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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 HDO reactor could ensure removal of oxygen down to <1 wt%. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup has been constructed at DTU Chemical Engineering for proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.

2 RESULTS

Experiments were performed with 50 g of sulfided CoMo/MgAl₂O₄ catalyst in the fluid bed reactor and 173 g of sulfide NiMo/Al₂O₃ catalyst in the HDO reactor. Hydrolyropyolysis of beech wood was performed at 25 bar with gas composition 470 ppm H₂S, 6 % N₂ balance H₂. The effect of varying the temperature (365-511 °C) and hydrogen pressure (15-35 barg) on the product yield and organic composition was studied. The mass balance closed between 90 and 101 wt. % dry ash free basis (daf). The combined condensed organics and C₄+ gasses yield varied between 17 and 22 wt. % daf (Figure 2), which corresponds to an energy recovery between 40 and 53 % in the organic product. The yield of non-condensable gasses varied between 24 and 32 wt. % daf and the char yield varied between 9.6 and 18 wt. %. Analysis of the condensed organics by GC simulated distillation showed that it consists of 20-40 vol. % naphtha and 60-80 vol. % diesel. The condensed organics contains 42 to 75 wt. % aromatics, based on GC×GC-FID chromatographic peak area, and the remainder was primarily naphthenes with minor amounts of paraffins. The condensed organics were essentially oxygen free (<0.001 wt. %) when both reactors were used. Bypassing the HDO reactor increased the oxygen concentration in the condensed liquid to 1.8 wt. %. In the ongoing work the effect of the choice of catalyst in the fluid bed is investigated and a combined organic and C₄+ gas yield of 25 wt.% daf has been obtained. The results show that catalytic hydrolyropyolysis may be a viable way to process solid biomass into liquid and gaseous fuels with high yields.

3 INNOVATION AND RELEVANCE

This study confirms that catalytic hydrolyropyolysis with hydrodeoxygenation is an attractive route for converting 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