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Influence of the Grain Direction on the Low-Temperature Pyrolysis of Large Wood Particles

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Pyrolysis is the thermal decomposition of a solid fuel in an inert atmosphere. Biomass pyrolysis products are non-condensable gases, char, and tars. The amounts and compositions of the products depend on several operating parameters i.e. temperature, pressure, heating rate as well as the biomass properties. For large particles, the pyrolysis rate is affected by chemical kinetics, mass transfer and heat transfer. Owing to the anisotropy of the woody material, transport processes depend on the heating and flow direction relative to the wood grain, as well as on temperature, density, and moisture content. The present work investigates the effect of grain orientation on the wood pyrolysis. For this purpose, dried white pine wood cylinders of 1.9 cm diameter and 4 cm length were pyrolyzed using a flow of nitrogen heated to a temperature between 374 and 464 ^{0}C. The cylinders have two different grain orientations: parallel and perpendicular to the cylinder axis. The pyrolysis was performed in a turbulent nitrogen flow at atmospheric pressure for 30 min. Temperature profiles at three locations within the particle were measured using a sheathed K-type thermocouples with sheath diameter of 0.5 mm. The temporal evolution of several volatiles released during sample pyrolysis was measured using Fourier Transform Infrared (FTIR) and Non Dispersive Infrared (NDIR) analyzers.

The data are compared in order to deduce the effects of sample grain orientation on the pyrolysis of woody biomass. It was noted that more gas and char were formed from the parallel gain orientation. This is due to the higher residence times of tars, such that there is a higher probability for their reacting to form secondary char and lighter gases prior to escaping from the particles.

1. Introduction

Conversion of biomass to transportation fuels and other high-value products can proceed through a variety of processes, both thermochemical and biochemical. Recently, pyrolysis of large wood particles, especially at relatively mild conditions, has received increased attention. These conditions are of practical interest when co-production of char is desired, either as biochar for agricultural treatment (Lehmann and Joseph, 2009) or for industrial purposes. Perhaps more importantly, they provide a good test of current models of the pyrolysis process (Gauthier et al., 2013a) a crucial building block in the modelling of all thermochemical processes.

Centimeter-scale biomass particles pyrolyze in the thermally thick regime, where significant variations in internal temperature exist (Di Blasi, 1997). These conditions imply that reaction thermochemistry can be observed through changes in internal temperature of the wood particles, and several recent investigations have interpreted internal temperatures as indicative of successive endothermic and exothermic processes as reported by Park et al. (2010) in their pyrolysis study of 2.54 cm maple heated mainly by radiation to a temperature ranging from 365 to 606 °C. Similar observations have been reported by Gauthier et al. (2013b) conducting their experiments with 1.9 cm diameter and 4 cm length beech wood cylinders pyrolysed over the temperature range 468-1050 °C. Bennadji et al., (2013) obtained also similar result with the pyrolysis of 1.9 cm diameter and 4 cm length dried poplar cylinders heated mainly by a convective heat flux.

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Also of interest in thick particles is the secondary reaction of tars on char surfaces which can increase char yields. Grieco and Baldi, (2011) proposed a mechanistic kinetic model which included secondary pyrolysis reactions involving solid and gaseous products. Experimental and modeling studies conducted by Sadhukhan et al. (2009) shown also that the pyrolysis of large biomass particles led to the secondary char formation owing to the secondary reactions of the released volatiles in the presence of primary char. More recently, Pattanotai et al. (2013) have studied experimentally the pyrolysis of large woody cylinders; they attributed the increase of the total gas and char yields to the intraparticle secondary reactions of the tar.

Wood grain orientation has an impact both on the thermal regime and on the secondary tar reactions. Along the wood grain orientation, thermal conductivity is higher, and resistance to gas transport is several orders of magnitude lower, as described in Grønli's review (1996). Thus both heat transfer and transport of volatiles occur disproportionately along the direction of the grain. Because of the huge differences in intrinsic permeability, gas flow can be neglected in directions perpendicular to the wood grain. This study investigates the pyrolysis of wood cylinders with an aspect ratio of approximately two, with the wood grain oriented either parallel to the cylinder axis (parallel-grain) or perpendicular to it (cross-grain). When the wood grain is along the long dimension of the wood particle, the interior of the particle is more thermally isolated from the surface, thus having longer pyrolysis times and being more strongly affected by reaction thermochemistry. The parallel-grain orientation also implies that volatiles must travel a longer distance before exiting the particle, as they travel along the grain direction. Thus the volatiles have more likelihood to react on char surfaces within the parallel-grain cylinders. By comparing the behaviour of the two grain orientations, the importance of these effects can be evaluated.

2. Method

Wood cylinders of diameter 1.90±0.01 cm, length 3.97±0.04, and mass 4.90±0.43 g, were turned on a lathe from a single block of white pine, using only heartwood. Two types of cylinders were obtained: "parallel-grain," with the wood grain parallel to the cylinder axis, and "cross-grain," with the wood grain perpendicular to the cylinder axis. The properties of the wood are listed in Table 1. Both mean values and standard deviations are listed in the tables, based on three samples. Proximate analysis was performed following ASTM E870-82 (2006) with minor changes. Ultimate analyses were obtained using a Thermo Delta V isotope ratio mass spectrometer interfaced to a NC2500 elemental analyser. C, H, O, and N were all measured, not obtained by difference.

Table 1: White pine heartwood proximate and ultimate analyses

Proximate Analysis	Wt %, dry basis	Ultimate Analysis	Wt %, dry basis
volatiles	86.86±0.04	C	52.25±0.42
fixed carbon	13.02±0.06	H	6.71±0.34
ash	0.12±0.02	O	38.96±1.70
		N	0.04±0.002

Prior to pyrolysis, wood cylinders were dried until no further weight change was observed, then cooled to room temperature in a dessicator. Three sheathed, 0.5-mm-OD thermocouples were inserted into each wood cylinder through holes drilled radially. The thermocouple junctions were positioned along the cylinder centerline at different axial locations (1, 2, and 3 cm from one end of the cylinder).

The cylinder was mounted in a holder and inserted abruptly into a heated turbulent flow reactor, where a heated nitrogen flow of 5.80 g/s provided rapid dilution of volatile products. The cylinder axis was perpendicular to the flow reactor axis, with the thermocouples inserted perpendicular to the flow direction. Downstream of the cylinder, at a location where the volatiles are well mixed with the nitrogen flow, samples were drawn continuously from the reactor and through the gas cell of a Fourier-transform infrared (FTIR) analyser with sampling time of approximately one minute and typical detectability limits of a few parts per million (ppm). A parallel sample flow passed through a nondispersive infrared analyser for analysis of CO with a more rapid response rate. Sample flowrates are chosen such that the residence time in the sampling system and reactor was approximately 4 seconds, which is negligible on the time scale of the pyrolysis process. The cylinders were kept in the heated part of the reactor for 30 min. At the end of this time, they were withdrawn from the heated flow, cooled, and removed from the reactor. Experiments were performed with nitrogen temperatures of 374, 418, and 464 ^{o}C, with run-to-run deviation in temperature from the average of at most 4 ^{o}C. Under these temperature conditions, gas-phase reactions of tars and gases are negligible (Morf et al., 2002); thus measured products reflect only pyrolysis reactions and char-catalyzed secondary decomposition of tars within the solid particle. Further details of the reactor and sampling and analysis systems are provided in a previous publication (Bennadji et al., 2013).

3. Results and Discussion

Figure 1 shows the temperatures measured near the center of the wood cylinders. Three repeats of each gas-temperature condition and grain orientation are superimposed on the plot, showing good repeatability. Following the step change in surface heat flux at t=0, all cases show temperatures rising and eventually asymptoting to the final (gas) temperature. At the two higher temperatures, there is clear evidence of an endothermic process (plateau or reduced slope of temperature curve), followed by an exothermic process (maximum in the temperature history). The timing of the heating process and the magnitude of the thermochemical effects differ for the different grain orientations. As anticipated, cross-grain cylinders heat more rapidly, in keeping with their greater thermal contact with the surface. The impact of grain orientation on thermochemical effects is more complex, with the grain orientation affecting the magnitude of the exothermic reaction peak only at the low and mid temperature conditions.

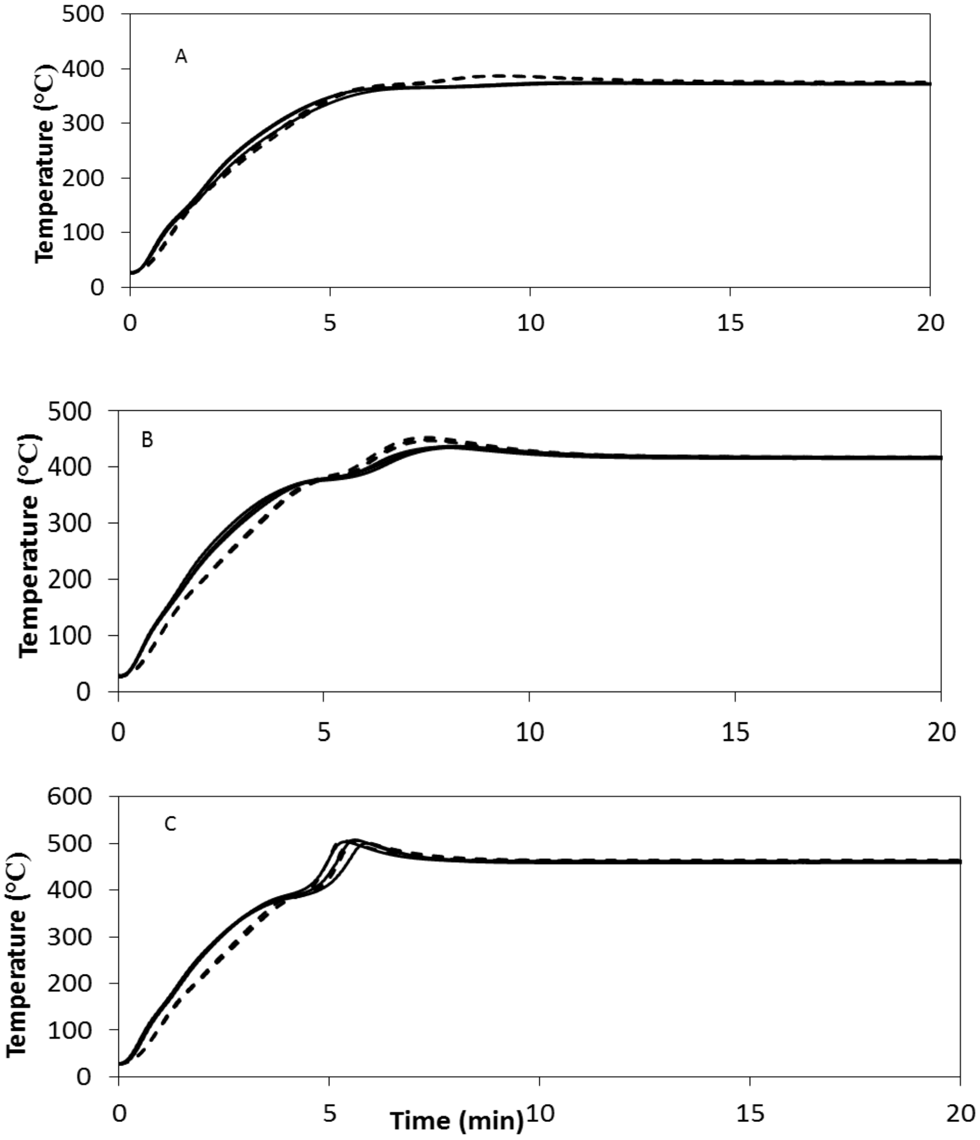

Figure 1: Temperatures measured at the center of the cylinder with nitrogen temperatures of 374 °C (A), 418 °C (B), and 464 °C (C). Solid lines represent experiments with cross-grain wood; dashed lines represent experiments with parallel-grain wood

Figure 2 shows time histories of selected species emitted from the two grain orientations, during heating to 418 °C. Again, results of three separate runs for each condition are superimposed. The parallel-grain cylinders (B) produce larger amounts of CO and CO_2, and slightly smaller amounts of formaldehyde. The peaks of CO and CO_2 are shifted to slightly to later times, while the formaldehyde peak is unchanged a the time resolution available.

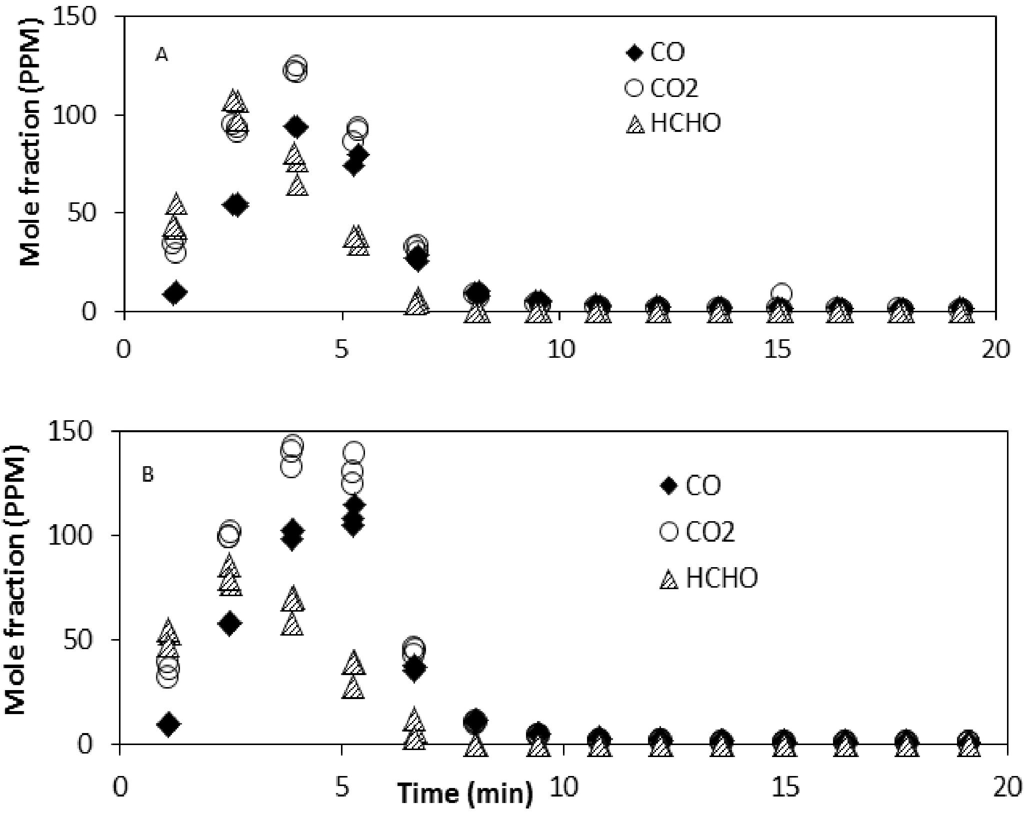

Figure 2: Representative time histories of species evolved during pyrolysis: Major species observed during pyrolysis of (A) cross-grain wood and (B) parallel-grain wood, with a nitrogen temperature of 418 °C

In Figure 3, the product yields are summarized for the same temperature conditions, both for individual species (A) and for char, gas (defined as CO, CO_2, and CH_4), and tar (obtained by difference) (B). Permanent gases CO, CO_2, and CH_4 have higher yields for the parallel-grain cylinders than for the cross-grain cylinders, while yields of the volatile compounds formaldehyde, formic acid, acetic acid, and methanol are lower for the parallel-grain cylinders. The yields of char and gas are higher for the parallel grain than for the cross-grain cylinders. In all cases except acetic acid, the difference between the two orientations is larger than the standard deviation of the measurements. The species results are consistent with the increased time for secondary reactions converting tar to char and gases, as the tar species pass through longer passageways, to exit the pyrolyzing parallel-grain wood cylinder.

4. Conclusions

The experimental results presented above are generally consistent with the anticipated effects of wood grain orientation. When the wood grain is parallel to the long dimension of the biomass particle, greater impact of reaction thermochemistry and greater conversion of tars to char and gases are observed. These observations appear to be due to the differences in thermal conductivity and gas permittivity with grain orientation. Thus in the parallel-grain cases, temperature conditions at the surface have less influence on interior temperatures because of the longer distance for heat conduction along the grain, and tar species have longer times for conversion through secondary reactions as they exit the particle.

These findings can provide a useful data set for comparison to models of biomass kinetics and transport processes. They also have important implications for the pyrolysis of wood chips. Because wood fractures more readily along the grain than across the grain, natural wood chips tend to be longer in the direction parallel to the grain than in the direction perpendicular to the grain. The current study implies that the processes along the grain direction dominate the transport of heat and gases through the particle. Thus it appears that the length along the grain orientation is the most relevant physical dimension to consider in predicting pyrolysis behaviour of wood chips.

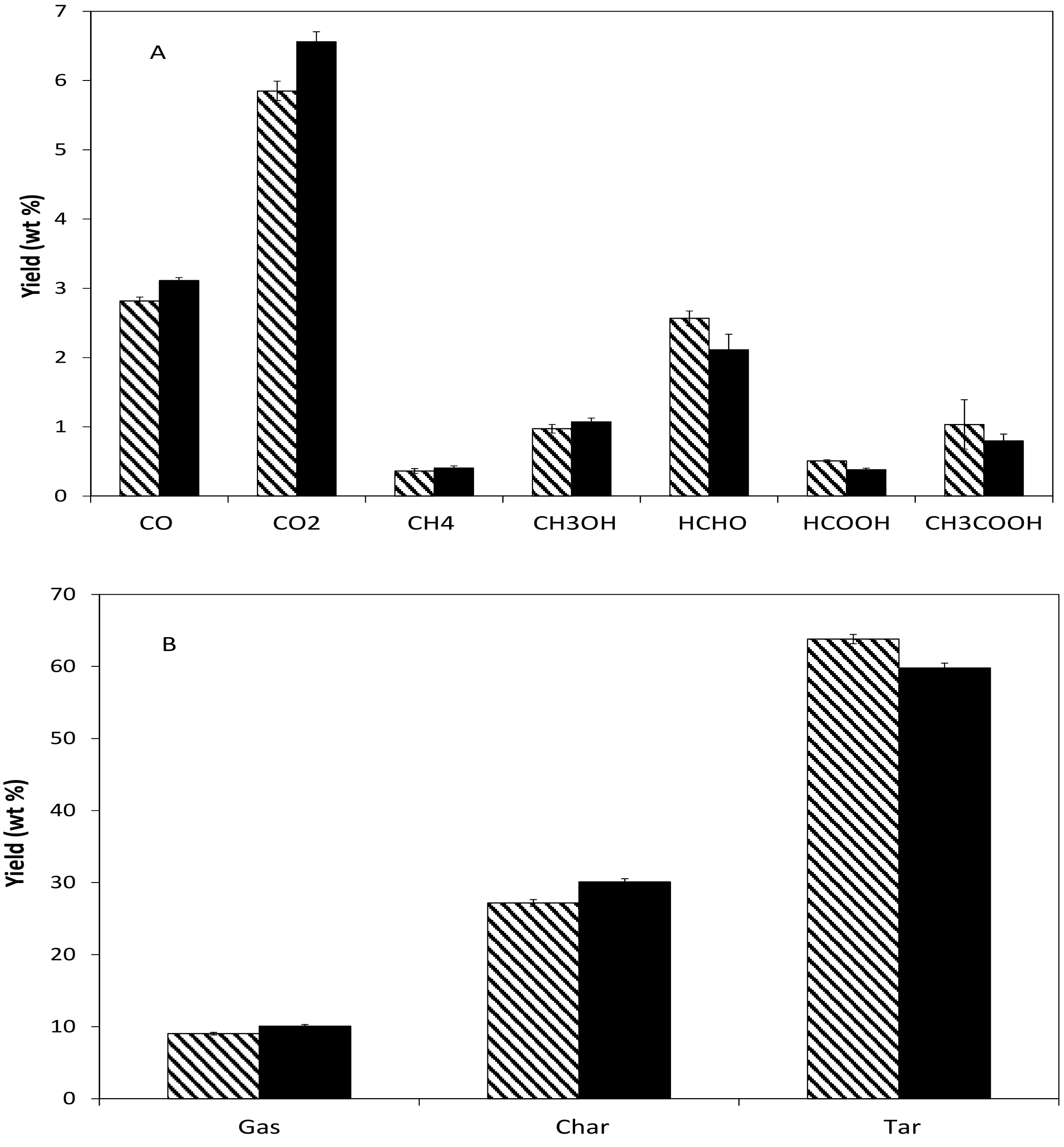

Figure 3 Representative yields of (A) individual species and (B) classes of compounds evolved during pyrolysis of cross-grain wood (cross-hatched bars), and parallel-grain wood (solid bars) at a nitrogen temperature of 418 ^{o}C. Error bars represent the standard deviations of three measurements.

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