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Efficient Method of Lignin Isolation Using Microwave-Assisted Acidolysis and Characterization of the Residual Lignin

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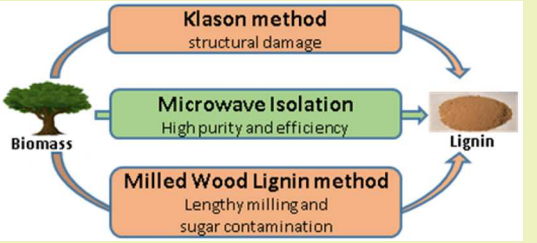
Supporting Information

ABSTRACT: Microwave heating is characterized by high efficiency and selectivity in biomass treatment. Due to the high thermal stability and low polarity of lignin, isolation of lignin by high-temperature microwave treatment is a promising subject for investigation. In this paper, microwave treatment is applied to polysaccharide liquefaction and lignin isolation from softwood at 160−210 °C for 10 min with dilute sulfuric acid. Mass balance/element analysis/FTIR/TG/solid-state ^{13}C NMR/Py-GC/MS are applied to investigate the processed residues (residual lignin). At 190 °C processing temperature, the residual lignin is a material rich in aromatics. High lignin purity (93 wt %) and yield (82 wt %) could be achieved by a simple protocol, which usually takes days or even weeks using conventional milled wood lignin protocols. The Py-GC/MS is applied to check the structure of lignin by a newly developed approach. The liquid phase after isolation is analyzed by GC-MS and liquid carbon NMR. Most chemicals in processed liquid are from cellulose and hemicellulose, suggesting that lignin is preserved well in the residue. By comparison, we found that microwave isolation causes less lignin degradation than conventional acidolysis under equivalent conditions. It is concluded that microwave treatment is potentially a promising tool for isolation of polysaccharide-free lignin with high efficiency.



KEYWORDS: *Lignin, Microwave, Acidolysis, Lignocellulosic biomass*

INTRODUCTION

Since 1838 when Anselme Payen first found "encrusting material" that was later named "lignin" embedded between cellulose and hemicellulose, numerous studies have been carried out to investigate the structure and characteristics of lignin. Lignin ranks second in quantity in the terrestrial regions of Earth's surface, playing an important role in plants allowing water conduction and protecting them against pathogen attacks.[1] From the viewpoint of chemical structure, lignin can be a potential source of valuable phenolic compounds by degradation.[2,3] Compared with other sustainable carbon-based resources, these vast resources constitute a potential advantage for lignin utilization.

However, the extraction of polysaccharide-free lignin with high efficiency using conventional methods is still a challenge because in biomass lignin acts as "glue" adhering the plant polysaccharides layers together with strong covalent bonding to cellulose and hemicellulose.[4] Extraction of lignin is accompanied by structural damage and polysaccharide contamination.[5] The lack of high-quality lignin on the market coupled with difficulties in degrading it selectively and efficiently into useful low molecular weight products make it undervalued and underdeveloped compared with cellulose and hemicellulose.[6] Therefore, lignin is still widely used as an energy source in chemical pulp and paper mills and in some industrial biorefinery processes.[7,8] One advancement in pure lignin isolation was proposed by Klason. The two-step Klason acidolysis protocol and its modified versions have been mostly used as standards of lignin content and purity determination, as in the TAPPI T222 method.[9] The drawback with the Klason protocol is that as concentrated sulfuric acid is applied the structure of Klason lignin (KL) is modified. In a KL procedure, lignin condenses to become water-insoluble. As a result, the repolymerization is serious. Another commonly used lignin in laboratory studies is milled wood lignin (MWL). This milder protocol uses neutral solvents for isolation affords and a product that is widely regarded to offer the best material for the structural analysis of the "native lignin" originally present in the plant tissue.[5,10] The linkages in lignin−carbohydrate complexes (LCC) are broken by milling, and then lignin is extracted by dioxane−water solvent. The disadvantage is that the intensive and lengthy milling (taking between 1 h to 3 weeks depending on milling machine) is energy-consuming, which in turn increases the cost of the isolation. Low lignin yield,[5] polysaccharide contamination,[11] and the tendency for dioxane−water to dissolve only the lower molecular weight fractions of the lignin are also drawbacks of MWL protocol. MWL is generally representative of total lignin in wood except that phenolic content is higher than that in native lignin because MWL is extracted by dioxane−water solvent. On the

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basis of the MWL protocol, cellulolytic enzyme lignin (CEL) protocol was proposed to increase lignin yield, but it was still low at 27−29 wt %.[11] Furthermore, CEL protocol requires a high dosage of enzymes, and the process is tedious. Therefore, both MWL and CEL methods are used mainly by lab-scale research but are not suitable for industrial production.[5,11] Although there are many improvements based on these methods, efficient lignin isolation with high yield and low contamination is always a difficult task and calls for new protocols.

With efficient and selective heating, microwave heating provides a promising approach in thermal treatment of biowaste, especially lignocellulose.[12−14] Until now, there have been only a few studies focusing on microwave-assisted lignin isolation. Zhou et al.[15] investigated microwave-assisted lignin extraction from birch in formic acid and compared it with conventional isolation methods. A higher delignification was achieved by microwave heating than oil bath heating. Li et al.[16] also performed microwave lignin extraction from bamboo at 90 and 109 °C separately. It was found that increasing temperature would benefit lignin extraction. Zoia et al.[17] performed microwave-assisted lignin isolation in inorganic acid solution, and a high yield of 55 wt % (total amount of acid soluble and insoluble lignin) was achieved. All these studies prove the advantages of microwave-assisted lignin isolation, especially lignin purity and processing time. However, these studies only focus on low-temperature isolation. High-temperature isolation still needs investigation. With elevated temperature, better performance is expected to be achieved because acidolysis lignin is more stable to thermal degradation than cellulose and hemicellulose. This thermal stability can be expected to be further enhanced during microwave treatment because of the selectivity of microwave treatment. Microwave heating is based on the high-frequency rotation of polar molecules. Therefore, compounds with high polarity are more rapidly heated during microwave irradiation. Lignin, having higher aromaticity and lower polarity than polysaccharide,[18,19] is likely to degrade less severely in a microwave isolation than conventional acidolysis under equivalent conditions of total energy input.

Based on the discussion above, in this paper a new method for fast microwave-assisted lignin isolation is proposed. Dilute sulfuric acid is used for acidolysis, as previous studies have shown that lignin−carbohydrate complexes (LCC) are reduced to negligible levels when acidolysis is conducted in this medium.[20] High-temperature isolation (160−210 °C) is carried out to ensure LCC can be cleaved in a short time. Systematic analysis is performed to investigate lignin quality. A new analysis approach based on Py-GC/MS is applied to check the structure of lignin after isolation.

MATERIALS AND METHODS

Materials. Mixed softwood pellets (MSP, UK Biochar Research Centre, School of Geosciences, University of Edinburgh) were used as feedstock for lignin isolation. The elemental and ICP analyses are shown in Tables S1 and S2. Compared with hardwood and herbaceous biomass, softwood has the least acid-soluble lignin, only about 0.2−0.5 wt %,[9] and thus is the most suitable for acidolysis lignin isolation. Sulfuric acid was purchased from Fischer Chemicals (>95 wt %). Creosol (99 wt %), vanillin (99 wt %), and phenol, 2-methoxy- (98 wt %) were purchased from Sigma-Aldrich. *trans*-Isoeugenol (99 wt %) was purchased from Acros Organic.

Experimental Methods. All biomass was milled to 60 mesh powders using a cutting mill (Retsch SM300, Germany) in Biorenewables Development Center (BDC), University of York. The microwave treatment was performed in a Discovery SP microwave reactor (CEM Corporation, USA) in capped vessels. Maximum power (300 W) of the microwave reactor was applied in all the experiments to make sure that the holding temperature could be achieved as quickly as possible. Diluted sulfuric acid (0.2 mol/L) was applied for isolation. The processing temperature of 160−210 °C at intervals of 10 °C was used for isolation. The holding time was 5/10/20 min (in this paper, the abbreviation microwave residual lignin (MRL) only refers to the 10 min sample). During microwave treatment, 0.2 g of MSP and 15 mL of acid solvent were heated in a capped vessel with stirring. After microwave treatment, the residue was recovered by filtration. Then, the residue was washed several times with deionized water until the rinsed water was neutral. In order to prepare the microwave residual lignin obtained in this way for further analysis, the residue was dried (105 °C, 24 h) and then weighed. All the experiments were repeated 3 times.

Lignin isolation by conventional heating (acidolysis lignin, AL) was performed using a benchtop autoclave (Anton Paar Monowave 50). MSP (0.08 g) and aqueous sulfuric acid (0.2 mol/L, 6 mL) were heated with stirring in a sealed vessel. The temperature was ramped up to 190 °C (within 5 min, similar to microwave experiments) and was held for 10 min. The residue (190 °C AL) after isolation was washed and dried as in the microwave residual lignin preparation. Most conditions of AL protocol are the same as those in the microwave experiment. By comparing AL and MRL, the characteristics and advantages of microwave treatment can be investigated.

The purity and yield was calculated by TAPPI T222 method.[9] The method is shown schematically in Figure S1. About 0.1 g of dewaxed sample was treated with 10 g of sulfuric acid (72 wt %) at 20 °C for 2 h. The solution was then diluted with deionized water to 3 wt % sulfuric acid and refluxed for 4h. The insoluble residue (lignin) was isolated by filtration. After washed with hot water, the residue was dried at 105 °C for 24 h. This dried residue is Klason lignin (KL). The purity and yield were calculated according to the equation in Table 1. The purity result was adjusted by subtracting the ash content measured by TG analysis.

Table 1. Purity and Yield of MSP and 190 °C MRL/AL[a]

	purity (wt %)		
	dry basis	extractive-free basis	yield (wt %)
MSP	30.37[b]	39.08[c]	
190 °C MRL	80.64[d]	92.85[e]	82.31[f]
190 °C AL	75.91[d]	87.51[e]	65.60[f]

[a]For definitions of M_0, M_d, M_{a1}, M_i, M_{di}, and M_{a2}, see Figure S1. [b]M_{a1}/M_0. [c]M_{a1}/M_d. [d]M_{a2}/M_i. [e]M_{a2}/M_{di}. [f]M_{a2}/M_{a1}.

Elemental analysis and ICP analysis data were obtained from the analytical service offered by Department of Chemistry, University of York.

Thermogravimetric (TG) analysis was performed using a Netzsch STA 409 analyzer (Germany). The following parameters were applied: temperature ramp rate 20 K/min, final temperature 600 °C, and carrier gas 50 mL/min pure nitrogen gas. To measure ash content, the following parameters were applied: temperature ramp rate 20 K/min, final temperature 625 °C holding for 1 h, and carrier gas 50 mL/min N_2 and 100 mL/min O_2. The final mass % was used as the ash content.

FTIR data was obtained using a PerkinElmer FTIR/FTNIR Spectrum 400 analyzer (USA). The spectra were acquired between 700 and 4000 cm^{-1} with resolution of 2 cm^{-1} and scan time of 64 s.

Solid-state ^{13}C NMR spectroscopy (SSNMR) results were obtained at the EPSRC UK National Solid-State NMR Service at University of Durham. The spectra were obtained at 100.562 MHz. The chemical shift range from 0 to 240 ppm was recorded.

Py-GC/MS results were obtained from BDC, University of York. The units used were CDS Analytical 5250-T Trapping Pyrolysis Autosampler (UK) as the pyrolysis unit, Agilent Technologies 7890B GC System (USA) as gas chromatography unit, and Agilent

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Technologies 5977A MSD (USA) as mass spectrum unit. The sample was loaded into the pyrolysis unit and pyrolyzed at 600 °C for 10 s. The volatile materials released were carried into the GC/MS unit by nitrogen for analysis. The following GC/MS parameters were applied: GC inlet temperature at 350 °C, initial temperature at 40 °C for 2 min, ramp rate at 10 K/min until 300 °C, holding at 300 °C for 30 min, and split ratio with 50:1. Volatile compounds were identified by comparing the mass spectra with NIST Lab database. A standard sample mixture of four compounds, creosol/vanillin/2-methoxyphenol (guaiacol)/*E*-isoeugenol, was also subjected to pyrolysis and GC/MS in order to verify the mass spectral identities.

After microwave isolation at 190 °C, the aqueous phase was neutralized and dried using freeze-dryer for 24 h, preparing for liquid-state ^{13}C NMR and GC/MS analysis. Liquid-state ^{13}C NMR spectroscopy results were obtained by JEOL ECS 400 NMR Spectrometer (Japan). D_2O was used as the solvent for analysis. The number of scans was 8192.

GC/MS results were obtained using a PerkinElmer Clarus 500 GC/MS (USA). Ethanol was chosen as solvent for analysis. The GC program used was as follows: initial temperature at 50 °C holding for 4 min, ramp rate with 10 K/min until 290 °C and holding for 10 min, split ratio with 5:1, and injector temperature at 290 °C. The identities of the compounds were determined by comparing the mass spectra with NIST lab database.

RESULTS AND DISCUSSION

Mass Balance and C/H Contents. Figure 1 shows the influence of temperature and holding time on the yield of residue and C/H content. It was found that major changes of residue mass and C/H content took place from 160 to 190 °C. At 170 °C, the residue mass could be still affected by holding time; above 190 °C, the masses of the residues obtained did not vary significantly with holding time, showing the high efficiency of microwave heating. The residue mass of KL was 31 wt %, which was close to that of 190/200 °C residues. Adler[21] reported that the equivalent formula of the purest softwood lignin he could produce from spruce was $C_9H_{7.92}O_{2.40}(OCH_3)_{0.92}$, which suggested the C/H content of pure softwood lignin should be close to 65.12/5.47 wt %. Lin et al.[22] also measured the C/H content of an industrial lignin which was 65.00/6.43 wt %. Compared with these values, the C/H content of 190 °C MRL was similar to those isolated lignins. The H content of KL was low because concentrated sulfuric acid was likely to dehydrate the lignin. The C/H of 190 °C AL was similar to that of 190 °C MRL; however, the residue mass was lower, showing conventional acidolysis at high temperature caused more mass loss than microwave treatment and indicating that lignin is in fact more thermally stable under microwave heating than when subjected to conventional heating as expected.

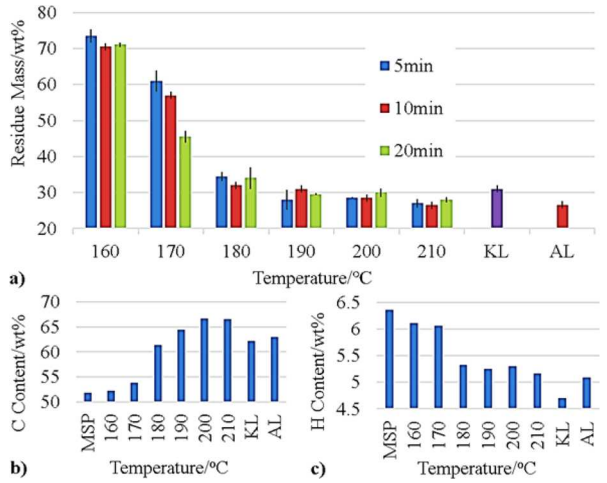

Figure 1. Comparisons of KL, 190 °C AL, and microwave-isolated lignin under different conditions: (a) mass balance; (b and c) C/H content.

Purities (Acid-Insoluble Lignin Content) and Yields. The yields and purities of 190 °C MRL and 190 °C AL (10 min sample) shown in Table 1 were calculated according to TAPPI method T222 shown in Figure S1. After 10 min of microwave treatment at 190 °C, the isolation produced lignin with high purity (93 wt %) and yield (82 wt %), both of which were higher than those of lignins obtained using MWL methods. Wu and Argyropoulos[11] produced MWL with a 14 day milling process on the softwood (black spruce (*Picea mariana*)). The extractive-free basis purity and yields were 88.3 wt %/28.5 wt % respectively. Compared to MWL methods, the much shorter duration required by microwave heating is probably the main reason for the higher lignin yields obtained during this study. Within such a short processing time, lignin loss is reduced to a great extent. Sulfuric acid offers an environment where carbohydrate can be hydrolyzed and solubilized, while most lignin is insoluble.

Another reason for high purity and yield is possibly the selectivity of microwave treatment.[12−14] Different from conventional heating, microwave heating is achieved by the high-frequency rotation of polar molecules. Compared to nonpolar compounds, polar molecules and functional groups are treated more intensely and faster in microwave radiation. Compared with carbohydrate, lignin is generally regarded as having higher aromaticity and lower polarity.[18,19] Therefore, carbohydrate and lignin can be expected to behave in significantly different ways under microwave radiation, particularly in the presence of dilute aqueous sulfuric acid. Such a hypothesis explains why in Table 1 the yield of 190 °C AL was much lower than that of 190 °C MRL. These data provide further strong support for the mechanism by which microwave heating exerts its selectivity in mixtures containing materials of differing polarities.

Liquid-Phase Analysis. After isolation at 190 °C (10 min), the solution after microwave treatment was analyzed by GC/MS and liquid ^{13}C NMR. The GC/MS list of aqueous phase compounds are showed in Table S3. The GC/MS results showed that the majority of compounds in solution were chemicals derived from sugars characterized by the presence of ketone, aldehyde, and furan groups, while aromatic compounds occurred in much lower proportions. This result was consistent with liquid ^{13}C NMR results (Figure S2). The peaks in 20−40 ppm were ascribed as saturated carbon which were mainly from polysaccharide. The peaks of ketone were located in 205−220 ppm, suggesting that dehydrated sugars were probably the main products in liquid phase. Of greatest significance is the absence of intense peaks between 100 and 150 ppm, where carbons in benzenoid rings typically resonate, indicating that aromatic compounds remained predominantly in the insoluble solid residue. The absence of these peaks provides further evidence for lack of thermal depolymerization when lignin is heated by microwaves for 10 min at 190 °C.

Thermogravimetric Analysis. Figure 2 shows the TG curves of MSP, KL, 170/190 °C MRL, and 190 °C AL. For MSP, the DTG curve had a very strong peak at around 350 °C that corresponds to the decomposition of cellulose.[23,24] This peak was accompanied by a well-pronounced shoulder at

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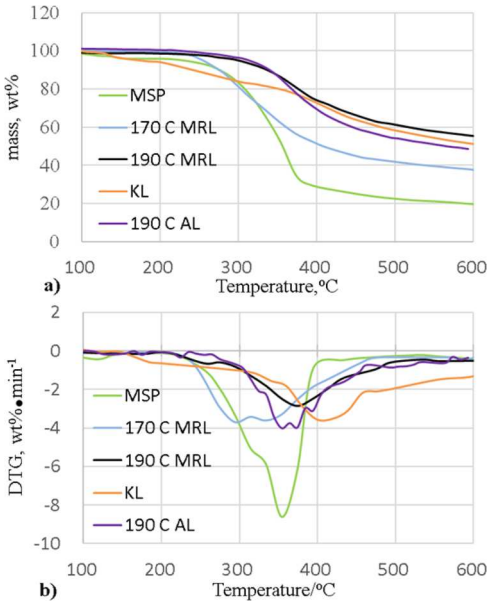

Figure 2. Pyrolysis curves of samples (MSP, KL 190 °C AL, and 170/190 °C MRL) at heating rate of 20 K/min. (a) TG curves; (b) DTG curves.

around 300 °C, attributable to hemicellulose decomposition.[23,24] For 170 °C MRL, the final mass loss was lower than that of MSP. These results illustrated that microwave isolation at 170 °C was already able to remove the carbohydrate to some extent. However, there were two strong DTG peaks (294 and 330 °C) in the range of 290−350 °C, showing that 170 °C MRL was still severely contaminated by cellulose and hemicellulose.

The mass and DTG curves of KL and 190 °C MRL had similar trends in general. Compared with linear structure of cellulose and hemicellulose (with some branches), the complex 3D structure of lignin and predominance of aryl−alkyl ether linkages make it recalcitrant to thermal degradation. These factors resulted in the 190 °C MRL and KL samples having high residual mass at 600 °C, a higher peak zone for degradation. The final residual masses were high at 52 and 55 wt % respectively, showing that fewer degradable compounds existed in these two samples than those in 170 °C MRL. Their DTG peaks were located between 370 and 410 °C, where pure lignin displays its DTG peak according to previous studies.[23,24] Unlike the DTG curves of MSP and 170 °C MRL, the DTG curves showed no peaks between 290 to 350 °C, confirming that polysaccharides were mostly removed in the 190 °C MRL and KL samples. A subtle difference between KL and 190 °C MRL was that the degrading peak of 190 °C MRL was slightly lower, which was either caused by structural changes brought about by the 190 °C treatment, or by dehydrations promoted by the 72 wt % sulfuric acid used in the Klason protocol.

Comparing 190 °C MRL and 190 °C AL, it was found there was more polysaccharide in 190 ° AL sample. The two DTG curves both had peaks at around 375 °C, showing lignin was a main component in both isolated residues. However, for the DTG curve of 190 °C AL, there was also a well-pronounced peak at 354 °C that was attributable to the degradation of polysaccharide.[23,24] Furthermore, the DTG peaks of 190 °C AL were stronger than those of 190 °C MRL, showing that 190 °C AL was less thermally stable. The data indicate that 190 °C MRL is less contaminated by polysaccharides and more thermally stable than lignin produced by conventional acidolysis at 190 °C.

FTIR. Figure 3 shows the FTIR spectra of MSP and MRL. As the treatment temperatures were increased, the bands assigned

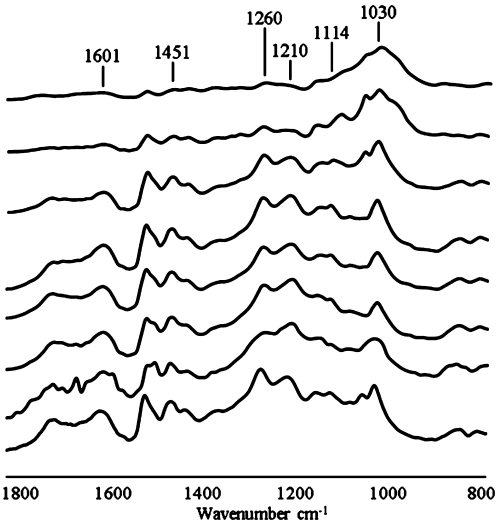

Figure 3. FTIR spectra of MSP and isolated lignin. From top to bottom: MSP, 170/180/190/200/210 °C MRL, KL, and 190 °C AL.

as aromatic skeleton (1601/1508/1451/1424 cm^{-1})[25−28] were strengthened significantly. These strong peaks suggested high aromaticity of the residues after treatment. The peak at 1030−1060 cm^{-1} was assigned as C−O stretching of primary alcohol.[25,27,28] It weakened as temperature rose, indicating a better removal of polysaccharide at high temperature. The overall trend of the FTIR spectra demonstrated that temperature acts as an important factor in lignin isolation. At treatment temperatures higher than 190 °C, the spectra of MRL were very similar to that of KL. From 190 to 210 °C, the peaks at 1114 cm^{-1} (secondary alcohol)[29] and 1030 cm^{-1} were further weakened slightly. This may suggest that 210 °C MRL was purer than 190 °C MRL. However, as shown in Table 1, the 190 °C treatment rendered 18 wt % of the lignin acid soluble. Therefore, an isolation at 210 °C would solubilize more lignin, result in lower lignin yield, and perhaps trigger further structural changes away from native lignin. Furthermore, the tube pressure of the 210 °C experiment was 100 psi higher than that of 190 °C (Figure S3). Therefore, due to lignin yield and safety reasons, 190 °C seemed a suitable temperature for this current protocol.

The FTIR spectra of 190 °C MRL and 190 °C AL showed similar general trends. However, the peak at 1260 cm^{-1} was stronger in 190 °C AL than that in 190 °C MRL. This peak could be ascribed to ether bonds, especially alkyl aryl ethers.[25]

SSNMR. Figure 4 shows the spectra of SSNMR spectra of MSP and various isolated lignin samples. The peak at 55 ppm was as being attributable to methoxyl carbons.[29,30] This peak was strengthened in isolated lignin samples, because the monomer of softwood lignin, the guaiacyl unit (G-unit), contains one methoxyl side chain. Comparing the spectra of MSP and 170/190 °C MRL, it was obvious that the peaks between 109 and 162 ppm were much stronger after microwave treatment. According to Mao et al.,[29] the peaks in the range between 108 and 60 ppm can be attributed to aliphatic carbons

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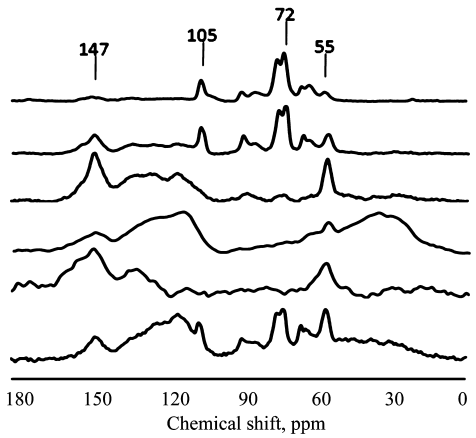

Figure 4. SSNMR spectra of MSP and isolated lignin. From top to bottom: MSP, 170 °C MRL, 190 °C MRL, KL, KL (CPNQS), and 190 °C AL.

mainly from carbohydrates and side chains of lignin, such as the peaks at 72 and 105 ppm characteristic of C2, C3, C5, and C1 carbons of cellulose,[31] while peaks between 162 and 109 ppm were attributed to carbon atoms in benzenoid rings that provided strong evidence for the existence of lignin in their samples. The major peaks in this zone were located at 147 ppm (aromatic C−O),[30,32] 130 ppm (aromatic carbon bearing alkyl group),[32] 125 ppm (hydrogen-bearing aromatic carbon not adjacent to oxygen functionalities),[32] and 114 ppm (aromatic carbon ortho to phenolic C−OH moieties).[32]

The spectra of 190 °C MRL and KL showed significant differences. There were two wide bands at 30−50 ppm and 120−135 ppm for KL spectrum. Research[29,33,34] showed that these two bands can be attributed to CH_2 carbons and CH carbons, respectively. When processing the KL spectrum using the CPNQS methodology that suppresses the CH_2/CH band, the spectrum became similar to that of 190 °C MRL. These data suggested that microwave isolation can keep the aromatic part of lignin intact; however, it appears to remove the aliphatic part to some extent. The monomers of lignin are phenylpropanoid in structure. They are based on a C_6−C_3 structure that contains both aliphatic and aromatic carbons. Compared with the aromatic C_6 moieties, the C_3 aliphatic side chains of lignins are characterized by higher polarities, having higher O/C ratios than the aromatic parts of the structure. Microwaves are more efficient in heating polar compounds and functional groups,[12] so the side chain is more likely to be modified or cleaved during lignin isolation. As a result, lignin isolated using microwave heating has a higher proportion of intact aromatic rings and a lower proportion of intact side chains than does the lignin isolated using conventional heating at the same temperature. This fact will benefit the application of isolated lignin as a potential source for production of low molecular weight aromatic compounds.

The SSNMR spectrum of 190 °C AL showed a strong peak at 72 ppm, suggesting severe sugar contamination. Similar to the spectrum of KL (normal CP spectrum), there was a band at 120−135 ppm, suggesting a high content of CH_2 group in lignin isolated by conventional acidolysis. These data add further evidence to the hypothesis that MRL has a proportionately higher aromatic carbon content and that microwave heating at 190 °C results in significant cleavage of the side chains of this type of lignin.

Py-GC/MS. MSP and the isolated lignin samples (190 °C MRL, KL, and 190 °C AL) were analyzed by Py-GC/MS. From the changes of peak area % of typical pyrolytic products, especially phenolic compounds, the structure change and degradation extent during lignin isolation can be investigated. Because most polysaccharide had been removed, the phenolic compounds were dominant in pyrolytic products of the three lignin samples, while there were more pyrolytic products from cellulose and hemicellulose in MSP, such as 2-propanone, 1-hydroxy-/furfural/cyclopentane-1,2-dione. In Table 2, nine of the compounds identified in highest proportions from the Py-GC/MS are listed together with their measured ion current peak areas. In Table 1 it was shown that the lignin content of 190 °C MRL (80.64 wt %, dry basis) was 2.67 times that of MSP (30.37 wt %, dry basis). When the ratios between the ion current peak areas for the 190 °C MRL and those for MSP are compared as shown in Figure 5a, it is apparent that the trend line has a slope of 2.99, which is in acceptable agreement with the expected ratio of 2.67, suggesting that lignin was well-preserved without significant degradation. Notably, two of the nine compounds were significant outliers from the trend line, 2-methoxy-4-vinylphenol and (*E*)-isoeugenol. There are two possible reasons that can explain why these two compounds do not conform to the expected trend: (1) The precursors for these compounds are concentrated around the periphery of the 3D lignin structure and are bonded covalently to carbohydrates as part of the LCC, resulting in chemical modification of the alkene groups during acid hydrolysis. (2) The compounds are more or less evenly distributed through the 3D structure of the lignin and do not survive the acidic conditions at 190 °C for reasons that cannot be explained at present. The fact that compound numbers 6 and 7 in Table 2 also contain double bonds in the side chain and do fit closer to the trend line may be seen as evidence favoring the former explanation. The trend line between KL and MSP (Figure 5b) was also somewhat lower than that in Figure 5a, showing that there were

Table 2. Comparisons of Phenolic Compounds Peak Area (%) of MSP and Isolated Lignin

no.	compounds	MSP	190 °C MRL	KL
1	1,2-benzenediol, 4-methyl-	0.42	2.51	2.62
2	phenol, 4-ethyl-2-methoxy-	1.20	3.66	3.70
3	creosol	6.20	18.67	13.90
4	phenol, 2-methoxy-	3.17	8.45	9.73
5	vanillin	1.36	2.67	1.29
6	phenol, 2-methoxy-5-(1-propenyl)-, (*E*)-	0.99	1.87	1.43
7	phenol, 2-methoxy-4-(1-propenyl)-, (*Z*)-	0.39	0.65	0.31
8	2-methoxy-4-vinylphenol	4.04	4.92	3.58
9	*trans*-isoeugenol	3.78	3.20	1.37

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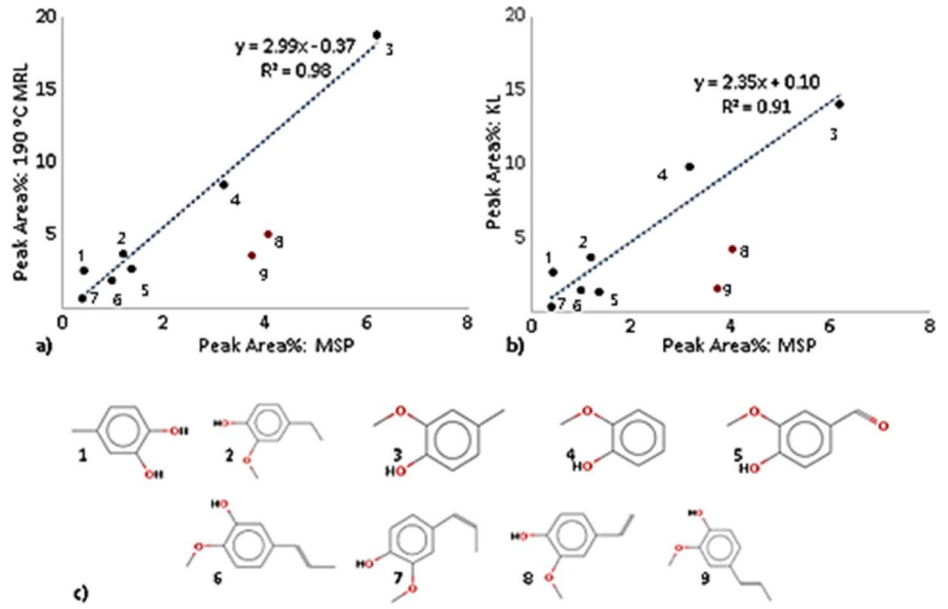

Figure 5. Peak area % of phenolic compounds according py-GC/MS analysis. (a) MSP vs 190 °C MRL; (b) MSP vs KL. (c) Compound structures.

proportionately fewer aromatic compounds in pyrolytic products of KL than that of 190 °C MRL. This was probably becasue there were more aliphatic compounds in KL due to less side chain modification than that in 190 °C MRL, which is consistent with the results of SSNMR analysis presented above.

When the volatile products produced by Py-GC/MC of 190 °C AL were compared with those obtained from 190 °C MRL, it was evident that pyrolysis products derived from carbohydrates, such as 5-hydroxymethyl furfural (0.60% in 190 °C AL, 0.22% in 190 °C MRL) and D-allose (2.06% in 190 °C AL, undetectable in 190 °C MRL), were evident with higher peak areas in the case of 190 °C AL. An interesting fact was that one of main pyrolytic products, creosol, showed a higher peak area % in 190 °C AL (25.0%) than that in 190 °C MRL (18.7%), though the latter was purer lignin and less contaminated with carbohydrates. Fleck[35] observed that some model lignin dimers, such as conidendrin and di-isoeugenol in which the two monomers are linked by a saturated ring, did not produce creosol during pyrolysis. Fleck found that certain interlinkages, such as an indane ring, could effectively prevent the formation of creosol under pyrolytic conditions. Furthermore, Fleck[35] pointed out that creosol was one of the main pyrolytic products of coniferin which is a glucoside of coniferyl alcohol, so sugar contamination actually could increase the yield of creosol to some extent. It is arguable that these two factors explain why 190 °C AL with the higher carbohydrate content produced more creosol. It is also possible that some of the structural changes in the side chains of the lignin promoted by microwave heating lead to formation of new cyclic aliphatic interlinkages between monomeric units that are in close proximity within the 3D stucture and that these changes also serve to reduce creosol yields from Py-GC/MS of 190 °C MRL.

CONCLUSIONS

It has been demonstrated that a pure form of lignin relatively uncontaminated by residual carbohydrates can be produced rapidly and efficiently by brief (10 min) microwave heating of mixed softwood pellets (MSP) at 190 °C in dilute aqueous sulfuric acid. The type of lignin produced by this new method, designated as 190 °C MRL, has both higher yield and purity than equivalent material produced by conventional heating to 190 °C in aqueous sulfuric acid at the same concentration in an autoclave for the same time. The latter material has been designated 190 °C AL (acidolysis lignin). It has been shown that 190 °C MRL is of high aromaticity due to the modification of lignin side chains. The Py-GC/MS results from the two types of lignin indicate that some formation of cyclic aliphatic linkage occurs between the side chains of monomeric units that are in close proximity when microwave heating at 190 °C is applied. The techniques applied using comparative Py-GC/MS on lignin samples obtained by differing techniques have general application in identifying structural changes occurring during lignin isolation.

In general, the research results show that high-temperature microwave treatment is a powerful tool for lignin isolation. High efficiency, a simple protocol, and high lignin yield are its most significant advantages. It is potentially a very promising method for high-quality lignin preparation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02545.

Element and ICP analysis of feedstock; TAPPI T222 method; GC/MS spectra and compounds lists; pressure and temperature comparisons during experiment (PDF)

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Notes

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