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Hydrogen assisted catalytic biomass pyrolysis for green fuels

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1 INTRODUCTION

This extended abstract includes further experimental details, additional results and outlook.

2 EXPERIMENTAL

2.1 SETUP

All experiments have been conducted at the catalytic hydrolysis setup constructed at DTU-Chemical Engineering. It consists of a feeding section with gas mixing (H_2 , H_2S and N_2), liquid feeding (for catalysts activation by sulfidation) and a 4 L pressurized biomass screw feeder with stirring and feed screw rotation through magnetic couplings with additional gas feeding for biomass entrainment. A reactor section with gas preheater, fluid bed reactor (29.5 mm i.d.) with disengager zone (49.3 mm i.d.), heated filter (SS316 sinter metal tube) and char collector and a fixed bed HDO reactor (32.5 mm i.d.). Finally, a makeup section with three stage cooling (25 °C, 2 °C, -35 °C), condensation and liquid collection, pressure reduction, online gas analysis by GC and flaring of exhaust gasses.

2.2 EXPERIMENTAL CONDITIONS

Experiments have been performed with 50 g of a commercial $CoMo/MgAl_2O_4$ catalyst (180-355 μm sieve fraction) in the fluid bed reactor and 173 g of a commercial $NiMo/Al_2O_3$ catalyst (trilobe extrudates) in the fixed bed HDO reactor. The catalysts were sulfided at 25 barg with 2-7.5 % of H_2S , 5 % N_2 in balance H_2 by feeding liquid DMDS to the system. The setup was pressurized to 25 barg in N_2 and the reactors heated to 170 °C, then the gas/liquid feed was changed to the sulfidation conditions and temperatures ramped to 350 °C at 10 °C/min and held at 350 °C for one hour.

The hydrolysis of biomass have been performed at 25 barg with gas composition 470 ppm H_2S , 6 % N_2 balance H_2 at a total flow of 87 NL/min, of which 52 NL/min is through the gas preheater and 35 NL/min for entrainment of the biomass from the feeder (preheated to 200 °C). The actual total flow at reaction temperature and pressure corresponds to approximately three times the minimum fluidization velocity ($3u_{mf}$) for the employed catalyst sieve fraction.

The biomass was pulverized bark free beech wood (Dansk Træmel, DT 64) produced for smokehouses, with approximate particle size of 200 to 700 μm , water content of 5.75 wt.% (bone dry at 102 °C) and ash content of 0.58 wt.% (dry basis).

The effect of temperature and pressure was investigated by varying the temperature in the fluid bed reactor between 365 and 511 °C, the temperature in the HDO reactor between 350 and 400 °C, and the total pressure varied between 15 and 35 barg. The catalyst in the fluid bed reactor was replaced between each experiment. The HDO reactor was in one experiment bypassed to investigate the effect of the fluid bed reactor.

During the experiments the online GC analyzes (once every 12 min) for all C_1 - C_5 alkanes and alkenes and C_{6+} as one lumped peak using an FID detector and CO , CO_2 , H_2S , N_2 and H_2 using two TCD detectors.

At the end of each experiment the liquid collection bottles were isolated from the gas flow, depressurized slowly to minimize evaporation and water and oil were collected. Char and catalyst were recovered from the fluid bed and filter and the char yield determined by subtracting the mass of catalyst loaded in the fluid bed from the total mass of catalyst and char recovered. The wood left in the screw feeder was recovered to determine the total amount fed and the average feed rate.

The yield of liquid oil, liquid water, char, $CO+CO_2$, non-condensable C_1 - C_3 gasses and potentially condensable C_{4+} gasses were calculated using the total biomass fed (dry, ash free basis).

3 EXTENDED RESULTS

Varying the temperature in the fluid bed reactor changed the product distribution as shown in Figure 3 (A). Increasing the temperature in the fluid bed reactor mainly decreased the char yield, while increasing the gas yield, in agreement with the results obtained with IH²[®] process [1]. The organic yield including condensed organics and C₄₊ gasses increased when the temperature increased from 365 to 400 °C above which it remained constant within the experimental uncertainty. The influence of pressure on the product distribution is shown in Figure 3 (B). Increasing the total pressure did not affect the liquid organic yield, but decreased the CO and CO₂ yield. The hydrogen consumption also increased from 35 g/kg biomass at 15 barg to 46 g/kg biomass at 25 barg, but did not increase further when the pressure increased to 35 barg. The char yield also increased with increasing pressure.

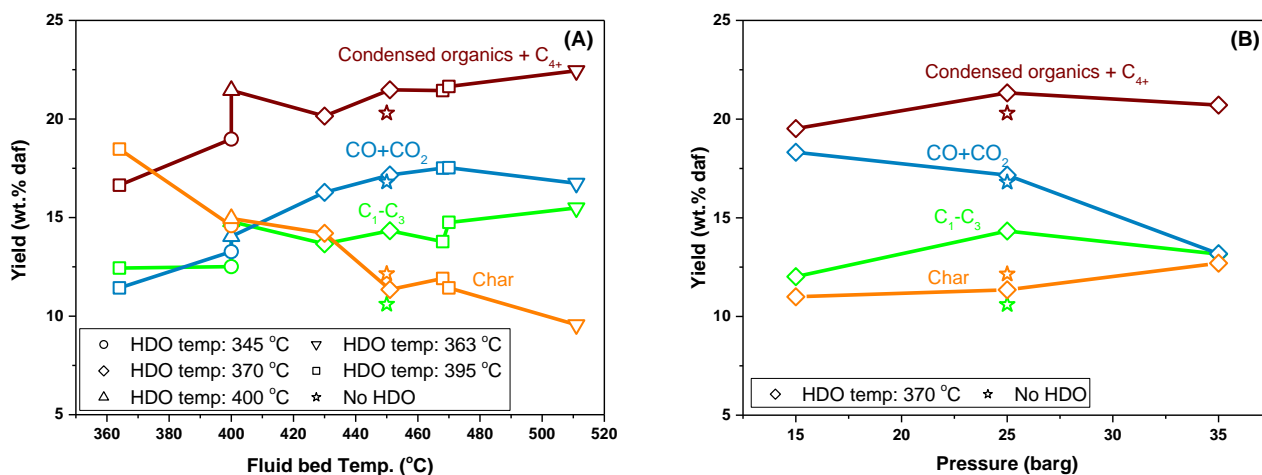


Figure 3: Effect of varying the fluid bed temperature (A) and the pressure (B) on the product distribution

The concentration of aromatics and naphthenes are shown as a function of the fluid bed temperature and the total pressure in Figure 4 (A). The concentration of aromatics decreased when the temperature in the fluid bed was increased from 365 to 430 °C, but increased when the temperature was further increased. Equilibrium calculations for monoaromatics have shown that they are favored over the corresponding naphthenes when the temperature is above 405 °C. This indicates that the hydrogenation of aromatics to naphthenes was kinetically controlled below 430 °C and equilibrium controlled at higher temperatures. The HDO reactor has only minor influence on the aromatic concentration. As shown in Figure 4 (B), increasing the total pressure at 450 °C in the fluid bed decreased the aromatic concentration and increased the naphthenes concentration, which is most likely due to the increased hydrogen pressure shifting the equilibrium towards the saturated products and increasing the rate of hydrogenation.

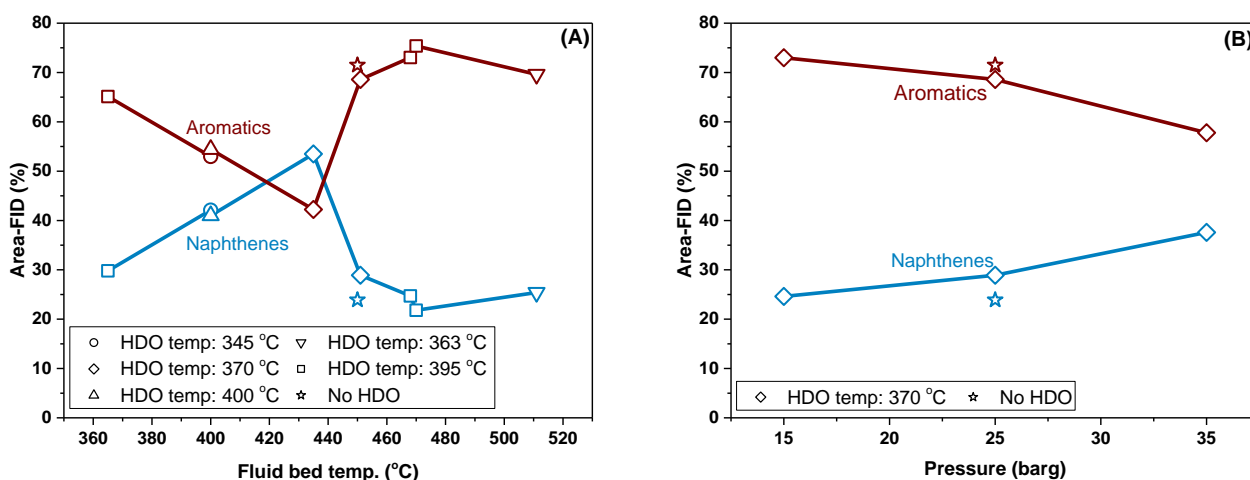


Figure 4: Effect of varying the fluid bed temperature (A) and the pressure (B) on the aromatic (including phenols) and naphthene content in the condensed organic liquid.

Oxygen specific GC-AED showed that when the HDO reactor was bypassed the total oxygen content in the condensed organics was 1.8 wt. % and that the main oxygenates were different phenols. When the HDO reactor was used the oxygen content was below 100 ppmw and only traces of phenols, naphthol, and dibenzofurans were detected in the condensed organics.

The energy recovery was calculated on the basis of the amount of biomass fed to the setup and the heating value of the different phases. The resulting energy recoveries for each product are shown in Figure 5. The energy recovery for the condensed organics and C₄₊ was between 40 and 53 %, the energy recovery for the gas was between 36 and 48 %, and the energy recovery for the char was between 14 and 19 %. The total energy recovery for all of the experiments was more than 100 %, which is due to incorporation of hydrogen that increases the heating value of the products. The energy added to the products by hydrogen corresponded to between 0.26 and 0.34 MJ/MJ biomass used.

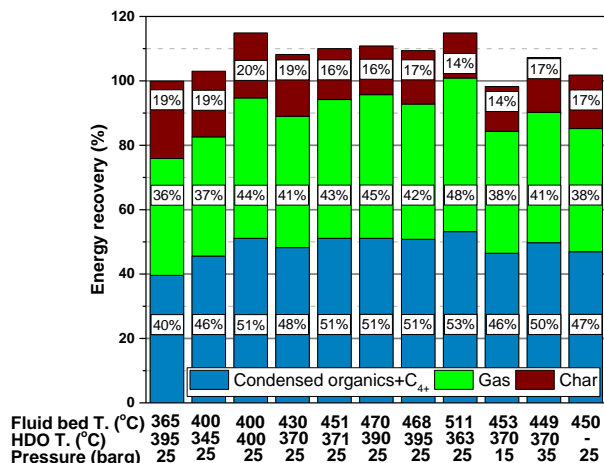


Figure 5: The effect of the process conditions on the energy recovery

4 RELEVANCE AND OUTLOOK

This project has demonstrated that catalytic hydrolysis is an attractive route for conversion of biomass into liquid fuels, thus it confirms the findings of the IH² project at GTI [1]. Furthermore it shows that product distribution and oil composition can be controlled by varying the process conditions.

The process is further investigated by testing different catalysts in the fluid bed. Recent work has shown that it is possible to archive a condensed organics and C₄₊ yield of 25 wt. % daf with a cheap and non-toxic catalyst. Furthermore the process stability will be investigated by running longer experiments and testing different types of biomass.

5 REFERENCES

[1] T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, Environ. Prog. Sustain. Energy 31 (2012) 191–199.