



The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions

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ABSTRACT

The goal of this study was to investigate the effect of pyrolysis temperature on the recovery of various products from the pyrolysis of red oak using a fractionating bio-oil recovery system. Within the temperature range investigated, the maximum bio-char yield of 31.1 wt% occurred at 350 °C, the maximum bio-oil yield of 66.7 wt% occurred at 400 °C and the maximum non-condensable gas (NCG) yield of 26.3 wt% occurred at 550 °C. The maximum production of sugar from cellulose and hemicellulose of 13.5 wt% occurred at 450 °C. The sugars, in the form of anhydrosugars, were condensed in stage fractions (SF) 1–2. Production of phenolic compounds was highest at 400 °C yielding 29.4 wt% dry basis (db) with the majority collected as oligomers in SF 1–2. Moisture content was highest at 550 °C yielding 57.9% in SF5, which is 91% of the total moisture. Gel permeation chromatography (GPC) indicated that the majority of compounds found in the heavy ends of bio-oil (SF 1–2) ranged from oligomeric monomers to tetramers.

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1. Introduction

Fast pyrolysis is the thermal decomposition of biomass into liquid (bio-oil), solids (bio-char), and non-condensable gases (syngas). It is widely recognized that pyrolysis temperature affects the yield of these products; the goal of most pyrolysis research is to maximize the yield of liquids, which can be upgraded to transportation fuels. Little research has been directed toward the effect of temperature on the individual organic components of the bio-oil, possibly because they are recovered together as “whole bio-oil” with limited prospects for separating them after recovery.

Bio-oil is a multicomponent mixture containing 35–40 wt% oxygen, which is present in most of the more than 300 identified compounds in bio-oil [1]. It is comprised of both volatile compounds, including water, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, quaiacols, syringols, vanillins, and furans, and non-volatile compounds, especially viscous phenolic oligomers [2–5].

Bio-oil's complex chemical composition causes many problems including poor stability, both in storage and when heated for upgrading. Bio-oil constituents have a very wide range of boiling temperatures. Bio-oil starts to boil below 100 °C but distillation

ceases at 250–280 °C leaving 35–50% of the starting material as residue [1,5]. Typical methods of separation and purification include liquid chromatography, extraction, centrifugation, and distillation, which are high cost and difficult to scale up [6].

These problems prompted us to develop a bio-oil recovery system that separates bio-oil into SFs with distinctive chemical and physical characteristics [5]. This separation is accomplished by a combination of condensers with carefully controlled coolant temperatures to recover vapors and electrostatic precipitators (ESP) to recover aerosols.

The ability to fractionate bio-oil opens the possibility of optimizing pyrolysis operating conditions for the production of desired products [7]. For example, for the purpose of producing asphalt or resins, pyrolysis conditions that increase the yield of higher molecular weight phenolic oligomers should be optimized. If monomeric sugar production is the goal, conditions that encourage depolymerization of polysaccharides should be favored. This study investigates the effect of pyrolysis temperature on the recovery of various products from the pyrolysis of red oak using the fractionating bio-oil recovery system. Of particular focus is cellulose-derived levoglucosan and lignin-derived phenolic oligomers.

2. Methods

Biomass used for the pyrolysis experiments was Red oak (*Quercus rubra*) procured from Wood Residual Solutions of Montello,

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WS. As-received biomass was passed through a 60 hp hammer mill equipped with a 3 mm screen, resulting in a particle range of approximately 200 μm to 3 mm. The moisture content of the red oak was approximately 10%.

Experiments were performed in a fluidized bed pyrolyzer and bio-oil recovery system that separates the bio-oil into distinctive stage fractions, as previously described by Pollard et al. [5]. Stage 1, a condenser, captures high boiling point compounds such as levoglucosan and phenolic oligomers. It is a shell-and tube heat exchanger operated with gas inlet and outlet temperatures of 345 °C and 102 °C, respectively. The coolant water is controlled to 85 °C. Stage 2 uses an ESP to collect aerosols formed either during pyrolysis or during cooling in Stage 1. The ESP is operated at 40 kVDC and heat traced to 129 °C to prevent premature condensation of vapors. Stage 3, another shell-and-tube heat exchanger, collects compounds with dew points near that of phenol. It operates at gas inlet and outlet temperatures of 129 °C and 77 °C, respectively. The coolant water is controlled to 65 °C. Stage 4, an ESP, is insulated and has an operating temperature of approximately 77 °C. Stage 5 is a shell-in-tube heat exchanger using water at 18 °C as coolant for the purpose of removing water, furans, and light oxygenated compounds (i.e. acids) [5].

Several improvements have been made to the system since first described by Pollard et al. [5]. Knife gates in the feed system were improved to provide continuous batch feeding and allow extended test runs. Four Omega Type K thermocouple sensors (Omega Engineering, Inc., Stamford, CT) were inserted along the central axis of the fluidized bed spaced every 50 mm to improve monitoring and control of pyrolysis. The thermocouple located at the top of the fluidized bed region controls power to the external bed heaters and thus sets the reaction temperature of the bed. Enhanced preheating of nitrogen entering the plenum of the reactor further improves temperature control of the reactor. The bio-char disengagement section was heat traced to improve its operational reliability. Better temperature control was added to the inlet of SF 1, which was previously prone to fouling. The collection efficiency of the ESPs was improved with changes to its geometry to improve corona discharge. These changes to the pyrolysis system allow for significant improvements in bio-oil yield and allow more reliable sustained operation compared to previously reported results with the pyrolyzer [5].

Five pyrolysis tests were performed at 350, 400, 450, 500, and 550 °C with a biomass feed rate of 6 kg/h. Bio-oil was collected and weighed to determine yield for each SF. Bio-oil was stored in polypropylene containers at 5 °C in the dark until analyzed. Non-condensable gas flow rate was determined by injecting helium into the reactor plenum at a known mass flow rate as determined by an Alicat Mass Flow Controller (Alicat Scientific, Tucson, AZ). An Agilent Varian® CP-4900 Micro-GC (Gas Chromatograph) (Agilent Technologies, Inc. Santa Clara, CA) interfaced with Galaxie® Chromatography 1.9 software (Bruker Corporation, Bruker Daltonics, Inc., Fremont, CA) was used for NCG analysis at the gas exit of the bio-oil collection system. The micro-GC was programmed to sample for 30 s followed by 120 s of run time. The average composition over steady state operation was then used to calculate NCG yields. In principle, bio-char could be determined directly from the cyclone catch, but sand often elutriated from the fluidized bed along with the bio-char, making problematic accurate measurement of bio-char yield from the cyclone catch. Accordingly, bio-char yield was determined by difference rather than direct gravimetric measurement.

Specific analyses of the bio-oil were from methodologies described in detail in the literature. The Association of Analytical Communities, International (AOAC) Method 988.12 (44.1.30) (Phenol–Sulfuric Acid Assay for Total Carbohydrate Determination) was used to quantify the water-soluble sugar fraction in SF

1–5 [7]. Levoglucosan was used as the standard with the ultraviolet visible range spectrophotometer wavelength set to 490 nm. Oasmaa and Kuoppala [8] describe bio-oil sample preparation for extracting the water-soluble fraction of bio-oil for sugar determination. The acids analyzed in each bio-oil SF included acetic, formic, glycolic, and propionic by ion chromatography (IC) [9]. These were done in triplicate with the standard deviation $\leq \pm 0.9$ wt% wet basis (wb). Gas chromatography/mass spectroscopy was used for bio-oil chemical analyses. The samples were done in triplicate. The standard deviation for phenol and alkylated phenols was $\leq \pm 0.10$ wt% wb, monomethoxyphenols was $\leq \pm 0.41$ wt% wb, and dimethoxyphenols was $\leq \pm 0.60$ wt% wb. The standard deviation for furans was $\leq \pm 0.01$ wt% wb. A complete description of the methodology is found in Pollard et al. [5]. The Folin–Ciocalteu colorimetry method [10] was used to determine total phenols in bio-oil [11]. The samples were done in triplicate. The standard deviation was $\leq \pm 2.16$ wt% db. The water-insoluble content was determined by an in-house method previously described in the literature [5]. The standard deviation for the water-insoluble content evaluation was $\leq \pm 2.34$ wt% db.

Gel permeation chromatography (GPC) was used to determine the relative molecular weight distribution (relative to polystyrene standards) of the bio-oil constituents at 254 nm utilizing a diode array detector. The high performance liquid chromatography (HPLC) system used was a Dionex Ultimate 3000 (Sunnyvale, CA) equipped with a Shodex Refractive Index (RI) and Diode Array detector (DAD). The software used to control the instrument and evaluate the samples was Dionex Chromeleon version 6.8. For the GPC analyses, the eluent for the phenolic oligomers was tetrahydrofuran (THF) with two Agilent PLgel 3 μm 100 Å 300 x 7.5 mm and one Mesopore 300 x 7.5 mm. The column flow rate and temperature was 1.0 mL min^{−1} at 25 °C. The phenolic oligomers samples were prepared using 10 mL of THF and 0.02 g of heavy ends from the bio-oil. All samples were filtered with a Whatman 0.45 μ Glass Microfiber syringe filter before analysis. The GPC standards were purchased from Agilent (Agilent Technologies, Inc. Santa Clara, CA). These standards contained polystyrene ranging from 162 – 38,640 g mol^{−1}. The polystyrene standards were diluted with JT Baker HPLC grade Stabilized THF.

Moisture content of the bio-oil was determined by a MKS 500 Karl Fischer Moisture Titrator (Kyoto Electronics Manufacturing Co., Ltd, Kyoto, Japan) using ASTM E203 Standard Test Method for Water Using Karl Fischer Reagent. The reagent used was Hydranal Composite 5 K and the solvent was Hydranal Working Medium K purchased from Thermo Scientific® (Hanover Park, IL). The percent moisture of the bio-oil samples was determined in a minimum of four trials with a standard deviation of $\leq \pm 3.08\%$.

The ultimate analysis was performed using LECO TruSpec (LECO Corp., St. Joseph, MI) carbon, hydrogen, and nitrogen (CHN) analyzer with the determination of oxygen by difference. Ethylene diamine tetra acetic acid (EDTA) was used as a standard for carbon and hydrogen determinations. Calibration lines were prepared using four different concentrations of EDTA. The standard was purchased from LECO Corporation. A minimum of 3 trials were run for each sample. The standard deviation for the ultimate analyses was $\leq \pm 0.42$ wt% carbon and $\leq \pm 0.17$ wt% hydrogen.

3. Results

The yields (weight of product/weight of feedstock) of bio-char, NCG, and bio-oil stage fractions were determined at five different temperatures: 350, 400, 450, 500, and 550 °C using red oak as feedstock (Table 1). Maximum yield of whole bio-oil was obtained in the temperature range 400–450 °C where approximately 67 wt% of the biomass was converted to bio-oil. However, there was

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