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Publication date:
2017

Document Version
Peer reviewed version

Citation (APA):

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H₂CAP - Hydrogen assisted catalytic biomass pyrolysis for green fuels

Magnus Zingler Stummann1, Martin Høj1, Jostein Gabrielsen2, Peter Arendt Jensen1, Anker Degr Jensen1*
1DTU Chemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby (Denmark)
2Haldor Topsoe A/S, 2800 Kgs. Lyngby (Denmark)
*aj@kt.dtu.dk

Introduction

Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies [1]. To utilize this oil as liquid fuel the oxygen content must be reduced from 15-30 wt.% down to <1 wt.%, which increases heating value and stability and decreases acidity [1]. Upgrading bio-oil by catalytic hydrodeoxygenation (HDO) is challenged by severe polymerization and coking upon heating the oil. Alternatively, performing fast pyrolysis in high-pressure hydrogen atmosphere in a fluid bed reactor with a HDO catalyst as bed medium could immediately stabilize reactive pyrolysis vapors [2]. An additional vapor phase HDO reactor ensures removal of oxygen down to <1 wt.%, resulting in separate hydrocarbon oil and water phases being recovered. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup has been constructed at DTU Chemical Engineering. With a capacity of 100 to 300 g/h solid biomass, the aim is to provide a proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.

Materials and Methods

Experiments have been performed using 50 g of CoMo/MgAl₂O₄ catalyst in the fluid bed reactor and 173 g of NiMo/Al₂O₃ catalyst in the HDO reactor. The catalysts were sulfided at 25 bar with 2-7.5 % of H₂S, 5 % N₂ in balance H₂ by feeding liquid DMDS to the system. The hydropyrolysis of biomass have been performed at 25 bar with gas composition 470 ppm H₂S, 6 % N₂ balance H₂ at a total flow of 87 NL/min. The actual total flow at reaction temperature and pressure corresponds to approximately three times the minimum fluidization velocity (3umf) for the employed catalyst size fraction. The biomass used was beech wood, bark free and approximate particle size 200 to 700 μm. Moisture 5.75 wt.% (bone dry at 102 °C) and ash content 0.58 wt.% (dry basis).

Table 1 summarizes the reaction conditions in the four experiments performed so far. For each experiment a fresh load of catalyst in the fluid bed reactor and the same load of catalyst in the HDO reactor was used, but both catalyst were sulfided before each experiment.

<table>
<thead>
<tr>
<th>Table 1: Reaction conditions employed in the first four experiments</th>
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<tbody>
<tr>
<td>Exp. #1</td>
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<tr>
<td>Biomass feed rate [g/min]</td>
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<tr>
<td>Fluid bed Temp. [°C]</td>
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<tr>
<td>Filter Temp. [°C]</td>
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<tr>
<td>HDO Temp. [°C]</td>
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</tbody>
</table>

Results and Discussion

A photograph of the condensed liquids from Exp. #4 and the yields obtained from Exp. #1 to #4 are shown in Figure 2.

The products are phase separated aqueous and hydrocarbon fractions. The produced oil has low viscosity, is free flowing, transparent and very different from conventional wood pyrolysis oil. The best oil yield is 22.2 wt.% of the wood, corresponding to approximately 39 % carbon atom yield and an energy yield of approximately 53 %. The oxygen content of the condensed oil has been measured to <1 wt.%, the hydrogen content approximately 12 wt.% and the carbon content approximately 88 wt.%, showing that the oil is hydrocarbons. Simulated distillation (SimDist by GC) showed that approximately 25 vol.% of the condensed oil is gasoline and 75 vol.% diesel. The main oxygenates left in the oil are 4-ethylphenol, dimethylphenol, benzofuran, dibenzofuran, methylidenbenzofurans and 2-naphthol, some of the least reactive compounds in HDO, as measured with O-specific GC-AED.

These very first results show that the process performs excellently as intended. The liquid yield may be further improved by choice of catalysts and reaction conditions, which is the focus of ongoing work.

Significance

This study confirms that catalytic hydropyrolysis with hydrodeoxygenation is an attractive route for biomass to liquid fuels. The reaction conditions employed are significantly milder than gasification, potentially resulting in lower capital and operating costs, and the energy yield is significantly better than second-generation bio-ethanol. The oil yields are comparable to those reported in literature [2,3].

References