Characterization of Fast Pyrolysis Bio-oils Produced from Pretreated Pine Wood

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Abstract The pretreatment of biomass prior to the fast pyrolysis process has been shown to alter the structure and chemical composition of biomass feed stocks leading to a change in the mechanism of biomass thermal decomposition. Pretreatment of feed stocks prior to fast pyrolysis provides an opportunity to produce bio-oils with varied chemical composition and physical properties. This provides the potential to vary bio-oil chemical and physical properties for specific applications. To determine the influence of biomass pretreatments on bio-oil produced during fast pyrolysis, we applied six chemical pretreatments: dilute phosphoric acid, dilute sulfuric acid, sodium hydroxide, calcium hydroxide, ammonium hydroxide, and hydrogen peroxide. Bio-oils were produced from untreated and pretreated 10-year old pine wood feed stocks in an auger reactor at 450 °C. The bio-oils' physical properties of pH, water content, acid value, density, viscosity, and heating value were measured. Mean molecular weights and polydispersity were determined by gel permeation chromatography. Chemical characteristics of the bio-oils were determined by gas chromatography–mass spectrometry and Fourier transform infrared techniques. Results showed that the physical and chemical characteristics of the bio-oils produced from pretreated pine wood feed stocks were influenced by the biomass pretreatments applied. These physical and chemical changes are compared and discussed in detail in the paper.

Keywords Pretreatment · Bio-oil · Pine wood · Fast pyrolysis · Chemical characterization

Introduction

As a result of the increase in energy demand, high costs of fossil fuels, global climate change, and predicted future reduction of fossil fuel feed stocks, there is a high interest in development of liquid fuels from renewable sources [1, 2]. It is estimated that within 50 years, biomass will provide up to 35–40% of the total world energy consumption [3]. To

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attain this level of supply, a wide variety of alternative biomass feed stocks such as wood and agricultural residues, animal waste, and energy crops will be required. New biochemical and thermochemical conversion processes will be necessary to convert these feed stocks to various forms of energy and chemicals [4, 5]. Among the available thermochemical processes, fast pyrolysis is considered to be one of the promising technologies for converting biomass into a feed stock for both fuels and chemical production [6].

Fast pyrolysis involves heating biomass rapidly at a high temperature (450–600 °C) in the absence of oxygen to produce organic vapors, pyrolysis gases, and char. The vapor is then cooled to room temperature to obtain the pyrolysis liquid product, widely known as bio-oil [5, 7]. Bio-oil typically consists of a complex mixture of organic compounds, with the ratio of these compounds varying with feed stock type and applied pyrolysis process conditions.

Lignocellulosic biomass is composed of three major components: cellulose, hemicellulose, and lignin. Each of the three components exhibits unique thermal decomposition and kinetic characteristics during the pyrolysis process. As a result, pyrolysis of lignocellulosic biomass results in a complex chemical mixture of degradation products from cellulose, hemicellulose, and lignin [4, 8]. In the last two decades, extensive studies have been conducted to understand the complexity of the fast pyrolysis process and the factors affecting bio-oil characteristics. Three process factors known to affect the yield and the properties of bio-oil are pyrolysis temperature, heating rate, and residence time [9–12]. Feed stock relative chemical composition and particle size are also important factors that influence bio-oil characteristics [7].

Feed stock pretreatment has become an important tool for ethanol production. 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 [13]. Numerous pretreatment methods for this purpose have been investigated, including physical [14], chemical [15], and a combination of both [16]. For example, steam explosion [17], hot compressed water treatments [18], and applications of dilute acids [19] or bases [20] have been utilized. Various pretreatment processes were also used prior to fast pyrolysis to improve bio-oil characteristics, produce useful selected chemicals, and increase the yield of sugars [21–24]. However, the comparison between the effect of different pretreatment chemicals on physical and chemical properties of bio-oil have not been reported before in the literature.

The aim of the present study was to investigate the effect of a limited number of chemical pretreatment regimes on pine wood feed stocks to determine their influence on bio-oil physical and chemical properties. The bio-oil physical properties of pH, water content, acid value, density, viscosity, and heating value were determined by standard methods. Bio-oil chemical characterization was determined by gas chromatography/mass spectrometry (GC/MS), gel permeation chromatography (GPC), and Fourier transform infrared (FTIR) techniques.

Materials and Methods

Materials

Ten-year old loblolly pine wood trees were harvested from the Starr Memorial Forest of the Forest and Wildlife Research Center, Mississippi State University, Starkville, MS. Tree

stems were debarked and the debarked stems were reduced to paper-chip size (19.0 to 31.75 mm). The paper-chip-sized chips were then dried to about 8–10% moisture content and subsequently ground in a hammer mill to smaller particle size. These particles were then sieved to a particle size of 2–6 mm and kept in sealed plastic buckets to prevent moisture loss. Ultimate, proximate, and higher heating value (HHV) for untreated pine wood were determined by Hazen Research, Inc., Golden, CO, USA with results as shown in Table 1. Lignin content was determined as Klason lignin according to the method of the Institute of Paper Chemistry [25]. Holocellulose content was estimated by the method developed by Wise et al. [26].

Pretreatments

The pine wood was treated with six different acidic and alkaline solutions. Wood samples were immersed in the dilute pretreatment solutions (sample/solution liquid ratio=1:5) in conical flask. The treatment conditions such as temperature, time, treatment reagent loading, and water loading are described in Table 2; all pretreatments were done in a water bath. After pretreatment, the biomass was filtered and washed with distilled water till neutralization then dried in an oven at 100 °C. After drying, the biomass was kept in sealed plastic buckets until pyrolyzed. For each chemical reagent, the pretreatment process was repeated several times to produce a biomass quantity sufficient for pyrolysis in the auger reactor.

Pyrolysis

Pyrolysis of the six pretreated pine wood specimens plus control was performed by a proprietary stainless steel auger reactor described in previous research [27]. The reactor has a ~1 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 air-tight bottles and refrigerated immediately at 4 °C to prevent aging.

Table 1 Main characteristics of untreated 10-year pine wood.

Characteristics	Value
Ultimate analysis (%)	
Sulfur	0.01
Carbon	51.30
Hydrogen	5.83
Nitrogen	0.07
Oxygen[a]	35.99
Proximate analysis (%)	
Water	6.34
Ash	0.46
Volatile matter	78.54
Fixed carbon	14.66
Components analysis (%)[b]	
Lignin	27.7
Holocellulose	68.1
HHV (MJ/kg)	18.6

[a] By difference

[b] Weight percentage on dry basis

Table 2 Pretreatment conditions for 10-year pine wood.

Pretreatment	Temperature (°C)	Time (min)	Pretreatment agent loading (g/g dry biomass)	Water loading (ml/g dry biomass)
H_3PO_4	100	60	0.140	5
H_2SO_4	100	60	0.104	5
N_aOH	100	60	0.106	5
$Ca(OH)_2$	100	60	0.100	5
NH_4OH	100	60	0.344	5
H_2O_2[a]	80	60	0.143	5

[a] pH=11

Bio-oil Characterization

The bio-oils' physical properties of pH, water content, acid value, density, viscosity, and heating value were measured. Percent water was determined by ASTM Method D-1744. Viscosity was determined with a Stony Brook Model PDVa-100 viscometer at 50 °C. Acid value was obtained by dissolving one gram of bio-oil in an isopropanol/water mixture and titrating to a pH of 8.5 with 0.1 N NaOH. The pH was determined indirectly by adding 1 g of bio-oil to 50 ml of water, stirring, and measuring the pH with an Orion Model EA920 pH meter. The density of bio-oil was determined at 20 °C. The calorific value was measured as calorimetric value (higher heating value) by a Parr 1341 Oxygen Bomb Calorimeter (Parr Instrument Co., Moline, IL, USA).

Gel Permeation Chromatography Analysis

GPC analysis was performed on a Waters HPLC system, consisting of a Waters 600E System Controller and a Waters 410 Differential Refractometer. Five polystyrene standards with peak molecular weights of 2,900, 1,990, 1,200, 1,050, 580, and 162 were used for molecular weight calibration. Using a 100-μl syringe, approximately 80-μl aliquots of each standard and sample were individually flushed through a 20-μl sample loop and injected for analysis. The analytical column was a Varian Polymer Labs Plgel 3 μm, 100A, 300× 7.5 mm. The mobile phase was 100% tetrahydrofuran with a flow rate of 1 ml/min and the total sample run time was 16 min. Data from the differential refractometer was acquired and processed by PC-based Viscotek GPC Software.

Gas Chromatography/Mass Spectrometry Analysis

The GC/MS analyses of the pyrolysis oils from the six pretreated and control feed stocks were performed with a Hewlett-Packard HP 5890-Series II gas chromatograph (GC) equipped with a Hewlett-Packard HP 5971 series mass detector (MS). The calibration method for determining bio-oil chemical components was described in previous paper reported by Leonard et al. [27]. Briefly, a representative sample (0.2 g) of each bio-oil was weighed to the nearest 0.1 mg and diluted to 10.00 ml with methanol. One milliliter of this solution was transferred to an autosampler vial and spiked with 10 μl of a 4,000 μg/ml (ppm) internal standard just prior to analysis. A dilute sample of 1.00 μl was injected into ZB-5 capillary column of (30 m×0.32 mm ID×0.25 μm film thickness). The initial oven temperature of the GC was 40 °C for 4 min and the temperature then programmed at a rate of 5 °C/min to 270 °C. The injector and detector temperatures were 270 °C and 250 °C,

respectively, and the carrier gas was He of 99.99% purity. The ratio of mass to charge (m/z) values, which represent the fragment ions of the compounds were recorded for each compound.

Fourier Transform Infrared Analysis

The bio-oils' functional group compositional analyses were investigated by FTIR Spectrophotometer (Varian 3100 FTIR). All measurements were performed with the KBr disc technique.

Results and Discussion

Bio-oil Physical Characterization

The physical characteristics of pH, density, acid value, water percent, viscosity, and calorific values for the pretreated and control bio-oils are summarized in Table 3. Pine wood control had a pH value of 3.08 and acid value of 69.5. Pretreatments with sulfuric and phosphoric acids had respective pH values of 2.81 and 2.92 with acid values of 95.6 and 74.9, respectively. Respective pH values for the alkaline pretreatments were 3.76, 3.55, 3.49, and 3.60 for sodium hydroxide, calcium hydroxide, ammonium hydroxide, and hydrogen peroxide; respective acid values were 51.1, 62.8, 66.2, and 55.5. As a result of removing acids and bases from wood before pyrolysis through neutralization step, the difference in acid values and pH of bio-oil are not directly related to the presence of acid or base in the bio-oil but due to their effects. The lower pH and higher acid value for bio-oils of acid pretreated wood are probably due to the removal of base metals and alkaline compounds contained in the wood [22]. On the other hand, the higher pH and lower acid values for bio-oils of alkaline pretreated pine wood may be related to removal of some acidic groups such as acetyl and uronic acid substitution on hemicelluloses during alkaline pretreatment [28]. Both acid and alkaline pretreatments had little effect on the density of the bio-oils which ranged from 1.15 to 1.19 ml/g.

As shown in Table 3, the water contents of all pretreated bio-oils increased compared to the control. This increase was of a magnitude of 1 to 2 percentage points with the exception of the ammonium hydroxide and hydrogen peroxide pretreatments which increased by 2.5 and 7.1 percentage points, respectively. It is clear that the chemical reactions caused by the pretreating chemicals resulted in the production of water. Reference to the viscosity values in Table 3 indicates that the bio-oils produced by the acid pretreatments increased viscosity

Table 3 Physical properties of different bio-oils.

	Bio-oil of untreated pine wood	Bio-oil of H_3PO_4 treatment	Bio-oil of H_2SO_4 treatment	Bio-oil of NaOH treatment	Bio-oil of $Ca(OH)_2$ treatment	Bio-oil of NH_4OH treatment	Bio-oil of H_2O_2 treatment
pH	3.08	2.92	2.81	3.76	3.55	3.49	3.62
Acid value	69.5	74.9	95.6	51.1	62.8	66.2	55.5
Density (g/ml)	1.18	1.19	1.19	1.19	1.17	1.17	1.15
Water (%)	16.9	17.8	18.9	17.6	17.9	19.4	24.0
Viscosity (cSt at 50 °C)	55.2	84.4	91.6	53.6	43.5	31.9	12.3
HHV (MJ/kg)	22.49	22.70	23.83	24.4	21.9	19.66	7.28

considerably above that of the control (55.2 cSt) with respective cSt values of 84.4 and 91.6 for the phosphoric and sulfuric acid treatments. The respective viscosity increases were 53% and 65% for the phosphoric and sulfuric acid treatments. The expected viscosity change, based on increased water content, would be a decrease. However, the actual result is a dramatic viscosity increase of over 50%. The high viscosity for the acid-treated bio-oils indicates that the acid treatments resulted in additional polymerized bio-oil components with resultant higher bio-oil viscosity. Accordingly, the increase in water content for the bio-oils of acid pretreated pine wood may be related to the formation of water as a by-product of the polymerization reaction [22].

In contrast to the increased bio-oil viscosity resulting from the acid pretreatments, the viscosity of the alkaline pretreated bio-oils decreased. The viscosities of the alkaline pretreated bio-oils were 53.6, 43.5, 31.9, and 12.3, respectively, for the sodium hydroxide, calcium hydroxide, ammonium hydroxide, and hydrogen peroxide pretreatments; this gave respective reductions of 2.3%, 21.2%, 42.2%, and 77.7%. The water content for alkaline treated bio-oil with ammonium hydroxide and hydrogen peroxide was increased by 14.8% and 42.0%, respectively. Therefore, the viscosity change appears to be related to the increase in water content of the alkaline pretreated bio-oils.

Bio-oil calorific higher heating values are given in Table 3. With one exception, the HHVs of the pretreated study bio-oils, which ranged between 19.7 and 24.4 MJ/kg, differed little from the control bio-oil HHV of 22.5. The finding that bio-oil HHV values are approximately one-half of the 42 MJ/kg value for petroleum fuels is the expected one as this is the generally accepted value for raw bio-oil. The bio-oil produced from biomass pretreated with hydrogen peroxide, however, was exceptionally low at 7.3, an HHV about one third of the remaining values. This low value was produced by the bio-oil with the highest water content at 24%. The influence of higher water content in lowering bio-oil calorific value is a well known result. This phenomenon is also shown for the bio-oil produced from the ammonium hydroxide treated biomass. This bio-oil had a water content of 19.4% that resulted in an HHV of 19.7.

Bio-oil Chemical Characterization

GPC Analysis

Table 4 shows the weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydespersity index (PD$=M_w/M_n$) for the bio-oils produced from the study pine wood feed stocks. The M_w for these bio-oils ranged from 320 and 500 g/mol while M_n ranged from 230 and 310 g/mol. The bio-oils of phosphoric and sulfuric acid pretreated pine wood gave the highest M_w values of 450 and 500 g/mol, respectively. The high molecular weights may be related to the increased polymerization reactions catalyzed

Table 4 GPC analysis of different bio-oils.

	Bio-oil of untreated pine wood	Bio-oil of H_3PO_4 treatment	Bio-oil of H_2SO_4 treatment	Bio-oil of NaOH treatment	Bio-oil of $Ca(OH)_2$ treatment	Bio-oil of NH_4OH treatment	Bio-oil of H_2O_2 treatment
M_w	430	450	500	400	360	340	320
M_n	280	270	310	240	240	250	230
M_w/M_n	1.53	1.66	1.61	1.66	1.50	1.36	1.39

by the presence of acidic compounds. The bio-oil produced from untreated pine wood had a moderate M_w of 430 g/mol. The bio-oils of alkali pretreated pine woods gave lower M_w values (320–400 g/mol) compared with acid pretreated and untreated pine wood. The lowest M_w value of 320 g/mol was obtained for the bio-oil of hydrogen peroxide treated wood. This result appears to be related to the high water content (24%) for this bio-oil. The polydespersities (PD=M_w/M_n) were relatively higher for acid pretreated (1.61 and 1.66) compared with (1.36 to 1.53) for untreated and alkaline pretreated pine wood bio-oils.

GC/MS Analysis

The major chemical constituents of all wood species are carbohydrates (cellulose and hemicelluloses) and lignin. Accordingly, the major wood pyrolysis products and condensed bio-oil are derived from these components with different proportions depending on the pretreatment process. Table 5 summarizes the concentrations of 33 bio-oils components which were quantitatively determined by GC/MS. The total concentration % of quantitated GC/MS components in Table 5 not representing the total bio-oil components and represent only a fraction from more than 200 chemical components that usually exist in the bio-oil. Also, at least 30% bio-oil contents are of higher molecular weight species (dimmer, trimer, and oligomeric cellulose and lignin pyrolysis products) cannot get through the injector and GC column and this portion was characterized by GPC.

Furfural, 5-hydroxymethyl-furfural, 2-furanmethanol, 2-methyl-2-cyclopentene-1-one, 2-(5H)-furanon, 5-methyl-2-furancarboxyaldehyde, 3-methyl-2-cyclopentene-1-one, acetaldehyde, hydroxyacetaldehyde, levoglucosan, and acetic acid are some degradation products of cellulose and hemicelluloses pyrolysis [29]. It is clear from Table 5 that the concentration of furfural and 5-hydroxymethyl-furfural (main hemicelluloses degradation products) in the bio-oil of both acid and alkaline pretreated pine wood was less than that for the bio-oil of untreated pine wood. This can be attributed to the removal of hemicelluloses during the acid and alkaline pretreatments [15]. Also, the decrease in the concentrations of most other carbohydrate pyrolysis products in the bio-oil of acid and alkaline pretreatment may be related to the same effect.

Levoglucosan has been determined to be the major chemical compound in bio-oils produced by cellulose pyrolysis. Based on 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 [21, 22]. 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 followed by chemical analysis of the bio-oil product. The GC/MS chromatograms in this study showed that the levoglucosan peak was merged with other anhydrosugars' peaks. Thus, this anhydrosugar peak group was examined as a single group and the concentration was approximated by using the levoglucosan ion current quantitation for the entire peak region. It was found that the concentration of levoglucosan and other anhydrosugars in the bio-oil for most acid and alkaline pretreated pine wood was lower than that for the bio-oil of untreated pine wood. This may be due to thermal instability and breakdown of levoglucosan and other anhydrosugars into smaller fragments during condensation of pyrolysis gases into bio-oil. It was found that only calcium hydroxide pretreatment leads to an increase in the concentration of levoglucosan and other anhydrosugars in the produced bio-oil.

Pyrolysis of lignin produces numerous phenolic compounds. *Trans*-isoeugenol, 4-methyl-1, 2-benzenediol, 1, 2-benzenediol, *cis*-Isoeugenol, phenol, 2, 6-diethylphenol,

Table 5 GC/MS characterization of different bio-oils.

Compound name	Concentration (%)						
	Bio-oil of untreated pine wood	Bio-oil of H₃PO₄ treatment	Bio-oil of H₂SO₄ treatment	Bio-oil of NaOH treatment	Bio-oil of Ca(OH)₂ treatment	Bio-oil of NH₄OH treatment	Bio-oil of H₂O₂ treatment
Furfural	0.54	0.32	0.30	0.41	0.06	0.05	0.31
5-Hydroxymethyl-furfural	0.43	0.00	0.00	0.00	0.00	0.00	0.00
2-Furanmethanol	0.34	0.03	0.03	0.09	0.18	0.24	0.40
2-Methyl-2-cyclopenten-1-one	0.12	0.05	0.09	0.18	0.09	0.06	0.20
2-(5H)-Furanone	0.67	0.34	0.46	0.42	0.48	0.46	0.43
5-Methyl-2-furancarboxaldehyde	0.10	0.18	0.31	0.11	0.05	0.03	0.08
3-Methyl-2-cyclopenten-1-one	0.17	0.00	0.15	0.13	0.16	0.13	0.16
3-Methyl-1,2-cyclopentanedione	0.76	0.54	0.56	0.42	1.01	0.79	1.29
Levoglucosan and other anhydrosugars[a]	5.06	2.34	1.97	2.59	8.72	7.12	0.84
Phenol	0.81	1.49	0.99	0.64	0.59	0.51	0.54
2-Methylphenol	0.44	0.51	0.49	0.37	0.32	0.25	0.29
3-Methylphenol	0.62	0.64	0.64	0.53	0.59	0.46	0.61
2,3-Dimethylphenol	0.05	0.05	0.05	0.03	0.06	0.03	0.08
2,4-Dimethylphenol	0.36	0.23	0.37	0.23	0.3	0.22	0.29
2,6-Dimethylphenol	0.04	0.02	0.04	0.04	0.03	0.02	0.07
2-Methoxyphenol (o-Guaiacol)	0.49	0.45	0.42	0.42	0.37	0.30	0.31
2-Methoxy-4-methylphenol	0.54	0.31	0.57	0.36	0.43	0.32	0.41
2,6-dimethoxy-phenol	0.02	0.05	0.00	0.02	0.00	0.00	0.00
2-Methoxy-4-propylphenol	0.05	0.02	0.03	0.03	0.04	0.03	0.07
4-Ethyl-2-methoxy-phenol	0.15	0.08	0.14	0.14	0.14	0.10	0.16
3-Ethylphenol	0.13	0.07	0.07	0.1	0.14	0.11	0.30
1,2-Benzendiol	1.66	1.71	1.87	1.04	1.93	1.66	1.72
3-Methyl-1,2-benzenediol	1.22	0.84	1.00	0.64	1.13	1.01	1.10
4-Methyl-1,2-benzenediol	0.37	0.3	0.47	0.29	0.49	0.39	0.36
4-Ethylcatechol	0.00	0.00	0.00	0.00	0.00	0.01	0.00
3,4-Dimethylbenzoic acid	0.00	0.00	0.05	0.00	0.00	0.00	0.00
Naphthalene	0.03	0.03	0.02	0.10	0.02	0.01	0.02
Eugenol	0.23	0.12	0.14	0.13	0.17	0.14	0.24
Cis-Isoeugenol	1.36	0.55	0.64	0.69	1.08	0.81	1.73
Trans-Isoeugenol	4.81	1.49	1.49	2.34	3.05	3.18	3.68
Vanillin	0.20	0.20	0.25	0.19	0.26	0.15	0.28
Acetovanillone	0.14	0.09	0.13	0.11	0.16	0.11	0.17
Oleic Acid	0.73	0.56	0.42	0.52	0.34	0.27	0.32
Total	22.64	13.66	14.11	13.31	22.39	18.97	16.46

[a] The levoglucosan peak was broad and it merged with other anhydrosugar peaks. Thus, the entire area of this peak group was taken and the concentration was approximated by using the levoglucosan ion current quantitation for the entire peak region

and 2, 3-dimethylphenol had the highest concentrations as shown in Table 5. Generally, it was observed that the concentrations of most lignin degradation products in the bio-oils of acid and alkaline pretreated pine wood were less than that in the bio-oil of untreated pine wood. This result may relate to the partial removal of lignin following acid and alkaline

Fig. 1 FTIR spectra for the bio-oil of *A* untreated pine wood, *B* H$_3$PO$_4$ treatment, *C* H$_2$SO$_4$ treatment, *D* NH$_4$OH treatment, *E* Ca(OH)$_2$ treatment, *F* H$_2$O$_2$ treatment, and *G* NaOH treatment
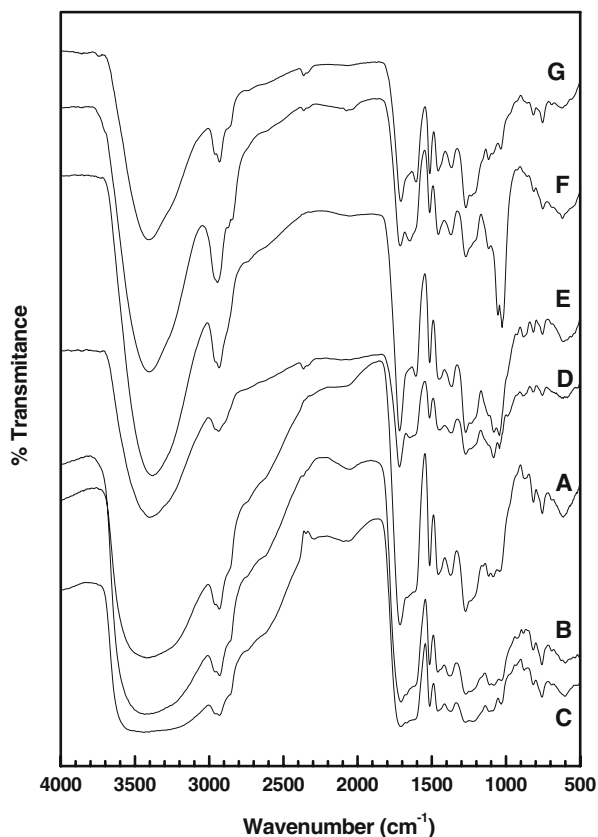
pretreatment. Recent research has shown that some lignin is deposited on feed stock surface as droplets during mild acid hydrolysis and can be removed by a washing step as employed in this study [30]. Generally, we can conclude that both acid and alkaline pretreatment prior to biomass fast pyrolysis leads to a decrease in the concentrations of most bio-oil compounds.

FTIR Analysis

Figure 1 shows the FTIR spectra representing functional group compositional analysis from pretreated and control bio-oils. The broad absorbance band between 3,050 and 3,600 cm^{-1}

Table 6 FTIR functional group compositional of different bio-oils.

Group	Absorbance (cm^{-1})	Class of compounds
O–H (stretching)	3,050–3,600	Phenols, alcohols, water
C–H (stretching)	3,000–2,800	Alkanes
C=O (stretching)	1,750–1,650	Ketones, quinones, aldehyde groups, carboxylic acids
C=C (stretching)	1,680–1,580	Alkenes
C–H (bending)	1,470–1,350	Alkanes
C–O (stretching)	1,300–950	Primary, secondary, and tertiary alcohol aromatic groups
C–H (bending)	900–700	

are ascribed to ν(O–H) vibrations of hydroxyl groups which indicate the presence of alcohols, phenols, and water in the bio-oil. The presence of the O–H absorbance peak together with the presence of C=O stretching vibrations between 1,650 and 1,750 cm^{-1} indicates the presence of carboxylic acids and their derivatives. In addition, the presence of the peaks between 1,650 and 1,750 cm^{-1} may also indicates the presence of ketones, quinones, and aldehyde groups [31]. The absorbance peak of C–H stretching vibrations between 2,800 and 3,000 cm^{-1} and the C–H deformation vibrations between 1,350 and 1,470 cm^{-1} indicates the presence of methyl and methylene groups of alkanes in pyrolysis oil. The C–H stretching vibrations band for alkanes was more pronounced in case of alkaline pretreatment with calcium hydroxide, sodium hydroxide, and hydrogen peroxide which indicates more hydrocarbon compounds in those bio-oils. Increasing the absorbance for alkenes compounds was associated with shrinking of the hydroxyl group absorbance band. The presence of alkenes in the pyrolysis oil may be indicated by the absorbance of stretching vibration of C=C peaks between 1,680 and 1,580 cm^{-1}; this absorbance peak is also indicative for aromatics. Absorbance peaks between 700–900 cm^{-1} may be related to out of plane C–H bending of mono, polycyclic, and substituted aromatic groups [32]. The peaks between 950 and 1,300 cm^{-1} are due to the presence of primary, secondary, and tertiary alcohols [33]; these peaks were more pronounced in the case of hydrogen peroxide pretreatment. A summary of the most important functional groups present in the study bio-oils are presented in Table 6.

Conclusions

In this study, fast pyrolysis experiments of six different pretreated pine woods and untreated control were performed in an auger-fed reactor at 450 °C and the produced bio-oils were physically and chemically characterized. Acid pretreated pine wood produced bio-oils with lower pH, higher acid values, and viscosity compared to the bio-oils of untreated and alkaline pretreated pine wood. The HHV for all bio-oils ranged from 19.7 to 24.4 MJ/kg except that, for the bio-oil of hydrogen peroxide pretreatment, the HHV was 7.28 MJ/kg due to very high water content (24%). The average molecular weights for the bio-oils of acid pretreated pine wood were higher than for untreated and alkaline pretreated pine wood. GC/MS chemical characterization showed also that the chemical concentrations for most bio-oil components that arise from the degradation of hemicelluloses, cellulose, and lignin were lower than that in the bio-oil of untreated pine wood. Calcium hydroxide pretreatment increased the concentration of levoglucosan and other anhydrosugars in the produced bio-oil. FTIR spectra indicated that most bio-oils had similar chemical compositions with the possibility of increased hydrocarbon compounds in the bio-oil of calcium hydroxide, sodium hydroxide, and hydrogen peroxide pretreated pine wood.

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