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Effect of Acid, Alkali, and Steam Explosion Pretreatments on Characteristics of Bio-Oil Produced from Pinewood

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ABSTRACT: Bio-oil produced from pinewood by fast pyrolysis has the potential to be a valuable substitute for fossil fuels. Pretreatment prior to the fast pyrolysis process has been shown to alter the structure and chemical composition of biomass. To determine the influence of biomass pretreatments on bio-oil produced during fast pyrolysis, we tested three pretreatment methods: dilute acid, dilute alkali, and steam explosion. Bio-oils were produced from untreated and pretreated pinewood feedstocks in an auger reactor at 450 °C. The bio-oils' physical properties including pH, water content, acid value, density, viscosity, and heating value were measured. Chemical characteristics of the bio-oils were determined by gas chromatography–mass spectrometry. Results showed that bio-oil yield and composition were influenced by biomass pretreatment. Of the three pretreatment methods, 1% H₂SO₄ pretreatment resulted in the highest bio-oil yield and best bio-oil quality.

1. INTRODUCTION

As a result of the increase in world energy consumption, the arrival or impending arrival of peak petroleum production, and concern over global climate change, there has been an urgent need for development of alternative energy sources.^{1,2} Biomass is a source that planners are looking to for future production of significant amounts of renewable energy. It is estimated that within 50 years, biomass will provide up to 35–40% of the total world energy consumption. A variety of new technologies and methods, including biochemical and thermochemical processes, are being developed to convert biomass to various forms of energy and chemicals. Among these available processes, one of the promising technologies for converting biomass feedstock into fuels is fast pyrolysis for producing bio-oil with yields around 70%.^{3–6}

Any form of biomass can be a feedstock for fast pyrolysis. Wood,⁷ bark,^{8–12} agricultural wastes/residues,^{13,14} nuts and seeds,^{15,16} grasses,⁷ forestry residues,^{17,18} and cellulose and lignin¹⁹ represent various potential feedstocks for bio-oil production. However, most of the research performed to date has focused on wood feedstocks.⁵

Fast pyrolysis involves heating biomass rapidly at a moderately high temperature (350–600 °C) in the absence of oxygen to produce organic vapors, pyrolysis gases (mainly CO₂, H₂, CO, and light hydrocarbons), and char. The vapor is then cooled to obtain the pyrolysis liquid product (tars, high molecular hydrocarbons, and water) widely known as bio-oil.²⁰ Bio-oil typically consists of a complex mixture of organic compounds, with the ratio of these compounds varying with feedstock type and pyrolysis process conditions. Variations in heating rate, applied temperature, and residence time significantly influence bio-oil characteristics as well as the distribution of the gas, liquid, and solid products produced during pyrolysis. Pyrolysis may be conducted slowly or quickly. Bio-oil production from charcoal is minimized at low temperatures, low heating rates, and long residence times. For biomass, it is generally recognized that fast pyrolysis gives the highest liquid yields at high heating rates (>100–1000 °C/min), at fast

heat transfer rates, and with the use of finely ground biomass feed (<1–3 mm).²¹

In thermal analysis, there are great differences of the pyrolysis behavior among the three main components, cellulose, hemicellulose, and lignin. Hemicellulose is easily degraded, and its pyrolysis occurs mainly at 220–315 °C. The pyrolysis of cellulose occurs mainly at 315–400 °C, while lignin was more difficult to decompose and the weight loss happens in a wide temperature range (150–900 °C).²² Previous studies showed that biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition, and lignin decomposition.^{23,24}

Feedstock pretreatment has become an important tool to increase cellulosic ethanol production yields. Pretreatment processes break down lignin and disrupt the crystalline structure of cellulose, rendering it more accessible to enzymes to allow more ready fermentation to sugars.²⁵ Numerous pretreatment methods for cellulosic ethanol production have been investigated, including physical²⁶ and chemical.²⁷ For example, steam explosion,²⁹ hot compressed water treatments,³⁰ and application of dilute acids^{27,31} or bases³² have been utilized. These pretreatment processes may have potential to be used prior to fast pyrolysis to improve bio-oil yield and characteristics, to produce useful selected chemicals, or to increase the anhydrosugar yields.^{33–35} However, limited research is available on the influence of biomass pretreatment chemicals and methods on bio-oil yield and properties.

The aim of the present study was to investigate the effect of the following pretreatments on yield and characteristics of bio-oil from pinewood feedstock: (a) particle size reduction (grinding) followed by sieving, (b) steam explosion, (c) acid (H₂SO₄) treatment, and (d) alkali (NaOH) treatment. Lignocellulosic compositions of pretreated materials were determined; characterization

Received: March 31, 2011

Revised: June 20, 2011

Published: June 21, 2011

was performed by scanning electron microscope (SEM) imaging. The bio-oil physical properties of pH, water content, acid value, density, viscosity, and heating value were determined. Bio-oil chemical characterization was determined by gas chromatography/mass spectrometry (GC/MS) and Fourier transform Infrared (FTIR) methods.

2. EXPERIMENTAL SECTION

2.1. Materials. Loblolly pine lumber was purchased from East Mississippi Lumber Co, Starkville, MS. The lumber was reduced to paper-chip size (19.0–31.75 mm) by a wood chipper. The paper-chip-sized chips were then dried to about 10% moisture content and subsequently ground with a 29.8 kW (40 hp) bliss full circle hammer mill with a 6.35 mm (1/4 in.) screen. These particles were then sieved with a vibratory sifter (model ZS30-S6666, SWECO Vibro-Energy Separator, Florence, KY) with two screen sizes, one screen at a time. The screen sizes applied were 12 mesh (1.532 mm) and 30 mesh (0.68 mm). The particles retained by the 12 mesh screen were termed “large”. The particles that passed through the 12 mesh screen and that were subsequently retained by the 30 mesh screen were termed “medium”. Particles that passed through the 30 mesh screen were termed “small”.

2.2. Acid and Alkaline Pretreatments. Yang et al.²⁷ evaluated the effect of three H₂SO₄ concentrations (0.5, 1.0, and 1.5%) on the composition of germplasms and found significant effect of acid concentration on hemicellulose solubilization. Sharma et al.²⁸ treated sunflower stalks with 0.25–1.5% NaOH to improve enzymatic saccharification.²⁸ On the basis of the above literature, 0.5% and 1% H₂SO₄ concentrations and 0.5% NaOH were evaluated for pinewood in our study. The particulate feedstocks were treated with dilute solutions (sample/liquid ratio = 1:17) in a stainless steel container, immersed in a temperature-controlled water bath maintained at 100 °C for 1 h. Following pretreatment, the pretreated biomass was filtered through a 50 mesh sieve and washed with distilled water until a neutral pH was achieved. The wet biomass was then dried in an oven at 105 °C to a moisture content of 10% or less, similar to the procedure followed by Yang et al.²⁷ The dry biomass was stored in airtight plastic buckets. For each chemical reagent, the pretreatment process was repeated 10 times under same conditions to produce a biomass quantity of 8 kg, the minimum quantity required for production of meaningful yields of bio-oil by auger pyrolysis.

2.3. Steam Explosion Pretreatment. Steam explosion pretreatment was performed by a vertical stainless steel reactor (Figure 1). The reactor was designed and operated by the Department of Agricultural and Biological Engineering, Mississippi State University. The chips were loaded into the steam explosion vessel through the charge inlet. Tap water was added to pinewood chips (water/pine ratio = 5:1). All openings of the charged vessel were then sealed to prevent steam escape. The vessel was then heated to a pressure of 1.3 MPa; at this pressure, heating was discontinued. The temperature attained in the vessel at the maximum pressure typically ranged between 173 and 193 °C. The maximum temperature and pressure conditions were maintained for 10 min, at which time the discharge valve was opened. The particles exited the discharge valve under high pressure and were captured by a collection bin. The steam-exploded material was dried at 105 °C overnight.

2.4. Physical Characterization of Treated Pinewood. The morphology of all samples were investigated with SEM equipped with an energy-dispersive X-ray spectroscopy (EDX) attachment (JEOL JSM-6500F field emission scanning electron microscope) which provides the material surface information. The samples were precoated with gold prior to their introduction into the SEM vacuum chamber.

2.5. Lignocellulosic Composition Analysis of Pinewood. Lignocellulosic composition, including cellulose, xylan, arabinan, galactan, mannan, and lignin, was determined by the NREL method for “Determination of Structural Carbohydrates and Lignin in Biomass”.³⁶ By this

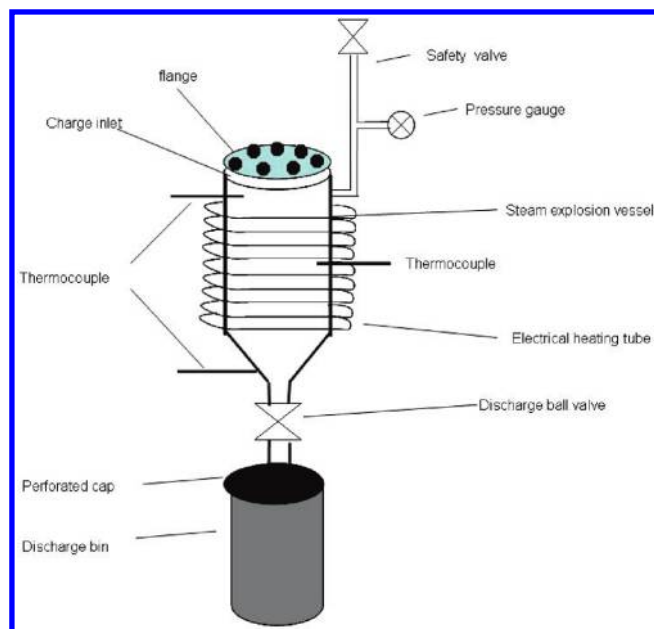


Figure 1. Schematic of steam explosion equipment.

procedure, specimens (0.3 g) were treated with 72% H₂SO₄ for 1 h. The mixture was hydrolyzed by adding 84 mL of water and autoclaving at 121 °C for 1 h. The resultant hydrolysis solution was then filtered through the crucibles with a filtering disk to separate the filtrate and residue. The filtrate was used to determine the content of cellulose, hemicellulose, and acid-soluble lignin, while the residue was used to determine acid-insoluble lignin. The filtrate was analyzed for glucose, xylose, arabinose, galactose, and mannose by HPLC analysis. Conversion factors were used to convert monomer sugar concentrations into polymeric compositions in the starting materials. The acid-soluble lignin in the filtrate was determined by spectrophotometry. The residue was dried at 105 °C for 16 h and the weight of the residue comprised ash and acid-insoluble lignin. Ash content was determined by NREL method for “Determination of Ash in Biomass”,³⁷ wherein the quantity of residual material remaining after heating biomass at 600 °C is the ash content. Lignocellulosic compositional determination was performed for all samples, and the values reported are the mean value of duplicate results.

2.6. Pyrolysis. Pyrolysis was performed in a proprietary auger reactor described by Ingram.³⁸ The reactor is designed and operated by Department of Forest Products, Mississippi State University. The reactor has a 7 kg/h feed rate and an auger speed of 13 rpm. The pretreated samples were pyrolyzed at a temperature of 450 °C. The condensed bio-oil was collected directly in airtight bottles and refrigerated immediately at 4 °C to prevent aging.

2.7. Bio-Oil Physical Properties. The bio-oils’ physical properties of pH, water content, acid value, density, viscosity, and heating value were measured. Percent water was determined by ASTM D1744 method. Viscosity was determined at 40 °C with an Ubbelohde viscometer (Norristown, PA) based on the ASTM D445 method. Acid value was obtained by dissolving 1 g of bio-oil in 35% 2-propanol with titration to a pH of 8.5 with 0.05 N NaOH.³⁹ The pH was determined directly with a calibrated Orion 4 Star pH meter. The density of bio-oil was determined at 20 °C. Higher heating value (HHV) was measured using a Parr 6200 oxygen bomb calorimeter (Parr Instrument Co., Moline, IL).

2.8. Gas Chromatography/Mass Spectrometry Analysis of Bio-Oil. The GC/MS analyses of the pyrolysis oils were performed with a Hewlett-Packard HP 5890-Series II gas chromatograph (Santa Clara, CA) equipped with a Hewlett-Packard HP 5971 series mass detector. The calibration procedure used for bio-oil component concentrations

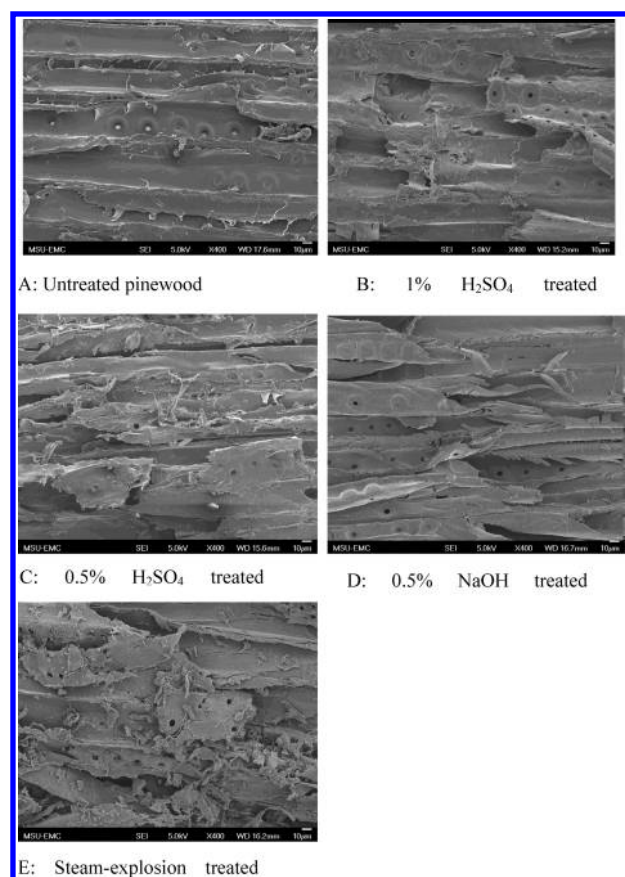


Figure 2. SEM images of pinewood surface before and after treatment: (A) untreated pinewood, (B) 1% H_2SO_4 treated pinewood, (C) 0.5% H_2SO_4 treated pinewood, (D) 0.5% NaOH treated pinewood, and (E) steam explosion treated pinewood.

was that described by Hassan et al.³⁹ Briefly, a representative sample (0.2 g) of each bio-oil was weighed to the nearest 0.1 mg and diluted to 10 mL with methanol. One milliliter of this solution was transferred to an autosampler vial and spiked with 10 μL of a 4000 $\mu\text{g}/\text{mL}$ (ppm) internal standard just prior to analysis. A dilute sample of 1 μL was injected into ZB-5 capillary column of 30 m \times 0.32 mm i.d. \times 1 μm film thickness. The initial oven temperature of the GC was 40 $^\circ\text{C}$ for 4 min and the temperature was programmed to increase at a rate of 5 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$. The injector and detector temperatures were 280 and 250 $^\circ\text{C}$, respectively. The carrier gas was He of 99.99% purity and flow rate is 1 mL/min. The ratio of mass to charge (m/z) values, which represent the fragment ions of the compounds, were recorded for each compound.

2.8. Statistical Analysis. Analysis of variance (ANOVA) and Tukey's test (SAS Institute, Cary, NC) were used to compare means of compositions of samples. Statistical significance level was 5% ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Physical Characterization of Treated Pinewood. The surface morphology of untreated, acid pretreated, alkaline pretreated, and steam explosion treated specimens are shown in Figure 2. It can be observed that untreated pinewood had a fibrous structure, while pretreated materials had a loose and porous structure. The SEM images showed that steam-exploded material had a more disrupted structure than the specimens treated by H_2SO_4 and NaOH .

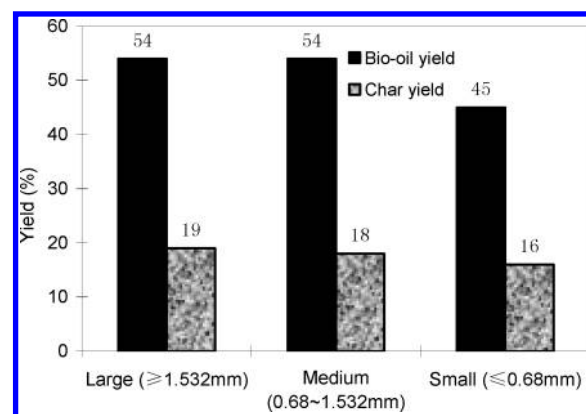


Figure 3. Bio-oil and char yields of large (1.532 mm), medium (0.68–1.532 mm), and small (≤ 0.68 mm) pinewood chips.

3.2. Size Reduction and Bio-Oil Yield. Figure 3 shows the yields of both pyrolysis oil and solid char in relation to the mass of pinewood feed for the three particle sizes tested. All yields are expressed as a percentage of dry biomass. The maximum bio-oil yield (54 wt %) was obtained for both large (>1.532 mm) and medium (0.68 to 1.532 mm) particle sizes with char yields of 19% and 18%, respectively. In general, larger particles are expected to have poor mass transfer and heat transfer characteristics because of the lower surface area to mass ratio; this effect was not observed in this study in terms of bio-oil yield, perhaps because the surface area to mass ratio for the “large” size used in this study was not low enough to be the limiting mechanism. The small particle size (<0.68 mm) produced a bio-oil yield of 45 wt % with a char yield of 16 wt %. The char yield for the small particle size was reduced by two percentage points compared to the larger particles. The bio-oil yield decreased by 9% by contrast. It is clear, therefore, that much of the bio-oil yield lost for small particles was lost as increased gas production. This increased gas production is likely the result of the increased temperature reached during pyrolysis of the small particles. This higher temperature to which the small particles were subjected results in a suboptimum temperature application that produces increased gas. The increased gas production results in loss of yield of liquid bio-oil and char, with the highest impact on liquid bio-oil production. Similar results on effect of particle size on bio-oil yield were observed by Sensoz⁴⁰ and Islam et al. also,⁴¹ wherein the largest particle size resulted in the highest bio-oil yield.

Table 1 gives the lignocellulosic composition for each of the pinewood particle sizes. The hemicellulose contents for small particle size were less than for the other sizes, while the ash content was higher. Bauer et al.⁴² also found differences in compositions of size fractions (ranging from 0.149 to 19.0 mm) obtained by size reduction of wheat and barley straw. This could be due to differences in hardness of the biomass components that would result in varying milling effects on components, which would lead to differing concentrations in size fractions.

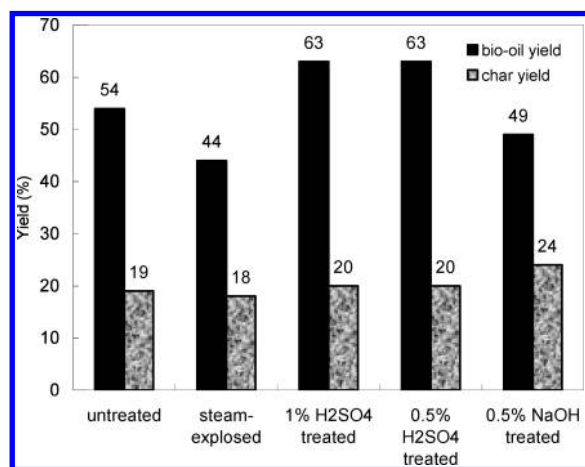
3.3. Chemical/Steam Explosion Pretreatments and Bio-Oil Yield. Figure 4 shows the relative bio-oil yields by pretreatment type. Maximum bio-oil yield was obtained for 1% and 0.5% H_2SO_4 pretreatment. Alkaline and steam explosion pretreatment decreased the bio-oil yield. It can also be seen that bio-oil yield was not affected by the concentration of H_2SO_4 .

Table 2 shows composition of pinewood from different pretreatments. It can be observed that steam explosion degraded

Table 1. Bio-Oil Yield and Lignocellulosic Composition of Untreated Pinewood by Particle Size^a

size	composition (%)							
	cellulose	xylan	arabinan	galactan	mannan	hemicellulose ^b	lignin	ash
large (>1.532 mm)	33.5a	6.45a	0.33a	4.25a	16.32a	27.34a	39.9a	0.39b
medium (0.68–1.532 mm)	35.97a	6.25a	1.89a	3.62a	14.83a	26.58a	37.36a	0.42ba
small (<0.68 mm)	32.7a	5.07a	0.87a	3.63a	13.96a	23.53b	22.16a	0.49a

^a Values are mean of duplicates. Values in the column followed by the same letter are not different ($p < 0.05$). ^b Hemicellulose is the sum of xylan, arabinan, galactan, and mannan.

**Figure 4.** Bio-oil and char yield of large size pinewood with different pretreatment.

all the hemicellulose (xylan, arabinan, galactan and mannan). Hemicellulose is an important source of compounds in bio-oil, like 5-hydroxymethylfurfural and 2-furanmethanol.³⁹ The absence of hemicellulose explains the decrease of bio-oil yield from steam exploded pinewood. The decomposition of hemicellulose also explains the higher contents of cellulose and lignin steam exploded material compared to untreated material (Table 2).

Although steam explosion is effective in biomass pretreatment for bioconversion to cellulosic ethanol, it is not useful for fast pyrolysis, because of the loss of hemicellulose into water despite the disintegration of the structure, as shown by the SEM image (Figure 1). Steam explosion is useful in other biofuel production processes, such as cellulosic ethanol production, where the solution also is used in production.

Dilute-acid treatment at moderate temperatures has been shown to decrease the hemicellulose content of biomass.⁴³ Table 2 results showed no significant change in xylan, arabinan, and galactan contents in pinewood treated with 0.5% and 1% H₂SO₄. Perhaps, the acid-treatment condition applied in this study was mild and degraded hemicellulose very little. However, the structure of the pinewood was damaged by the acid treatment, as seen in Figure 2. Dilute H₂SO₄ dissolves a little lignin, and lignin is disrupted, increasing cellulose susceptibility.⁴⁴ It has also been shown by previous researchers that dilute acid treatment can remove most of the ash in the pinewood. The presence of metals (ash) decreases the yield of bio-oil and increases yields of char and incondensable gas.⁴⁵ Table 2 results show that the ash contents of large pinewood particles following 1% and 0.5% H₂SO₄ treatment were significantly lower compared to ash content of the untreated control (0.39% content of ash).

Bio-oil yield from NaOH-treated pinewood was lower than from untreated pinewood (Figure 4). Using alkaline chemicals to remove lignin has been known for years to improve cellulose digestibility.⁴³ Lignin content of NaOH-treated pinewood was lower compared to that of untreated pinewood (Table 2). In addition, unlike acid pretreatments, a limitation occurs because some of the alkali is converted to irrecoverable salts or is incorporated as salts into the biomass by the pretreatment reactions.²⁵ Alkali metal ion, part of the ash in the biomass, can inhibit bio-oil production and enhance char production.^{33,46} The ash content after 0.5% NaOH pretreatment was 2.49%, substantially higher than for untreated pinewood (0.39%). Expectedly, the lowest bio-oil yield (49%) and the maximum char yield (24%) were obtained from the NaOH-pretreated pinewood (Figure 4).

3.4. Bio-Oil Physical Characteristics. The physical characteristics of pH, density, acid value, water percent, viscosity, and calorific values for the bio-oils are summarized in Table 3. Untreated large size pinewood produced bio-oil with pH value of 2.65 and acid value of 90.06. Materials were sufficiently washed with water after acid/alkali treatment. Hence, any differences in acid values and pH of bio-oil would not be due to the presence of the acid/alkali but would be due to the effects of pretreatment. The lower pH and higher acid value for bio-oils of acid pretreated wood were probably due to the removal of base metals and alkaline compounds contained in the wood.³⁴ On the other hand, the higher pH and lower acid values for bio-oils of alkaline pretreated pinewood may be related to removal of some acidic groups such as acetyl and uronic acid substitution on hemicelluloses during alkaline pretreatment.⁴⁷ Density of bio-oil was the lowest for alkaline treatment, 1.09 g/mL (Table 3). There was no significant difference in densities of bio-oil between acid and steam explosion pretreatments and untreated sample.

As shown in Table 3, pretreatment increased the water content of bio-oils compared to the untreated pinewood. This increase in water content was of a magnitude of 31.8–40.8% with the exception of NaOH pretreatment, which resulted in an increase of 166.8%. Chemical reactions caused by the pretreating chemicals resulted in the production of water. It can be concluded that NaOH is not useful to treat pinewood because of high water content (55.57%) in the bio-oil.

Bio-oils produced by the 1% and 0.5% H₂SO₄ had higher viscosity than that from untreated pinewood (6.49 cSt) with values of 7.08 and 7.31 cSt, respectively (Table 3). The expected viscosity change, based on increased water content, would be a decrease. However, the actual result was a viscosity increase of more than 9%. The high viscosity for the acid-treated bio-oils indicates that the acid treatments resulted in additional polymerized bio-oil components. Accordingly, the increase in water content for the

Table 2. Bio-Oil Yield and Lignocellulosic Composition of Large Size Pinewood for Different Pretreatments^a

pretreatment condition	composition (%)							
	cellulose	xylan	arabinan	galactan	mannan	hemicellulose ^b	lignin	ash
1% H ₂ SO ₄	32.1b	4.72a	1.44ba	2.92b	15.51a	24.58a	44.26b	0.68b
0.5% H ₂ SO ₄	34.6b	5.15ba	0b	3.16ba	15.95a	24.25a	45.23b	0.71b
0.5% NaOH	31.62b	6.10a	2.48a	3.03b	13.21b	24.8a	38.26b	2.49a
steam explosion	46.21a	0c	0b	0c	0c	0b	45.16a	0.64b
untreated	33.55b	6.45a	2.48a	0.33ba	16.32a	27.34a	39.90b	0.39b

^a Values are mean of duplicates. Values in the column followed by the same letter are not different ($p < 0.05$). ^b Hemicellulose is the sum of xylan, arabinan, galactan, and mannan.

Table 3. Physical Properties of Bio-Oils from Different Pretreatments of Large Size Pinewood^a

	pH	acid value	density (g/mL)	viscosity (cSt at 40 °C)	water (%)	heating value (MJ/kg)
bio-oil of untreated pinewood	2.65cb	90.06a	1.17ba	6.49a	20.83c	16.1a
bio-oil of 1% H ₂ SO ₄ treatment	2.77b	65.06b	1.18a	7.31a	27.45cb	16.53a
bio-oil of 0.5% H ₂ SO ₄ treatment	2.52c	65.23b	1.20a	7.08a	29.51b	15.00b
bio-oil of 0.5% NaOH treatment	3.15a	41.41c	1.09c	1.49b	55.57a	misfire ^b
bio-oil of steam explosion treatment	2.78b	64.16b	1.14b	3.93ba	29.32b	misfire ^b

^a Values are mean of duplicates. Values in the column followed by the same letter are not different ($p < 0.05$). ^b Bio-oil from steam explosion and NaOH treatment cannot be burned and no heating values were gotten.

bio-oils of acid pretreated pinewood may be related to the formation of water as a byproduct of the polymerization reaction.³⁴

In contrast to the higher bio-oil viscosity resulting from the acid pretreatments, the viscosity of the alkaline and steam explosion pretreated bio-oils was lower than that from untreated pinewood. The viscosities of the alkaline and steam explosion pretreated bio-oils were 1.49 and 3.93, with respective reductions of 77% and 39.4%, which can perhaps be attributed to the higher water content and lack of polymerization in the bio-oils.

Bio-oil calorific higher heating values (HHV) are reported in Table 3. The HHVs of the acid pretreated study bio-oils were 15.00 and 16.53 MJ/kg, similar to the control bio-oil HHV of 16.0. Bio-oil HHV values were approximately half the 42 MJ/kg value for petroleum fuels, as reported in earlier studies also.³⁹ The HHVs of bio-oils produced from biomass pretreated with NaOH and steam explosion could not be determined because of the high water content.

As shown in Table 3, bio-oil from 1% H₂SO₄ had higher HHV, higher viscosity, and lower acid value compared to other pretreatments. It can be concluded that 1% H₂SO₄ pretreatment resulted in bio-oil with the most desired physical characteristics.

3.5. Chemical Composition of Bio-Oils. It can be expected that bio-oil composition of the condensed bio-oil being derived from biomass components, which vary in proportion depending on the pretreatment process, would vary as biomass composition varied. Table 4 summarizes the concentrations of 33 bio-oil components that were quantitatively determined by GC/MS. Table 4 represents only a portion of more than 200 chemical components that usually exist in the bio-oil. Also, at least 30% of bio-oil contents are high molecular weight species (dimer, trimer, and oligomeric cellulose and lignin pyrolysis products) that cannot flow through the injector and GC column. Furfural, 5-hydroxymethylfurfural, 2-furanmethanol, 2-methyl-2-cyclopentene-1-one, 2(5H)-furanone, 5-methyl-2-furancarboxyaldehyde, 3-methyl-2-cyclopentene-1-one, acetaldehyde, hydroxyacetaldehyde, levoglucosan, and acetic acid

are some of the products of cellulose and hemicelluloses pyrolysis.⁴⁸ From Table 4, it is evident that the concentrations of furfural and 5-hydroxymethylfurfural (main hemicelluloses degradation products) in the bio-oil from acid, alkaline, and steam explosion pretreated pinewood were less than that for the bio-oil from untreated large size pinewood. This can be attributed to the removal of hemicelluloses during the pretreatments.⁴⁹ The decrease in the concentrations of most other carbohydrate pyrolysis products in the bio-oil of acid and alkaline pretreatment may be attributed to the same effect.

Levoglucosan has been determined to be the major chemical compound in bio-oils produced by cellulose pyrolysis. On the basis of pyrolysis–gas chromatography (PY–GC) analysis, researchers have reported that phosphoric acid pretreatment prior to fast pyrolysis of cellulose can significantly increase the concentration of levoglucosan.³⁴ However, the effect of pretreatment on levoglucosan production has been reported only for PY–GC and not for bio-oil produced by a fast pyrolysis reactor. It was found that the concentration of levoglucosan and other anhydrosugars in the bio-oil for alkaline pretreated pinewood was lower than that for the bio-oil of untreated pinewood. This may be due to alkali metal ion attached in pinewood after NaOH pretreatment, which modifies the composition of bio-oils and decreases the content of levoglucosan.⁵⁰ It was found that acid and steam explosion pretreatment leads to an increase in the concentration of levoglucosan and other anhydrosugars in the produced bio-oil. This may be due to the removal of alkali ion by acid treatment.

Pyrolysis of lignin produces numerous phenolic compounds. *trans*-Isoeugenol, 4-methyl-1,2-benzenediol, 1,2-benzenediol, *cis*-isoeugenol, and phenol had the highest concentrations, as shown in Table 4. Generally, it was observed that the concentrations of most lignin degradation products in the bio-oils of acid- and alkaline-pretreated pinewood were less than that in the bio-oil of untreated pinewood. This result may be due to the decrease in lignin content following acid and alkaline pretreatment (Table 2).

Table 4. GC/MS Characterization of Bio-Oils from Large Size Pinewood^a

compound name	concentration (%)				
	untreated pinewood	1% H ₂ SO ₄ treatment	0.5% H ₂ SO ₄ treatment	0.5% NaOH treatment	steam explosion treatment
furfural	0.07	0.07	0.07	0.03	0.09
5-hydroxymethyl-furfural	0.09	0.00	0.00	0.00	0.03
furfuryl alcohol	0.00	0.08	0.03	0.00	0.10
2-methyl-2-cyclopentenone	0.18	0.00	0.00	0.00	0.15
2(5H)-furanone	0.00	0.00	0.00	0.00	0.00
3-methyl-2-cyclopentenone	0.06	0.06	0.03	0.02	0.09
phenol	0.15	0.16	0.13	0.20	0.33
3-methyl-1,2-cyclopentane	0.00	0.39	0.24	0.00	0.67
2-methylphenol	0.09	0.11	0.00	0.13	0.19
3-methylphenol	0.12	0.19	0.16	0.16	0.34
2-methoxyphenol (<i>o</i> -guaiacol)	0.54	0.61	0.46	0.43	0.62
2,4-dimethylphenol	0.01	0.00	0.01	0.02	0.03
3-ethylphenol	0.06	0.08	0.07	0.06	0.14
2,3-dimethylphenol	0.05	0.03	0.07	0.01	0.01
2-methoxy-4-methylphenol (<i>p</i> -methylguaiacol)	0.01	0.01	0.01	0.02	0.08
1,2-benzenediol	0.00	0.00	0.00	0.00	0.00
4-ethyl-2-methoxy-phenol (4-ethylguaiacol)	1.08	0.79	0.75	0.34	0.65
2,6-dimethoxyphenol	1.81	1.20	0.00	0.75	0.00
eugenol	0.01	0.01	0.00	0.00	0.02
2-methoxy-4-propylphenol (4-propylguaiacol)	0.22	0.30	0.22	0.16	0.28
vanillin	0.00	0.01	0.01	0.00	0.00
<i>cis</i> -isoeugenol	0.05	0.00	0.01	0.00	0.02
<i>trans</i> -isoeugenol	0.12	0.14	0.09	0.06	0.13
levoglucosan	0.05	0.07	0.04	0.03	0.08
oleic acid	0.22	0.00	0.00	0.00	0.00

^a The following components were analyzed, but they were not present: 5-methylfurfural, 2,6-dimethylphenol, naphthalene, 3-methyl-1,2-benzenediol, 4-methyl-1,2-benzenediol, 3,4-dimethylbenzoic acid, 4-ethylresorcinol, and acetovanillone.

4. CONCLUSIONS

In this study, fast pyrolysis of pinewoods pretreated with four different methods and untreated control were performed in an auger-fed reactor at 450 °C. The produced bio-oils were physically and chemically characterized. Pinewood pretreated with 1% and 0.5% H₂SO₄ produced bio-oils with the highest yield, 63%, compared to the bio-oils of untreated and other pretreated pinewood. GC/MS chemical characterization showed that the chemical composition of the bio-oils was influenced by pretreatment method. The quality of bio-oil obtained from 1% H₂SO₄ pretreatment was the best because of higher HHV, less water content, higher pH, and higher viscosity.

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ACKNOWLEDGMENT

Partially funded by Sustainable Energy Research Centre (SERC) and Combined Heating and Power (CHP) fundings of Mississippi

State University (MSU). Thanks to Aditya Samala, Graduate Research Assistant, Department of Agricultural and Biological Engineering, MSU, for HPLC analysis.

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