



Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood

Shi-Shen Liaw^a, Shuai Zhou^a, Hongwei Wu^b, Manuel Garcia-Perez^{a,*}

^a Biological Systems Engineering, Washington State University, WA 99164, USA

^b Fuels and Energy Technology Institute, Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth WA 6845, Australia

HIGHLIGHTS

- ▶ Treating biomass below 300 °C does not have a major effect on product yields.
- ▶ Guaiacyl (G) units decrease when the biomass is heated over 300 °C.
- ▶ The yield of levoglucosan reduces when the biomass was heated over 260 °C.
- ▶ The yield of water increases in the whole range of temperature studied.

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ABSTRACT

This paper investigates the effect of thermal pretreatment temperatures between 200 and 370 °C on the yield and composition of products (bio-char, gas, water and organics) obtained when Douglas-fir wood was subsequently pyrolyzed in an auger reactor at 500 °C. The yield of products was reported for the pre-treatment and pyrolysis steps separately, and for the two steps added. The maximum yield of bio-oils achieved without pretreatment was close to 59 mass%. A decrease in total liquid yield was observed when the biomass was pretreated at 300 °C. At higher temperatures, the yields of Douglas-fir primary degradation products (lignin oligomers, anhydrosugars and alkylated and methoxylated phenols) decreased. The overall water yield increased gradually to 14 mass% at a pretreatment temperature of 290 °C. The yield of lignin oligomers also decreased as the pretreatment temperature increased. A drastic reduction in the yield of methoxylated phenols derived from guaiacyl (G) was observed when the biomass was pretreated at temperatures over 300 °C. This drastic reduction in the yield of methoxylated lignin derivatives can be explained by the formation of liquid intermediates that facilitate the formation of ionic species, enhancing dehydration reactions leading to the production of o-quinone methide intermediates critical for bio-char formation.

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1. Introduction

The production of transportation fuels derived from forest and agriculture wastes is a promising alternative to reduce our over-dependence on imported oil and to reduce the green house gases emissions associated with the combustion of fossil fuels. In 2007, the United States Energy Independence and Security Act (EISA) urged the industry to produce 9 billion gallons of renewable fuel by 2008 and an additional 36 billion gallons annually by 2022 to replace 20% of the transportation fuels consumed [1]. Meanwhile, the European community also established a target of 10% renewable fuels by 2020 [2]. To produce such quantities, new technologies need to be developed to convert lignocellulosic materials into trans-

portation fuels. Among the technologies studied, pyrolysis is very promising because it allows the conversion of between 60 and 75 mass% of lignocellulosic materials into a crude bio-oil [3,4] that can be further refined via hydrotreatment to produce transportation fuels [5].

Improving the quality of bio-oils is a major research goal for the biomass thermo-chemical community [6–13]. The properties of the feedstock [14], pyrolysis conditions [8,9], and particle size [13,15] are the three main factors affecting bio-oil quality. Thermal pretreatment in the range of temperature between 200 and 300 °C in the absence of oxygen (torrefaction) could modify some of these parameters and affect bio-oil yield and quality [16,17]. When biomass is heated between 200 and 300 °C hemicellulose is typically thermally degraded and the weak glycosidic bonds of amorphous cellulose break resulting in the formation of cellulose with between 150 and 400 glucose units [18,19]. This cellulose with constant degree of polymerization is often called “activated

* Corresponding author. Tel.: +1 509 335 7758; fax: +1 509 335 2722.

E-mail address: mgarcia-perez@wsu.edu (M. Garcia-Perez).

cellulose”, and is considered by some authors an intermediate product of pyrolysis reactions [18,20]. In this temperature range (200–300 °C), biomass weight loss is mainly due to dehydration, decarboxylation and deacetylation of xylan-containing hemicellulose polymers [21].

Thermal pretreatment at temperatures between 275 and 300 °C could reduce grinding energy [22,23]. This is critical for fast pyrolysis given the sensitivity of bio-oil yield and composition to biomass particle size [13,15]. High yields of bio-oil can only be achieved if biomass particles with diameters below 2 mm are used.

Despite the potential of thermal pretreatment to reduce grinding energy, there are few reports discussing its effect on the yield and quality of pyrolysis products [24–26]. The effect of thermal pretreatment at a temperature of 280 °C on the yield of products obtained from an auger pyrolysis and fluidized bed reactor at 350 °C, using beech, poplar, spruce and straw, was studied by De Wild et al. [25]. The authors concluded that staged pyrolysis could be a promising route to appreciate lignocellulosic materials. The main goal of this paper is to evaluate the effect of thermal pretreatment on the yield and composition of bio-oils obtained from Douglas-fir wood in an auger pyrolysis reactor in the range of temperature between 200 and 370 °C.

2. Experimental methods

2.1. Biomass preparation

The Douglas-fir wood studied was grown in Port Angeles, Washington and was kindly donated by Herman Brothers Logging & Construction, Incorporated (Port Angeles, WA). The samples were stored in a refrigerator at 4 °C and ground by a pioneer mill (Model number 400 HD, serial number 2404, Bliss Industries, Inc.) to a particle size below than 2 mm [27].

2.2. Thermal pretreatment and pyrolysis

Between 500 and 600 g of Douglas-fir wood samples were thermally pretreated in every experiment with an auger reactor [27]. Briefly, the dried biomass in the hopper was fed with a volumetric feeder (Barbender Technologies) into the auger reactor at a feed rate of 10–12 g/min. A stainless-steel tube 58.5 cm length and 10 cm diameter was heated by a Lindberg/Blue M (model HTF55322A) furnace. The biomass was pushed through the hot zone of the reactor with an auger screw driven by a 1 hp variable speed motor. Nitrogen at 10 L/min was used as the carrier gas and the auger speed was set at 5 rpm for the torrefaction process, corresponding to a residence time of 72 s. The thermally pretreated biomass obtained between 270 and 370 °C was collected in a pot. The pretreated biomass was left to cool in the pot and was then pyrolyzed in the same auger reactor at 500 °C. The estimated residence time of the vapors inside the pyrolysis reactor was approximately 8 s. All the pyrolysis experiments were conducted at auger speeds of 13 rpm which corresponds to a biomass residence time of approximately 30 s. For both the thermal pretreatment and the pyrolysis tests the temperature on the external wall was set and recorded as well as the temperature of the biomass bed at the exit of the heating zone and at the entrance into the collection pot. The vapors resulting from the pretreatment and the pyrolysis steps were condensed in three condensation units as described elsewhere [27]. The pressure inside the reactor was kept under a very slight vacuum of -2 mm H₂O by sucking the pyrolytic vapors and the carrier gas through the condensers with a vacuum pump. The yield of liquid was determined by weighing the liquid collected in the traps, the vacuum pump and the condensers. The non-condensable gases were calculated by difference.

2.3. Pretreated biomass analyses

The contents of extractives, cellulose, lignin, and hemicelluloses in thermally pretreated Douglas-fir wood were measured following ASTM methods (ASTM D1105-96, D1106-96, E1758-01). The extractives were measured by soxhlet extraction using ethanol and toluene as solvents. The cellulose and hemicelluloses contents were calculated by the mono-sugar content after two step sulfuric acid hydrolysis and analysis in an ionic exchange chromatograph. Lignin content includes acid soluble and acid insoluble fraction. The acid soluble lignin was obtained by UV spectroscopy and the acid insoluble lignin was calculated as the solid residues left after acid hydrolysis.

2.4. Thermogravimetric analyses

The thermally pretreated samples were dried at 105 °C and analyzed thermogravimetrically in a Mettler-Toledo TGA/SDTA851 analyzer. Between 5 and 10 mg of the different samples were put into the pans and heated at 10 °C/min. The final temperature inside the furnace was 600 °C and the nitrogen carrier gas flow rate was 20 ml/min.

2.5. Bio-oil analysis

The chemical composition of the liquid collected during the thermal pretreatment and pyrolysis step was determined using the methods described below.

2.5.1. Water content

The water contents of thermal pretreatment and pyrolysis liquids were measured by Karl-Fisher Titration (Schott Titroline KF) using Hydranal Composite 5K as reagent (ASTM E203-08).

2.5.2. GC/FID and GC/MS

The content of methanol in the liquids collected was determined with a GC/FID (Shimadzu GC-2014 with AOC-5000 auto injector) equipped with a head space analyzer (oven temperature 85 °C) [27]. Briefly, the vapor in contact with the sample (250 μ l) was injected into a 30 m \times 0.25 mm ID column with a 0.25 μ m film (HP-INNOW) using helium at 27.9 cm/s as the carrier gas. The GC/FID was operated in split mode (split ratio: 1:25), with an inlet and the FID at 180 °C and 210 °C respectively. The oven temperature of the GC was held at 45 °C for 1 min followed by heating at a rate of 5 °C/min until 70 °C (holding time at the final temperature: 2 min). The column was then heated to 200 °C (at a heating rate of 65 °C/min) and held at this temperature for 5 min to ensure the removal of all heavy molecules.

The content of selected volatile organic compounds heavier than water was measured with a GC/MS (Agilent 6890N). The instrument was calibrated with solutions of standard (selected) compounds at five different concentrations. Phenanthrene was the internal standard used to determine the response factor for each of the compounds analyzed in the conditions used in the GC/MS. Methanol solutions containing 5 mass% of oil sample and 0.2 mass% of phenanthrene were analyzed. All of the solutions were filtered (0.45 μ m) to remove bio-char particles from the oil. Filtered solutions (1 μ l) were injected into the inlet at 200 °C and working with a split ratio of 20:1. The vapors from the inlet were separated by capillary column (Agilent HP-5 MS, HP19091S-433) using helium as a carrier gas (1 mL/min). The column was held at 40 °C for 1 min, heated at 3 °C/min until 280 °C, and held for another 10 min at the final temperature. The mass spectrometer was operated with a transfer line temperature at 150 °C, an ion

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