

Upgrading of model bio-oil by catalytic hydrodeoxygenation using CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts

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Abstract:

Bio-oil produced from fast pyrolysis of biomass is a potential candidate to replace conventional fossil-derived fuels. However, the fast pyrolysis derived oil generally has a high oxygen content (15-25% wt) that makes it unstable, corrosive and low in heating value. The aim of this study is to upgrade the properties of pyrolysis bio-oil by catalytic hydrodeoxygenation (HDO). To eliminate the inconsistent properties of real bio-oil for the experiment, a model bio-oil, which was a mixture of chemicals at proportions simulating bio-oil derived from eucalyptus bark reported in a previous study, was used as the sample. The experiment was conducted in a high pressure autoclave reactor operated on a batch mode at temperatures of 250-350°C, and under pressure of H₂ in the presence of CoMo and NiMo catalysts. The results show that oxygen removal could be achieved and was favored by the increase in temperature. The NiMo/Al₂O₃ catalyst exhibited a higher activity for oxygen removal than did the CoMo/Al₂O₃ catalyst. Initial pressure of H₂ was another factor that affects deoxygenation efficiency. The higher the initial pressure, the higher the deoxygenation efficiency.

Keywords: Bio-oil; Pyrolysis; Catalytic Hydrodeoxygenation

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1. Introduction

The steady increase in the demand for transportation fuel and depleting source of petroleum oil poses a threat to global energy security especially for oil importing countries. Biomass is currently used to produce liquid biofuels to substitute petroleum oil. Commercial liquid biofuels are bioethanol from sugar or starch-rich crops or biodiesel from oil-rich crops. Lignocellulosic biomass can also be used as feedstock for liquid biofuel production via fast pyrolysis process. However, the high oxygen content in fast pyrolysis oil or so-called bio-oil results in negative effects to the properties of oil, including oil instability, high acidity and low heating value (Qi et al., 2007). Therefore, upgrading the bio-oil by reducing its oxygen content is necessary before it can be further used such as in automotive engines. Hydrodeoxygenation (HDO) is a bio-oil upgrading process in which oxygenic compounds and unsaturated hydrocarbon are transformed into saturated hydrocarbon. In this paper, the catalytic hydrodeoxygenation of the model bio-oil was carried out using a lab-scale high pressure autoclave operated on a batch mode. To eliminate the inconsistent properties of real bio-oil, model bio-oil was used for the experiment. The catalysts used were the commercial CoMo and NiMo catalysts. This study aims to observe the effects of operating conditions and characteristics of the upgraded products, especially oxygen content.

2. Methodology

The model bio-oil in this study refers to a mixture of high purity grade chemicals that were prepared before each experiment. The components of model bio-oil used simulated the bio-oil derived from eucalyptus bark as reported in a previous study (Yuenyongchaiwat, 2010) which contained acetone 34%, phenol 33%, furfural 14%, ethanol 12% and acetic acid 7%. The bio-oil upgrading experiment was conducted in a mechanically stirred stainless steel autoclave, as shown in Fig. 1. The reactor volume was 100 ml and operated on a batch mode. Bio-oil was loaded in the reactor with catalyst, pressurized with 3-15 bar initial pressure of H₂ and heated to temperatures in the range of 250-350°C. The reaction time was 3 hours, after which the liquid product was collected for elemental

analysis, while the gas product was collected for GC analysis. The HDO catalysts in the upgrading experiment were CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts, which are commercially available.



Fig. 1 Mechanically stirred stainless steel autoclave.

3. Results and Discussion

The results clearly show that, under the studied conditions, the oxygen removal could be achieved and was favored by the increase in temperature for both CoMo and NiMo catalysts. Fig. 2(a) shows the product distribution from the experiment with the best oxygen removal condition for both catalysts (at 5%wt catalyst, 325°C, 5 bar initial pressure of H₂ and 3 hours reaction time). The formation of solid product or coke was observed at the operating temperature at 300°C or above suggesting the occurrence of heat induced polymerization reactions at sufficiently high temperature (Badawi et al., 2011). The experiment with CoMo catalyst clearly yielded higher content of solid than NiMo catalyst. The catalytic hydro-deoxygenation activity, reported as %HDO, which was determined from the oxygen reduction from bio-oil, was higher when using NiMo catalyst compared to CoMo catalyst as presented in Fig. 2(b).

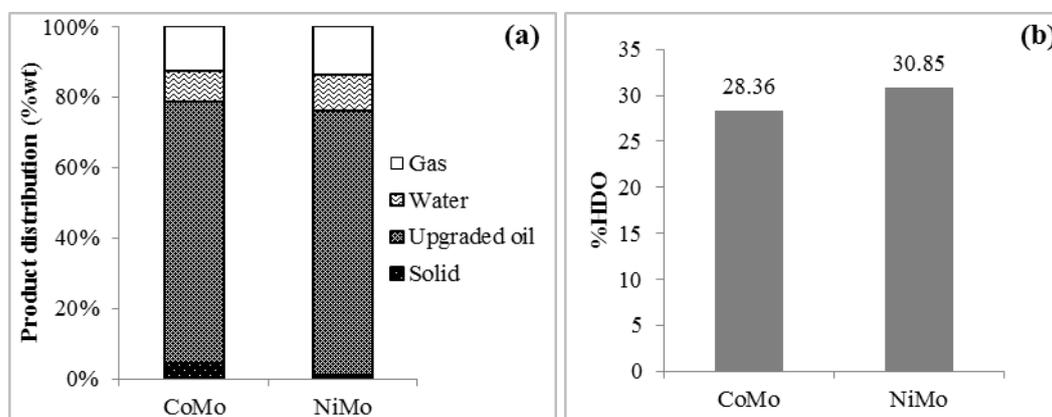


Fig. 2 The effect of catalyst type on (a) product distribution and (b) %HDO.

The H₂ consumption and the amount of the major product gas species were determined by the GC analysis and the direct measurement of the total product gas volume. The results of gas product are shown in Fig. 3 for CoMo- and NiMo-based catalyst. The gas product was composed mainly of CO, CO₂ and hydrocarbon gases i.e. CH₄, C₂H₄, C₂H₆ and C₃H₈, which were derived from oil cracking reaction, while water was formed by the hydrogenation reaction.

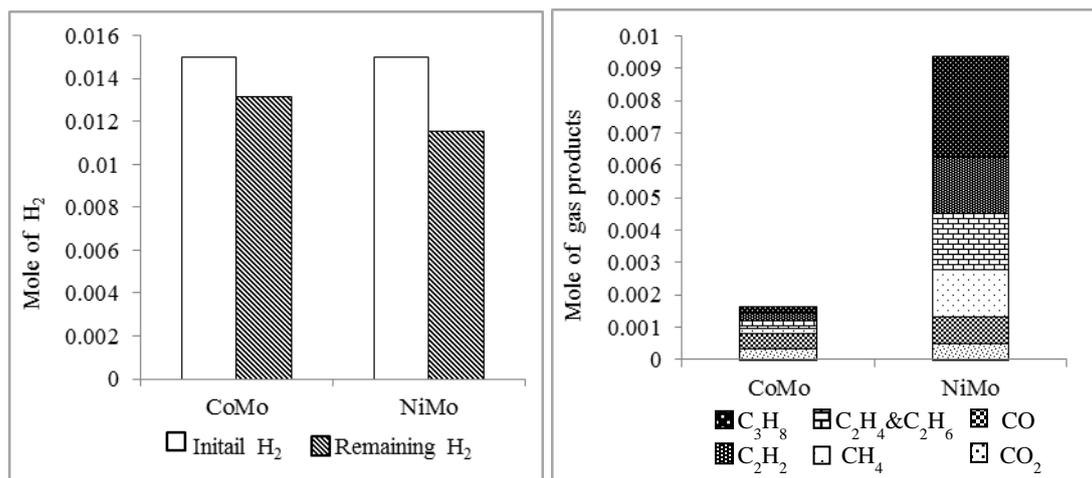


Fig. 3 The effect of catalyst types on catalytic hydrodeoxygenation and the compositions of gas products.

Since the NiMo catalyst showed the higher hydrodeoxygenation performance than CoMo catalyst (referring to Fig. 2), NiMo catalyst was selected to test the effect of initial H₂ pressure on hydrodeoxygenation performance. The initial pressure of H₂ was varied in the range of 5-15 bar under otherwise similar conditions. Due to the maximum pressure of the autoclave reactor, the operating temperature was 300°C to keep the final pressure below 100 bar. The product distributions were not significantly different as seen in Fig. 4(a); however, the %HDO (see Fig. 4(b)) increased from 30.27 to 37.38% when the initial pressure of H₂ was increased from 5 to 15 bar. The high pressure has been found to result higher solubility of H₂ in the oil and thereby a higher availability of H₂ in the vicinity of the catalyst. This increases the reaction rate and further decreases coking in the reactor (Venderbosch et al., 2010; Oasmaa et al., 2010; Kwon et al., 2011).

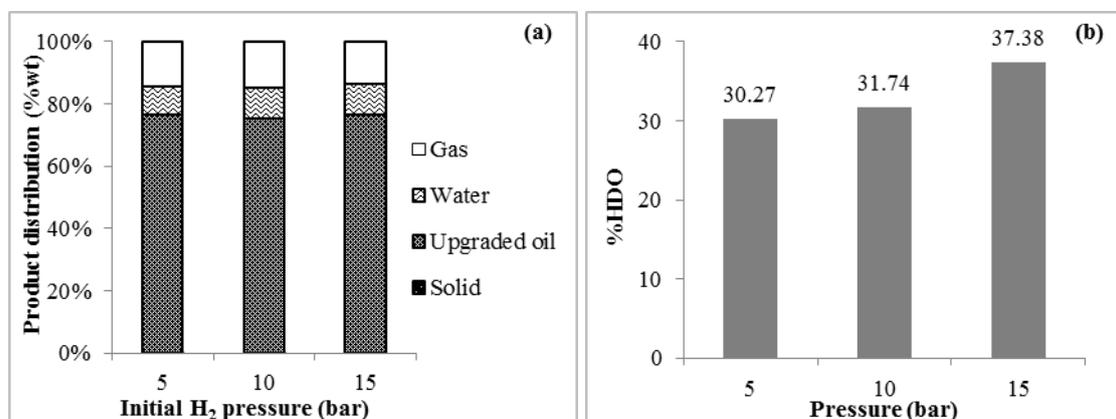


Fig. 4 The effect of initial H₂ pressure on (a) product distribution and (b) %HDO

The compositions of the gas products from bio-oil upgrading using various initial pressure of H₂ are presented in Fig. 5. The H₂ remaining as well as other gas products such as CO, CO₂, CH₄, etc., increased when higher initial pressure of H₂ was used.

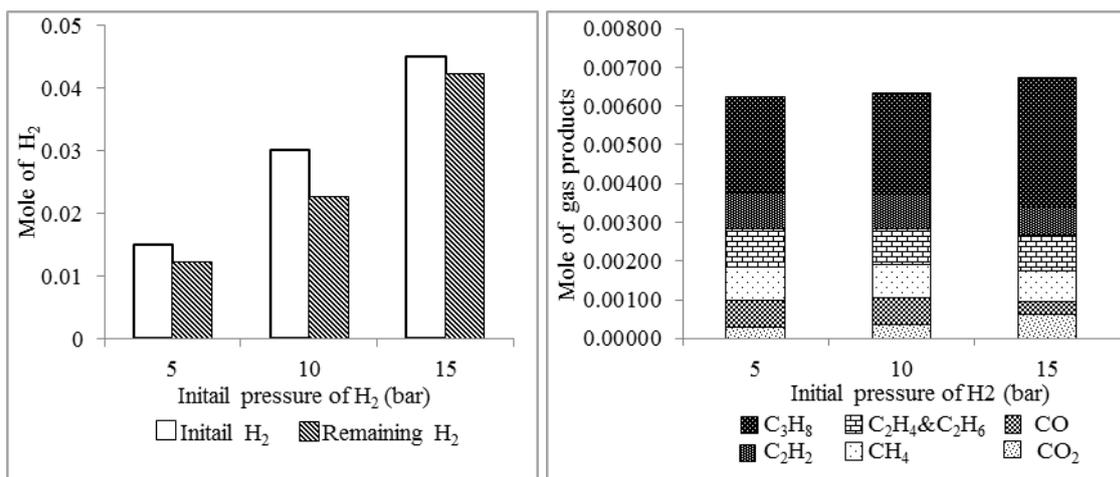


Fig. 5 The effect of initial pressure of H₂ on catalytic hydrodeoxygenation on the compositions of gas products.

4. Conclusion

The problematic property of bio-oil -- high oxygen content -- was improved by catalytic hydrodeoxygenation (HDO) reaction. In this study, the hydrodeoxygenation in the presence of CoMo and NiMo catalyst could remove oxygen from the model bio-oil.

- The NiMo catalyst showed the high efficiency of oxygen removal than CoMo catalyst. However, the catalytic hydrodeoxygenation using CoMo and NiMo caused loss of upgraded bio-oil products by solid formation (coke) and oil cracking into gas production (CO, CO₂ and hydrocarbon gases).
- For the effect of initial pressure of H₂, the %HDO increased from 30.27 to 37.38 when the initial pressure of H₂ was increased from 5 to 15 bar.

5. References

- Badawi, M., Paul, J.F. and Cristol, S. et al. 2011. Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study. *Journal of Catalysis* 282: 155-164.
- Kwon, K.C., Mayfeld, H., Marolla, T., Nichols, B., and Mashburn M. 2011. Catalytic deoxygenation of liquid biomass for hydrocarbon fuels. *Renew. Energy* 36: 907-915.
- Oasmaa, A., Kuoppala, E., Ardiyanti, A.R., Venderbosch, R.H., and Heeres H. 2010. Characterization of hydrotreated fast pyrolysis liquids. *Energy Fuels* 24: 5264-5272.
- Qi, Z., Jie, C., Tiejun, W. and Ying, X. 2007. Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management* 48: 87-92.
- Venderbosch, R.H., Ardiyanti, A.R., Wildschut J., Oasmaa A. and Heeres H.J. 2010. Stabilization of biomass-derived pyrolysis oils. *Journal of Chemical Technology & Biotechnology* 85(5): 674-686.
- Yuenyongchaiwat, P. 2010. Bio-oil Production from Various Biomass Feedstocks by Vacuum Pyrolysis. M.Eng Thesis, JGSEE.