]. The waste cooking oil was provided by a local company *Naturalmente Social Recikla, S. L.* in Zaragoza, Spain. In a typical run of HDO, 25 g of distilled water, 2.5 g of previously degummed waste cooking oil and 0.25 g of catalyst are added into a 50 mL 316SS batch reactor (OLT-HP-50 provided, *Ollital*). The reactor is purged with N₂ and subsequently loaded with 10 bar of N₂ pressure. Next, the reactor is heated with a stirring of 300 rpm up to reach 350 °C and maintained at this temperature with 1000 rpm for 3 h. Once residence time is completed, the reactor is quenched by immersion in cold water. At ambient temperature, a gas sample is analyzed by gas chromatography (Perkin Elmer – GC Refinery Gas Analyzer – 1157). The remaining product is filtered with cyclohexane, and the solid residue is dried at 100 °C overnight. The liquid mixture (water and cyclohexane and oil) is separated by decantation. Finally, the cyclohexane and oil mixture is analyzed by gas chromatography with an FID detector (Perkin Elmer – GC, Clarus[®] 690) and by GC-MS (Clarus-690-SQ8T). Conversion, selectivity and yields were calculated by carbon atomic balance.

3. Results and discussion

During the H₂-free catalytic HDO of waste cooking oil, different carbon nanofibers-supported catalysts (Pd-, Ru-, Mo₂C- and Ni-based) were studied for their influence on the gas and liquid product

distribution. First, Fig. 1a) shows the gas product composition after hydrodeoxygenation with different catalysts along with the gas generated (in mmol). The use of a catalyst promoted H₂ formation. Also, CO in large quantities was detected, which is related to decarbonylation reactions during HDO and gasification. Other compounds in high proportions were CH₄ and CO₂, meanwhile, the “others” fraction involves light hydrocarbons (C₂-C₆) in minor quantities. From the “others” propane proportion was calculated, and the propane mmol production for the catalysts was ordered as follows: Ni/CNF (0.088) > Pd/CNF (0.070) > Mo₂C/CNF (0.029) > Ru/CNF (0.017) > Blank (0.007). Additionally, by comparing the gas production (mmol) and the H₂ proportion, it was found that the catalysts that formed more H₂ *in situ* in descending order were: Ni/CNF (21.1) > Mo₂C/CNF (9.8) > Ru/CNF (5.9) > Pd/CNF (5.4) > Blank (1.4). Conversions are shown in Fig. 1b), where the blank experiment and the Mo₂C/CNF catalyst exhibit the lower values. Meanwhile, Ru/CNF and Pd/CNF show conversions of 12 and 17%, respectively, and the highest selectivities to diesel-range hydrocarbons. Finally, Ni/CNF achieved the highest conversion (42%) and a selectivity to diesel and gasoline of 66 and 33%, respectively.

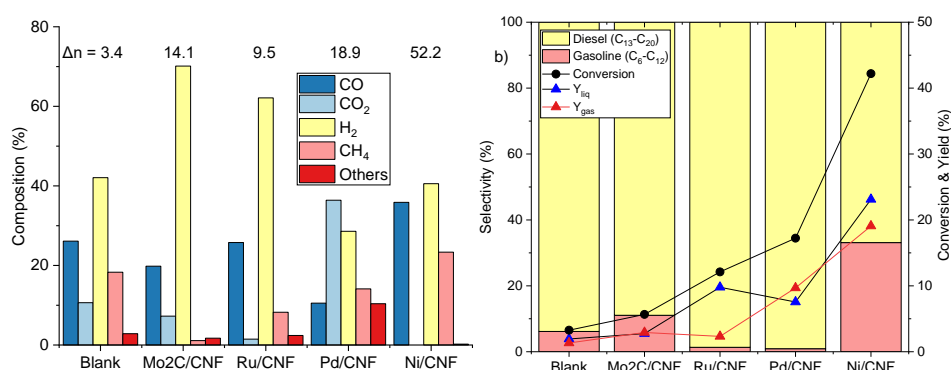


Figure 1. a) Gas composition and mmol generated after H₂-free hydrodeoxygenation and b) conversion and selectivity on the liquid product distribution influenced by different catalysts.

4. Conclusions

Catalytic HDO of waste cooking oil without an external source of H₂ was performed. H₂ was supplied by the water dissociation. It was found that below the critical point of water, H₂ formation can be produced to hydrodeoxygenate waste cooking oil and produce linear hydrocarbons, mainly in the range of diesel. In this regard, Mo₂C/CNF catalyst was insufficient to reach high conversion. Meanwhile, Ru and Pd-based catalysts showed conversions of 12 and 17% to liquid and gas products, along with high selectivity to linear hydrocarbons in the carbon length of diesel. On the other hand, the Ni/CNF catalyst showed the highest conversion (42%) and a selectivity to diesel and gasoline hydrocarbons of 66 and 33%. In future work, Pd, Ru and Ni loadings will be analyzed to improve the conversion and selectivity to diesel fraction.

References

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Keywords

Hydrodeoxygenation, H₂-free, waste cooking oil, metal catalysts.