



# Effect of blending ratio of loblolly pine wood and bark on the properties of pyrolysis bio-oils



Xueyong Ren<sup>a,b</sup>, Jiajia Meng<sup>a</sup>, Jianmin Chang<sup>b</sup>, Stephen S. Kelley<sup>a</sup>, Hasan Jameel<sup>a</sup>, Sunkyu Park<sup>a,\*</sup>

<sup>a</sup> Department of Forest Biomaterials, North Carolina State University, Raleigh, NC 27695, USA

<sup>b</sup> MOE Key Laboratory of Wood-based Material Science and Application, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, PR China

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## ABSTRACT

Bark, which is available in abundance, has recently become a topic of interest when considering alternative materials for the production of pyrolysis bio-oil. Previous studies have revealed that the pyrolysis behavior of bark differs remarkably from that of wood in that bark typically generates a phase-separated bio-oil. In this study, blends of loblolly pine wood and bark were pyrolyzed to investigate the effect of blending ratio on the yield and properties of derived bio-oils. Trends of lower decomposition rate, decreased organic yield, and increased bio-char yield were observed as bark percentage in the feedstock increased, while the amount of levoglucosan in bio-oil increased. Pyrolysis reactivity, which includes yield and physical properties of the bio-oil, was found to have a linear relationship with the blending ratio of pine bark. It was found that blending up to 50% bark in the feedstock still produced a homogeneous bio-oil.

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## 1. Introduction

Lignocellulosic biomass is an abundant renewable feedstock used for the production of bio-based chemicals and fuels [1]. Among the many biomass resources, forest residue is one of the most highly under-utilized resources. Residue is usually left behind at logging and forestry sites to help maintain soil conditions for future logging operations. However, this debris has been identified as a potential source of forest fires and environmental pollution. Forest residue consists primarily of bark, needles, leaves, sap, and heated wood chips [2]. In fact, an estimated 30.3 million tons of bark are generated every year from timber processing in the United States alone. Approximately 90% of the bark generated is used as a low grade heating source at present [3].

Fast pyrolysis is one of the most promising technologies for biomass conversion because it efficiently converts solid biomass into a liquid, which provides logistical advantages including easy transportation and storage compared to its bulky parental biomass [4–7]. Therefore, bio-oil production from bark via the fast pyrolysis process is of significant interest considering the great availability of feedstock. The softwood bark was pyrolyzed in a vacuum reactor and the derived bio-oil was separated into top and bottom layers. Following separation, the layers' chemical properties and storage stability were studied [8–10]. Fast pyrolysis of forestry residue yields less liquid product compared to bark-free wood. Also, phase-separation was found to take place

when forestry residue was used as the feed for bio-oil production because of the significant differences in polarity, solubility, and density between extractives and the highly hydrophilic pyrolysis liquid compounds in the bio-oil matrix [11]. Pyrolysis of mallee bark was conducted between the temperatures of 300 and 580 °C and the results indicated that the temperature of pyrolysis process played a significant role in determining the yield and composition of the resulting bio-oil. Properties that were linked to changes in temperature include the presence of aromatic compounds and phase separation [12]. Many previous studies have found that the pyrolysis behavior of bark (rich in extractives, waxes, and lignin) differs significantly from that of wood because phase-separation is often observed in the derived bio-oil when bark is used [9–13]. The inhomogeneous liquid derived from bark is considered poor quality and has very limited applications.

Co-pyrolysis is a promising strategy which would allow companies to profit from the properties of different raw material. However, to the best of the author's knowledge, the co-pyrolysis of different biomass for bio-oil production at desired conditions has rarely been reported. Previous studies have shown that differences in biomass composition can influence the conversion efficiency and bio-oil product yield and quality [14–15]. Moreover, it is still an open question as to how individual components of different materials will interact during the co-pyrolysis process. Mixing different types of biomass may generate a “desired” feedstock that meets certain chemical component specifications. These specifications may eventually help to reduce product costs and promote the standardization of bio-oil production by integrating low-grade biomass resources into the parental feedstock strategy. In practice, pulp

\* Corresponding author.

E-mail address: [sunkyu\\_park@ncsu.edu](mailto:sunkyu_park@ncsu.edu) (S. Park).

and paper mills generate a large volume of loblolly pine bark, available in US southern east area, which could be a potential source of bio-oil feedstock.

The objective of this study is to examine how the blending ratio of wood and bark affects pyrolysis reactivity and properties of derived bio-oils. Samples of bark-free loblolly pine wood, loblolly pine bark, and three blends at different ratios were subjected to both analytical pyrolysis and lab-scale fast pyrolysis. The physical and chemical properties of bio-oils were analyzed to understand the impact of bark blending on the quality of pyrolysis bio-oil.

## 2. Materials and methods

### 2.1. Raw material and sample preparation

The materials used in this study included an approximately 20-year-old loblolly pine tree (*Pinus taeda*), which was harvested from Schenck Memorial Forest in Wake County, North Carolina, USA. The pine tree was first debarked to separate the bark-free stem fraction and bark fraction. The stem fraction (“wood”) and bark fraction (“bark”) were air-dried for one week and then milled with a Wiley mill equipped with 0.50 mm sieve. In addition to the individual wood and bark samples, three blend samples were prepared with different oven-dry weight ratios (weight of wood to bark at 80:20, 50:50, and 20:80) and were labeled as WB82, WB55, and WB28. The different mixtures of wood and bark were physically blended for 3 min using a Ro-Tap shaker.

### 2.2. Feedstock analysis

The ash yield of the pine wood and bark were determined at 525 °C for 4 h in a muffle furnace. The extractives in the feedstock were recovered with acetone using a Soxhlet extractor for 24 h. The extracted solution was rotationally evaporated below 40 °C with low-pressure to acquire the weight of the extractives. Following the Soxhlet extraction, the air-dried acetone extractive-free samples were then extracted with a methanol-water mixture (3:1, v/v) for 48 h to recover the tannin.

Lignin and carbohydrate content of the pine wood and bark samples were determined using the NREL standard procedure with slight modification [16]. Hydrolysis with 72% H<sub>2</sub>SO<sub>4</sub> for 2 h was conducted first to achieve a quantity of 0.3 g OD powder of wood (40–60 mesh). The hydrolyzed samples were diluted to 3% H<sub>2</sub>SO<sub>4</sub> and autoclaved at 120 °C for 1 h. The biomass hydrolysate was then filtered and oven-dried to determine the amount of insoluble lignin present (Klason lignin). A UV-Vis (Lambda XLS, Perkin Elmer, Waltham, MA, USA) at 205 nm was used to measure the acid soluble lignin in the remaining filtrate. Sugar analysis was also carried out via a high-performance liquid chromatography (HPLC) system (Agilent 1200, Agilent, Santa Clara, CA, USA) with a refractive index detector.

Carbon, hydrogen, and nitrogen content of the samples were measured using a Perkin Elmer CHN/O elemental analyzer. Oxygen content was calculated by difference.

### 2.3. Analytic pyrolysis by TGA

Analytical pyrolysis was conducted on the samples using a thermogravimetric analyzer (Q500, TA instruments). Proximate analysis and a decomposition behavior study were integrated into one operation process, as shown in Fig. 1; (1) a heating rate of 50 °C/min from ambient temperature to 110 °C with nitrogen purge, (2) an isothermal period for 5 min, (3) a heating rate of 100 °C/min from 110 °C to 900 °C, (4) an isothermal period for 15 min, (5) purge gas change from nitrogen to air at the same temperature to provide oxidative environment, and (6) a final isothermal period for 10 min. A sample containing approximately 15 mg of biomass was used in each run. Industrial grade nitrogen and air were used as the purge gas at a flow rate of 100 mL/min both for pyrolysis and

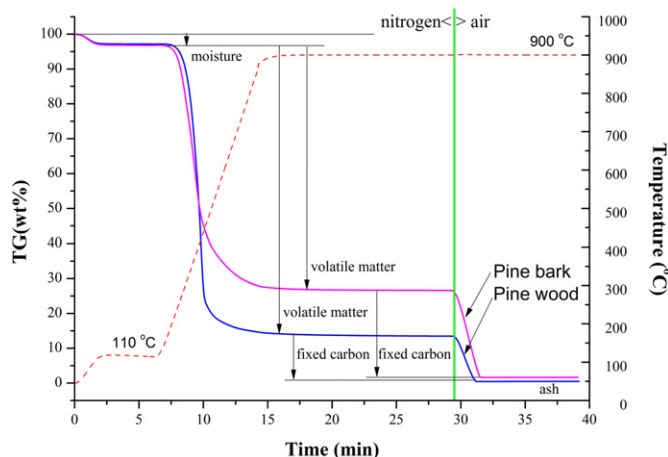


Fig. 1. Diagram for proximate analysis of pine wood and bark.

combustion conditions. TA Instruments Universal Analysis 2000 software was used to analyze the data.

### 2.4. Fast pyrolysis operation

Fast pyrolysis experiments were conducted on a lab-scale fluidized bed pyrolysis system at North Carolina State University (Raleigh, NC, USA). The reactor system and operation has previously been described elsewhere [17]. The reactor consists of a screw feeder with a carrier gas tube, a fluidized-bed with a diameter of 4.3 cm, a cyclone for char separation, and a liquid collecting system. A quantity of 200 g sand was used as a fluidizing agent and heat transfer medium in the pyrolysis reactor. Biomass Fast pyrolysis was performed at 500 °C with a feed rate of 150 g/h. The produced bio-oils were collected in the two water-cooling condensers at temperatures below 4 °C followed by an electrostatic precipitator (ESP) at 14 kV. The bio-oil samples collected from the two locations were mixed together and stored in the refrigerator for later analysis. Bio-oil and char yield distributions were determined gravimetrically, and the non-condensed gas (NCG) yield was determined by difference. The reaction water yield was calculated based on the product bio-oil yield and water content of the bio-oil and the organic yield was the difference between total bio-oil yield and reaction water yield.

### 2.5. Characterization of bio-oils

Physical and chemical properties of the derived bio-oils including elemental composition, water content, pH value, viscosity, GPC molecular weight, ATR spectrum, and GC-MS analysis were characterized and compared.

A Shimadzu gel permeation chromatography (GPC) was used to obtain the average molecular weight and molecular weight distribution of the pyrolysis oils. The GPC column was calibrated on polystyrenes by a refractive index detector (RID). The GPC instrument was set-up with two columns (Waters Styragel HR 5E and Styragel HR 1) in tetrahydrofuran as the eluent (0.7 mL/min). Approximately 50 mg of pyrolysis oil was diluted in 10 mL of THF and then filtered with a 0.2 µm PTFE syringe filter. Approximately 20 µL of the solution was injected into the system. Data processing was conducted using the Shimadzu LC solution-GPC Postrun software, where the number-average molecular weight (M<sub>n</sub>), weight-average molecular weight (M<sub>w</sub>), and the poly-dispersity index (PDI = M<sub>w</sub>/M<sub>n</sub>) were reported from an RI detector.

The ATR spectra of the bio-oil were recorded in the transmission mode between 4000 cm<sup>-1</sup> and 650 cm<sup>-1</sup> using a PerkinElmer Frontier FT-IR Spectrometer.

GC with mass spectrometric (MS) analysis of bio-oil was performed on a Finnigan Polaris Q Plus system with a DB-1701 column. The same

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