Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils

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Pyrolysis of Wood and Bark in an Auger Reactor: Physical Properties and Chemical Analysis of the Produced Bio-oils

Leonard Ingram,*,† Dinesh Mohan,‡ Mark Bricka,§ Philip Steele,† David Strobel,† David Crocker,|| Brian Mitchell,† Javeed Mohammad,§ Kelly Cantrell,† and Charles U. Pittman, Jr.#

Forest Products Department, Mississippi State University, Mississippi State, Mississippi 39762, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, Department of Chemical Engineering, Mississippi State University, Mississippi State, Mississippi 39762, and National Renewable Energy Laboratory, Chemistry Department, Mississippi State University Golden, CO 80401

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Bio-oil was produced at 450 °C by fast pyrolysis in a continuous auger reactor. Four feed stocks were used: pine wood, pine bark, oak wood, and oak bark. After extensive characterization of the whole bio-oils and their pyrolytic lignin-rich ethyl acetate fractions by gas chromatography/mass spectrometry (GC/MS), gel permeation chromatography (GPC), calorific values, viscosity dependences on shear rates and temperatures, elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, water analyses, and ash content, these bio-oils were shown to be comparable to bio-oils produced by fast pyrolysis in fluidized bed and vacuum pyrolysis processes. This finding suggests that portable auger reactors might be used to produce bio-oil at locations in forests to generate bio-oil on-site for transport of the less bulky bio-oil (versus raw biomass) to biorefineries or power generation units. The pyrolysis reported herein had lower heat transfer rates than those achieved in fluidized bed reactors, suggesting significant further improvements are possible.

1. Introduction

Resource conservation needs and the development of value-added products from biomass have promoted the development of technologies to utilize biomass more efficiently. Many efforts have been made to convert biomass to liquid fuels and chemicals since the oil crises in the mid-1970s.[1,2] Oil from fossil sources is nonrenewable. The United States, China, and others are heavily reliant on foreign sources for energy from liquid fuels, providing strong incentives for developing renewable energy sources. The accelerated rate of growth of energy consumption in Asia, particularly China and India, raises this incentive for all countries. In addition, fossil fuel burning causes net addition of carbon dioxide to the atmosphere, which contributes to global warming. In contrast, biomass combustion is more CO_2 neutral. Furthermore, in countries like India or subtropical Africa, biomass represents about 80% of energy resources (38% on a worldwide scale).[3] Thermochemical conversion is an efficient way to utilize biomass for fuels. Thus, several types of pyrolysis reactors are being used to generate liquid fuels from biomass.[1]

Fast-pyrolysis-derived bio-oils have potential as feed stocks for chemical production[4–9] and as a promising route to liquid fuels.[1,9–12] Virtually any form of biomass can be considered as a feed stock for fast pyrolysis.[13] Wood,[14,15] bark,[16–20] agricultural

* To whom correspondence should be addressed. E-mail: lingram@cfr.msstate.edu (L.I.); cpittman@chemistry.msstate.edu (C.U.P.). Phone: (662) 325-7616(C.U.P.). Fax: (662) 325-7611 (C.U.P.).

† Forest Products Department, Mississippi State University.

‡ Department of Chemistry, Mississippi State University. Current address: Environmental Chemistry Division, Industrial Toxicology Research Centre, Post Box No. 80, Mahatma Gandhi Marg, Lucknow 226001, India.

§ Department of Chemical Engineering, Mississippi State University.

|| National Renewable Energy Laboratory.

Chemistry Department, Mississippi State University.

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wastes/residues,[21,22] nuts and seeds,[23,24] grasses,[25] forestry residues,[26,27] and cellulose and lignin[28] represent various potential bio-oil feed stocks. However, most of the work has been carried out on wood.[1,10–12,29]

Biomass pyrolysis in an inert atmosphere produces gaseous products (mainly CO_2, H_2, CO, CH_4, C_2H_2, C_2H_4, and C_6H_6), liquid products (tars, high molecular hydrocarbons, and water), and solid products (char). Changing the heating rate and the temperature, along with other factors, modifies the properties and distribution of the gas, liquid, and solid products. Pyrolysis may be conducted slow or fast. Charcoal can be maximized at lower temperatures, low heating rates, and longer residence times. It is generally recognized that fast pyrolysis gives the highest liquid yields at very high heating rates (>100 to 1000 °C/min), at fast heat transfer rates, and with the use of finely ground biomass feed (<1 to 3 mm).[1] Controlling temperature (425–500 °C) and employing rapid condensation produces liquid biocrude products. Maximum pyrolysis oil yields are achieved in the 425–557 °C temperature range.[11,30,31] Most pyrolysis studies to generate bio-oils were conducted within this temperature range.[15,25]

Fast thermal decomposition of wood at 425–557 °C in the absence of molecular oxygen causes depolymerization/fragmentation of the wood's macromolecular structure.[11,30,31] These products may continue to depolymerize via cracking processes to yield lower molecular weight products. Cross-linking via condensation reactions and water loss simultaneously results in char formation.[32] Very high heat transfer rates and short residence times minimize char formation due to rapid volatilization of low molecular weight derivatives. This minimizes second-order polymerization reaction rates.[33] Longer residence times permit further secondary decomposition and cracking reactions. This generates gases, water, formic acid, and other low molecular weight products,[30] so rapid vapor quenching is necessary. Water has a large heat of vaporization. Thus, excess moisture suppresses the rate of substrate temperature rise. Some free water content, however, aids heat transfer and can help further fragment biomass particles via a "steam explosion"-like process.

Typical wood-derived pyrolytic bio-oil is acidic (pH 2.5–3.4), contains 20–30% water and 0.04–0.24% ash, and exhibits viscosities between 35 and 53 cSt at 40 °C.[34] Bio-oils have complex multiphase fluid morphologies due to the presence of char particles, waxy materials (e.g., fatty acids, fatty alcohols, sterols, and aliphatic hydrocarbons), and aqueous droplets and micelles formed from heavy compounds in a matrix of hollocellulose-derived compounds and water.[35,36] Heating values can be raised by catalytic deoxygenation, but upgrading is complicated by instability, viscosity increases, and catalyst coking.[14] Aging reduces the amount of water-soluble compounds, and higher molecular weight, lignin-derived species contribute to network formation.

Fast biomass pyrolysis methods to maximize the pyrolytic oil include application of ablative fluidized bed, rotating cone, vacuum moving bed, entrained flow, and transported bed reactors.[1,10–12,29,37] Recently, Renewable Oil International, LLC (ROI), Florence, AL, demonstrated modular and transportable ROI bio-oil plants based on auger reactors.[38] These can be located close to biomass sources, reducing the cost of transporting the biomass[38] as long as suitable bio-oil is produced.

Prior to this research project, little was known about the chemical and physical proerties of bio-oil produced from auger reactors and only a few bio-oil properties had been characterized.[39] More recently, the results from research that was done during the same time period as work reported in our paper were published.[40] Selected fuel properties of bio-oil/biodiesel blends

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and physical properties of bio-oil produced from pine were reported along with manufacturing technical details.

2. Experimental Section

2.1. Feed Preparation. Bio-oils were produced by pyrolyzing oak wood, pine wood, oak bark, and pine bark in an auger reactor. The oak and pine wood feed stocks were supplied by Fiber Resources, Southern Arkansas, in the form of wood pellets. The pine bark and oak bark were supplied by PCA, Ackerman, MS, and Rives & Reynolds, Louisville, MS, respectively. The pine bark and oak bark samples were air-dried for 1–2 days to 8–10% moisture content. The oak and pine wood pelletized samples were pyrolyzed at the moisture content received (6–8% moisture). Each feed was ground in a Bauer mill (Bauer Brothers Co) and sieved (Universal Vibrating Screen) to a particle size of 2–4 mm prior to pyrolysis.

2.2. Bench-Scale Pyrolysis in the Auger Reactor. Pyrolysis of wood and bark samples was conducted at an ~1 kg/h feed rate in a stainless steel proprietary auger reactor. The auger reactor is compact, does not use a carrier gas or a heat carrier, and operates continuously. The auger reactor pipe is 7.6 cm in diameter and 102 cm in length. The auger speed applied was 12 rpm at a pyrolysis temperature of 450 °C. The approximate time/temperature exposure profile which we employed for feed to traverse this reactor has been described previously.[41] Multiple band heaters along the reactor length were employed to supply heat. Feed stock was preheated to 110–120 °C prior to arrival in the pyrolysis zone to speed heat transfer. The auger reactor was operated for this study such as to require about 30 s to traverse the 450 °C pyrolysis temperature zone and took about 50 s for the initial feed to move to the char exit point. However, as vapors or aerosols form, they move to the condenser within a few seconds. The experiments performed with this auger-fed pyrolysis reactor involved longer solid residence times and slower heat transfer rates than are typical for fast pyrolysis. The slower heating rate and longer residence time exhibited by our current laboratory-scale reactor are not inherent properties of auger reactor designs in general. ROI, in particular, has developed a proprietary auger reactor design with much higher heating rates and lower residence times with correspondingly higher yields compared to our current laboratory-scale reactor.

Bio-oil was collected after the pyrolysis reaction had been continued for 40–60 min with continuous biomass feeding. Therefore, the entire process had reached a steady state. Pyrolysis produced a mixture of gases, aerosols, and some very fine char particles. A solid char residue is also formed which is moved through the reactor by the rotating screw (auger) to a removal pot. The gases and aerosol were condensed as bio-oil (entrapping some entrained fine char particles) in a proprietary condenser. The noncondensed products exited the condenser at 24–25 °C.

2.3. Bio-oil Characterization. Pyrolysis liquid samples obtained from different treatments of wood or bark were stored in firmly closed glass/plastic bottles in darkness at 4–5 °C as previously described.[42,44] Karl Fischer analyses for water showed no changes in water content over 8 months when stored this way.

Condensed, multiphase morphology bio-oil liquids can react during storage. Bio-oils contain aldehydes, carboxylic acids, hydroxyaldehydes, ketones, phenolics, levoglucosan, mono-, di-, and higher saccharides, and so forth. Some products are volatile. Lignin fragments may resemble syringol and quaiacol structures, and monomeric, dimeric, trimeric, and even higher molecular weight structures can be present. Bio-oil aging typically produces some higher molecular weight compounds. Micro- and macrophase changes contribute to variations in the oil's chemical and physical properties. Loss of volatiles also affects bio-oil aging. The stability of pyrolysis liquids has been previously monitored by following multiple parameters which were all correlated.[42,43]

2.3.1. Ethyl Acetate Solvent Fractionation of Pyrolytic Lignin-Rich Fractions. The lignin-derived portion of bio-oil usually constitutes 25–30% of the whole bio-oil.[45] Since the lignin-rich fraction is of interest as a phenol formaldehyde resin extender and a wood preservative,[46,47] the lignin-rich fraction of the four bio-oils derived from the auger reactor pyrolysis was isolated by the ethyl acetate fractionation method developed by the National Renewable Energy Laboratory.[48] Bio-oil samples (1 kg) were dissolved in ethyl acetate (1:1 wt/wt). The oil was vacuum-filtered through Whatman No. 42 filter paper to remove fine char. On standing, the ethyl acetate/bio-oil mixture formed two phases: an organic-rich ethyl acetate top phase and an ethyl acetate-insoluble bottom phase. The phases were separated, and the ethyl acetate-soluble portion was water washed twice and then extracted with $NaHCO_3$ (5% wt/wt, 10 × 200 mL). The basic aqueous layer was saved for isolation of the acidic organic fraction containing carboxylic acids and other water-soluble compounds. Ethyl acetate was evaporated in order to concentrate the soluble nonvolatile organic material. This method has been reviewed along with other solvent fractionations of bio-oil.[1]

2.3.2. Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. A list of target compounds for quantitative determination was complied from information in previously published literature and from initial GC/MS analysis of bio-oil, followed by the qualitative identification based on mass spectral library matches. All chemicals for calibration standards were obtained from Sigma-Aldrich and used without further purification. Concentrated stock solutions were prepared by weighing 0.1 g of each individual compound to the nearest 0.1 mg, dissolving in 2 mL of methanol, and quantitatively transferring to a 100 mL volumetric flask. The mixture was diluted to volume with dichloromethane. Aliquots of the 1000 μg/mL stock solution were then diluted to concentrations of 20, 50, 80, 120, and 160 μg/mL in dichloromethane.

A commercial (US-108N, Ultra Scientific) mixture of six isotopically labeled compounds was used as an internal standard. This consisted of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} at a concentration of 4000 μg/ml. A 10 μL of the internal standard mixture was spiked into each working standard to calculate a response factor over a five-point concentration range for each compound of interest.

Each calibration standard solution was analyzed on a Perkin-Elmer Clarus model 500 GC/MS instrument by manual injection of 2.00 μL of solution using splitless conditions followed by injector venting at 0.5 min. The injector temperature was 270 °C, and the helium carrier gas flow was held constant at 2.0 mL/min. The GC was fitted with a 30 m × 0.32 mm i.d. fused silica capillary column, coated with 5% phenyl/methylpolysiloxane (DB-5, J&W Scientific). The GC oven was programmed from an initial temperature of 40 °C (4 min) followed by a 5 °C/min increase to a final temperature of 280 °C, and held for 15 min. After a solvent delay of 3 min, full

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scan mass spectra were acquired from 35 to 550 *m/z* at a scan rate of 0.2 s per scan, with an interscan delay of 0.1 s. The total time for each injection run was 67 min.

The mass spectrometer was configured for electron impact ionization at 70 eV, with an interface temperature of 225 °C and a source temperature of 210 °C. Prior to analysis, the spectrometer was mass calibrated and abundance tuned using heptacosafluorotributylamine CAS [311-89-7]. Full scan data were acquired and processed using Perkin-Elmer Turbomass software (2005 version 5.1.0.0944). Peak areas of the characteristic ions, usually the base peak, of the compounds of interest and a selected internal standard were used to calculate a response factor for each target compound.

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 dichloromethane. A 1 mL portion of this solution was transferred to an autosampler vial and spiked with 10 μL of a 4000 μg/mL (ppm) internal standard just prior to analysis. A 2.00 μL injection was used to acquire GC/MS peak area data as described for the calibration standards. The concentrations in samples were determined by comparing the integrated peak areas of characteristic ions to responses generated with the working standards (Tables 1 and 2).

2.3.3. Nuclear Magnetic Resonance Analysis. ^{13}C NMR spectra of whole bio-oils and lignin-rich fractions were recorded in DMSO-d_6 solutions at 100.6 MHz and 60 °C using a VARIAN Mercury 400 MHz spectrometer (Tables 3 and 4). ^{1}H NMR was run on a Bruker AMX-600-A 600 MHz spectrometer with *z*-gradient, inverse, and heteronuclear capabilities, respectively (Table 5). Solutions of 18−20 wt % bio-oil were employed. About 10^5 scans were accumulated for each sample ^{13}C spectrum using a 90° pluse width together with broadband proton decoupling. Tubes of 5 mm diameter were used. Inverse gated decoupling was applied to void NOE effects in the ^{13}C spectra. Tip angles of 45° for ^{1}H and 30° for ^{13}C were used.

The integrated ^{13}C spectra were divided into five general chemical shift ranges for analysis: 215–163 ppm (carbonyl carbons), 163–110 ppm (total aromatic carbons), 110–84 ppm (carbohydrate-type carbons), 84–54 ppm (methoxy- or hydroxy-bound carbons), 54–1 ppm (primary, secondary, tertiary, and most quaternary alkyl carbons). The aromatic region was further subdivided into 125–112 ppm (guaiacyl carbons) and 112–110 ppm (syringyl carbons). The alkyl region was also subdivided into 34–24 ppm (mostly secondary and tertiary carbons) and 24–6 ppm (most primary and some secondary carbons). These areas were also selected because the integral curves were flat at each of these breaks, facilitating more precise measurements, allowing accurate integrations as a fraction of the total carbons present. This protocol is similar to that developed at the National Renewable Energy Laboratories.[49,50] These assignments are also consistent with the bio-oil and model compound studies.[51] ^{1}H NMR spectral integrations were divided into the following ranges: 10.0−8.0 ppm, 8.0–6.8 ppm, 6.8–6.4 ppm, 6.4–4.2 ppm. 4.2–3.0 ppm, 3.0–2.2 ppm, 2.2–1.6 ppm, and 1.6–0.0 ppm (Table 5).

2.3.4. Gel Permeation Chromatography (GPC) Analysis Calibration. Six polystyrene standards with peak molecular weights of 2900, 1990, 1200, 1050, 580, and 162 were used for molecular weight calibration. Each standard (0.5 g) was weighed (analytical balance) into a beaker (50 mL), dissolved in tetrahydrofuran (THF), quantitatively transferred to a class A 10 mL volumetric flask, and diluted to volume. Standards were filtered through a 0.45 μm Millex syringe driven filter unit into a 4 mL vial, and capped for analysis.

GPC Analysis. Bio-oil samples and their ethyl acetate fractions (oak bark, oak wood, pine bark, and pine wood) were each weighed (~0.3 g) in a beaker (50 mL), dissolved in THF, quantitatively transferred to a 50 mL volumetric flask, and diluted to volume. All samples were filtered through a 0.45 μm Millex syringe driven filter unit into a 4 mL vial, and capped for analysis. GPC analyses were performed on a Waters HPLC system, consisting of a Waters 600E System Controller and a Waters 410 Differential Refractometer. Approximately 80 μL aliquots of each standard and sample were individually flushed through a 20 μL sample loop and injected for analysis. A Varian Polymer Laboratories Plgel 3 μm, 100 Å, 300 mm × 7.5 mm analytical column and a 100% THF mobile phase with a flow rate of 1 mL/min were employed. The total sample run time was 16 min Data (Table 6) were acquired and processed using PC-based Viscotek GPC Software, version 2.61.

2.3.5. Viscosity Measurements. Viscosities were obtained using both a BrookField viscometer, model LV-DVI+, and a TA Instruments, model 1000N, rheometer. Rheological analyses of the four bio-oil types and lignin-rich fractions, produced from evaporating the ethyl acetate solvent,, were performed at 25, 50, and 80 °C (Tables 7 and 8). A 4 cm diameter stainless steel rheometer plate was used for the bio-oils with a plate gap of 2000 μm. The viscosities of the lignin-rich ethyl acetate fractions were measured at a plate gap of 1000 μm. Shear rates from 0.05 to 300 s^{-1} were employed for oak wood, oak bark, pine wood, and pine bark bio-oils. Bio-oil aging was studied by examining the shear rate dependence of viscosity as a function of storage time at 4 °C at different measurement temperatures.

2.3.6. Collective Properties: Density, Water Content, Solids, Ash, Acid Value, Heating Value, Elemental Analysis, and pH. The pyrolysis liquid density was determined by picnometery according to ASTM standard D 4052. This method[52] is applied to oils which are liquids between 15 and 35 °C. Bio-oil density correlates well with its water content.[53] The density of the extractive-rich forestry residue liquid (top phase) is always lower than that of the bottom phase. The water content was determined by the Karl Fischer titration using standard methods.[54,55] The Karl Fischer titrations were performed with a Cole-Parmer model C-25800-10 titration apparatus. These quantities are summarized in Table 9.

The solids content refers to the methanol-insoluble portion of the bio-oil determined by a previously published procedure.[56] A Buchner filtration system and preweighed Whatman filter paper were used. Bio-oil (5 g) was dissolved in 100 mL of methanol and filtered. Then, the filter paper was washed with methanol until the filtrate was clear, oven-dried (105 °C) for 1 h, and stored in a desiccator prior to reweighing. The weight of the methanol-insoluble solids divided by the weight of the bio-oil sample is the fractional solids content (Table 9). The bio-oil samples were placed in a porcelain crucible and heated with a Bunsen burner. The ash content was determined by Hazen Research, Inc., Golden, CO. Ash contents are given in Table 10.

The acid value was determined by dissolving 1 g of bio-oil in 50:50 isopropanol/water and titrating with 0.1 N NaOH to a pH of 8.5. The acid value was calculated as the number of milligrams of KOH equivalent to 1 g of sample (Table 9). Bio-oil pH (Table 9) was determined in water using a method similar to the methods used for wood or soil. One gram (1.00) of bio-oil was stirred with 50 mL of water, and the pH of the water recorded using a calibrated pH meter model Orion EA 920.

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(55) ASTM E 203 Standard test method for water using volumetric Karl Fischer Titration. Easton, MD: American Society for Testing and Materials, 1996.

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(57) ASTM D5291 Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants. Easton, MD: American Society for Testing and Materials, 1992.

Table 1. GC/MS Analysis—The Quantitated Compounds in the Bio-oils and Their Lignin-Rich Ethyl Acetate Fractions

quantitated compounds in whole bio-oils	retention time	quantitation ion	concentration in bio-oil (percent)			
			pine wood	pine bark	oak wood	oak bark
furfural	10.181	96	0.47	0.85	1.10	0.71
2-furanmethanol	10.955	98	0.11	0.07	0.10	0.10
2-methyl-2-cyclopenten-1-one	12.865	96	0.12	0.06	0.10	0.10
5-methylfurfural	14.917	110	0.10	0.17	0.13	0.07
3-methyl-2-cyclopenten-1-one	15.014	96	0.17	0.02	0.13	0.13
phenol	15.457	94	0.77	0.87	0.50	0.68
3-methyl-1,2-cyclopentanedione	17.153	112	1.00	0.49	0.93	0.77
2-methylphenol	18.009	108	0.37	0.24	0.25	0.31
3-methylphenol	18.706	108	0.71	0.85	0.40	0.57
2-methoxyphenol (*o*-guaiacol)	19.231	124	0.39	0.28	0.22	0.34
2,6-dimethylphenol	19.903	122			0.01	0.01
2,4-dimethylphenol	21.105	122	0.27	0.22	0.12	0.14
3-ethylphenol	21.604	122	0.03	0.13	0.04	0.08
2,3-dimethylphenol	21.996	122	0.01			0.01
1,2-benzendiol	22.439	110	3.79	4.46	2.25	2.23
2-methoxy-4-methylphenol (4-methylguaiacol)	22.506	138	0.54	0.51	0.18	0.30
naphthalene	22.592	128				0.02
5-hydroxymethylfurfural	22.495	126			0.01	0.08
4-methyl-1,2-benzenediol (4-methylcatechol)	24.359	124	0.65	0.46	0.76	0.57
4-ethyl-2-methoxy-phenol (4-ethylguaiacol)	25.021	152	0.03	0.13	0.08	0.13
3-methyl-1,2-benzenediol (3-methylcatechol)	25.235	124	2.44	2.81	1.11	1.19
eugenol	27.216	164	0.19	0.13	0.06	0.09
2-methoxy-4-propylphenol (4-propylguaiacol)	27.502	137				
vanillin	28.479	152	0.24	0.22	0.08	0.13
3,4-dimethylbenzoic acid	28.632	150	0.09	0.08	0.09	0.08
4-ethyl-1,3-benzenediol (4-ethylresorcinol)	29.147	123	0.04	0.02	0.03	0.04
2-methoxy-4-(1-propenyl)phenol (isoeugenol)	29.793	164	0.62	0.46	0.15	0.42
1-(4-hydroxy-3-methoxyphenyl)-ethanone (acetovanillone)	30.725	166	0.16	0.15	0.08	0.10
1,6-anhydro-beta-D-glucopyranose (levoglucosan)	33.262	60	14.20	21.50	21.60	8.21
oleic acid	44.731	55	0.39	0.21	0.21	0.36

quantitated compounds in the lignin-rich, ethyl acetate fractions	retention time	quantitation ion	concentration in bio-oil (percent)			
			pine wood	pine bark	oak wood	oak bark
furfural	10.160	96	0.49	1.18	1.68	1.07
2-furanmethanol	10.909	98	0.22	0.09	0.33	0.21
2-methyl-2-cyclopenten-1-one	12.860	96	0.13	0.09	0.15	0.14
5-methylfurfural	14.902	110	0.18	0.40	0.35	0.17
3-methyl-2-cyclopenten-1-one	15.146	96			0.05	
phenol	15.467	94	1.82	2.28	1.51	1.45
3-methyl-1,2-cyclopentanedione	17.107	112	0.51	0.30	0.63	0.75
2-methylphenol	18.003	108	0.92	0.71	0.85	0.79
3-methylphenol	18.737	108	1.76	2.33	1.36	1.15
2-methoxyphenol (*o*-guaiacol)	19.231	124	0.90	0.69	0.60	0.76
2,6-dimethylphenol	19.878	122	0.08	0.03	0.14	0.09
2,4-dimethylphenol	21.095	122	0.81	0.68	0.44	0.36
3-ethylphenol	21.614	122	0.47	0.45	0.15	0.25
2,3-dimethylphenol	21.966	122	0.09	0.04	0.06	0.06
1,2-benzendiol	22.439	110	4.95	6.47	5.01	4.17
2-methoxy-4-methylphenol (*p*-methylguaiacol)	22.531	138	1.35	1.32	0.62	0.71
naphthalene	22.582	128			0.05	0.38
5-hydroxymethylfurfural	22.587	126		0.02	0.10	0.22
4-methyl-1,2-benzenediol (4-methylcatechol)	24.339	124	1.81	1.51	2.51	1.71
4-ethyl-2-methoxy-phenol (4-ethylguaiacol)	25.027	152	0.41	0.41	0.27	0.30
3-methyl-1,2-benzenediol (3-methylcatechol)	25.281	124	4.02	5.47	3.00	2.34
eugenol	27.242	164	0.45	0.37	0.22	0.26
2-methoxy-4-propylphenol (4-propylguaiacol)	27.517	137	0.06	0.01		
vanillin	28.495	152	0.26	0.33	0.15	0.27
3,4-dimethylbenzoic acid	28.632	150	0.10	0.10	0.09	0.10
4-ethyl-1,3-benzenediol (4-ethylresorcinol)	29.147	123	0.04	0.02	0.08	0.05
2-methoxy-4-(1-propenyl)phenol (isoeugenol)	29.819	164	2.29	1.81	1.32	1.48
1-(4-hydroxy-3-methoxyphenyl)-ethanone (acetovanillone)	30.741	166	0.25	0.29	0.17	0.20
1,6-anhydro-beta-D-glucopyranose (levoglucosan)	30.802	60	0.38	0.89	0.38	0.59
oleic acid	44.705	55	0.67	2.13	0.26	0.61

The calorific value was measured as the higher heating value (HHV) (Table 11). The lower heating value (LHV) was calculated from the HHV and the total weight percent of hydrogen (from elemental analysis) in the bio-oil according to LHV (J/g) = HHV (J/g) − 218.13 × H percent (wt %).[57] The free water does not have to be subtracted because it cannot be removed by centrifugation of the pyrolysis liquid, as is the case for heavy petroleum fuel oils. Calorific values (BTU/lb) and elemental analyses were determined by Hazen Research, Inc., Golden, CO (Table 10). Elemental carbon, hydrogen, and nitrogen analyses of the bio-oil samples were conducted by combustion in pure oxygen at ~950 °C and analysis of CO_2, H_2O, NO_x, N_2, and SO_x. Oxygen was determined by difference.

3. Results and Discussion

Four separate pyrolysis reactions were performed for each feed. The amount of char produced for each feedstock over the

Table 2. Estimated Amount of Total Analyzed Material Based on the Ratio of Integrated Total Ion Current of Known and Unknown Compounds, Percent Water, and Percent Acids in the Whole Bio-oils from Four Feed Stocks

	pine wood	pine bark	oak wood	oak bark
percent semivolatile compounds	67.6	64.7	68.3	70.8
percent water	13.0	23.1	18.1	25.4
percent carboxylic acids	7.6	7.8	10	11
total	**88**	**96**	**96**	**110**

four runs fell into the following ranges: pine wood, 17.5–19.8%; oak wood, 17.5–19.9%; pine bark, 9.7–23.2; oak bark, 21.3–27.8%. The range of total liquid yields over the four repetitions for each of these feeds were the following: pine wood, 48.7–55.2%; oak wood, 49.6–56.3%; pine bark, 42.8–44.2%; oak bark, 43.8–49.8%. The noncondensable gas (final condenser temperature, 24–25 °C) volumes were not measured.

Bio-oil yields are partially dependent on very rapid heating of the wood particles to the final pyrolysis temperature. Our reactor design did not attempt to optimize the rate of heat transfer. Therefore, the yields reported here are lower than those that will be achieved with improved heat transfer designs.

The chars produced in the pyrolysis have been extensively characterized and studied as adsorbents as previously reported (Mohan, Pittman, et al., 2007). The chars have higher heating values (HHVs) that were >27.9 MJ/kg. These HHVs were slightly higher for the wood chars (~31.4 MJ/kg) than for the bark chars (~30.4 MJ/kg).

3.1. Gas Chromatography/Mass Spectrometry (GC/MS) Analysis of Bio-oils. Wood from both oak and pine species is composed of approximately 50−70% carbohydrates: cellulose and hemicellulose. Cellulose throughout the plant kingdom is made up of D-glucose joined exclusively by β-1–4 bonds, while hemicellulose can differ between species.[58] Galactoglucomannans are the most abundant hemicelluloses in pines. The galactose/glucose/mannose ratio is approximately 0.1:1:4 in galactoglucomannans. *O*-Acetyl-4-*O*-methylglucurono-β-D-xylan, the most common hemicellulose found in red oak, contains α- or β-D-xylose as the principal polysaccharide. An acetyl group occurs on about 7 out of every 10 of its xylose units. Also, 4-*O*-methyl-α-D-glucrouronic is a side chain on about 1 out of 10 xylose units. Hemicellulose typically contains 200–250 monosaccharide units and may contain a variety of other monosaccharide units. Levoglucosan was observed to be the major product in conventional cellulose pyrolysis, with reported yields as high as 60%. Subsequent levoglucosan dehydration yielded substituted furan and pyran derivatives.[59] Pyrolysis of several hemicelluloses yielded furfural as the major product.

Despite these differences in hemicellulose compositions between pine and red oak, no obvious differences in the distribution of substituted furans or other compounds were observed in the GC/MS analyses of bio-oil samples produced in this study. Table 1 summarizes the compounds which were quantitatively determined by GC/MS as described in section 2.3.1. Less is known about the composition of bark hemicelluloses, but there did not appear to be major differences in the furan derivatives that were found in the pine or oak bark bio-oils generated in this study versus those from the wood. Levoglucosan was the major component in bio-oils produced in this study, ranging in concentration from 8 to 22% for the four different feed stocks (Table 1).

Approximately one-fourth of the compounds found in the bio-oil samples were furfural or furfural derivatives formed by dehydration of monosaccharides that occur in cellulose or hemicellulose. Many other compounds originating from wood carbohydrates were also observed by GC/MS, including acetic acid, hydroxyl acetaldehyde, hydroxyacetone, ethyl acetate, 1-hydroxy-2-butanone, and 5-hydroxymethyl furfural that were found in bio-oil derived from all four feed stocks. The origin of these compounds from specific wood components was reported previously.[59,60]

Pine lignin contains guaiacyl units biosynthetically derived from trans-coniferyl alcohol. Red oak and other hardwood lignins contain both guaiacyl and syringyl repeating units. Thus, softwood lignin contains 3-methoxy-4-hydroxyphenyl functional groups and hardwood lignin contains both 3-methoxy-4-hydroxyphenyl and 3,5-dimethoxy-4-hydroxyphenyl groups. The bio-oils produced in this study contained predominantly phenolic compounds with only one methoxy group. These structures resemble guaiacyl lignin components. 4-Methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, vanillin, and isoeugenol were most abundant (Table 1). Methylphenols, dimethylphenols, catechol, and methyl substituted benzenediols were also observed. Catechol was the most abundant, occurring at concentrations in the range 2−4.5% in bio-oils from all four feed stocks. Dimethoxyphenols originating from syringyl lignin were observed in bio-oil from oak but not pine feed stocks. The concentrations of syringol, methoxyeugenol, syringaldehyde, and acetosyringone were not quantitated, but these compounds were found only in bio-oil from oak wood and oak bark feed stocks.

Oleic acid was observed in samples of bio-oil from all four feed stocks (Table 1). Oleic acid likely originated from a triglyceride extractive component which commonly occurs in both hardwood and softwood. Terpenes and resin acids that are common extractives were not observed in bio-oil from pine wood or pine bark. Interestingly, bio-oils produced from pine wood and pine bark exhibited similar organic compound distributions. A similarity in the commonly occurring components was also noted between bio-oils produced from oak wood and oak bark.

The same 30 compounds quantitated in the whole bio-oils were also quantitated in the ethyl acetate fractions (see the second half of Table 1). The amounts of phenolic compounds such as the methylphenols, dimethylphenols, catechol, quaiacols, methycatechols, methoxy(propyl)phenols, and methoxy(propenyl)phenols were present in higher quantities in these ethyl acetate fractions, as expected. A substantial amount of the oleic acid also was found in the ethyl acetate fraction from pine bark bio-oil. Furfurals and furfurols were also present.

The sum of the specific 30 compounds in the whole bio-oil samples (listed in the first portion of Table 1) corresponds to 27.2, 35.4, 30.7, and 27.2% of the total bio-oil produced from pine wood, pine bark, oak wood, and oak bark, respectively. The total quantity of semivolatile products produced was estimated using the sum of the total ion currents for these compounds and the sum of the total ion current for compounds not included in the target quantitated compound list. The semivolatile material in this calculation represents the percent of the total bio-oil sample that is sufficiently volatile to pass

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(59) Elder, T. In *Wood and Cellulosic Chemistry*; Hon, D. N.-S., Shiraishi, N., Eds.; Marcel Dekker, Inc.: New York and Basel, 1991; Chapter 14.

(60) Branca, C.; Giudicianni, P.; Di Blasi, C. *Ind. Eng. Chem. Res.* **2003**, 3190–3202.

Table 3. ^{13}C NMR Integrations of Whole Bio-oils[a]

type of carbon	chemical shift region (ppm)	carbon content (% of all carbon in each spectrum) pine wood bio-oil	pine bark bio-oil	oak wood bio-oil	oak bark bio-oil
carbonyl	215–163	11.8	0.5	18.1	2.4
aromatic	163–110	48.4	43.9	40.1	35.3
carbohydrate	110–84	5.8	1.4	10.3	2.1
methoxy/hydroxy	84–54	16.1	20.8	16.1	12.5
alkyl carbons	54–1	17.9	33.4	15.5	47.7
	34–24	8.5	13.2	6.0	19.2
	24–6	9.4	20.2	9.5	28.5

[a] Spectra were obtained at 60 °C in DMSO-d_6 at 100.6 MHz on a Varian Mercury 400 MHz spectrometer using inverse gated decoupling to avoid NOE effects.

Table 4. ^{13}C NMR Integrations for Lignin-Rich Fractions Derived by Ethyl Acetate Fractionation[a]

type of carbon	chemical shift region (ppm)	carbon content (% of carbon) pine wood bio-oil	pine bark bio-oil	oak wood bio-oil	oak bark bio-oil
carbonyl	215–163	8.6	9.5	6.7	12.0
total aromatic	163–110	47.1	43.4	51.4	52.5
general aromatic	163–125	27.1	24.9	28.7	31.8
aromatic (guaiacyl)	125–112	17.3	16.7	15.3	14.7
aromatic (syringyl)	112–100	2.7	1.8	7.4	6.0
carbohydrate	110–84	0	0	0	0
methoxy/hydroxy	84–54	10.6	14.8	20.1	12.5
alkyl carbons	54–1	33.8	32.3	21.7	23.0
	36–1	33.8	32.3	21.7	23.0

[a] Spectra obtained at 60 °C in DMSO-d_6 at 100.6 MHz on a Varian Mercury 400 MHz spectrometer using inverse gate decoupling to avoid NOE effects.

Table 5. ^{1}H NMR Integrations of the Whole Bio-oils versus the Chemical Shift[a]

Chemical shift region (ppm)	Type of protons	Hydrogen content (% of all hydrogen) Pine wood bio-oil	Pine bark bio-oil	Oak wood bio-oil	Oak bark bio-oil
10.0 – 8.0	-C**H**O, -COO**H**, downfield Ar**H**	2.63	6.58	1.55	0.94
8.0 – 6.8	Ar**H**, **H**C=C (conjugated)	4.35	7.13	2.79	4.04
6.8 – 6.4	**H**C=C (nonconjugated)	5.30	5.10	3.64	3.85
6.4 – 4.2	>C**H**O, ArO**H**, **H**C=C (nonconjugated)	16.54	20.72	16.86	20.34
4.2 – 3.0	CH_3O-, -CH_2O-, >C**H**O	37.56	37.65	40.29	34.80
3.0 – 2.2	$CH_3C(=O)$-, CH_3-Ar, -CH_2Ar	9.04	6.79	9.21	8.95
2.2 – 1.6	-CH_2-, aliphatic O**H**	13.69	9.14	15.97	16.10
1.6 – 0.0	-CH_3, -CH_2-	10.88	6.89	9.70	10.98

[a] These chemical shift regions overlap somewhat and O**H** protons from water, alcohols, and carboxylic acids are pH-dependent and can be found over a wide range. $-CO_2$**H** protons can exist from 13 to 10 ppm, phenolic protons can exist from 8.0 to 4.0 ppm, and water, hydroxyaldehyde, hydroxyketone, and alcohol can vary widely with pH.

Table 6. Molecular Weight Analysis by Gel Permeation Chromatography (GPC) in THF of Whole Bio-oils and Their Ethyl Acetate Fractions Produced from Four Different Feed Stocks

feed stock	bio-oil fraction	M_w	M_n	M_w/M_n
pine wood	whole	420	330	1.27
pine bark	whole	390	310	1.26
oak wood	whole	460	380	1.21
oak bark	whole	450	370	1.22
pine wood	EA[a]	540	420	1.29
pine bark	EA[a]	520	410	1.27
oak wood	EA[a]	460	380	1.21
oak bark	EA[a]	540	440	1.23

[a] EA = ethyl acetate fraction of that specific bio-oil.

through a GC column under the conditions described. These values ranged from 64.7 to 70.8% for all bio-oil samples produced in this study (Table 2). If the known amount of water and the estimated carboxylic acid concentrations are added, then the total amount of volatile material is estimated to be in the range between 88 and 110% for bio-oil from these four feed stocks. This result suggests that the amounts of nonvolatile material present in these four bio-oils may actually be less than 5–10%. Other reports and determinations of the composition of bio-oil from different feed stocks, reactors, and temperatures can be found in recent literature.[37,61,62]

Table 7. Temperature Dependence of Whole Bio-oil Viscosities at Two Different Shear Rates

biomass feed (shear rate in s^{-1})	bio-oil viscosities (cP) 25 °C	50 °C	80 °C
pine wood			
(0.05)	200	154	92
(300)	264	51	17
oak wood			
(0.05)	206	171	38
(300)	154	36	14
pine bark			
(0.05)	7253	2529	70
(300)	563	76	25
oak bark			
(0.05)	7289	5047	131
(300)	270	45	19

3.2. NMR Analysis. The ^{13}C NMR spectra are particularly instructive because of their large chemical shift regions. Table 3 summarizes the integrated ^{13}C spectra of the whole bio-oils, while Table 4 contains this same information for their corresponding lignin-rich ethyl acetate fractions. The pine and oak wood bio-oils exhibited far more carbonyl carbon content (11.8 and 18.1%), respectively, than the pine or oak bark oils (0.5 and 2.4%, respectively). This is consistent with the far higher content of cellulose and hemicellulose pyrolysis products present in the whole bio-oils (e.g., formic, acetic, propionic, and other

(61) Bridgwater, A. V., Ed. *Fast Pyrolysis of Biomass: A Handbook*; CPL Press, Liberty House: Newbury, U.K., 2002; Vol. 2.
(62) Bridgwater, A. V., Ed. *Fast Pyrolysis of Biomass: A Handbook*; CPL Press: Newbury Berks, U.K., 2005.

Table 8. Temperature Dependence of the Viscosities for Lignin-Rich Ethyl Acetate Bio-oil Fractions at Two Different Shear Rates (Viscosities Given in Centipoise)

	ethyl acetate fraction dynamic viscosities (cP)		
biomass feed (shear rate in s^{-1})	25 °C	50 °C	80 °C
pine wood			
(0.05)	9561	232	36
(300)	1372	159	37
oak wood			
(0.05)	9021	3467	101
(300)	5533	336	57
pine bark			
(0.05)	8154	102	47
(300)	719	106	31
oak bark			
(0.05)	32 820	423	182
(300)	1018	121	29

Table 9. Average Values for Percent Water, Acid Value, pH, Density, Percent Solids, and Viscosity for Bio-oils from Pine Wood, Oak Wood, Pine Bark, and Oak Bark

sample type	percent water[a]	acid values[a]	pH/water	density (g/cc)	percent solids	kinematic viscosity 50 °C (cSt)
pine wood	16.0	90	3.1	1.19	0.19	60.9
oak wood	22.5	120	3.1	1.20	0.80	41.6
pine bark	19.8	84	3.2	1.17	2.10	nd[b]
oak bark	22.0	120	3.2	1.20	1.83	nd[b]

[a] The percentages of water in the ethyl acetate fractions were lower than those in the whole bio-oils. The water percentages in the ethyl acetate fractions were 8.7 (pine wood), 9.4 (oak wood), 8.7 (pine bark), and 8.4 (oak bark). The acid values for these four fractions were remarkably similar. All were between 18.0 and 19.1. [b] nd = not determined.

Table 10. Percent Ash, Elemental Analysis, and BTU Content of Composite Bio-oil Samples from Pine, Oak, Pine Bark, and Oak Bark Feed Stocks[a]

component	pine wood	oak wood	pine bark	oak bark
carbon (%)	52.64	47.19	53.99	45.47
hydrogen (%)	7.53	4.51	6.97	6.05
nitrogen (%)	0.09	0.12	0.37	0.32
sulfur (%)	0.019	0.022	0.035	0.28
oxygen (%)	39.52	47.97	38.21	47.75
ash (%)	0.197	0.184	0.428	0.080
heat content (MJ/kg)	21.9	18.7	18.3	19.0

[a] These analyses give the wt % of the whole bio-oil including their water contents.

Table 11. Comparison of the Physical and Chemical Characteristics of Bio-oil from This Study to Characteristics in Other Published Results

quality	MSU pine	ROI[39]	Other Bio-oils[37]
water (%)	16	21	10–31
solids (%)	0.19	0.66	0.17–1.14
visc. (cSt50)	53	2.4	9–137
density (g/cc)	1.19	1.10	1.21–1.24
C (%)	61	62	48–60
H (%)	7.0	8.0	5.9–7.2
O (%)	32	29	32–46
HHV (MJ/kg)	21.9	20.0	15.0–19.0

carboxylic acids, aldehydes, hydroxyaldehydes, hydroxyketones, levoglucosenone, and related products). Ethyl acetate fractionation largely removes these products.

The lignin-rich fractions from pine and oak wood (Table 4) had substantially more aliphatic carbon content (33.8 and 21.7%) than their corresponding whole bio-oils (17.9 and 15.5%). This is consistent with the aliphatic chain linkages that cross-link the phenolic units of lignin. The oak bark whole bio-oil has a much higher aliphatic carbon content (47.7%) than the oak bark ethyl acetate fraction (23.0%), whereas the pine wood whole oil and lignin-rich fractions (33.4 and 32.3%, respectively) each have about the same aliphatic carbon content. The bark oils have less carbohydrate carbon (pine, 1.4%; oak, 2.1%) than the whole oils from either wood (pine, 5.8%; oak, 10.3%). Clearly, both whole bark bio-oils have a greater content derived from lignin or other polyphenolic precursors.

It was of interest to examine the aromatic region of the lignin-rich ethyl acetate fractions for quaiacyl versus syringyl phenolic components (Table 4). Pine wood and pine bark lignin-rich fractions had slightly higher quaiacyl contents (17.3 and 16.7%) than oak wood or oak bark lignin-rich fractions (15.3 and 14.7%). However, the oak wood and oak bark fractions had much higher syringyl contents (7.4 and 6.0%) than the pine wood and pine bark fractions (2.7 and 1.8%). This trend was also clear in the whole bio-oils (data not divided out in Table 3).

Another pronounced difference can be observed in the carbohydrate carbon chemical shift range from 110 to 84 ppm. No resonances occurred in this region for any of the four lignin-rich ethyl acetate fractions (Table 4). By contrast, pine wood and oak wood whole bio-oils exhibited 5.8 and 10.3% of their respective carbons in this region (Table 3).

^{1}H NMR whole bio-oil spectra were similar to those previously reported (Bozell, 1992). Since the ^{1}H chemical shift range is compressed relative to that of ^{13}C, considerable overlap of various types of proton resonances occurs. Furthermore, the presence of phenolic, carboxylic alcohol, and water hydroxyl groups acidic pH values causes a variety of rapid equilibrations, peak width broadening, and the chemical shift changes. The integrated areas in specific chemical shift ranges are summarized in Table 5.

Aliphatic protons occur between 0.0 and 1.6 ppm, and others are found from 1.6 to 2.2 ppm along with aliphatic hydroxyls. Protons located alpha to ketone, aldehydes, or carboxyl groups and benzylic protons occur from 2.2 to 3.0 ppm. On the basis of the integrated areas, substantial amounts of aliphatic protons exist which are consistent with the ^{13}C NMR spectra.

Significant quantities of methoxy, $-CH_2O-$, and $=CHO-$ functionality appear from 3.0 to 4.2 ppm. Further $=CHO-$ groups, phenolic OH, and nonconjugated olefinic protons are seen from 4.2 to 6.4 ppm. Olefinic protons on double bonds conjugated to carbonyls are found from 6.4 to 6.8 ppm and at lower fields (6.8–8.0 ppm) where the bulk of the aromatic protons occur. Lower field aromatic protons and aldehyde protons are found from 8.0 to 10.0 ppm. Given the complications resulting from the wide chemical shift range over which hydroxyl protons are found and the overlapping of the chemical shift ranges, further quantitation was not attempted. However, direct comparisons of the ^{1}H NMR spectra of the four whole bio-oils produced in the auger pyrolysis reactor with bio-oils produced from a fluidized bed reactor revealed similar overall patterns.

3.3. Gel Permeation Chromatography (GPC) Analysis. Weight average molecular weights (M_w) for the four bio-oils were in the range 390−460 with M_w. The bio-oils from oak feed stocks exhibited slightly higher M_w values than the bio-oils from pine feed stocks (Table 6). The polydispersities (PD $= M_w/M_n$) were 1.27 and 1.26 for the pine wood and pine bark bio-oils. These values were slightly higher than the respective values for oak wood (1.21) and oak bark (1.22) bio-oils. The fractional composition of compounds in the 300−400 molecular

weight range for whole bio-oil is not known. A weight average molecular weight (M_w) of 540 was previously reported for oak bio-oil prepared in the NREL vortex reactor.[8] The M_w value of this bio-oil was also reported to increase with storage time and increased temperature.

In a detailed characterization of multiple solvent fractionated portions of bio-oil produced by fast vacuum pyrolysis, it was demonstrated that the water-soluble and water-insoluble/CH_2Cl_2-insoluble fractions should both be analyzed using dimethylformamide (DMF) as a solvent with calibration performed using polyethylene glycols.[63] DMF is very effective at dissolving lignins over a wide molecular weight range.[64–66] Our GPC studies on both whole bio-oils and their ethyl acetate fractions were performed in THF using polystyrene standards. This method is the most extensively used procedure for studying unfractionated whole bio-oils.[8,33,48,67–70] When examining these previous studies and those summarized in Table 6, it must be remembered that all of the reported M_n and M_w values could be somewhat low because the water-insoluble/CH_2Cl_2-insoluble fraction contains the heaviest molecules (molecular weights from 1475 to 1967).[63,67] These will not be fully soluble or analyzed using THF.

The THF-soluble portions of the ethyl acetate fractions exhibited higher M_n and M_w values than the whole bio-oils for all feed stocks except for oak wood, which showed the same molecular weight values for both.

3.4. Viscosity Measurements. Pine and oak bark bio-oils had higher viscosities at 25 and 50 °C than pine and oak wood oils. Both bark bio-oils were non-Newtonian at low shear rates but became Newtonian at higher shear rates at all temperatures between 25 and 80 °C. The non-Newtonian shear thinning behavior decreased as temperature increased. This behavior is illustrated in Figure 1 for oak bark bio-oil where the viscosity (in poise) is plotted versus shear rate at 25, 50, and 80 °C. Pine and oak wood whole bio-oils, by contrast, were essentially Newtonian at 25 °C but exhibited mild shear thinning behavior at both 50 and 80 °C. This behavior is illustrated in Figure 2 for oak wood bio-oil. The viscosities of all four bio-oils and the four corresponding lignin-rich ethyl acetate fractions are summarized in Tables 7 and 8, respectively, for shear rates of 0.05 and 300 s^{-1} at these three temperatures.

The lignin-rich ethyl acetate fractions exhibited higher viscosities at low shear rate than the unfractionated bio-oils. This is not surprising, since their water contents were significantly lower, a consequence of the solvent fractionation process. At 25 °C, all of the ethyl acetate fractions were non-Newtonian (shear thinning). Shear thinning became less pronounced at 50 and 80 °C for oak wood, pine wood, and oak bark, while the pine bark ethyl acetate fraction became Newtonian. Loss of shear thinning as the temperature increased is illustrated in Figure 3 for pine bark's ethyl acetate fraction.

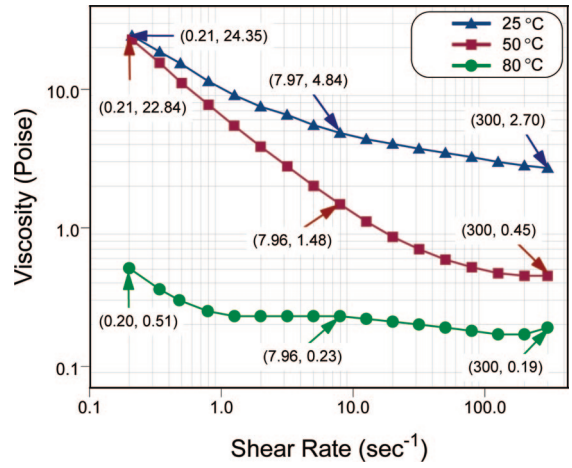

Figure 1. Viscosity of oak bark bio-oil as a function of shear rate at 25, 50, and 80 °C.

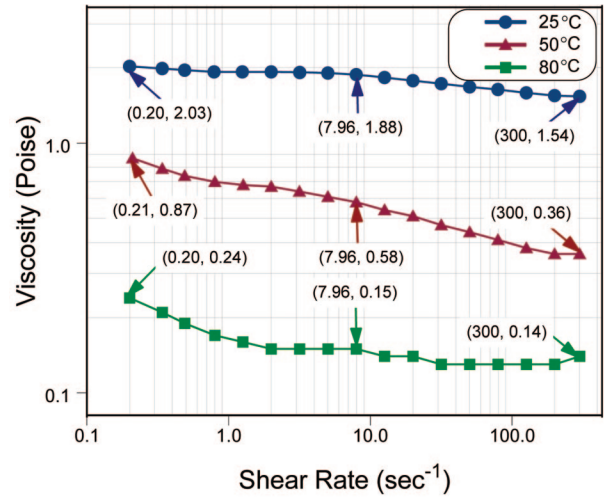

Figure 2. Viscosity of oak wood bio-oil as a function of shear rate at 25, 50, and 80 °C.

The rheological behavior is extremely difficult to try to interpret because of the complex multiphase nature of all of these bio-oils. As the temperature changes, the phase behavior changes, and this, in turn, influences the viscosity. Microscopic images (Figures 4 and 5) show these phases. For example, oak bark bio-oil at magnifications of 40× and 200× reveal multiple phases at 25 °C. At 80 °C, these phases appear to disappear and disperse into a single phase. Thus, the drop in viscosity between 25 and 80 °C is the result of several factors, including phase changes, operating simultaneously. This is also true of the viscoelastic properties obtained from dynamic studies.

Dynamic studies were conducted to obtain storage (G') and loss (G'') moduli. These values were obtained at angular frequencies of 0.10−100 rad·s^{-1} at 25, 50, and 80 °C. Pine wood bio-oil exhibited a crossover frequency to gel behavior of 105 rad·s^{-1} at 25 °C. The value of G' for pine wood bio-oil increases and, eventually, $G' > G''$, indicating gel-type behavior.

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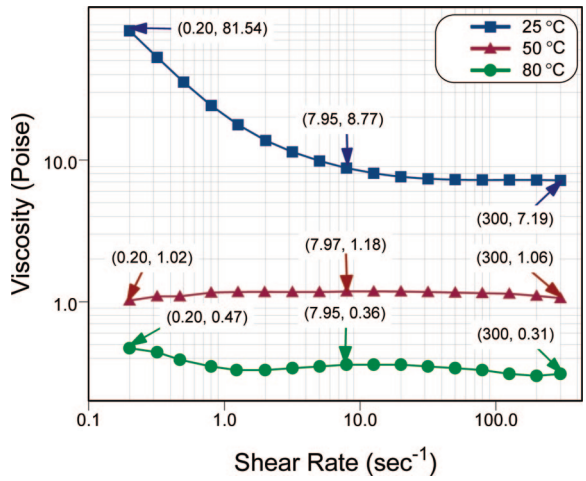

Figure 3. Viscosity of the ethyl acetate fraction of pine bark bio-oil as a function of shear rate at 25, 50, and 80 °C.

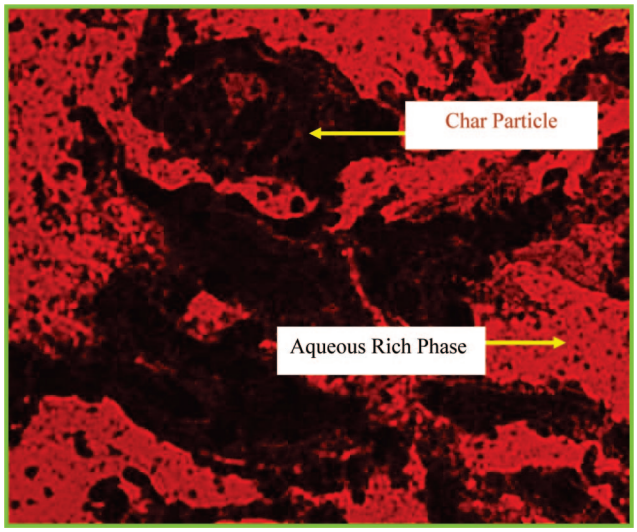

Figure 4. View of phases present in oak bark bio-oil at 25 °C and a magnification of 40×.

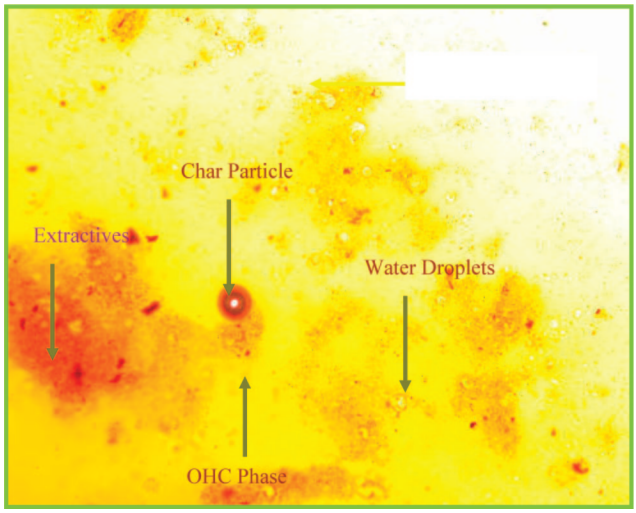

Figure 5. View of phases present in oak bark bio-oil at 25 °C and a magnification of 200×.

At 50 °C, the crossover frequency to gel behavior was 3.5 rad·s^{-1}. Thus, loss of permanent fluid structure and alignment occurs on heating. At 80 °C, the complete melting or phase disappearance, which had been observed microscopically, was also inferred from the values of the storage moduli (G'). The values of G' did not build up during the test period and remained significantly lower than the loss modulus (G''). Detailed viscosity and rheology studies of these bio-oils and lignin-rich ethyl acetate fractions will be published elsewhere.

3.5. Collective Properties: Density, Water Content, Solids, Ash, Acid Value, Heating Value, Elemental Analysis, and pH. Density, water content, solids, ash, acid values, heating values, elemental analyses, and pH values are summarized in Tables 9 and 10. Table 9 shows that bio-oil from pine wood had a lower water content (16.0%) versus the bio-oils produced from oak wood (22.5%), oak bark (22.0%), and pine bark (19.8%). Pine wood bio-oil consistently had the lowest water content in multiple auger reactor pyrolysis experiments under different pyrolysis conditions during this study, and these results have already appeared.[72] The water contents of all four ethyl acetate fractions were lower, ranging from 8.4 to 9.4%. This reflects the amount of water carried into the ethyl acetate solvent containing the pyrolytic bio-oil components. It is a function of the fractionation procedure used.

The acid values of bio-oils from both oak and pine wood were lower than those from bark (Table 9). Furthermore, pine-derived bio-oil had a lower acid value (90) than oak-derived bio-oil (120). Hardwoods typically have a higher content of acetyl groups associated with their hemicellulose than softwoods. The formation of acetic acid from the acetyl groups is a likely cause of the higher hardwood acid values. The pHs of oak and pine bio-oils were the same (3.1). The bark bio-oils had pH values of 3.2, just slightly higher than the upper end of the range of 2.5−3.0 reported for values measured with a pH meter.[73] All four ethyl acetate fractions had far lower acid values (from 18.0 to 19.1). This is consistent with the removal of formic, acetic, and propionic acids and hydroxyl carboxylic acids derived largely from cellulose and hemicelluloses.

Bio-oil from pine wood had the lowest percent filterable solids, while bio-oil from pine bark and oak bark tended to have higher values (Table 9). The filterable material had the physical appearance of fine charcoal. Entrained charcoal and ash particles carrying over into the biomass pyrolysis condensate is frequently reported in the literature. Other methanol-insoluble solids would also be collected by this filtering technique. With the 25 μ filter used in these experiments, filtered bio-oil remained dark in color. However, samples of bio-oil were transparent after they were filtered through the much smaller pore openings of a 0.45 μ filter, used for GPC analysis.

The kinematic viscosities of the wood-derived bio-oil samples were in the range 40−65 cSt at 50 °C. Bio-oils from both bark feed stocks were extremely viscous, making it impossible to apply the same viscosity determination procedure for analysis; hence, the viscosity of these samples was not determined. The falling needle viscometer is easier to load and use than the reverse flow Canon-Fenske instrument that is required for opaque liquid.

Elemental and ash analyses are summarized in Table 10. Bio-oil from pine wood had the highest hydrogen content (7.53%) and also the highest heat value at 21.9 MJ/kg. Bio-oil from pine bark and oak wood ranked next in hydrogen content (6.97 and 6.05%). The heat value of pine wood bio-oil (21.9 MJ/kg) was

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Table 12. Comparison of Auger Reactor Bio-oils with Bio-oils Produced in Other Fast Pyrolysis Reactor Systems

										elemental analysis					
feed	reactor/process	temp (°C)	residence time (solids) (s)	water (wt %)	pH	viscosity[a]	density (g/cc)	HHV (MJ/kg × 10^{-3})	LHV (MJ/kg × 10^{-3})	C (wt %)	H (wt %)	N (wt %)	O (wt %)	ash	ref.
pine wood	auger	450	−30	16.0	3.1	60.9 cSt (50 °C)	1.19	18.7	20.9	52.6	7.53	0.09	39.5	0.20	this study
oak wood	auger	450	−30	22.5	3.1	41.6 cSt (50 °C)	1.20	21.9	17.0	47.2	4.51	0.12	48.0	0.18	this study
pine bark	auger	450	∼30	19.8	3.2	70 cP (80 °C)[b]	1.17	19.0	17.0	54.0	6.97	0.37	38.2	0.43	this study
oak bark	auger	450	∼30	22.0	3.2	131 cP (80 °C)[b]	1.20	18.3	17.5	45.5	6.05	0.32	47.8	0.08	this study
oak/maple	ensyn process Canada			19.9	3.7	11 cSt (50 °C)	1.19		16.9	55.3	6.6	0.4		0.14	71
oak wood	abiatic process	625	<1	16.1	2.9	159 cP (25 °C)	1.29			46.3	6.8	0.1	46.8	0.05	8
maple oak	ensyn from RTP facility	525	0.35	26		107 cP (25 °C)	1.19	21		55.1	6.7	0.15	38.0		74
softwood bark	vacuum pyrolysis	500 (at 14 kPa)		13	3.0	62 cSt (50 °C)	1.19	27.9		62.6	7.0	1.1	29.0	0.3	16
softwood	fluidized bed (Hamburg)		<1	14.6	2.3	40–200 cP (40 °C)	1.2	20		55	7				32
fir wood	rotating cone, BTG (Netherlands)			4.5		250 cP (60 °C)		22.2		58.1	6.6	0.5	38.4	<0.05	12
beach wood	rotating cone, BTG (Netherlands)			14.0	2.7	10 cP (70 °C)	1.22	20.9		55.1	7.2	2.0	35.1		12
wood	ensyn, transported bed (Canada)			22	2.5	450 cP (40 °C)		23.1		56.4	6.2	0.2	37.1	0.1	12

[a] This column contains both dynamic (cP) and kinematic viscosity (cSt) measurements. [b] At a 0.5 s^{-1} shear rate. These viscosities drop at a shear rate of 300 s^{-1} to 25 cP (pine bark bio-oil) and 19 cP (oak bark bio-oil).

the highest, while that for pine bark bio-oil was the lowest (18.3 MJ/kg). The higher value for pine wood bio-oil correlates with its lower water content. Ash contents ranged from 0.080 to 0.197% for the pine and oak wood and oak bark bio-oils. However, the pine bark bio-oil had a much higher ash content at 0.428%.

Pine bark whole bio-oil had the highest ash content and lowest heat value, while also exhibiting the highest carbon content of all the bio-oil samples and more hydrogen than oak wood or bark (Table 10).

The characteristics of pine wood whole bio-oil from the auger reactor are summarized and compared in Tables 11 and 12 with characteristics described in the literature for bio-oils produced by other pyrolytic reactors. The bio-oils from the auger reactor were totally soluble in methanol, acetone, and isopropanol and partially soluble in methylene chloride and toluene, consistent with published results from bio-oils produced in other reactors.[27] Overall, the chemical and physical properties, heating values, elemental analyses, etc., of the four bio-oils produced in the auger reactor are generally similar to the properties of bio-oils produced in other types of fast pyrolysis reactors.

4. Conclusions

The major conclusion of this study is that the bio-oils formed in the auger pyrolysis reactor are very similar to bio-oils formed in a variety of other reactors where the biomass heating rates are substantially higher. This auger reactor process has a relatively slow heating rate. The transit time for solids through the reactor was about 50 s (~30 s in the pyrolysis zone at 450 °C), and the time that vapors and aerosols are in contact with the pyrolyzing solid as it becomes char is greater than that for a typical fast pyrolysis system. All of these factors raised doubts that the bio-oil from an auger reactor would be of similar quality to bio-oils produced in fluidized bed or vacuum pyrolysis reactors. However, the nature of the bio-oils produced in this study lends support to the notion that portable auger reactors could be taken to sites of tree harvesting or thinnings, in order to convert biomass to bio-oil for subsequent delivery to power generating locations or biorefineries. Raw harvested biomass is bulky (even after compaction). It would be cheaper to transport the more energy-dense bio-oil to their destinations for further use.

The pyrolysis auger reactor used in this work must be viewed as a first-generation research prototype. An improved design has been incorporated into a second-generation reactor, just completed at Mississippi State University. This unit is designed to provide higher heating rates and improved thermal transfer of heat to the feed stocks.

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