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H₂CAP - Hydrogen assisted catalytic biomass pyrolysis for green fuels

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1 INTRODUCTION AND PURPOSE

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 could ensure 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 of this process 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.

![Schematic diagram for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.](image)

Figure 1: Simplified H₂CAP process diagram including fluid bed catalytic hydropyrolysis (20 to 40 bar and 350 to 500°C), char separation, temperature adjustment, vapor phase HDO reactor (20 to 40 bar and 300 to 400°C), cooling, condensation and liquid separation. These parts have been constructed at DTU Chemical Engineering. Additionally, steam reforming and water gas shift (WGS) of non-condensable gasses to H₂ and CO₂ and wind-powered electrolysis of water to H₂ is envisioned.

2 RESULTS

Experiments were performed with 50 g of CoMo/MgAl₂O₄ catalyst in the fluid bed reactor and 173 g of Ni-Mo/Al₂O₃ catalyst in the HDO reactor. The catalysts were sulfided before experiments. Hydropyrolysis of beech wood was performed at 25 bar with gas composition 470 ppm H₂S, 6 % N₂ balance H₂. A photograph of the condensed liquids from Exp. #1 and the yields obtained from Exp. #1 to #4 are shown in Figure 2.

![Photograph of the recovered liquids from Exp. #1.](image)

Figure 2: Photograph of the recovered liquids from Exp. #1. Oil is top phase in bottle 1 and bottle 2, only oil in bottle 3. Yields of char, C₁-C₃ hydrocarbons, CO + CO₂, condensed aqueous phase and condensed oil with potentially condensed oil (C₄+) in gas phase on dry, ash free basis for Exp. #1 to #4. The mass balance sum to 100, 98, 100 and 101 % respectively.

These very first results show that the process performs excellently as intended. The products are phase separated aqueous and hydrocarbon fractions. The low viscosity, free-flowing oil with <1 wt.% oxygen is very different from conventional wood pyrolysis oil. The best oil yield obtained is 22.2 wt.% of the wood, corresponding to approximately 39 % carbon atom yield and an energy yield of approximately 53 %. The liquid yield may be further improved by choice of catalysts and reaction conditions, which is the focus of ongoing work.

3 INNOVATION AND RELEVANCE

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 2nd generation bio-ethanol.

References