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## Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor

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#### ABSTRACT

A fast pyrolysis process produces a high yield of liquid (a.k.a. bio-oil) and has gained a lot of interest among various stakeholders. Nonetheless, some of the properties inherent by the bio-oil create significant challenges for its wider applications. Quality of the bio-oil and its yield are highly dependent on process parameters, such as temperature, feedstock, moisture content and residence time. In this study, the effect of temperature on bio-oil quality and its yield were examined using pine wood, an abundant biomass source in the southeastern part of the United States. Physical properties of bio-oil such as pH, water content, higher heating value, solid content and ash were analyzed and compared with a recently published ASTM standard. Bio-oil produced from pine wood using an auger reactor met specifications suggested by the ASTM standard. Thirty-two chemical compounds were analyzed. The study found that the concentration of phenol and its derivatives increased with the increase in pyrolysis temperature whereas the concentration of guaiacol and its derivatives decreased as the temperature increased. Concentration of acetic and other acids remained almost constant or increased with the increase in temperature although the pH value of the bio-oil decreased with the increase in temperature.

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#### 1. Introduction

Over the last few years, interest in using biomass derived energy/fuels has increased because of diminishing fossil fuel supply and growing concerns about its environmental issues. The Billion-Ton study showed that approximately 1.3 billion dry tons of biomass is available annually in the US, which potentially can be used to replace about 60 billion gallons of the country's annual petroleum consumption (Perlack et al., 2005), Many efforts have been made to convert biomass to liquid fuels via thermochemical and biochemical platforms. Among the various options within the thermochemical platform, a fast pyrolysis process has gained a lot of interest from academia and industries due to a high liquid yield. The fast pyrolysis process is preferred over a slow pyrolysis because of the high liquid yield and low solid yield (Bridgwater, 1999). Since the major product of fast pyrolysis is in the liquid form, it can be readily stored and transported. Further, there is a growing interest in utilizing bio-char (solid left from the pyrolysis process) as a soil amendment.

In the fast pyrolysis process, biomass is rapidly heated in the absence of oxygen (Gupta and Demirbas, 2010). As a result, biomass is decomposed to char, vapors/aerosols and gas. The vapors/aerosols are quickly condensed to a liquid called bio-oil. It is a complex mixture of more than 200 compounds containing water, sugars, acids, esters, aldehydes, ketones, furans, phenols, cresols, and guaiacols (Diebold, 2000; Milne et al., 1997). Bio-oil has many applications in the field of energy and fuels and can be used as a feedstock for many commodity chemicals. Bio-oil has been tested for static applications such as in boilers, furnaces, turbines and diesel engines for heat, power or electricity generations (Czernik and Bridgwater, 2004). Moreover, it can be upgraded as transportation fuels by improving its negative attributes, such as high acidity, high oxygen content, high viscosity, low heating value and instability. A detailed review of bio-oil production techniques, its applications and properties is documented elsewhere (Mohan et al., 2006). Some of these negative properties can be removed by upgrading the bio-oil through simple physical treatments while others need chemical treatments (Adjaye and Bakhshi, 1995; Chiaramonti et al., 2003; Diebold and Czernik, 1997; Qi et al., 2007; Senol et al., 2005; Zhang et al., 2006). An extensive review of bio-oil upgrading techniques is discussed in published documents elsewhere (Elliott, 2007; Furimsky, 2000).

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A variety of reactor configurations has been developed for the fast pyrolysis of biomass (Bridgwater and Peacocke, 2000). An auger reactor does not require a carrier gas and easy for handling and operation. These advantages make an auger reactor one of the promising reactor configurations for the fast pyrolysis process. An auger reactor was designed and operated to produce bio-oil in this study.

Many studies have reported an influence of pyrolysis parameters such as pyrolysis temperature, heating rate, feedstock composition, particle size and moisture content on the yield of bio-oil (Asadullah et al., 2007; Demirbas, 1998; Park et al., 2008; Sensoz et al., 2006). However, a handful of studies (He et al., 2009: Horne and Williams, 1996; Lee et al., 2008) reported an influence of these parameters on the physiochemical properties of bio-oil but those studies did not examine how each parameter would be influenced if the bio-oil is produced at different temperatures. In this paper, the physical and chemical properties of bio-oil produced at different temperatures were investigated to understand the influence of pyrolysis temperature in order to make the downstream process (upgrading) easier. Major physical properties such as density, pH, water content, heating value, ash and solid contents were measured and compared with the ASTM standard (D 7544-09) published recently (ASTM, 2009). Chemical compounds were analyzed to quantify the effect of temperature during the fast pyrolysis process.

The biomass used for bio-oil production in this study was pine wood, and the justification for using woody biomass for bio-oil production is as follows. Wood residues are widely available biomass in the US and about 368 million dry tons/year of biomass could be sustainably removed from forestlands (Perlack et al., 2005). Another study conducted by Milbrandt (2005) showed that wood residues account for 39% of total biomass available in the US. Further, the state of Alabama's potential for annual wood residue was listed as 2.81 million dry tons of forest residues, 6.45 million dry tons of primary mill residues, 63 thousand dry tons of secondary mill residues, and 532 thousand dry tons of urban wood residues. Pine wood is widely available biomass in the southern part of the US. The South's market for forest products has weakened in recent years due to increasing global competition in the pulp and paper industry and mill closures due to aging facilities. Landowners are looking for new markets for their timber, and it is anticipated that a new bioenergy sector could make up for previous setbacks.

#### 2. Methods

#### 2.1. Biomass preparation and characterization

Pine wood chips used in this study were obtained from a local wood chipping plant in Opelika, Alabama. Wood chips were dried

in an oven at 75 °C for 12 h and ground in a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm (1/16 in.) screen size. The ground biomass sample was then fractionated using screens with sieve numbers 20 (0.84 mm opening) and 30 (0.60 mm opening). The sample that was retained on the 0.60 mm screen but passed through the 0.84 mm screen was used for bio-oil production. Moisture content of the biomass (wet basis) was determined by calculating weight loss of a sample by heating it in an oven at 103 °C for 16 h according to the ASTM E 871 standard (ASTM, 2006). Ash content in the biomass sample was measured using the ASTM E 1755 standard (ASTM, 2007). Higher heating value (HHV) of the biomass sample was measured using an oxygen bomb calorimeter (IKA, model C200).

#### 2.2. Bio-oil production using auger reactor

An auger reactor was used for bio-oil production and four different temperatures (425, 450, 475 and 500 °C) were selected in order to obtain the highest bio-oil yield. The temperature range of 425-500 °C was based on trial studies that were carried out prior to conducting this experiment. A schematic diagram of the reactor configuration is given in Fig. 1. Two condensers were used for bio-oil collection. The second condenser, maintained at 0 °C, was used to condense the vapors which escaped from the first condenser. In each experiment, about 500 g of biomass was fed into the reactor using a screw feeder. An inert atmosphere in the reactor was maintained by purging nitrogen gas before the pyrolysis process. Liquid products from the first and second condensers were collected and mixed together to determine the total yield of liquid. For each temperature, experiments were run in triplicate and the average of three values is reported in this paper. Bio-oil and char yields were calculated by measuring their weights at the end of each experiment whereas the gas yield was determined from the difference (100 minus the sum of the weight of bio-oil and char).

#### 2.3. Bio-oil analysis

Physical and chemical properties of bio-oil produced at various temperatures were measured. Physical analysis of the bio-oil includes density, pH, viscosity, water, ash, and solid content, and heating value measurements while chemical composition was determined with a gas chromatograph/mass spectrometer (GC/MS). To measure density of bio-oil, a 2 mL, calibrated density bottle (Cole-Parmer Model EW-34580-40) was filled with a known mass of bio-oil. The pH measurements were performed with a digital pH meter (Oakton, Model PC 510). Water content of bio-oil samples was calculated by Karl-Fischer (KF) analysis using a Barnstead aquametry II apparatus (Cole-Parmer Model EW-25800-10). In the volumetric KF titration, the known amount

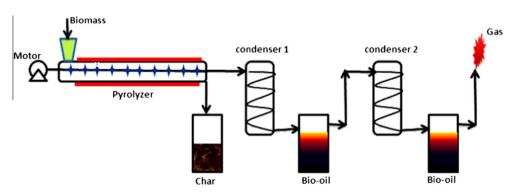


Fig. 1. An auger reactor configuration for pyrolysis of pine wood.

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