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Compositional Characterization and Pyrolysis of Loblolly Pine and Douglas-fir Bark

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Abstract Two potential biofuel resources, Douglas-fir and Loblolly pine bark, were subjected to extensive chemical and compositional analysis. The barks were initially extracted with dichloromethane, and the resulting extracted compounds were characterized by gas chromatography coupled with mass spectrometric analysis. Characterization of the major bark biocomponents indicated that Douglas-fir and Loblolly pine bark contained 22.5 and 13.2 % tannins, 44.2 and 43.5 % lignin, 16.5 and 23.1 % cellulose, and 7.6 and 14.1 % hemicellulose, respectively. Of particular interest is the high content of tannins and lignin, which make these barks excellent potential precursors for bio-oils and/or other value-added chemicals. ^{13}C nuclear magnetic resonance (NMR) was used to characterize the chemical structure of the lignin and tannins. These samples were also analyzed by ^{31}P NMR after phosphitylation of the hydroxyl groups in lignin and tannins. The NMR spectral data indicated that the lignin in both barks contained *p*-hydroxyphenyl (*h*) and guaiacyl (*g*) of lignin monomers with an *h*/*g* ratio of 10:90 and 22:78 for Douglas-fir and Loblolly pine bark, respectively. Gel permeation chromatography was used to analyze the molecular weight distributions of extracted tannins, isolated cellulose, and ball-milled lignin. The pyrolysis of Douglas-fir and pine bark at 500°C in a tubular reactor generated 48.2 and 45.2 % of total oil, of which the light oil contents are 14.1 and 20.7 % and heavy oil are 34.1 and 24.4 %. Similarly, fast pyrolysis at 375°C yielded 56.1 and 49.8 % of total oil for Douglas-fir and pine bark, respectively.

Keywords Loblolly pine bark · Douglas-fir bark · Extractive · Inorganic elements · Ball-milled lignin · Tannin · Cellulose · ^{13}C · ^{31}P NMR spectroscopy

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Introduction

The use of renewable energy resources is now considered an essential component to address energy security and sustainable economic development. Lignocellulosics are an abundant renewable feedstock for the global production of biofuels and valuable chemicals [1–3]. Among lignocellulosic bioresources, bark is a highly under-utilized material. Apart from extractives and plant polysaccharides, softwood barks usually contains 40–55 % lignin which is a biocomponent with higher energy density.

Every year in the USA, an estimated 30 million tons of bark is generated whereas 27 million tons of the bark is currently employed as a low value thermal resource [4]. Therefore, the conversion of bark to bio-oils or chemicals is of significant interest and a topic of considerable research effort. Many researchers have attempted to convert barks by liquefaction [5–7] or pyrolysis [8–10] to bio-oils that could be further upgraded to transportation biofuels. These bio-oils have also been identified and evaluated as a potential feedstock for a variety of other fine and bulk chemicals. For example, pyrolysis-derived phenols are being examined to synthesize bio-based phenol-formaldehyde resins [11, 12]. However, the challenge of efficiently and cost-effectively

converting barks to bio-oils while also minimizing the residual char formation continues to the present day.

A detailed survey of the chemical characteristics of bark and its various biocomponents is essential to understanding and optimizing the conversions taking place throughout the process of generating bio-oils from bark. Complicating this effort is the fact that bark is a highly heterogeneous material and the composition and properties of bark vary from species to species. There has been considerable work done to characterize the relative proportions of biocomponents in bark from several sources. McGinnis and Parikh investigated the chemical constituents of Loblolly pine bark via standard chemical methodology suggesting that the Klason lignin content of the extractive-free bark was 46.0 %. They demonstrated appreciable amounts of carbohydrates could also be extracted by both neutral and basic solvents, though this analysis did not provide a complete accounting of the cell wall components in all the samples because of the overlapping solubilities of some of the constituents [13]. Laver et al. reviewed the chemical constituents of Douglas-fir bark and reported that it includes wax, carbohydrates, cork, and tannins [14]. Labosky researched the chemical constituents of four southern pine barks including Loblolly pine bark and reported that within- and among-species variation in alcohol–benzene extractive content was appreciable. However, for Virginia and Loblolly pine bark, no within-species differences in the polar or non-polar extractable yields were observed [15]. A second study by Harun and Labosky analyzed the chemical constituents of five northeastern barks including white pine, red pine, shagbark hickory, red oak, and red maple. The results again showed that both within- and among-species variation in ash, ethanol–benzene extractives, and suberin content occurred significantly. In general, the softwood bark species contained a higher Klason lignin content (42 to 50 %) than in hardwood barks (36 to 38 %) [16]. In an effort to study the potential utilization of *Pinus pinaster* bark from the trees located in Santiago, Spain currently used to produce particleboards, researchers verified that the fraction formed by formaldehyde-condensable polyphenolics and polysaccharides is over 60 wt.% of bark [17]. Besides determining the content of extractives, Klason lignin, cellulose, and hemicellulose, literature studies indicate that the lignin within bark from maritime pine grown in Portugal is composed mainly of *p*-hydrophenyl and guaiacyl units in the proportion of 20:80 [18]. More recently, Huang et al. compared the lignin structures isolated from Loblolly pine stem wood, residue, and bark which were acquired from wood product industry [19]. Although a considerable effort has been devoted to the chemical characterization of various individual bark constituents, a detailed and comprehensive study of the entire bark composition and its constituents taken from a single source has not been performed, and most research is limited to reports of the bark mass fractions.

The burgeoning biofuels industry, in partnership with the forest products industry, has begun to examine what resources could be utilized for the generation of biofuels while still addressing existing commercial markets for wood and pulp/paper. Based on these concerns, the utilization of softwood bark for pyrolysis bio-oil production has become an attractive area of study given the volume of bark generated and limited established markets [20]. The Douglas-fir wood industry in northwestern USA and the pulp and paper industry in the southeast mainly utilizing southern pine generate large volumes of bark which is under active investigation as a resource for pyrolysis oils and is a driving factor for this investigation. In this paper, we examine in detail the compositional profile and the chemical structures present in the major bark constituents of these two valuable biofuel precursors secured from industrial wood conversion operations.

Materials and Methods

Chemicals All chemicals used in this study were purchased from VWR International and used as received with the exception of *p*-dioxane which was distilled over $NaBH_4$ prior to being used.

Sample Preparation Commercial sources of Loblolly pine and Douglas-fir bark were received from kraft pulp mills located in Georgia and Washington State, respectively. The Douglas-fir bark sample consisted solely of bark, but the Loblolly pine bark sample contained a mixture of bark and wood. A pure Loblolly pine bark sample was acquired by hand-sorting. The bark samples of different batches were mixed and then dried in a convection oven at 45°C for 1 day and subsequently milled with a Wiley mill equipped with a 0.50-mm sieve. The bark powders were stored at 0°C prior to use.

Ash and Extractive Content and Heating Value The ash content of Loblolly pine and Douglas-fir bark was determined by heating the samples at 525°C in a furnace [21] with a yield error of ±0.1 %. The acid-insoluble ash, mainly silica or silicates, was determined according to TAPPI method T-244; 6.0 M HCl (5.0 mL) was added to the ash and evaporated to dryness and then repeated a second time. A third aliquot of 6.0 M HCl (5.0 mL) was then added to the ash sample and the sample was heated to 100°C for 0.5 min, and the suspension was then diluted with 20 mL of deionized (DI) water. The suspension was filtered through ash-free filter paper, and the solid residue was washed with hot DI water (3×100 mL). Finally, the acid-insoluble ash

was determined by heating the samples at 525°C in a muffle furnace. The inorganic elements in the bark samples were determined by inductively coupled plasma emission spectroscopy according to methodology previously employed by Allison et al. [22]. According to TAPPI method T-204, the extractives were recovered with dichloromethane (DCM) using a Soxhlet extractor with a yield error of ±0.2 %. The heating value of bark was acquired according to TAPPI method T-684 using a 1261 Isoperibol Bomb Calorimeter [23].

GC/MS Analysis A DCM extractive aliquot and internal standard (heptadecanoic acid) were added to a 1.50-mL vial, and the solvent was subsequently removed under a stream of nitrogen. The dried residues were derivatized with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide, and 1 μL derivatized mixture was injected into a gas chromatography coupled with mass spectrometry (GC/MS) for the analysis. The instrument used was a Hewlett-Packard 5890 II GC equipped with a Hewlett-Packard 5971A mass selective detector. A 0.25-mm×60-m DB-5 fused silica capillary column with a 25-μm coating stationary phase was used for the chromatographic separations. The GC conditions were as follows: initial temperature, 150°C; initial time, 5 min; rate, 15°C/min; final temperature, 280°C; final time, 25 min; and injection port temperature, 250°C. The mass detector was operated using the following conditions: EI mode, 70 eV; filament on delay time, 8 min; and mass scan range, 45–650 amu. Quantification of individual components was based on the total ion peak area. GC response factor of each individual compound was assumed to be one for all calculations. It is worth noticing that only ~40 % of the extractives could be detectable and identified by GC/MS [24].

Tannin After Soxhlet extraction with DCM for 48 h, the air-dried DCM extractive-free bark samples were Soxhlet-extracted with a methanol–water mixture (75:25, *v*/*v*) for 48 h. The filtered solution underwent low-pressure rotational evaporation at 40°C and freeze-dried to recover the tannins with yield errors of ±0.1 and ±0.4 % for Douglas-fir and Loblolly pine bark, respectively. To avoid heat-initiated condensation of tannins, a second set of tannin samples were acquired (for structural characterization) by stirring bark samples (10.00 g) in a methanol–water mixture (75:25, *v*/*v*, 100 mL) at 40°C for 24 h. The solution was then filtered and the extracted bark samples were stirred in methanol–water mixture, an additional three times under the same conditions. The combined filtrates were concentrated under reduced pressure at 40°C and then freeze-dried [25].

Carbohydrate and Lignin Composition Bark samples for carbohydrate analysis and acid-insoluble lignin (Klason lignin) analysis were prepared using a two-stage acid hydrolysis protocol based on TAPPI methods [26] with a slight modification. The first stage utilizes a strong acid and a low reaction temperature (i.e., 72 % H_2SO_4 at 30°C for 1 h). The second stage is performed at much lower acid concentration and higher temperature (i.e., 3 % H_2SO_4 at 121°C for 1 h) in an autoclave. The resulting solution was cooled to room temperature and filtered through G8 glass fiber filter (Fisher Scientific, USA). The remaining residue which is considered as Klason lignin was oven-dried and weighed to obtain the Klason lignin content. The filtered solution was analyzed for carbohydrate constituents of the hydrolyzed bark samples determined by high-performance anion-exchange chromatography using a Dionex ICS-3000 system (Dionex Corp., USA) equipped with a pulsed amperometric detector [27]. The acid-soluble lignin content present in the filtrate was determined using an UV/Vis spectrophotometer (UV160U, Shimadzu) from the absorbance at 205 nm according to Lin and Dence [28].

Holocellulose, Cellulose Holocellulose was obtained by treating the DCM extractive-free/tannin-free bark samples with a mixture of acetic acid and sodium chlorite in a shaking water bath at 70°C until the sample became white and displayed a low measured Klason lignin content (<4 %). The cellulose samples were isolated by stirring the holocellulose sample (1.00 g) in NaOH solution (17.5 %, 50.0 mL) at 25°C for 30 min, and the solution was then diluted to 8.75 % NaOH solution by addition of 50.0 mL DI water and stirred at 25°C for 30 min. The solids were collected by filtration and then washed with 1 % acetic acid (50 mL) and DI water (100 mL). The solids were removed, washed with DI water, and allowed to dry overnight in a fume hood.

Isolation and NMR Characterization of Ball-Milled Lignin Lignin was isolated from DCM extractive-free/tannin-free bark by ball milling and organic solvent extraction. Ball-milled lignin (BML) samples of Douglas-fir bark and Loblolly pine bark were prepared according to the procedures described by Guerra et al. [29] and Holtman et al. [30] with the yields of 3.38 and 1.58 % of oven-dried bark, or the yields of 7.65 and 3.63 % based on Klason lignin contents which are 44.2 and 43.5 % of oven-dried bark, respectively; the BML yields of the two barks were comparable with literature data [31–34]. BML samples (100 mg) were dissolved in DMSO-d_6 (~500 mg) and analyzed by quantitative ^{13}C NMR using a Bruker Avance-400 MHz spectrometer at a frequency of 100.59 MHz over 32 K data points with acquisition time 0.67 s with an inverse gated decoupling pulse sequence using a pulse delay of 12 s and 10 K scans. Quantitative ^{31}P NMR analysis of BML (~25 mg) was accomplished by using a pyridine/$CDCl_3$ (1.6:1, *v*/*v*) solvent, cyclohexanol as an internal standard, and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as the derivatization

Table 1 Ash, extractive, and other biomass constituent contents and heating values of Loblolly pine and Douglas-fir bark

	Douglas-fir bark	Loblolly pine bark
Ash (%)	1.7	1.1
Acid-insoluble ash (%)	0.91	0.20
Extractive by DCM (%)	7.4	4.0
Tannins (%)	22.5	13.2
Lignin (%)	44.2	43.5
Cellulose (%)	16.5	23.1
Hemicellulose (%)	7.6	14.1
Heating value (MJ/kg)	23.6	21.7

agent following literature methods [35]. The quantitative ^{31}P NMR spectra were acquired at a frequency of 161.93 MHz over 32 K data points with acquisition time 1.29 s using an inverse gated decoupling pulse sequence with a 25-s pulse delay and 128 scans.

NMR Analysis of Tannins Quantitative ^{31}P and qualitative ^{13}C NMR were performed to characterize the chemical structure and composition of tannins. ^{31}P NMR experiments were conducted using the same NMR conditions as employed to characterize BML described above. ^{13}C NMR analysis was performed at a frequency of 100.59 MHz over 32 K data points with acquisition time 0.67 s using a gated ^{1}H decoupling sequence with a 1-s pulse delay and 10 K scans.

Gel Permeation Chromatography Analysis of Cellulose, BML, and Tannins The weight average molecular weight ($\overline{M}_w$) and number average molecular weight ($\overline{M}_n$) of cellulose, BML, and tannin samples were determined by gel permeation chromatography (GPC). This was accomplished for cellulose by drying cellulose samples (20.00 mg) over P_2O_5 in vacuum oven at 40°C for 24 h and then derivatizing this material using anhydrous pyridine (5.70 mL) and phenyl isocyanate (0.70 mL). The sealed reaction flask was kept at 65°C in oil bath with stirring until the cellulose was completely dissolved. After cooling to room temperature, methanol (2 mL) was added into the solution to quench the unreacted phenyl isocyanate. The mixture was added into a water–methanol mixture (3:7, *v*/*v*, 200 mL) to precipitate the cellulose tricarbanilates. The precipitated cellulose tricarbanilate

Table 3 Composition in DCM extractives of Loblolly pine and Douglas-fir bark

Compounds	Loblolly pine	Douglas-fir
	mg/kg of oven-dried bark	
Aromatic compounds	0	94
Vanillin	0	20
Vanillic acid	0	22
4-Hydroxycinnamic acid	0	10
Ferulic acid	0	42
Fatty acids and other carboxylic acids	879	1,701
Azelaic acid	0	24
C-16:0 (palmitic acid)	116	141
9,12-Octadecadienoic acid	77	20
Oleic acid	0	52
C 18:0 (stearic acid)	0	58
C 22:0 (behenic acid)	165	572
C 24:0 (lignoceric acid)	374	774
C 26:0 (Cerotic acid)	147	60
Alkanols	420	0.86
C 22:OH	0	0.41
C 24:OH	330	0.45
C 26:OH	90	0.01
Resin acids	2,657	4,780
Pimaric acid	365	105
Sandaracopimaric acid	71	0
Isopimaric acid	299	679
Palustric acid	239	141
Dehydroabietic acid	1,340	3,347
Abietic acid	343	256
Dehydro-9-ketoabietic acid	0	252
Alkanes	293	0
Monoglycerides	333	0
Sterol	117	210
Sitosterol	117	210
Others	0	77
Ergosterol derivative	0	40
Stigmasterol derivative	0	37

Table 2 Inorganic element profiles of Loblolly pine and Douglas-fir bark

Barks	Elements (mg/kg of oven-dried bark)															
	Ca	K	Al	Mg	S	P	Fe	Si	Na	Mn	Ba	Zn	Cu	Ti	Sr	B
Douglas-fir	1,535	959	343	199	268	222	243	168	82	29	19	10	20	15	11	4
Loblolly pine	2,140	1,000	740	454	297	266	69	38	27	75	15	21	5	1	6	10
Douglas-fir [38]	2,800	–	240	250	–	220	60	280	–	92	100	–	5.6	–	–	–
Loblolly pine [38]	1,800	–	230	360	–	140	56	420	–	91	15	–	3.2	–	–	–

was separated by centrifugation at 3,000 rpm for 10 min and purified by repeated washing and centrifugation with water–methanol (3×200 mL) and water (2×200 mL). The cellulose tricarbanilate samples were then freeze-dried and vacuum dried prior to GPC analysis [36]. The weight average degree of polymerization (DP_w) of bark cellulose was obtained by dividing M_w by 519, the molecular weight of the cellulose tricarbanilate monomer.

The BML and tannin samples (100 mg) were treated with a mixture of pyridine and acetic anhydride (1:1, *v*/*v*, 4.0 mL) with stirring at room temperature for 24–36 h. The reaction mixture was diluted with ethanol (30 mL) and stirred for 30 min and then concentrated under lower pressure. The addition and removal of ethanol was repeated seven times to remove trace acetic acid and pyridine from the sample. The acetylated BML and tannin samples were dissolved in chloroform (2 mL) and added dropwise into diethyl ether (100 mL) to precipitate the sample followed by centrifugation. The precipitate was washed with diethyl ether and centrifuged three times. After air drying, the acetylated samples were dried for 24 h in a vacuum oven at 40°C prior to GPC analysis.

Molecular weight determination was conducted using a Polymer Standards Service GPC SECurity 1200 system equipped with four Waters Styragel columns (HR0.5, HR2, HR4, HR6) at 30°C, Agilent isocratic pump, Agilent auto-sampler, Agilent degasser, Agilent refractive index detector, and Agilent UV detector (270 nm) using tetrahydrofuran (THF) as the mobile phase (1.0 mL/min) with injection volumes of 20 μL.

The molecular weight of the derivatized cellulose, tannin, and lignin samples was acquired by using a relative calibration curve. The calibration curve was created by fitting a third-order polynomial equation to the retention volumes obtained from a series of narrow molecular weight distribution polystyrene standards (1.36×10^6, 1.97×10^5, 5.51×10^4, 3.14×10^4, 7.21×10^3, 1.39×10^3, and 5.80×10^2 g/mol). The curve fit had an R^2 value of 0.9984.

Pyrolysis of Douglas-fir and Pine Bark The pyrolysis of Douglas-fir and pine bark was conducted in a tubular reactor and by a fast pyrolysis setup. Bark samples were placed in aquartz sample boat and then pyrolyzed in a split tube furnace at different operating temperatures with a heating rate of ~2.7°C/s. The split tube furnace was first preheated to the operating pyrolysis temperature. The pyrolysis tube was flushed with nitrogen, and as the pyrolysis proceeded, the pyrolysis product was passed through two condensers which were maintained in liquid nitrogen. Upon completion of the pyrolysis, the pyrolysis char and bio-oil samples were collected for subsequent chemical analysis. In general, two bio-oil fractions were collected. The first fraction, termed "heavy oil," condensed mainly near the end of the pyrolysis tube and the "light oil" was found in the first condenser. Only trace materials were collected in the second condenser. The mass of non-recovered material was determined by subtracting the weights of all recovered char and oil from the original weight of oven-dried bark samples. Conversely, fast pyrolysis was conducted by adding bark powder into a reactor submerged in a sand bath at a preset temperature. This setup immediately pyrolyzed bark powder, eliminating the need for ramp-up heating. The pyrolysis gaseous products were swept out with the nitrogen stream and condensed as described above. After the light oil fraction was decanted from the system, the heavy oil was recovered with a THF wash and filtering. The fraction was further concentrated by vacuum rotary evaporation.

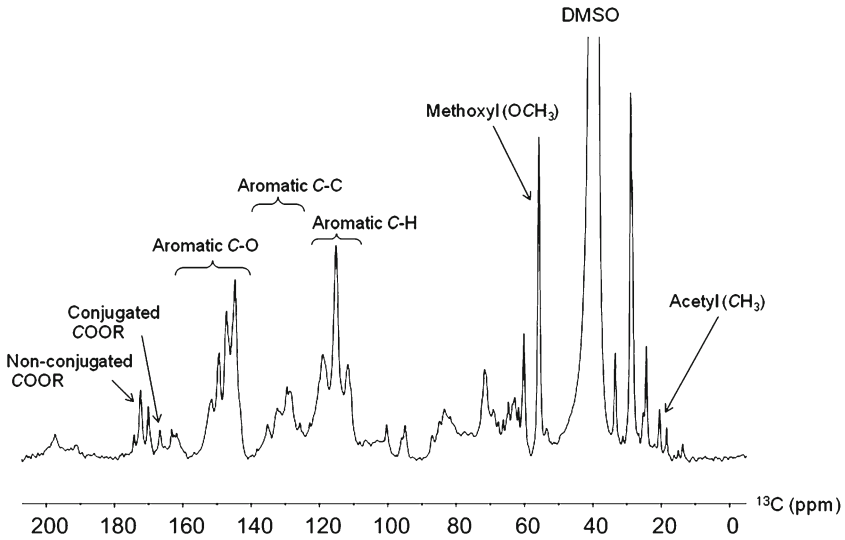

Fig. 1 Quantitative ^{13}C NMR spectrum of BML isolated from Douglas-fir bark

Table 4 Signal assignments in ^{13}C NMR spectra of Loblolly pine and Douglas-fir bark BML (expressed as number of C per aromatic ring)

^{13}C Chemical shift (ppm)	Structural moieties	Douglas-fir bark	Loblolly pine bark
195.0–190.0	Ar–CHO, Ar–CH=CH–CHO	0.03	0.05
174.0–169.1	Unconjugated COOR	0.37	0.16
167.1–166.1	Conjugated COOR	0.12	0.02
158.0–141.0	Aromatic C–O bond	2.21	2.21
141.0–123.0	Aromatic C–C bond	1.46	1.28
123.0–108.0	Aromatic C–H bond	2.34	2.50
61.5–58.0	Cγ in β-*O*-4	0.34	0.31
58.0–54.0	Methoxyl (OCH_3)	0.67	0.58
54.0–52.0	Cβ in β–β and β-5	0.13	0.11
	h/*g*	10:90	22:78
	Degree of condensation (%)	56	28

Results and Discussion

A chemical and structural characterization of the constituents within bark secured from industrial wood conversion operations is important to developing useful insight into the mechanisms of bark pyrolysis and optimized bio-oil production from these resources. Fang and McGinnis studied the decomposition behavior of components isolated from Loblolly pine bark by thermogravimetric analysis carried out in a nitrogen atmosphere. The results showed that Klason lignin and alkali-soluble material decomposed at a low rate, producing a high percentage of non-volatile residue and very broad differential thermogravimetric (DTG) curves whereas bark holocellulose decomposed at a much faster rate and yielded much less non-volatiles with a relatively sharp DTG curve [37]. In light of these types of observations, future bark pyrolysis studies would certainly benefit from an improved understanding of their starting chemical components/structures. Though previous investigations have examined the compositions of Loblolly pine and Douglas-fir bark [13, 14], little work has been done to determine their in-depth structure in the context of pyrolysis bio-oil feedstock. It is therefore important to correlate the detailed structural and compositional properties of these two barks with the optimized thermo-converting conditions and composition of bio-oils generated.

Bark Constituents The ash, DCM extractives, tannins, and other major cell wall biopolymer contents, as well as the heating values of the two bark samples, are summarized in Table 1. The inorganic elements of these samples are subsequently summarized in Table 2.

As shown in Table 1, Douglas-fir bark has a higher ash content than Loblolly pine bark. The Loblolly pine bark displayed an ash content that is comparable to what was reported by McGinnis and Parikh [13]. The decreased inorganic element content seen in Douglas-fir bark is most likely due to the higher acid-insoluble ash (silica or silicates) contents and the fact that the inorganic elemental measurements are based on the acid-soluble material. These inorganic elements will contribute to a process waste stream in future biofuel/bio-based chemical conversion operations and will need to be addressed in an environmentally compatible manner. The main inorganic elements in both bark samples are Ca, K, Al, Mg, S, and P, with the former two being the most prevalent elements. Table 2 indicates that Douglas-fir bark contains appreciably more Fe, Si, and Na than the Loblolly pine sample.

Harder and Einspahr investigated the bark of 42 pulpwood species including Douglas-fir and Loblolly pine bark [38], determining the levels of most metal elements in the bark. However, some of the most common metals like K, Na, and Zn as well as the content of sulfur were not analyzed. In comparison to data gathered in this study, the content of Si and Ca as well as Ba, P, Mn, Al, Fe, Mg, and Cu are quite different. Harder and Einspahr found higher relative contents of Ca, Mg, Si, Mn, and Ba, while lower contents of Al, Fe, and Cu in Douglas-fir bark. On the other hand, they also determined the relative content of Si which was significantly higher in value than what was detected in this study for Loblolly pine bark, whereas all other relative metal contents were found to be lower except Ba and Cu.

Tannins comprise a significant portion of carbon in terrestrial biomass, and it is well-known that barks contain

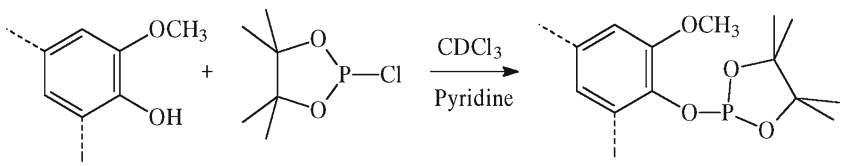

Fig. 2 Derivatization of hydroxyl structures using 2-chloro-4,4,5,5-tetramethyl-1,3,2 dioxaphospholane

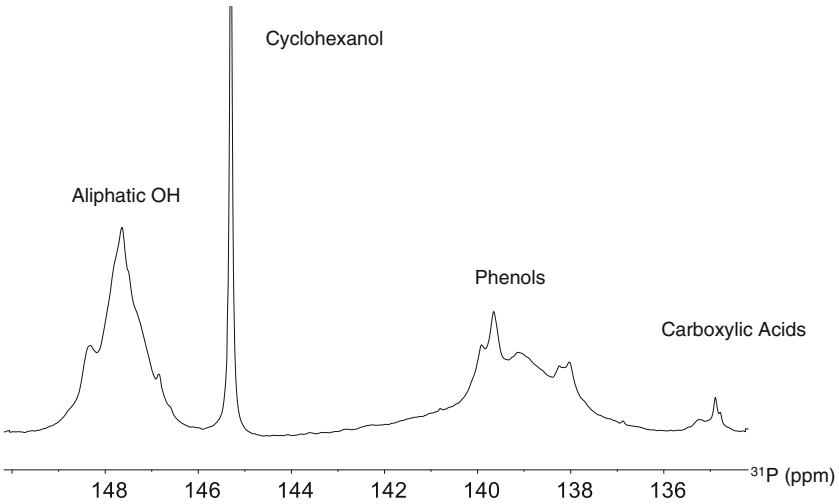

Fig. 3 Quantitative ^{31}P NMR spectrum of BML isolated from Loblolly pine bark

wide varying amounts of tannins [39]. Tannins are large polyphenolic compounds containing appreciable amounts of hydroxyl and carboxylic functional groups. The high mass content of tannins isolated from barks can be used in many fields including as coagulants for water and wastewater treatment [40], or as adhesives for wood and wood-based panels [41]. Alternatively, tannins can also be carbon-rich precursors for small aromatic structures via pyrolysis.

Table 1 also lists lignin and carbohydrate distribution data, which was acquired from the barks after being extracted by DCM and methanol–water (75:25, *v*/*v*) to remove small molecule extractives and tannins. The lignin value is the sum of Klason and acid-soluble lignin; the latter was 0.4 and 0.5 % for Loblolly pine and Douglas-fir bark, respectively. Klason lignin constitutes the acid-insoluble fraction of the bark and is typically used to describe the relative amount of lignin within biomass. The results shown in Table 1 also indicate that Douglas-fir bark contained slightly more lignin than Loblolly pine bark whereas the pine bark contains more cellulose and hemicellulose. The obtained cellulose and hemicelluloses contents of Loblolly pine bark are very similar to that of values reported in the literature [13, 15]. However, the content of extractives and lignin differed slightly, but are within the same order of magnitude, more than likely due to differences in the solvents used for extraction. The holocellulose content of Douglas-fir bark is ~6 % lower than the data reported by Laver et al. [14]; this difference may be due to the fact that their studies were performed on the inner part of Douglas-fir bark rather than the whole bark as in this study. Lignin, which was present in high amounts in both bark samples, has been shown to be an attractive resource for the thermal generation of bio-oils [37]. Likewise, cellulose and hemicellulose can also be readily converted to bio-oils by pyrolysis with or without the addition of pyrolysis catalysts such as K_2CO_3 and $ZnCl_2$ [42].

Data in Table 1 indicate that Douglas-fir bark has a 1.93-MJ/kg higher heating value (HV) than Loblolly pine bark, and this is attributed to the fact that Douglas-fir bark contains 3.52 % more carbon and 0.28 % more hydrogen than pine bark, as Douglas-fir bark contains 57.16 % carbon and 6.10 % hydrogen, while pine bark contains 53.64 % carbon and 5.82 % hydrogen. The HVs of the two barks were close in magnitude to the literature reported bark HV range (19.9–22.4 MJ/kg) [43], but Douglas-fir bark displayed a slightly higher value in this study. This natural variation in HV further highlights the need to monitor the chemical/heating properties of bark for commercial biopower and biofuel applications.

Table 5 Signal assignment in ^{31}P NMR spectra of Douglas-fir and Loblolly pine bark BML

^{31}P Chemical shift (ppm)	Structural moieties	Douglas-fir bark	Loblolly pine bark	Loblolly pine wood [51]	Douglas-fir wood [52][a]
		mM/g of lignin			
150.0–145.5	Aliphatic OH	2.08	2.47	4.16	1.60
143.0–140.0	Condensed phenolic OH	0.47	0.50	0.08	0.41
140.0–139.0	Guaiacyl OH	0.73	0.81	0.52	0.84
139.0–138.2	Catechol OH	0.43	0.57	0.05	0.94
138.2–137.3	*p*-Hydroxyphenyl OH	0.27	0.46	0.12	0.10
136.6–133.6	Carboxylic acid OH	0.61	0.26	0.02	0.13

[a] The lignin was referred to as isolated by enzymatic mild acidolysis lignin

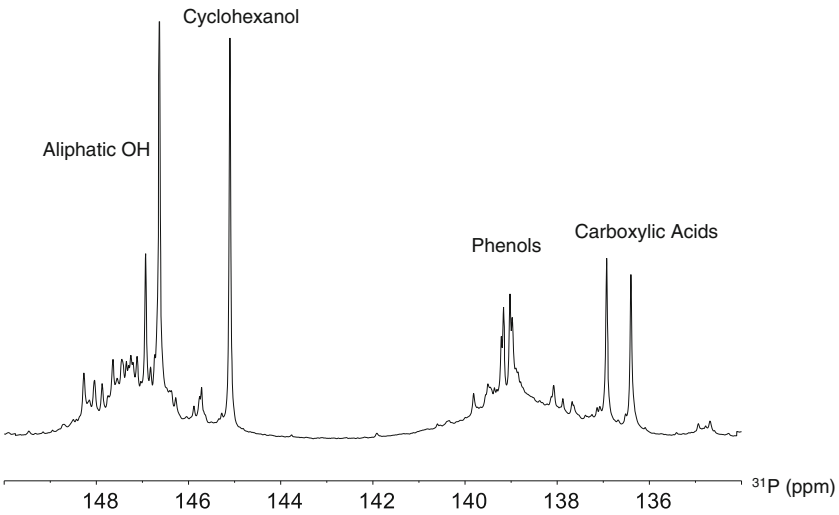

Fig. 4 Quantitative ^{31}P NMR spectrum of tannins isolated from Douglas-fir bark

Douglas-fir bark contains 3.4 % more DCM extractives than Loblolly pine bark, and compositions of these extractives by GC/MS are presented in Table 3. There are many compositional differences between the extractives of the two bark samples. Douglas-fir bark contains aromatic compounds such as vanillin, vanillic acid, 4-hydroxycinnamic acid, and ferulic acid which were not present in the Loblolly pine bark extractives. There were also traces of ergosterol and stigmasterol derivatives in Douglas-fir bark which were not detected in Loblolly pine bark extractives. Work by Gutarowska and Cichocka suggest that ergosterol derivatives in Douglas-fir bark may originate from a fungus associated with the bark [44]. Conversely, Loblolly pine bark contains some alkanes ($C_{16}H_{34}$–$C_{20}H_{42}$) and monoglycerides in the DCM extractives that are not detected in Douglas-fir bark. Lastly, the Douglas-fir bark was found to contain relatively more fatty acids and rosin acids than Loblolly pine bark, though the pine bark contains much more alkanols which are almost completely absent in Douglas-fir bark. The extractable fatty and rosin acids mentioned above, according to literature, can be used as biodiesel additive and bio-lubricant after transesterification [45–47].

Structural Analysis of Ball-Milled Lignin Using Quantitative ^{13}C NMR and ^{31}P NMR A major bark constituent, lignin, which was isolated from DCM extractive- and tannin-free bark, was analyzed by ^{13}C and ^{31}P NMR techniques. The ^{13}C NMR spectrum of the BML from Douglas-fir bark is shown in Fig. 1. BML, unlike Klason lignin, is a lignin fraction whose isolation method produces a material more chemically similar to the native lignin. The corresponding peak assignments and their relative amounts were calculated from the ^{13}C NMR spectra following literature methods [30, 48, 49] for the two bark lignin samples, and these data are presented in Table 4.

The integration of signals in ^{13}C NMR spectrum (Fig. 1) was performed by setting the area of the aromatic region (δ162–108 ppm) equal to 6.0, and all functional group results are reported as equivalences per aromatic ring. The *h*/*g* ratio of the lignins was calculated on the basis of the number of carbons per aromatic ring in corresponding to the C-4 carbon of *p*-hydroxyphenyl (*h*) units and C-2 carbon of guaiacyl (*g*) units. These are estimated from the integral value between approximate δ162–157 ppm (*h*) and δ112–108 ppm (*g*) [49, 50]

The NMR analysis demonstrated that Douglas-fir bark BML contains more carboxylic groups than Loblolly pine bark BML. The methoxyl group contents of Douglas-fir and Loblolly pine bark BML are 0.67 and 0.58 per aromatic ring, respectively, which are less than the methoxyl content reported by Holtman for Loblolly pine mill wood lignin (i.e., 0.96) [48]. The observed decreased methoxyl content in bark lignin was largely attributed to the considerable presence of *p*-hydroxyphenyl type units [39]. The ratio of *p*-hydroxyphenyl (*h*) to guaiacyl (*g*) was determined to be 10:90 and 22:78 for Douglas-fir and Loblolly pine bark BML, respectively. The *h*/*g* ratio of Loblolly pine bark

Table 6 Signal assignment in ^{31}P NMR spectra of Douglas-fir and Loblolly pine bark tannins

^{31}P chemical shift (ppm)	Structural moieties	Douglas-fir mM/g of tannin	Loblolly pine
150.0–145.5	Aliphatic OH	3.38	1.96
143.0–136.6	Phenols	3.76	2.13
136.6–133.6	Carboxylic acid OH	0.82	0.50

Table 7 GPC results of lignin, tannin, and cellulose isolated from Douglas-fir and Loblolly pine bark based on peak integrations

Samples	Bark source	$\overline{M}_w(g/mol)$	$\overline{M}_n(g/mol)$	PDI
BML	Douglas-fir	1.31×10^4	3.33×10^3	3.93
	Loblolly pine	5.12×10^3	2.43×10^3	2.11
Tannin	Douglas-fir	5.71×10^3	2.15×10^3	2.66
	Loblolly pine	1.16×10^4	3.28×10^3	3.54
Cellulose	Douglas-fir	8.41×10^5	1.12×10^5	7.51
	Loblolly pine	1.21×10^6	1.99×10^5	6.08

BML is comparable with lignin isolated from maritime pine bark (i.e., 20:80) [18]. The degree of condensation of bark lignin was estimated by subtracting the experimental integral value of $C_{Ar–H}$ from the theoretical value of $C_{Ar–H}$ which is obtained according to Eq. 1 [50]. The experimental integral values of $C_{Ar–H}$ for Douglas-fir bark and pine bark were 2.34 and 2.50 (Table 4), while the theoretical values of $C_{Ar–H}$ are 2.9 ($3\times0.9+2\times0.1=2.9$) and 2.78 ($3\times0.78+2\times0.22=2.78$), respectively. Douglas-fir bark BML has a higher condensation degree (56 %) compared to Loblolly pine bark BML (28 %).

$$\text{Theoretical}\, C_{Ar-H} = 2s + 3g + 2h \quad (1)$$

^{31}P NMR was used in this study to quantify the terminal hydroxy and phenolic functional groups present in BML after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as depicted in Fig. 2. This technique has been well documented for lignin [35], and our characterization of BML structure with ^{31}P NMR was based on literature methods [35]. The results from ^{31}P NMR can provide insight particularly into the relative amount of aliphatic hydroxyl, C-5 condensed, and C-5 non-condensed phenolics, *p*-hydroxyphenyl, and carboxylic hydroxyl groups present in a lignin sample [35].

The ^{31}P NMR spectrum of Loblolly pine bark BML is shown in Fig. 3, and the corresponding concentration of lignin functional groups is tabulated in Table 5. The data reveal that Loblolly pine bark BML contains more aliphatic hydroxyl, C-5 condensed phenol, *g* hydroxyl, and catechol groups than Douglas-fir bark BML. Loblolly pine bark lignin also contained more *h* hydroxyl groups than Douglas-fir bark lignin which is in agreement with ^{13}C NMR results in Table 4. The ratio values of *h*/*g* measured by ^{13}C NMR and ^{31}P NMR are not same because the ^{13}C NMR and ^{31}P NMR measure content of various lignin monomers differently. ^{13}C NMR measures internal units by indentifying the carbon percentage of the C-4 carbons in *h* units and C-2 carbons in *g* units whereas the ^{31}P NMR detects only terminal hydroxyl functionality. In addition, the content of carboxylic acid groups of Douglas-fir bark BML is higher than that of the Loblolly pine bark lignin which is also consistent with the prior ^{13}C NMR studies.

Comparing the ^{31}P NMR data of Loblolly pine bark BML to that of reported pine MWL [51] (Table 5), it can be seen that pine bark BML contains less aliphatic hydroxyl (−OH) groups, but about seven times more C-5 condensed phenols and 11 times more catechol groups, 13 times more the amount of carboxylic acid groups, almost four times more *h* hydroxyl, and one and half times more *g* hydroxyl groups than pine MWL. Douglas-fir bark BML contains more aliphatic hydroxyl groups, C-5 condensed phenols, *h* hydroxyl, and carboxylic acid groups than the reported values for Douglas-fir wood enzymatic mild acidolysis lignin (EMAL) [52]. Conversely, the Douglas-fir wood EMAL lignin contains more catechols and *g* hydroxyl groups than Douglas-fir bark BML.

NMR Analysis of Tannins There are two classes of tannins, condensed and hydrolysable. Condensed tannins are polymers of three-ring flavanols joined with C–C bonds, and the monomer units can be divided into two types: procyanidins (PC) which contains two hydroxyl groups on the B-ring and prodelphinidins (PD) with three hydroxyl groups on the B-ring. Hydrolysable tannins are also grouped into gallotannins

Table 8 Comparison of pyrolysis data between Douglas-fir bark and pine bark acquired at 450 and 500 and 350 and 375°C by tubular fixed-bed reactor and fast pyrolysis

Temperature (°C)	Bark	Char (%)	Light oil (%)	Heavy oil (%)	Light+heavy oil (%)	Noncondensable gas (%)
Pyrolysis in tubular reactor						
450	DF	42.2	9.3	37.3	46.7	11.1
	Pine	43.0	22.0	21.2	43.2	13.9
500	DF	38.1	14.1	34.1	48.2	13.7
	Pine	37.9	20.7	24.4	45.2	17.0
Fast pyrolysis						
350	DF	32.2	2.8	53.0	55.8	12.0
	Pine	33.6	15.0	35.5	50.8	15.6
375	DF	29.9	6.7	49.4	56.1	14.0
	Pine	32.5	16.6	33.2	49.8	17.7

DF Douglas-fir bark, *Pine* pine bark

and ellagitannins that are made up of gallic acid or hexahydroxydiphenic acid esters, respectively, linked to a sugar moiety [53]. Qualitative ^{13}C NMR spectra analysis of the methanolic extractives from the Douglas-fir and pine barks indicated that this material had not characteristics of hydrolysable tannins but characteristics of condensed tannins including PC and PD [25, 53–55].

Figure 4 is the quantitative ^{31}P NMR spectrum of tannins isolated from Douglas-fir bark. The integrated intensity data based on quantitative ^{31}P NMR spectra of two bark tannins is summarized in Table 6. The results indicate that Douglas-fir bark tannins contained more aliphatic hydroxyl groups, phenols, and carboxylic acid groups than Loblolly pine bark tannins.

GPC Analyses of BML, Tannins, and Cellulose The number ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weight as well as the molecular weight polydispersity index (PDI) determined by GPC for derivatized lignin, tannins, and cellulose isolated from Douglas-fir and Loblolly pine bark are shown in Table 7.

The GPC results indicate that Douglas-fir bark BML has higher molecular weight and greater PDI than Loblolly pine bark BML. Conversely, Loblolly pine bark tannins have higher molecular weight and greater PDI than Douglas-fir bark tannins. The molecular weights of BML and tannins for both barks were close, having a PDI<4. Pine bark cellulose has a higher molecular weight and narrower molecular weight distribution than Douglas-fir bark cellulose. The DP_w for cellulose isolated from Douglas-fir and Loblolly pine bark was of 1,620 and 2,330, respectively. These values are lower than molecular weights reported for wood-based cellulose with DP_w values ranging from 2,500 to 3,500 [56].

Pyrolysis of Douglas-fir and Pine Bark The pyrolysis of Douglas-fir and pine bark was performed under varying different conditions. A comparison of the pyrolysis data of Douglas-fir and pine bark acquired at 450 and 500°C using a tubular reactor and at 350 and 375°C by fast pyrolysis is shown in Table 8. The data in Table 8 show that at the conditions examined, the barks can be effectively pyrolyzed with a total bio-oil content produced of 46–56 % for the Douglas-fir bark and 43–51 % for the pine bark. The results also suggest that even under the same pyrolysis conditions, there was a significant difference in the relative portions of light vs. heavy oils generated from Douglas-fir bark vs. pine bark. These effects are undoubtedly due, in part, to differences in the chemical composition of the two bark samples including documented differences in cellulose, hemicellulose, extractives, and tannins content and chemical structure composition. As this paper mainly focuses on the chemical composition of barks, a more detailed pyrolysis study conveying how these differences in bark chemical composition affect bio-oil production and composition will be published shortly.

Conclusions

This paper presents a detailed biomass composition of Douglas-fir and Loblolly pine bark which can be used to potentially improve the conversion to bio-oils as a fuel precursor. A standard compositional analysis was performed. It was shown that Douglas-fir and Loblolly pine bark contained 22.5 and 13.2 % tannins, 44.2 and 43.5 % lignin, 16.5 and 23.1 % cellulose, 7.6 and 14.1 % hemicellulose, respectively. Tannins existing in the two bark sources are dominantly condensed tannins, while lignin contained methoxyl group contents in the two bark samples about half of that seen in normal softwood lignin. The structure of isolated lignin and tannins was chemically analyzed using NMR. The ratios of *h*/*g* lignin monomers were calculated as 10:90 and 22:78 for BML isolated from Douglas-fir and Loblolly pine bark, respectively.

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