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Analysis of Chemical and Physical Processes During Pyrolysis of a Single Cylinder of Poplar Wood in Flow Reactor

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Biochar for soil amendment is one of several possible desirable products from thermal processing of biomass. We investigate the decomposition of wood under conditions favoring biochar production: low temperatures (300 °C to 450 °C) and long residence times (60 minutes). Cylinders of poplar wood are inserted into a heated flow of nitrogen in a flow reactor, and gaseous pyrolysis products are sampled through a quartz probe and analyzed via Fourier Transform Infrared (FTIR) spectrometry. Profiles of CO, CO₂, CH₄, CH₃OH, and HCOOH are reported as functions of time after the insertion of the poplar wood. Condensable products are also collected and identified by gas chromatography/mass spectrometry (GC/MS), and yields of char are reported.

1. Introduction

Biomass pyrolysis has been studied both experimentally and numerically by numerous investigators, both in single-particle studies and in larger batch and continuous processes [1, 6]. Pyrolysis is of interest as a stage in combustion and gasification processes, and as a process to produce bio-oils. Tars, gases and chars are the three broad classes of products that result from wood pyrolysis, and models have been developed to describe how their evolution depends on the kinetics, fluid flow, and species and heat transfer processes in the wood [7, 8]. Recently, attempts have been made to describe the production of individual gaseous and tar species [9, 10]. Biochar produced via pyrolysis of biomass has attracted considerable recent attention as an additive to improve the water retention and productivity of poor agricultural soils [11]. Using chars in the soil rather than combusting them can be a net benefit to farmers even though it implies that about half the heating value of the initial biomass is forfeited. Biochar production is maximized under mild pyrolysis conditions, and the effects of pyrolysis conditions on the relevant properties of the char are still under investigation.

In the current study, we investigate pyrolysis of single cylindrical pieces of wood under conditions resulting in substantial char production. We continuously measure gas composition sampled from near the wood cylinder during the pyrolysis process, and also record temperatures inside the wood.

2. Experimental Method

Wood pyrolysis took place in a flow reactor with heat provided by a heated nitrogen flow. Nitrogen was preheated to the desired temperature, and flows through a heated 5-cm-ID, 1-m long tube at approximately 1 atm pressure, before entering a tee section. A cylindrical wood

sample was mounted in a holder and stored in the water-cooled side-arm of the tee, achieving temperatures of approximately 110 °C. Once steady nitrogen temperatures were reached in the main flow, the wood sample was inserted into the heated flow, without breaking the flow reactor seal. The wood cylinder was oriented with its axis perpendicular to the flow reactor axis.

Gas sampling took place through an open quartz sampling tube with OD of ¼", with its mouth 1.8 mm from the surface of the cylinder. The sampling train consists of quartz and PTFE tubing, glass cold traps in an ice water bath, and stainless steel fittings. Downstream of the cold traps, the flow enters a Teflon gas cell (~ 50 cm³) with ZnSe windows. The sample flowed continuously during the experiment, with a cell pressure of 300 torr and a residence time of ~ 2.3 s in the entire sampling and analysis system. Gas composition was determined via Nicolet 6700 FTIR (Fourier Transform Infrared Spectrometer) with an MCT detector, operated with a spectral resolution of 1 cm⁻¹. Concentrations were quantified via interactive subtraction of a reference spectrum of known concentration.

Tars were collected by rinsing the sample traps with acetone, and analyzed via Thermo Trace GC Ultra/DSQ II GC/MS [12]. Temperatures inside the wood cylinder were measured with a sheathed, 1/8"-OD, type K thermocouple with multiple thermocouple junctions grounded to the inside of the sheath, at ½" intervals starting at the tip, which was positioned at the center of the wood sample. The wood samples were cylindrical sections of a 1.9-cm-diameter poplar dowel; the grain of the wood was aligned with the axis of the cylinder.

3. Results and Discussion

Table 1 shows the flow reactor operating conditions as well as the char (solid) yields for the three conditions reported.

Table 1: Operating conditions for pyrolysis experiments.

Temperature, °C	318	400	440
Reynolds number based on reactor diameter	2763	2621	2448
Char yield (%); two duplicate runs	42, 46	24, 26	21, 22

Figure 1 shows species and temperature profiles for the 400 °C pyrolysis case. For each set of conditions, two runs were performed. The runs at other temperatures show similar behavior, with a strong peak for each species occurring sometime in the first 10 minutes of the experiment. Figure 2 summarizes the results of all three runs by displaying the peak value of each species mole fraction vs. the temperature. In both figures, the mole fractions shown are averages of the two runs, with error bars spanning the range of values.

The species observed via FTIR are three permanent gases: CO, CO₂, and CH₄, and two condensable species: methanol and formic acid. The measured partial pressures of these species are well below saturation values at the cold trap conditions; hence values measured in the FTIR cell should be unaffected by the cold traps. The FTIR spectra contain additional unidentified species. H₂, which is generally present in biomass pyrolysis gas samples, is not detectable by infrared absorption.

The peak values of all species increase with pyrolysis temperature; this trend is reasonable because higher temperatures produce a more rapid, more intense release of gases than lower temperatures do.

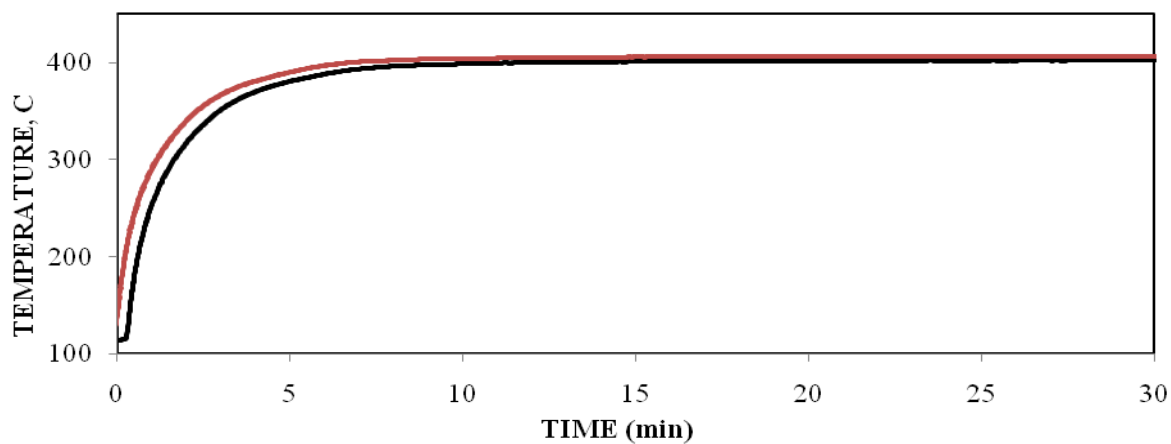
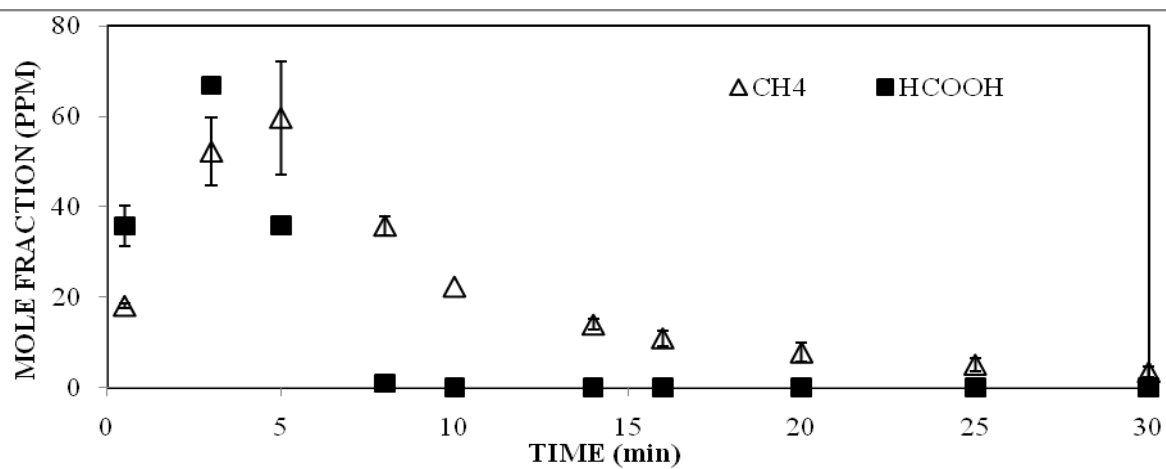
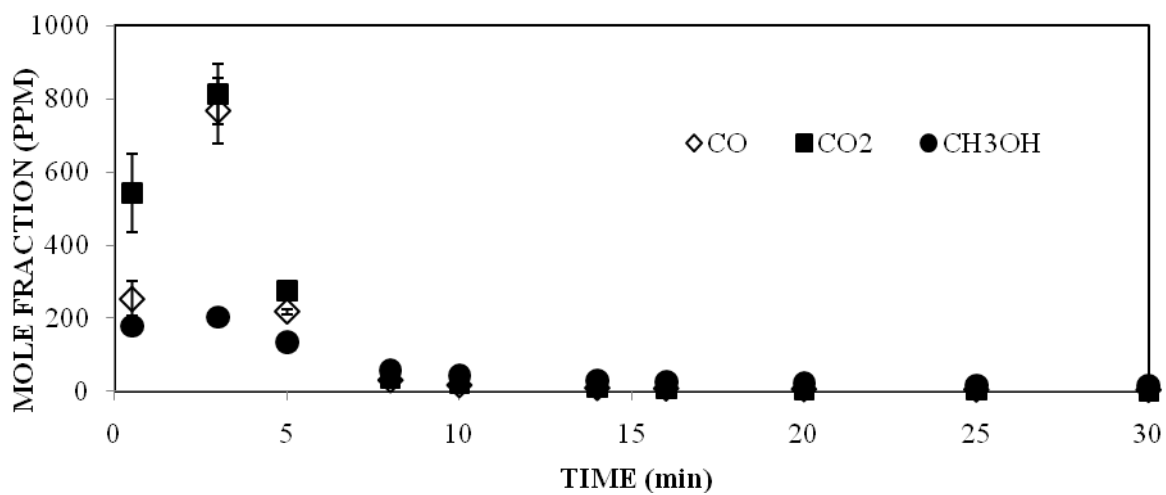


Figure 1: Species profiles and center temperature profiles for pyrolysis at 400 °C

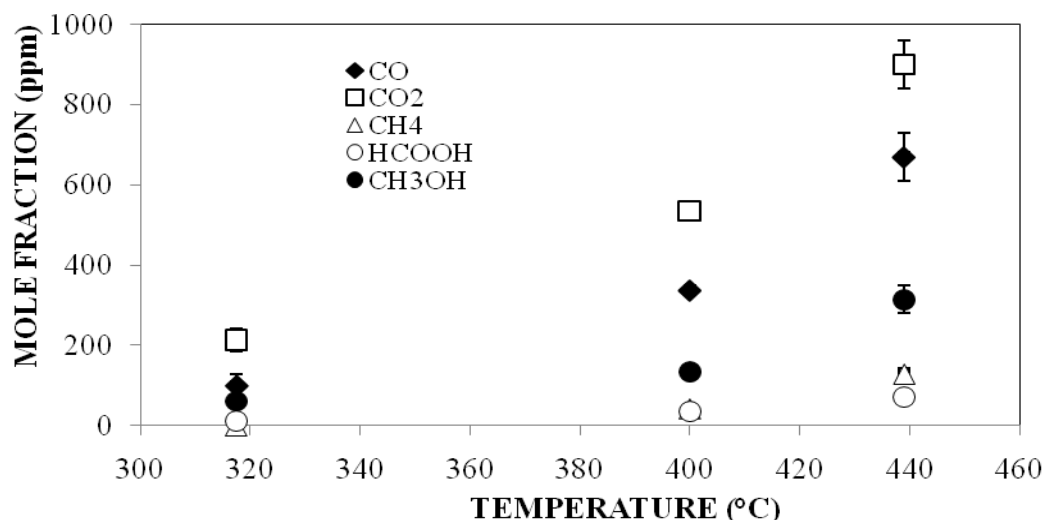


Figure 2: Peak mole fractions vs. pyrolysis temperature

GC/MS analysis of the cold trap contents indicated the presence of large quantities of oxygenated aromatic compounds (~30) such as phenols and methoxybenzenes, which are characteristic of lignin decomposition, as well as levoglucosan from cellulose pyrolysis.

4. Conclusions

We have obtained time histories of mole fractions of selected gases and volatile liquids evolved during pyrolysis of a cylinder of wood under low-temperature conditions with significant char yields. This data set should aid in validating combined transport and kinetic models of the pyrolysis of single particles of biomass.

Acknowledgments

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