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Catalytic upgrading of pyrolysis vapors

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INTRODUCTION

Currently, biomass is the only resource available for production of renewable, liquid transportation fuels. Within the thermochemical field, there are two process for the thermal decomposition of biomass: gasification and pyrolysis.

Gasification involves heating biomass to temperatures of 700-900°C in order to produce syngas, a mixture of carbon monoxide and hydrogen. The syngas then undergoes a catalytic reaction to form ethanol or other transportation fuels.

Fast pyrolysis is the rapid heating of biomass to temperature between 400 and 600 °C to produce a high yield of bio-oil. Bio oil is a dark viscous fluid with high water and oxygen content, is chemically unstable, and is not miscible with conventional fuels. Table 1 shows a comparison between bio-oil and heavy fuel oils.

Table 1: Typical Properties of Wood Pyrolysis Bio-oil and of Heavy Fuel Oil

Physical properties	Bio-oil	Heavy fuel oil
Moisture content, wt %	15-30	0.1
pH	2.5	--
Specific gravity	1.2	0.94
Elemental composition, wt %		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
ash	0-0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity, (at 50 °C), cP	40-100	180
Solids, wt %	0.2-1	1
Distillation residue, wt %	Up to 50	1

There are two methods used for upgrading the pyrolysis products: hydrotreating and catalytic cracking. Hyrdotreating involves the use of hydrogen to remove oxygen from the bio-oil forming water. Catalytic cracking reduces oxygen content through simultaneous dehydration, decarboxylation, and decarbonylation reactions in the presence of a zeolite catalyst.

MATERIALS AND METHODS

Samples of biomass were prepared as shown in Figure 1A and then loaded into the probe arm of a CDS Pyroprobe 5150 as shown in Figure 1B. The probe arm was then inserted into the Pyroprobe interface for the pyrolysis reaction. The interface was kept at 325 °C for the duration of the reaction to prevent condensation of pyrolysis vapors.

Biomass samples were rapidly heated to temperatures between 500 and 600 °C for 15 seconds. Condensables from the reaction are adsorbed onto the trap while non-condensables are vented into the hood. The condensables are then desorbed and sent to the GCMS for compound separation and identification.

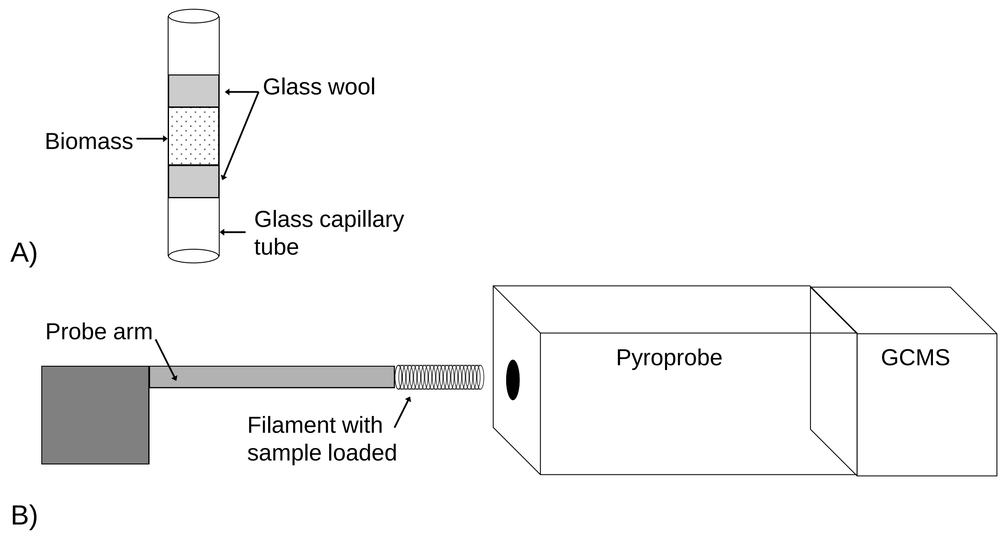

Figure 1: Sketch of sample tube and Pyroprobe layout

A) Diagram of sample tube loaded with biomass
B) Setup of Pyroprobe and GCMS

Preliminary tests showed that there was a discrepancy between the setpoint temperature on the software and the actual temperature of the sample. Calibration tests were run using a probe arm fitted with a thermocouple inside a sample tube.

RESULTS AND DISCUSSION

Calibrations for the Pyroprobe were done with washed cellulose and results were compared with previous data. Initial tests performed with a zeolite catalyst (developed by Mobil for conversion of methanol to gasoline), show a reduction of oxygen in the pyrolysis vapors as seen in Figure 2.

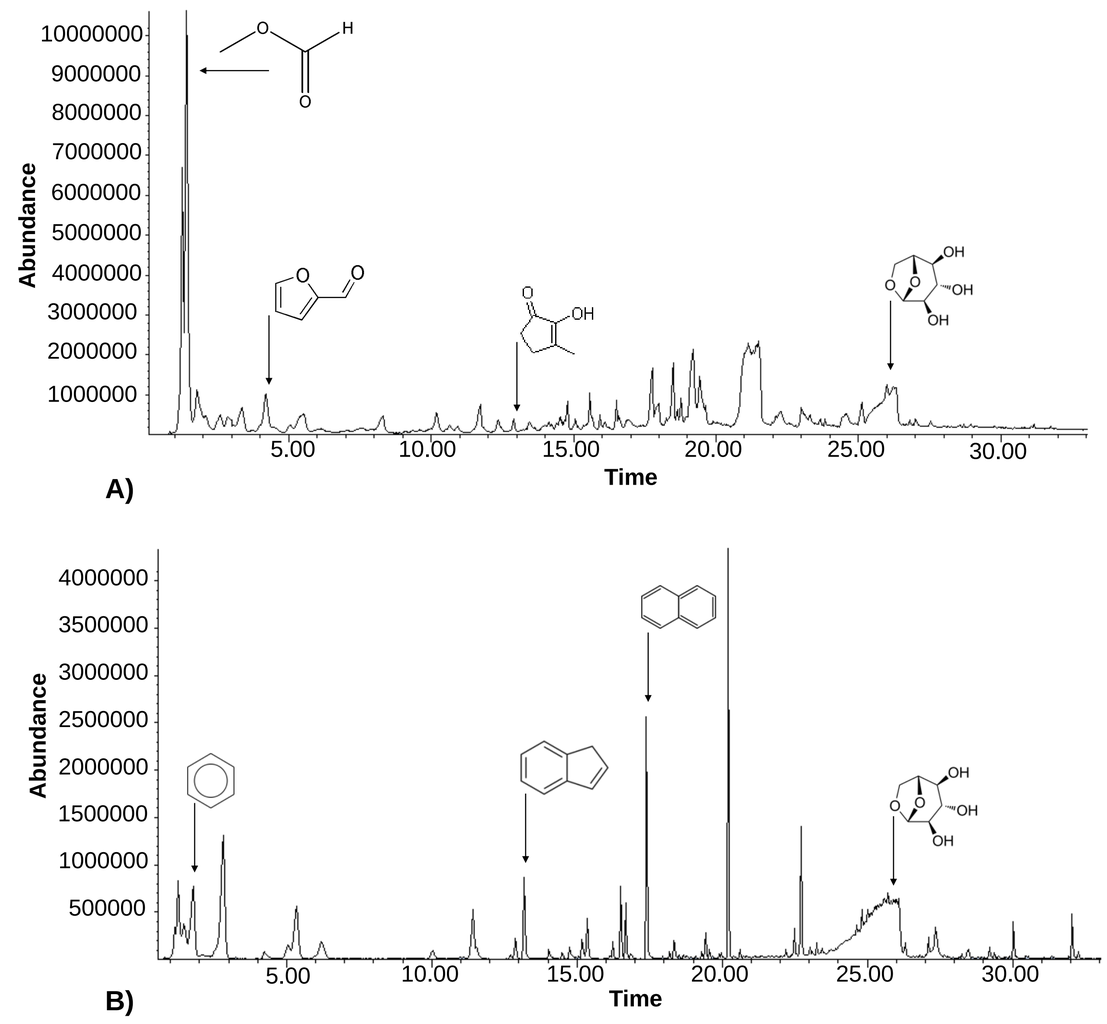

Figure 2: Chromatograms of washed cellulose pyrolysis products A) without catalyst and B) with zeolite catalyst.

FUTURE WORK

Future work will focus on the effect of catalyst loading on the pyrolysis vapors. The three methods are shown in Figure 3. Experiments will then be done at pressures of approximately 500 psi followed by reactions using hydrogen as a carrier gas.

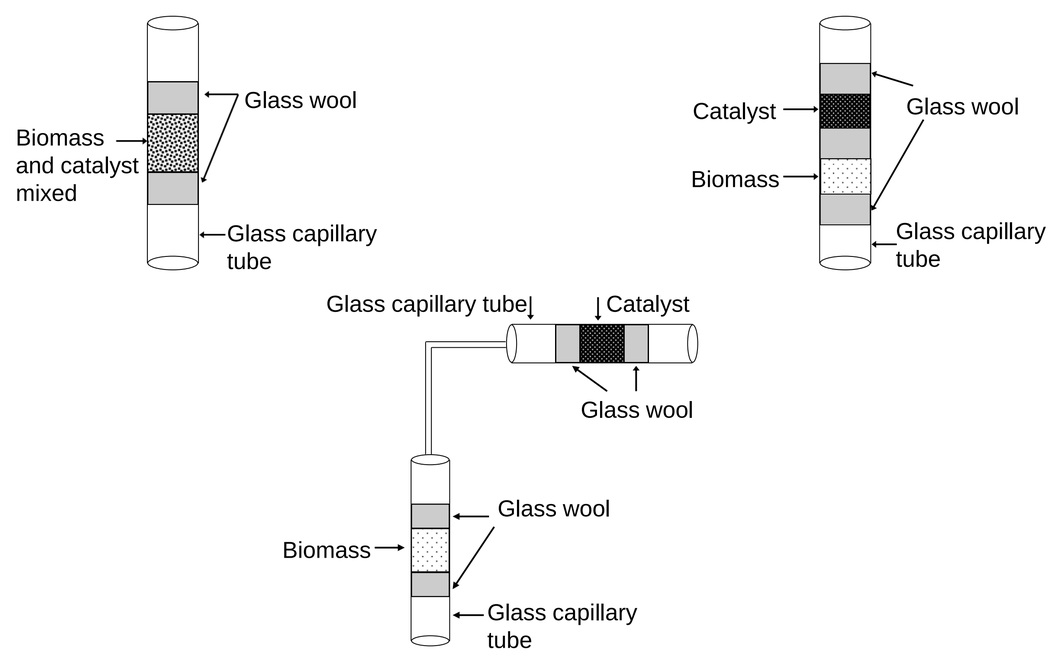

Figure 3: A diagram of A) sample tube loaded with mixture of biomass and catalyst B) sample tube loaded with biomass and catalyst separated by glass wool C) set-up for pyrolysis of biomass before the catalytic reaction

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