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Publication date:
2018

Document Version
Peer reviewed version

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Citation (APA):

Stummann, M. Z., Høj, M., Hansen, A. B., Wiwel, P., Davidsen, B., Jensen, P. A., ... Jensen, A. D. (2018). Hydrogen assisted catalytic biomass pyrolysis for green fuels. Effect of catalyst in the fluid bed. Abstract from The 10th International Conference on Environmental Catalysis, The 3rd International Symposium on Catalytic Science and Technology in Sustainable Energy and Environment, Tianjin, China.

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Hydrogen assisted catalytic biomass pyrolysis for green fuels. Effect of catalyst in the fluid bed

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Abstract: Fast pyrolysis of biomass is a well-known technology for producing bio-oil. However, in order to use the oil as transportation fuel the oxygen content must be decreased from approximately 40 wt.% to below 1 wt.% [1]. This can be achieved by catalytic hydrodeoxygenation (HDO). Unfortunately, deactivation due to coking of the catalyst is a severe problem for this technology [1]. The objective of the present work is to produce oxygen free gasoline and diesel from biomass by hydrogen assisted catalytic fast pyrolysis. Fast pyrolysis of beech wood (feeding rate: 275 g/h) has been performed in 26 bar hydrogen (flow: 55-90 NL/min) in a fluid bed reactor operated at 450 °C with several different catalysts as bed material followed by an additional vapor phase, fixed bed HDO reactor (operated at 370-400 °C) using a sulfided commercial NiMo/Al₂O₃ catalyst. The obtained bio-oil is essentially oxygen free. The tested catalysts in the fluid bed include olivine sand (OS), MgAl₂O₄ (MgAl), CoMo/MgAl₂O₄ (CoMo), zeolite HZSM5 mixed with alumina (ZA), NiMo impregnated on zeolite mixed with alumina (NiMoZA), and a cheap and non-toxic catalyst (HYCP).

The HYCP catalyst was tested both in reduced (HYCP-R) and sulfided forms (HYCP-S), while the other catalysts, with exception of OS, were sulfided prior to the experiment. The product distribution for the experiments where the

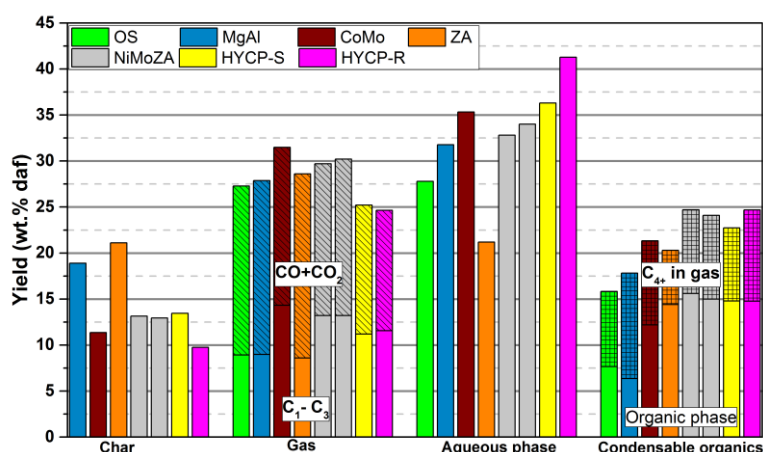


Figure 1. Effect of the catalyst in the fluid bed on the product distribution. Operating conditions: Fluid bed: 450 °C, HDO reactor: 370-400 °C, pressure 26 bar, H₂ flow: 55-90 NL/min, biomass feeding rate: 275 g/h.

HDO reactor was used is shown in Figure 1. Using the support materials (MgAl and ZA) gave a high char yield and a low yield of condensable organics compared to the supported catalysts (CoMo and NiMoZA). Using the HYCP-R catalyst gave a condensable organic yield of 25 wt. % daf corresponding to the highest obtained energy recovery of 58 %. Using the HYCP-R catalyst in the

fluid bed reactor and by passing the HDO reactor decreased the C_{1-3} yield from 12 to 3 wt. % daf and increased the condensable organic yield from 25 to 34 wt. % daf. However, oxygen concentration in the produced oil increased to 14 wt. % db. GC×GC-MS/FID showed that the oxygenates were mainly phenols (22 % FID-area) and oxygenated aliphatics (21 % FID area).

The carbon content on the spent catalysts was investigated using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). By varying the acceleration voltage it was possible to measure the carbon content both at the surface (at 3 kV) and in the bulk (at 15 kV). The carbon content is shown as a function of the acceleration voltage in Figure 2 for ZA and NiMoZA (2A), MgAl and CoMo (2B), and HYCP-S and HYCP-R (2C). It can be seen that the carbon content is significantly higher for ZA and MgAl compared to NiMoZA and CoMo, thus having a more active material in the fluid bed decreases the coking of the catalyst. For the MgAl the carbon content significantly decreases with increasing acceleration voltage, thus indicating that the concentration of coke on the catalyst is higher at the surface than towards the center. The carbon content on the spent HYCP catalysts are in the same range as for the CoMo and NiMoZA.

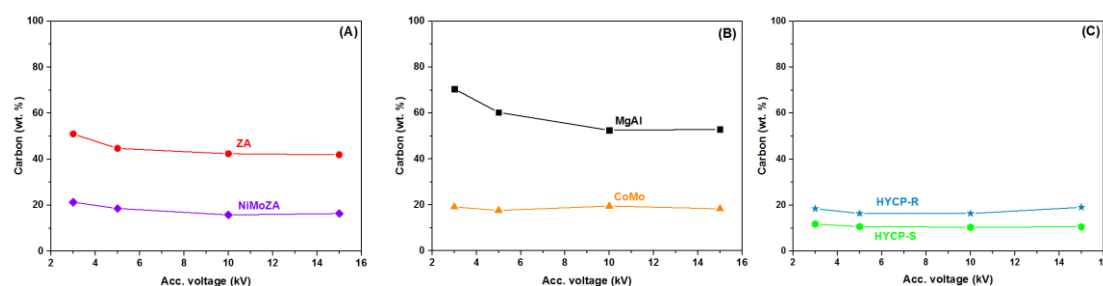


Figure 2 Carbon content on spent catalysts ZA and NiMoZA (A), MgAl and CoMo (B), and HYCP-R and HYCP-S (C) measure with different acceleration (acc) voltages

Our work indicates that hydrogen assisted catalytic pyrolysis is a feasible path for production of liquid renewable fuels. The presence of an active catalyst in the fluid bed is essential and has a significant impact on the product distribution. It is possible obtain a high yield of condensable organics with the cheap HYCP catalyst, thus showing that it is not necessary to use expensive formulated catalysts. In our ongoing research the differences between CoMo, NiMo and Mo catalysts in the fluid bed is further investigated. Furthermore the effect of the metal loading and the effect of using different supports are also studied and the spent catalysts characterized by use of SEM and transmission electron microscopy (TEM).

Key words: Hydropyrolysis; Bio-fuels; Hydrodeoxygenation

References

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