Research Article

Valorization of Bark Using Ethanol−Water Organosolv Treatment: Isolation and Characterization of Crude Lignin

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ABSTRACT: Bark serves multiple functions for a tree by combining protection and fluid transport. The tissue itself is composed of multiple types of material that includes typical cell wall structural polymers of cellulose and lignin, as well as extractives. With suitable fractionation, these bark constituents may serve to help valorize biomass when converted into feedstocks for polymeric precursors, such as aromatic polyols. In this study, organosolv processing was used to solubilize around 50% of pine bark (PB) and oak bark (OB), followed by the recovery of around 20% crude lignin. Two-dimensional $^1H-^{13}C$ heteronuclear single quantum coherence (2D HSQC) NMR and ^{13}C NMR revealed the crude lignin also contained mixed polyphenolics, suberin-compounds, and carbohydrate compounds, especially for PB. To optimize the extraction process, a two-level factorial design was used to study the impacts of temperature, ethanol concentration, and solid loading on the yield and related characteristics of crude lignin. Increased temperature and ethanol concentration during processing allowed more solubilization of the components along with the extraction of crude lignin with higher yield. The correlation analysis found that the thermal stability of crude lignin had a direct relationship with aromatic hydroxyl group content, while the glass transition temperature was impacted by the lower molar mass components contained in the crude lignin. Overall, the study showed promise to solubilize a high portion of bark material and provided insight into structure−property relationships of crude lignin-derived from an important, yet underutilized resource as a function of processing conditions.

KEYWORDS: Bark, Organosolv, Lignin, Compositional analysis, Polyol, Thermal properties
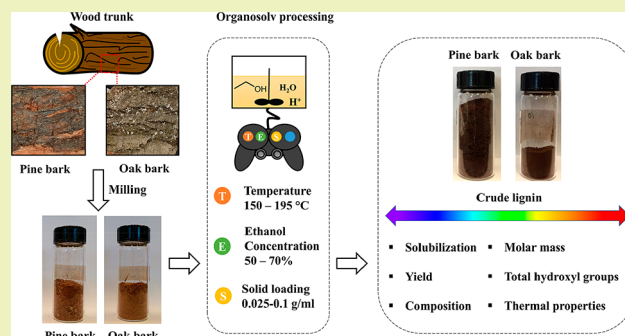
INTRODUCTION

The outer portion of woody-plants, bark, forms a remarkable barrier against fungi and insects as well as serves as a key component in regulating moisture.[1] While known for its protection, certain species such as cherry demonstrate surprising mechanical properties in its bark due to its hierarchical structure.[2] The composition of bark is dependent upon the species of woody plant, but it contains a higher amount of extractives such as tannins and fatty acids, along with suberin and minerals.[1,3] When trees are processed for lumber and pulp, the bark is stripped away from the log and is either utilized in value-added applications such as mulch or is burned for energy recovery. Owing to its multifunctionality of serving as a barrier and conductor of fluids, it contains typical structural polymers found in the xylem and high levels of potential extractives and suberin.[1]

On the basis of the above characteristics, it is clear that bark is a different feedstock filled with valuable components for the preparation of renewable materials and chemicals if it could be processed efficiently.[4] Previous approaches have shown that bark can be converted into various value-added materials such as nanocellulose,[5] epoxy,[6] and polyols.[7] Normand et al. adopted hot water to pretreat inner bark of Norway spruce for the isolation of nanocrystalline cellulose.[8] Oak bark had been used as a resource to extract tannins for polyphenolics in preparation of exterior adhesives[9] or antioxidants.[10] Owing to the abundant hydroxyl groups from polyphenolics and polysaccharides in the bark, Hartman et al. directly used bark powder as a heterogeneous polyol to react with highly active isocyanate compounds to produce PU foam.[11] Creatively, D'Souza and Yan obtained liquefied bark by using polyethylene glycol and glycerol as solvent and water/xylene as cosolvent, with sulfuric acid as catalyst, to extract the aromatic compounds.[12] These liquefied bark compounds were further used directly as polyols to make polyurethane foams.[13]

While research into bark utilization is growing, few published works describe the properties of the lignin fraction in the bark and their potential utilization. Renewable lignin resources have gained increasing attention as an alternative resource in replacing fossil-based compounds.[14−17] With a large amount of functional hydroxyl groups, researchers have developed a series of lignin-based materials such as bioplastics[18] and polyurethane foams[19−21] and coatings.[22−24] It is now possible to recover a large amount of technical lignin from the pulping industry by kraft or sulfite pulping.[25] These technical lignins are the most abundant available lignin resources; however, technical lignins have limited applications due to their nonuniform chemical structure, sulfur content, and broad molecular weight distribution. Alternative pulping methods for sugar access or fractionation have created technical lignins that outperform these lignins.[26] Different from traditional kraft and sulfite pulping using aqueous alkali or aqueous acid, the organosolv process utilizes organic solvents such as alcohols,[27] ketones,[28] or even organic acids[29] to treat the biomass at 90−200 °C in the presence of organic acid or mineral acid catalysts. Due to the relatively mild reaction conditions and high selectivity of organic solvent in dissolving lignin, the resulting organosolv lignin has a series of merits: more homogeneous chemical structure, lower molecular weight, lower glass transition temperature (T_g), and less contamination.[25] As a result, organosolv lignin typically outperforms other lignins in similar applications; for example, it has better compatibilities with polyols[21,30] and polyesters[31,32] and can be used for applications in foams and bioplastics, respectively. Currently, this process still has limited competitiveness in the market since the utilization of organic solvent will increase energy consumption and capital expenditure.[26]

Therefore, the utilization of low-cost feedstock like bark may help reduce the cost of organosolv processed biomass for substitution of petroleum products if there was an economically compelling reason to do so. In one attempt to valorize bark with a similar methodology, Karnaouri et al. used organosolv processing (ethanol/water) combined with steam explosion to treat bark, followed with the characterization of the chemical structure of lignin.[33,34] However, this study focused on the potential of treated bark residue as a source for potential hydrolysis sugars rather than extracted compounds in the liquor section. In the current study, both pine bark and oak bark were treated using an ethanol−water organosolv system to extract valuable crude lignin compounds. We hypothesized that the organosolv processing could help realize the valorization of bark resources, by extracting high-valuable lignin and removing part of the extractives that have a high hydroxyl content. A simple two-level factorial design was adopted to study the impact of temperature, ethanol concentration, and solid loading on the yield of solubilized and precipitated crude lignin. Further, the chemical structure, molecular weight, and thermal properties of the extracted crude lignin obtained with different reaction conditions were thoroughly characterized by NMR spectroscopy, gel permeation chromatography, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Through processing parameters, our objective was to control the performances of the resulting lignin with selected conditions and potentially create tailored crude lignin for new material applications.

■ RESULTS AND DISCUSSION

Compositional Analysis of Bark Resources. Besides common compounds such as polysaccharides, lignin, extractives, and ash, bark tissue was expected to contain additional compounds including polyphenols and suberin compounds with the number of extractives, lignin, and ash higher than values typically found in xylem due to its protective function for wood.[1] The original bark contained 34.3% (PB) and 31.0% (OB) of extractives, 30.1% (PB) and 30.5% (OB) of lignin, 13.1% (PB) and 10.5% (OB) of glucan, 9.6% (PB), and 9.6% (OB) of other sugar content derived from hemicellulose, with a level of 6.93% (PB) and 5.83% (OB) ash, Table S1. The extractive and lignin components were higher than those in the results of Miranda et al.[35] and Ruiz-Aquino et al.[36] most likely because the suberin content may be depolymerized and combined with phenolic extractives and lignin with the reaction conditions.

Change of Composition during the Organosolv Processing. The complex composition may limit the valorization of bark-based resources. As such, one of the hypotheses in this study was that the organosolv process (ethanol−water) can lead to the fractionation of bark by the isolation of extractives and lignin compounds, simultaneously. At the same time, we may obtain an extractive-free residue for applications such as biofuels. (Scheme 1)

Scheme 1. Potential Route for the Valorization of Bark Resources Including Biofuel, Chemicals, and Materials
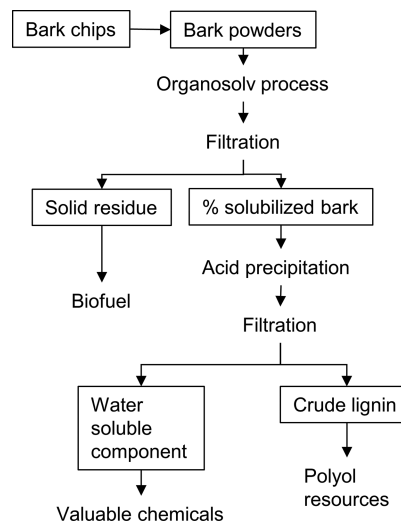
For the organosolv processing parameters, Zhang et al. summarized the reaction conditions and found that 50−80% ethanol−water solvent concentration was typically utilized to treat different types of biomass using sulfuric acid (catalyst, 1 wt % to biomass) in a temperature range between 140 and 210 °C.[26] Increased temperature led to increased yield of resulting lignin, but this also caused the condensation of the lignin.[37] Condensation of lignin was also impacted by tree species, as softwoods contain guaiacyl units (G) and p-hydroxyphenyl units (H), while hardwood species also contain syringyl units (S).[38] Syringyls are substituted by two methoxy groups that limit condensation reactions at the ortho positions on the aromatic ring.[39] As condensation will cause negative impact on the yield and chemical structure of lignin, in this study, we adopted a slightly lower temperature to treat pine bark

(softwood, 165 °C, 60%, 60 min, and 1% acid) relative to oak bark (hardwood, 180 °C, 60%, 60 min, and 1%).

Our initial process of organosolv treatment of 100 g of bark recovered 56 g (PB) and 47 g (OB) of solid residue after filtration and purification. Figure 1 showed that the major
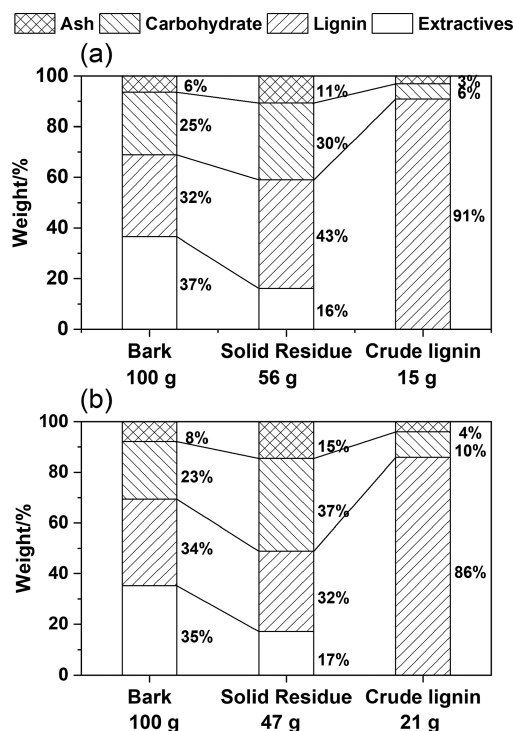
Figure 1. Compositional analysis during ethanol−water organosolv process for both oak bark and pine bark (reaction conditions in paraentheses): (a) pine bark (165 °C, 65% ethanol concentration, and 0.075 g/mL) and (b) oak bark (180 °C, 65% ethanol concentration, and solid loading (s: l, 0.0375 g/mL)

component in the solid bark residue changed significantly. These solid residues contained lower amounts of extractives than the original bark as 25 g (PB) and 24 g (OB) of extractives were removed from the solid residue during the organosolv process. An obvious reduction of extractives and hemicellulose components occurred since the aqueous ethanol dissolved degraded compounds at high temperature with an acid catalyst. As a result, the weight percentage of carbohydrate compounds in pine bark and oak bark residue had increased.

After the organosolv pretreatment, 44 g of pine bark compounds and 53 g of oak bark compounds (Figure 1) were dissolved into the supernatant, which were higher amounts than those from previous methods.[33] These results suggested a relatively high efficiency of this organosolv process to isolate various compounds from bark. The extraction liquor was concentrated, and the solids were recoved by precipitation in acidic water (Scheme 1, Figure S1). Within select conditions, 15 and 21 g of solids (crude lignin) were precipitated from pine bark and oak bark liquors, respectively. Around 30 g of bark (water-soluble compounds, Scheme 1), belonging to the low molar mass oligomers or chemical monomers such as flavone derivatives, terpenes, and nonstructural sugars compounds[1,40] were dissolved in the aqueous solution. A detailed analytical study of these abundant low molecular weight compounds is required in the future.

For the recovered solids from the supernatant, the Klason crude lignin was the predominant component at 12 g (pine bark) and 17 g (oak bark) in addition to the carbohydrates and ash. The amount of Klason crude lignin was higher than the calculated yield, based on the composition of solid bark residue before and after the organosolv process, which showed that 6 g of pine bark lignin and 17 g of oak bark lignin were removed. The increased yield was due to the mixed extractives, suberin, hemicellulose, and their degraded compounds that would form a condensed solid residue. Overall, the organosolv process was an efficient method to dissolve around 50% of bark, which may contain valuable products, if proper fractionation methods were adopted. The increased concentration of carbohydrate content in the resulting solid residue provides more valuable products for a biorefinery.[33] The mass intensity analysis reveals that reactants (mainly solvents) used per unit mass of product were greater in the case of oak bark compared to that in pine bark as a feedstock.[41] (Equation S1) Hence, solvent recovery and the complete utilization of isolated fractions of bark resources are critical to ensure that the process has a low environmental footprint.

Impacts of Reaction Conditions on the Solubilization of Bark and Crude Lignin Yield. To study critical factors on the solubilizatoin of bark and yield of crude lignin, we adopted a two-level factorial design (Table S2) revealing the impact of different reaction conditions including temperature (°C), ethanol concentration (%), and solid loading (S:L, g/mL).

The solubilization of bark (%) was an indicator of the efficiency of the organosolv process, which was in a range from 27%−46% for PB and 34%−53% for OB. The crude lignin yield (without ash) was in a range from 8.7% to 18.1% (PB) and from 13.9% to 21.3% (OB) with selected conditions (Table 1). Generally, the amount of ash content in the bark was 10% higher than wood.[1] These ash compounds were also extracted and mixed with the solubilized materials during the organosolv process. The selected reaction conditions had subtle impacts on their concentrations in the recovered crude lignin. The obtained crude lignin yield was thus recalculated by removing ash contents (Table 1).

Analysis of variance (ANOVA) showed that the ethanol concentration (%) and temperature (°C) had more significant impacts on the crude lignin yield and solubilization of bark than S:L (Table S3). The increased temperature with high ethanol (%) improved the yield of crude lignin and enhanced the solubilization of bark (Figure 2). In comparison, Pan et al. studied a wider range of temperatures (160−215 °C) on the delignification of hybrid poplar.[34] In the current study, the maximum yield and solubilization of oak bark were obtained as the temperature went up to 195 °C. Meanwhile, the increased ethanol (%) from 50% to 70% likely improved the solubility of the components in bark, especially extractives and suberin compounds; higher concentrations decreased the solubility of lignin due to the solvent parameter changes.[37,42]

By adopting a design of experiments approach, models were built to predict crude lignin yield and percent solubilization of bark under different experimental conditions (Table 2). The center point condition was performed to further indicate the accuracy of models. The variance between predicted values and actual values was around 15% (Table 2). With the same reaction conditions (160 °C and 60% ethanol, the solid loading was not involved), oak bark was more readily solubilized and had a higher yield than pine bark. Lignin in the hardwood generally has higher β-ether reactivity and a higher

Table 1. Organosolv Process Conditions on the Solubilization of Bark (%) and the Characterization of Organosolv Pine Bark Crude Lignin (OS-PB) and Organosolv Oak Bark Crude Lignin (OS-OB) Including Yield, Functional Groups, Molar Mass, and Thermal Properties

No.	Temp. (°C)	Ethanol (%)	S:L (g/mL)	% solub.	Yield %			Functional groups (mmol/g)[a]					Molar mass (g/mol)[b]			Thermal (°C)[c]	
					Solid	Ash	Crude lignin	AlOH	ArOH	Total OH	MeO	Methyl	M_w	M_n	PDI	T_{max}	T_g
								OS-PB									
1	150	70	0.05	38	9.75	2.16	9.54	4.64	4.87	9.51	1.61	1.19	4691	2144	2.19	455	116
2	150	70	0.1	41	13.48	0.00	13.48	3.75	4.92	8.67	1.3	1.17	5564	2340	2.38	483	104
3	150	50	0.1	28	11.12	4.25	10.65	3.23	3.69	6.92	1.12	0.98	7264	2413	3.01	412	109
4	150	50	0.05	27	9.59	0.00	9.59	3.85	4.48	8.33	1.29	1.07	5945	2556	2.33	454	137
5	180	50	0.1	36	9.02	3.65	8.69	3.17	4.93	8.10	1.52	1.04	4152	1705	2.44	455	106
6	180	70	0.1	43	18.11	0.00	18.11	3.34	4.05	7.39	1.4	1.5	4878	1761	2.77	440	127
7	180	70	0.05	46	17.42	0.00	17.42	3.65	5.22	8.87	1.76	1.13	3755	1651	2.27	445	115
8	180	50	0.05	40	12.10	7.47	11.20	5.03	6.12	11.15	1.69	1.55	3120	1513	2.06	413	166
								OS-OB									
1	165	70	0.025	44	14.39	0.17	14.37	4.25	4.81	9.06	3.55	1.01	3809	1868	2.04	480	156
2	165	70	0.05	34	16.48	2.85	16.03	3.82	4.38	8.20	1.26	0.68	3786	1914	1.98	520	148
3	165	50	0.025	48	15.79	0.56	15.70	3.04	3.45	6.49	2.55	0.73	4744	2009	2.36	464	121
4	165	50	0.05	42	17.41	0.08	17.41	4.54	7.04	11.58	3.42	0.92	3848	1841	2.09	421	150
5	195	50	0.05	49	14.18	1.81	13.92	3.85	5.71	9.56	4.95	0.55	2507	1400	1.79	524	127
6	195	70	0.025	53	22.33	6.25	20.93	3.29	4.1	7.39	3.85	0.55	3543	1575	2.25	445	140
7	195	70	0.05	49	22.58	5.53	21.33	3.69	4.3	7.99	3.93	0.73	3985	1686	2.36	457	127
8	195	50	0.025	52	16.25	1.26	16.05	3.66	5.33	8.99	4.51	0.79	2725	1477	1.84	516	139

[a]Aliphatic hydroxyl groups (AlOH), aromatic hydroxyl groups (ArOH), methoxyl groups (MeO), total hydroxyl groups (Total OH), methyl groups (related with fatty acid compounds, distinct from methoxyl groups on lignin). [b]Weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (PDI). [c]Maximum mass loss rate (T_{max}), glass transition temperature (T_g).
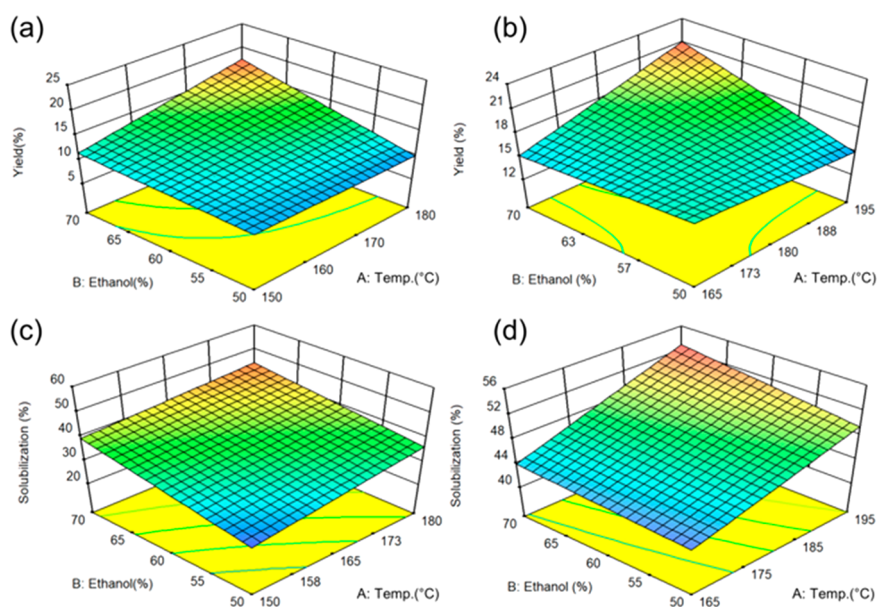
Figure 2. Interactive impact plots of temperature and ethanol concentration on the yield of crude lignin (a, organosolv pine bark crude lignin; b, organosolv oak bark crude lignin) and solubilization of bark (c, pine bark; d, oak bark).

Table 2. Models of Crude Lignin Yield and the Solubilization of Bark with the Selective Range of Reaction Conditions[a]

Response (% bark)	Equations	R^2	Predicted value, %	Actual value, %	Variance, %
Crude lignin yield (Pine bark)	12.85 + 1.39*A+1.99*B+1.53*AB	0.84	12.85	14.86	16.96
Solubilization (Pine bark)	37 + 3.5*A+5*B-A*B	0.97	37.00	44.00	15.90
Crude lignin yield (Oak bark)	17.43 + 1.41*A+1.52*B+2.10*A*B	0.92	17.43	20.09	13.69
Solubilization (Oak bark)	47.5 + 4*A+1.25*B+0.5*A*B	0.99	47.25	53.00	10.84

[a]A = temperature, (1, −1, or 0); B = ethanol concentration (%), (1, −1, or 0); AB = the interactive impacts of temperature and ethanol concentration, (1, −1, or 0).
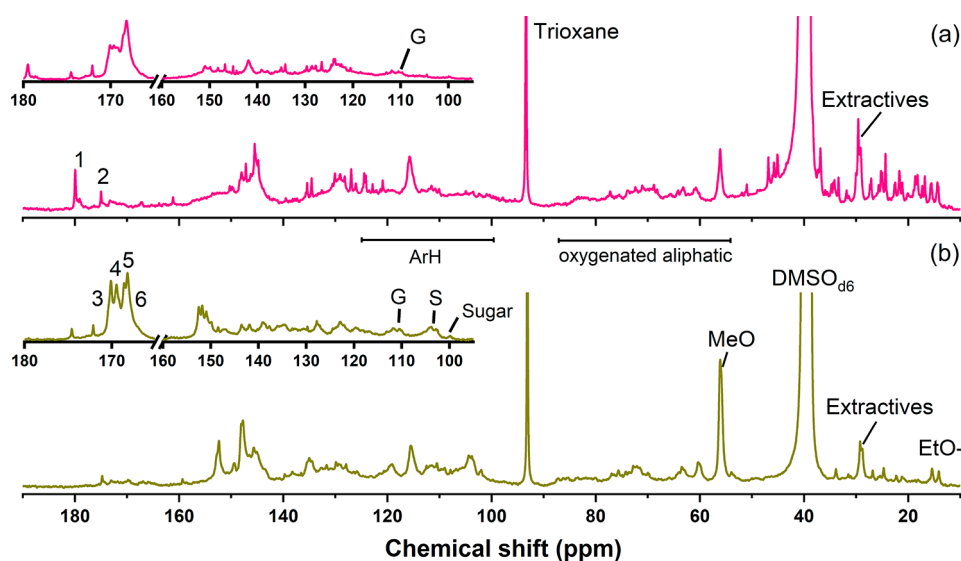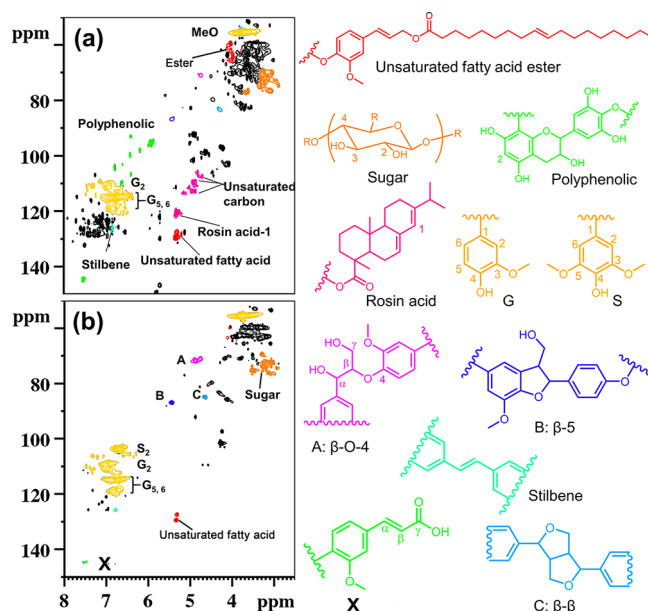
Figure 3. ^{13}C NMR spectrum of organosolv crude lignin, (a) pine bark (OS-PB, 165 °C, 65% ethanol concentration, and 0.075 g/mL), and (b) oak bark (OS-OB, 180 °C, 65%, ethanol concentration, and 0.0375); note that the insert of the spectra belong to acetylated lignin samples.

concentration of readily hydrolyzable α-ether linkages than lignin in softwood.[43] Besides, syringyl units in the hardwood are limited to undergo condensation reactions during the organosolv process. Shimada et al. studied model compounds and showed that the reactivities of guaiacyl carbocations were higher than syringyl carbocations to form condensed bonds with anionic aromatic ring sites.[44] On the basis of the reactivity, it was suggested that the condensation reaction was partially responsible for the low efficiency of the solubilization of bark using softwood as feedstock.[44] It is clear that softwood bark behaves similar to softwood xylem during the organosolv pulping.

Structural Analysis of Crude Lignin. In this study, we mainly focused on the characterization of isolated crude lignin. Semiquantitative ^{13}C NMR (Figure 3) and 2D HSQC NMR (Figure 4) revealed the chemical structure and major composition of crude lignin directly. As a comparison, milled pine wood lignin (MWL-Pine) and milled oak wood lignin (MWL-Oak) were used to represent the chemical structure of native lignin. (Table 3)[45] The acetylatation process was performed as a duplicate for the quantification of aromatic units and hydroxyl groups of the crude lignin. Note that for acetylation, filtration was adopted during isolation of the derivative and a small amount acid soluble acetylated lignin may not have been recovered (ca. less than 10%).

The spectrum of crude OB lignin showed both guaiacyl (G) and syringyl units (S), though their amounts were lower than those in MWL. The native bark lignin normally has a lower amount of methoxyl groups than those in native wood lignin due to the lower enzyme reactivity of methylation in the bark cell.[45,46] As such, the methoxy group content (MeO, 58−54 ppm, Table 3) in the crude lignin was lower than that in MWL. The demethylation during the organosolv process will also lead to the reduction of methoxy groups.[46] Also, for this group, OS-PB was lower than OS-OB since lignin from the hardwood sample contained syringyl units (Table 3).

Organosolv pretreatment of wood generally includes two steps during the delignification: (1) breakage of β ether bonds under higher temperature; (2) the condensation of benzyl cations under acidic conditions, as those degraded aromatic

Figure 4. HSQC NMR spectra of organosolv bark crude lignin, (a) pine bark (OS-PB, 165 °C, 65% ethanol concentration, and 0.075 g/mL), and (b) oak bark (OS-OB, 180 °C, 65% ethanol concentration, and 0.0375 g/mL).

monomers will become ionic compounds and easily react with other monomer/oligomers from lignin, polyphenols, and carbohydrates by condensation.[48] The native lignin linkages including β-O-4, $\beta-\beta$, and β-5 were tabulated in Table 3. The reduction of these linkages in the crude lignin (OS-PB and OS-OB) indicated the breakage of the β-O-4 bond during the isolation. In line with the previous organosolv treated wood lignin,[46,49] the excess amount of carbon−carbon linkages (degree of condensation, DC) and an increased amount of aromatic OH groups were formed or produced during the organosolv process.

These increased amounts of aromatic OH groups were also impacted by the polyphenolic compounds. As shown in the 2D HSQC NMR spectrum (Figure 4), the extractive compounds,

Table 3. Quantitative Structural Analysis of Milled Pine Lignin (MWL), Milled Oak Lignin (MWL), Organosolv Pine Bark Lignin (OS-PB), and Organosolv Oak Bark Lignin (OS-OB) (Per 100 Ar)[a]

Functional groups	Chemical shift (ppm)	MWL-Pine[46]	OS-PB	MWL-Oak[47]	OS-OB
G	114−108 (acetylated)	99	72	30	42
S	108−102 (acetylated)	n.a.	n.a.	64	24
X[b]	86.8 (δC)/5.49 (δH)	n.a.	4.0	n.a.	n.a.
EtO-	16.5−13	n.a.	15	n.a.	9
Methoxy content	58−54	97	35	169	82
Aliphatic OH	172−168.7 (Peak 3 and 4, acetylated	107	67	132	74
Aromatic OH	168.7−166 (Peak 5 and 6, acetylated)	33	91	29	79
Total OH	172−166	140	158	161	153
ArH	125−102 (acetylated sample)	253	226	211	217
DC	200+G-ArH	43	46	20	25
β-5[b]	86.8 (δC)/5.49 (δH)	10	5	3	3
$\beta-\beta$[b]	85.1 (δC)/4.63 (δH)	4	2	6	3
β-O-4[b]	70.9 (δC)/4.77 (δH)	42	11	60	12
Stilbene[b]	125.6 (δC)/6.97 (δH)/	n.a.	12	n.a.	minor
Sugar	102−98 (acetylated)	n.a.	yes	n.a.	yes
Polyphenolics[b]	94.9 (δC)/5.9 (δH)	n.a.	yes	n.a.	n.a.
Unsaturated fatty acid[b]	129.1 (δC)/5.70 (δH)	n.a.	yes	n.a.	yes
Rosin acid[b]	120.1 (δC)/5.3 (δH)	n.a.	yes	n.a.	minor

[a]G, guaiacyl units; S, syringyl units; X, cinnamyl acid; EtO-, extractives (typically found during the organosolv process); ArH, aromatic hydrogen; DC, degree of condensation. [b]Quantitative HSQC NMR analyzed results.

including polyphenolic compounds such as condensed tannins, rosin acid, and suberin-related compounds (unsaturated fatty acid ester), were blended or reacted with the resulting crude lignin.[50,51] OS-PB contained a greater amount of these compounds than OS-OB, as additional peaks appeared in the spectrum. These spectra also revealed that sugar compounds were found in both the extracts of OS-OB and OS-PB (Figure 3 and Figure 4). As such, it is in agreement with the compositional analysis of the OS-PB, relative to the oak bark, which had a greater mixture of lignin and extractive compounds and potentially suberin. Besides those extractive compounds, other unsaturated linkages or groups including stilbenes and cinnamyl acid end groups (X) were also found with OS-OB and OS-PB. Overall, the higher percentage of lignin related structural units and linkages reflected that the major component of the extract was lignin, especially for the OS-OB.

Impacts of Reaction Conditions on the Functional Groups. The chemical composition or functional groups for each sample were further quantitatively analyzed by ^{1}H NMR to study their correlation with organosolv reaction conditions (Figure 5). In the ^{1}H NMR spectrum, the acetylation of hydroxyl groups of crude lignin for analysis led to the
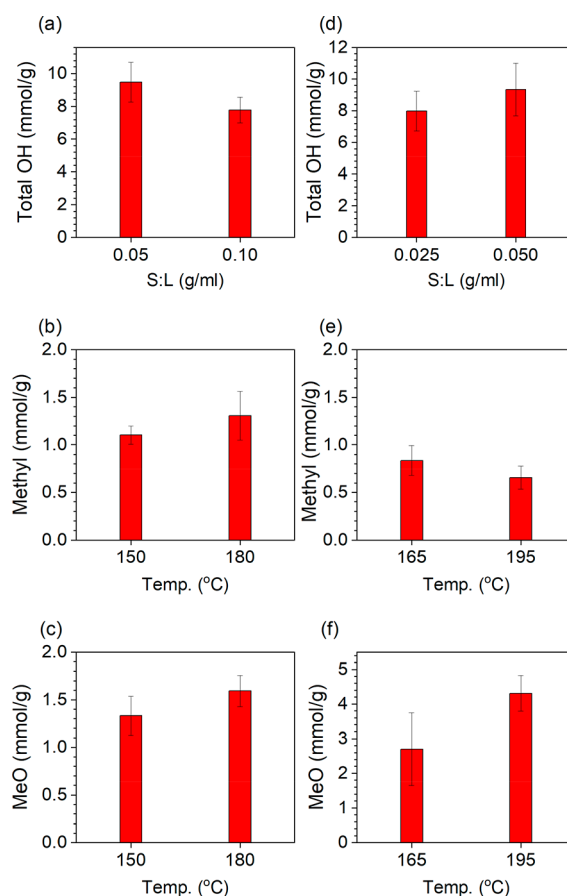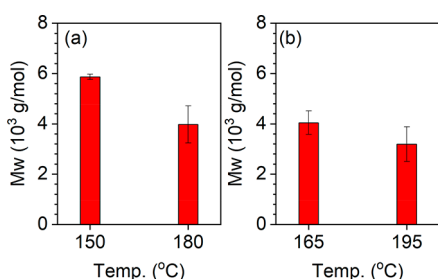
Figure 5. Impact of organosolv processing conditions on the functional groups of OS-PB (a, b, and c) and OS-OB (d, e, and f).

formation of two new peak clusters of the ester derivatives: aromatic hydroxyl groups (ArOH, 2.50∼2.17 ppm) and aliphatic hydroxyl groups (AlOH, 2.17∼1.70 ppm) (Figure S3). The hydroxyl groups are the "major handles" for lignin-based polymeric materials such as polyesters, polyethers, and polyurethanes.[16,52] Our later studies showed that the resulting lignins are excellent precursors in making polyurethane foam with comparable properties than original PU foam.[53] Overall, the crude lignin extracted had a total hydroxyl group ranging from 6.92 to 11.15 mmol/g (OS-PB) and 6.49 to 11.58 mmol/g (OS-OB) (Table 1). These numbers were higher than those of kraft lignin (Indulin AT, 6.40 mmol/g) and organosolv lignin (hardwood, 5.64 mmol/g) from wood resources.[21,54] Additional compounds enriched with OH groups, including carbohydrates and polyphenolics, will impact the hydroxyl group numbers as well. Therefore, the MeO groups (4.05−3.55 ppm) can more directly reflect the amount of lignin content in the crude lignin without considering impacts from nonlignin components, especially for OS-PB. The MeO groups of crude lignin ranged from 1.12 to 1.76 mmol/g (OS-PB) and from 1.26 to 4.95 mmol/g (OS-OB). The methyl groups (CH$_3$−, 0.93−0.47 ppm), separate from the methyls on methoxy groups, were related to suberin derived compounds or rosin acid, since most carbohydrate and lignin structures do not contain this group. The methyl group content in OS-PB (0.98−1.55 mmol/g) was larger than the amount found in OS-OB (0.55−1.01 mmol/g).

ANOVA revealed that the resulting models had a high p-value (>0.5), which means that we cannot build predictive

models for these compositions, based on selected reaction conditions. More conditions were required to improve the significance of the resulting models. Therefore, a single factor and multiple-factor analysis on these groups were discussed based on the sum of squares of each factor. The more significant sum of squares represented the factor that enhanced the effects and had a higher contribution to the formation of specific groups (Figure S2). The temperature caused a more significant impact on the number of MeO groups and methyl groups; the increasing temperature will drive the cleaveage of ether or ester bonds among those polymers thereby allowing the extraction of more lignin and suberin-derived compounds from the bark (Figure 5 b,e,c,f). This trend was in agreement with previous research using wood as feedstock to isolate lignin resources.[43,55] Further, the solid loading had a more significant impact on the total OH groups. The solid loading (S:L) significantly impacted the total OH groups for OS-PB and OS-OB (Figure 5a,d). With a higher solid loading (0.1 g/mL), the potential of increased concentration of lignin fragments led to more condensation reactions, accompanied by the reduction of the amount of hydroxyl groups through the release of the C_γ.[48]

Impacts of Reaction Conditions on the Molecular Weight. Organosolv bark lignin had molecular weights ranging from 3120 to 7264 g/mol for OS-PB and 2507 to 4744 g/mol for OS-OB. The molecular weight and its distribution for OS-PB (PDI = 2.06−3.01) were greater and broader than those for lignin from oak bark (PDI = 1.79−2.36). The molecular weight traces of bark lignin showed that both OS-PB and OS-OB had a sharp peak at the low molecular weight fraction (retention time >40 min). This peak was relatively high in OS-PB due to the higher amount of low molecular weight nonlignin compounds (Figure S4). Figure 6

Figure 6. Impact of organosolv processing conditions on the weight-average molecular weight (M_w) of OS-PB (a) and OS-OB (b).

revealed the impact of reaction conditions on the molar mass of crude lignin. For both oak bark and pine bark, low molecular weight lignin was found for the higher temperature reaction conditions (Figure 6 and Figure S5)

The correlation analysis between the molar mass and functional groups in crude lignin showed a linear relationship with ArOH, MeO, and total OH for both OS-PB and OS-OB (Table S4) The lower M_w of crude lignin has a higher amount of ArOH group and total OH groups, which was found with solvent fractionated lignin[56] (Figure 7). Interestingly, the MeO groups represented lignin components in crude lignin and for PB, this did not change with molar mass; in OS-OB, there was a correlation which may relate to the extraction of unsaturated fatty acid esters. The condensation reaction of lignin fragments was one of the main reasons to cause the increase of molar mass and reduction of ArOH groups. This reaction will occur if the isolated fragments contain a higher amount of G and H
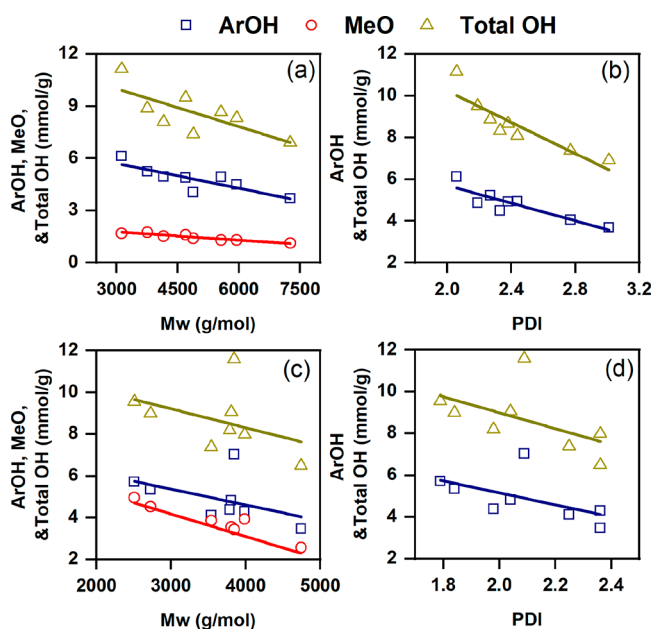
Figure 7. Correlation analysis of the chemical structure and molecular weight (weight-average) and its distribution of pine bark lignin (a,b) and oak bark lignin (c,d); ArOH, aromatic hydroxyl group; Total OH, total hydroxyl group; MeO, methoxy group.

(ortho-free) units rather than S. Therefore, the larger molar mass of crude lignin may have more of these linkages with lower MeO groups, ArOH groups, and higher PDI.

Impacts of Reaction Conditions on Thermal Properties of Crude Lignin. For the thermal decomposition of lignin, the weight loss during heating generally contains two-stages: (1) the degradation of phenyl propane side chains (150−300 °C); and (2) the degradation of the aromatic backbones (300−600 °C).[57] The temperature at the maximum mass loss rate (T_{max}) of lignin (Figure S6) was calculated to characterize the thermal stability of lignin (Table 1). For the OS-PB, the organosolv conditions had a slight impact on T_{max} of the isolated crude lignin (Figure S7). The change of T_{max} of OS-OB had a similar trend with the change of ArOH group content (Figure 8), since the aromatic backbones are the most stable groups. Overall, OS-OB had higher thermal stability
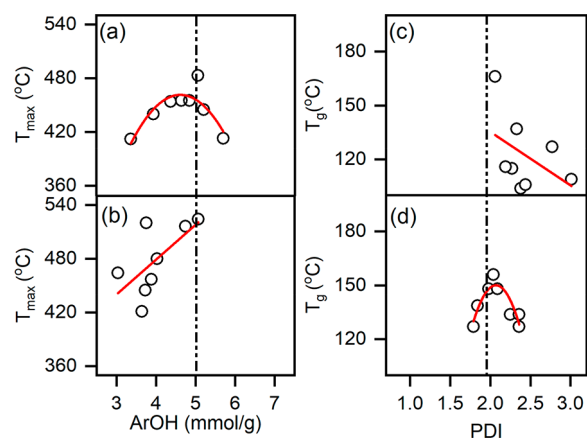
Figure 8. Correlation analysis of the chemical structure and molecular weight and its distribution of pine bark lignin (a, b) and oak bark lignin (c,d); ArOH, aromatic hydroxyl group; Total OH, total hydroxyl group; MeO, methoxy group.

than OS-PB because of the higher content of aromatic groups in the crude lignin.

In the preparation of polymeric materials, the glass transition temperature impacts material performance and hence, selection for a given application. After an annealing treatment, crude lignin had T_g ranging from 104 to 166 °C (OS-PB) (Table 1). This range was more extensive than the T_g of OS-OB (121- 156 °C) (Figure S8). The reaction temperature had a more significant impact on the T_g of OS-OB, but the organosolv conditions had subtle impacts on the T_g of OS-PB (Figure S5). The correlation analysis showed that T_g had a somewhat linear relation with the quantity of AlOH groups and polydispersity. An increasing amount of AlOH group content in the crude lignin led to stronger intramolecular hydrogen bonds and thus increased the T_g of crude lignin, for both OS-PB and OS-OB.[58] When PDI was around two, both OS-PB and OS-OB had the largest T_g (Figure 8). Hence, the T_g of the polymer was impacted by both chemical structure and molecular weight profile. With a higher PDI for crude lignin, the extractive and suberin compounds will act as a plasticizer, causing an increase of free volume in crude lignin. With a smaller PDI, lignin generally has a lower molar mass and should have more thermal mobility (Figure 8c,d). Overall, the organosolv conditions directly impacted the chemical structure and molecular weight of crude lignin. By selecting suitable conditions, we can partially control the thermal properties of crude lignin for a given application.

CONCLUSIONS

In summary, the organosolv process was used to treat pine and oak bark, solubilizing almost half of its mass to fractionate the components and extract crude lignin. Further analysis by composition analysis, ^{13}C NMR, and 2D HSQC NMR showed that extracted and precipitated compounds mainly contained lignin accompanied by polyphenolics, extractives, suberin, and a low amount of carbohydrate, especially for the organosolv pine bark crude lignin (OS-PB). With the temperature (°C), ethanol concentration (%), and solid loading (S:L, g/mL) values being available, predictive models on the solubilization of bark and crude lignin yield were built within the experimental range. The maximum solubilization of bark was 46% (PB) and 53% (OB), and the maximum yields of crude lignin were 18.11% (PB) and 21.33% (OB), respectively. These reaction conditions also had direct impact on the crude lignin's chemical structure, molecular weight, and thermal properties. Overall, we were able to manipulate the chemical structure, molecular weight, and thermal properties of lignin by selecting suitable reaction conditions of the organosolv process. With a relatively high number of hydroxyl groups, crude extracted bark lignin could be used as a polyol for polymeric materials such as rigid polyurethane foams and polyesters.

ASSOCIATED CONTENT

Ⓢ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06692.

Materials and methods section, characterization protocol, and the statistical analysis; composition of untreated and treated bark resources and the correlation analysis among characteristics of crude lignin; ^{1}H NMR spectra, gel permeation chromatography traces, thermal gravi-metric analysis curves, differential scanning calorimetry curves, and the impacts of reaction conditions on resulting crude lignin's chemical structure, molar mass, and thermal properties (PDF)

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Notes
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