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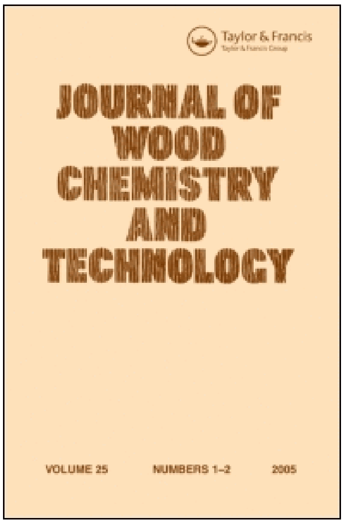

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Yong Sik Kim[a]; Hou-min Chang[b]; John F. Kadla[a]
[a] Faculty of Forestry, Department of Wood Science, University of British Columbia, Vancouver, BC, Canada [b] College of Natural Resources, North Carolina State University, Raleigh, NC, USA

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Yong Sik Kim
Faculty of Forestry, Department of Wood Science, University of British Columbia, Vancouver, BC, Canada

Hou-min Chang
College of Natural Resources, North Carolina State University, Raleigh, NC, USA

John F. Kadla
Faculty of Forestry, Department of Wood Science, University of British Columbia, Vancouver, BC, Canada

Abstract: The chemical structural changes of Lodgepole pine milled wood lignin (MWL) before and after polyoxometalate (POM) oxidation were investigated using gel permeation chromatography (GPC), Fourier Transform infrared spectroscopy (FTIR), and solution-state nuclear magnetic resonance spectroscopy (NMR). ^{13}C NMR spectroscopic data revealed an approximately 28% decrease in α-OH/β-O-4 inter-unit linkages after POM treatment. This was accompanied by an increase in carbonyl and phenolic hydroxyl content. These results suggest POM oxidation involved side chain (such as α-OH/β-O-4) oxidation and/or degradation of some of the inter-unit linkages. Quantitative ^{13}C NMR along with GPC analysis revealed an increase in the degree of condensation of the MWL as a result of POM treatment, suggesting radical coupling as a major reaction pathway.

Keywords: Lignin, milled wood lignin (MWL), polyoxometalate (POM), ^{13}C NMR spectroscopy

Address correspondence to John F. Kadla, Faculty of Forestry, Department of Wood Science, University of British Columbia, 2424 Main Mall, Vancouver, BC, Canada, V6T 1Z4. E-mail: john.kadla@ubc.ca

INTRODUCTION

Polyoxometalates (POMs) are a growing class of delignification reagents. They are environmentally benign alternatives to conventional bleaching chemicals that are well suited for total chlorine free (TCF) bleach plant processes.[1–3] POMs have been reported to efficiently and selectively remove lignin from pulps under both aerobic and anaerobic conditons.[1–4] Several investigations into the mechanisms of POM oxidation of lignin model compounds have been reported,[1,2,5–8] and some pulp bleaching experiments have been performed.[1,2,4,9] However, very little information is available on the effect of POM oxidation on the chemical structure of the lignin macromolecule at the molecular level. Detailed information on the mechanisms of oxidation of macromolecular lignin would significantly contribute to a more comprehensive understanding of the chemistry of POM-oxidation, and help improve process operation. In particular information is lacking regarding both fundamental mechanisms of homogeneous oxidation as well as the effects of interactions between POMs and polymeric (insoluble) lignin in wood-cell walls. In this article, we report the oxidation of a milled wood lignin by α-$[SiVW_{10}O_{40}]^{5-}$, the dominant oxidatively active species in the prototypical industrially relevant POM system, $Na_{5(+1.9)}[SiV_{1(-0.1)}MoW_{10(+0.1)}]$.[10]

EXPERIMENTAL

Materials

Air-dried Lodgepole pine (Pinus contorta) was milled in a Wiley mill using a 40-mesh screen. The coarsely milled wood (wood meal) was extracted with acetone for 48 h using a Soxhlet apparatus. After extraction, the wood meal was air-dried and stored in a 40°C vacuum oven and left at least 1 week prior to use. $K_5[SiVW_{11}O_{40}] \cdot 12H_2O$ (POM) was provided from the USDA Forest Products Laboratory (Madison WI, U.S.A).[1] $CDCl_3$ and DMSO-d_6 were purchased from Cambridge Isotope Laboratories. Anhydrous ethyl ether, 1,2-dichlorethane, 1,4-dioxane, tetrahydrofuran and pyridine were purchased from Sigma-Aldrich. All other chemicals were purchased from either Fisher Scientific or Sigma-Aldrich and used as received.

Planetary Ball Milling Method

The dried wood meal was ground using a planetary ball mill (Retsch PM 200) with two 50 mL zirconium oxide jars. Each jar contained 10 g of extractive-free wood meal and 6 zirconium oxide balls (20 mm diameter). Samples were ground under an argon atmosphere at 650 rpm for 15 h. To prevent overheating and thermal changes to the wood, the samples were milled for 30 min intervals, between which the samples were allowed to cool for 30 min. After milling, the milled wood was dried in a 40°C vacuum oven for at least 1 week prior to use.

Milled Wood Lignin (MWL) Isolation

MWL was isolated according to the method of Björkman.[11,12] Accordingly, 19 g of milled wood were put into a 500 mL capped centrifuge bottle and 200 mL of dioxane/water (96:4, v/v) was added. The solution was shaken at room temperature for 24 h under a nitrogen atmosphere. The mixture was centrifuged at 8000 rpm for 15 min and the supernatant collected. The remaining solid was resuspended in 200 mL of dioxane/water (96:4, v/v) and the earlier procedure repeated. The combined supernatants from centrifugation were concentrated and added dropwise to deionized water and then freeze-dried for 3 days using a VirTis EX freeze dryer. The resulting crude MWL (3.2 g) was stored in a 40°C vacuum oven for 1 week prior to purification. The crude MWL (3 g) was dissolved in 60 mL of 90% acetic acid. The acetic acid solution was then added dropwise with stirring to 660 mL of deionized water in order to remove carbohydrates. The precipitated lignin was centrifuged, freeze-dried, and then stored in a 40°C vacuum oven. The dried lignin was dissolved in 60 mL of 1,2-dichloroethane/ethanol (2:1, v/v) and centrifuged to remove any insoluble material. The resulting supernatant was added dropwise to 690 mL of anhydrous ethyl ether. After centrifugation, the precipitate was washed three times with fresh petroleum ether and dried in a 40°C vacuum oven for 1 week.

POM Treatment of MWL

The reaction of POM with MWL was performed by first weighing 150 mg of MWL into a septum-sealed serum bottle containing 20 mL of degassed sodium acetate buffer (0.2 M, pH 5.0). All of the air inside the bottle was displaced by purging repeatedly with argon. Ten mL of degassed POM stock solution was then added via syringe to the sealed bottle. The final concentration of POM in the buffer solution was 0.05 M and the weight per cent of MWL in the buffer suspension was 0.5%. The bottle was quickly immersed in an oil-bath maintained at 90°C with constant stirring. After 1 h of reaction, the bottle was rapidly cooled by immersion in an ice-water bath. The lignin was then filtered, washed with water and freeze-dried.

Acetylation of MWL

MWL and POM-treated MWL (POM-MWL) samples were acetylated for physical and chemical analysis. Acetylation was performed by dissolving

100 mg of purified lignin in 4 mL of pyridine/acetic anhydride (1:1, v/v), and stirring the reaction for 24 h at room temperature. The reaction solution was then added dropwise, with stirring, to 100 mL of ice-water. The precipitated lignin was collected by filtration through a Nylon membrane (0.45 μm, 47 mm), washed with ice-water and freeze-dried using a VirTis EX freeze dryer. This procedure was repeated to ensure complete acetylation.

Determination of Lignin Content in MWL

The lignin content of the purified MWL and extractive-free wood meal was determined using the Klason method (TAPPI Method T249 cm-85). Acid-soluble lignin was quantified by UV-Vis spectroscopy at 205 nm according to TAPPI Useful Method UM250. All samples were measured in duplicate.

Gel Permeation Chromatography (GPC) and Fourier Transform Infrared (FTIR) Analysis

The molecular mass distribution of the acetylated lignin samples were determined by GPC (Agilent 1100, UV and RI detectors) using styragel columns (Styragel HR 4 and HR 2) at 35°C, THF as the eluting solvent (0.5 mL $\min^{-1}$) and UV detection at 280 nm. The lignin concentration was 1 mg mL^{-1} and the injection volume was 75 μL. The GPC system was calibrated using polystyrene standards with molecular weights ranging between 580 and 1,800,000 Daltons.

Fourier transform infrared (FTIR) analysis was performed using a Perkin-Elmer Spectrum One FTIR equipped with an attenuated total reflectance (ATR) attachment. A total of 128 scans per sample were acquired at a spectral resolution of 4.0 cm^{-1}. FTIR absorbance spectra were directly obtained using vacuum oven-dried lignin samples.

The FTIR spectra were further analyzed using Peak Fit software (SPSS Inc., Chicago, IL). Deconvolution was performed using the Gaussian peak shape and a full width at half-maximum (fwhm) of 20–30 cm^{-1}; compared to ensure good resolution of peaks without overfitting. The number of peaks was analyzed using the second-derivative spectra prior to deconvolution. All peaks were fit until regression values (r^2) were greater than 0.995.[13]

Nuclear Magnetic Resonance (NMR) Analyses

Quantitative ^{13}C NMR and ^{1}H NMR spectroscopy were performed on a Bruker Avance 300 MHz spectrometer equipped with a BBO probe. For ^{1}H NMR, 40 mg of acetylated lignin was accurately weighed and dissolved in 0.75 mL of $CDCl_3$. The NMR spectra were recorded at 300 K, with a 90° pulse width and a 1.3 s acquisition time. A 7 s relaxation delay (d_1) was used to ensure complete relaxation of the aldehyde protons. A total of 128 scans were collected. Quantification of the relative amounts of the various functional groups was performed according to Adler et al.;[14] the integral of the aromatic proton region (7.2–6.4 ppm) was set equal to 2.7 and 2.6 for the MWL and POM-MWL, respectively. These values are based on 2 protons associated with C2 and C6, as well as 0.6 and 0.5 protons for the C5 of MWL and POM-MWL, as well as a small contribution from certain vinyl proton (~0.1). The number of C5 protons (0.6 and 0.5) was calculated based on the degree of condensation determined from ^{13}C NMR (MWL = 39/100 Ar and POM-MWL = 46/100 Ar, respectively).

Quantitative ^{13}C NMR spectroscopy was performed using 60 mg of acetylated lignin in 0.25 mL of DMSO-d_6. The sample solutions were filtered prior to NMR analysis, and analyzed using a Shigemi tube. Relaxation was facilitated by the addition of 10 μL of a chromium acetoacetonate solution (final concentration 10 mM).[15] Conditions for analysis included a 90° pulse width with a 1.4 s acquisition time, and a 1.7 s of relaxation delay (d_1). A total of 20,000 scans were collected.[15]

RESULTS AND DISCUSSION

Table 1 reports the yield and lignin content of the extractive-free wood and purified MWL. The yield of MWL was 26% with a 91% Klason lignin content after purification. The yield of POM-MWL was approximately 90% after POM reaction. As this was a heterogeneous reaction system, that is, the MWL was insoluble under the conditions used, the high yield of POM-MWL is likely the effect of POM oxidative reactions occurring primarily at the surface of the suspended lignin macromolecules.

Structural Analyses of MWL and POM-MWL Using NMR Spectroscopy

NMR spectroscopy has been extensively used to investigate the structure of lignin.[15,16] NMR provides a comprehensive view of the entire lignin

Table 1. Yield and Klason lignin content of the Lodgepole pine and purified MWL

		Klason lignin content (% ± 0.7%)		
Lignin yield (%)		Soluble	Insoluble	Total
Extractive-free Wiley wood	—	0.5	25.7	26.5
Purified MWL	26.0[a]	0.2	90.6	90.8

[a] Purified MWL lignin yield was calculated based on total lignin content as determined by Klason lignin content, referenced as 100%.

macromolecule. Quantitative ^{1}H NMR spectra were obtained for both acetylated MWL and acetylated POM-MWL (Figure 1). The relative amounts of the various functional groups was determined by setting the integral of the aromatic proton region (7.2–6.4 ppm) equal to 2.7 and 2.6 for acetylated MWL and acetylated POM-MWL, respectively[14] (see experimental). With the exception of the phenolic and aliphatic OH and methoxyl groups very little difference was observed between the ^{1}H NMR spectra of the two lignin preparations.

There is an increase in the phenolic hydroxyl group content from 17 to 23 per 100 aromatic rings for the acetylated MWL and acetylated POM-MWL, respectively. There is also a decrease in the aliphatic hydroxyl content from 101 to 99 per 100 aromatic rings MWL and POM-MWL, respectively. The generation of new phenolic hydroxyl groups is likely arising from the cleavage of α-O-4 and β-O-4 linkages (Scheme 1).

In order to obtain detailed information on the abundance of each inter-unit linkage, quantitative ^{13}C NMR spectroscopy was also performed for both acetylated and non-acetylated MWL and POM-MWL (Figure 2). ^{13}C NMR spectroscopy can be used to quantitatively estimate the abundance of each inter-unit linkage in the lignin macromolecule.[15,17,18] However, there still exists some overlap in the spectra, making estimations of the structural formations difficult.[17] Unfortunately, the non-acetylated POM-MWL did not completely dissolve at concentrations suitable for NMR analysis. This may be the result of changes in the chemical structure of the MWL after POM treatment. Quantitative carbon for this POM-MWL did not yield a spectrum with sufficient resolution to provide any useful data. As a result, only comparison between the acetylated MWL and POM-MWL are presented.

The ^{13}C NMR spectra can be separated into different structural regions and integrated to obtain structural information (Tables 2 and 3 and

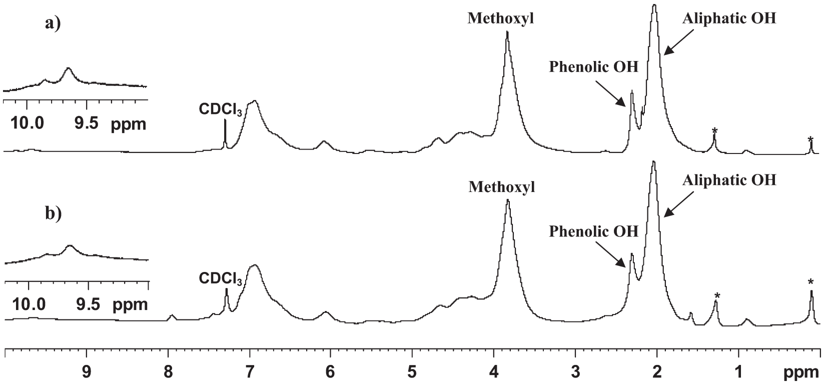
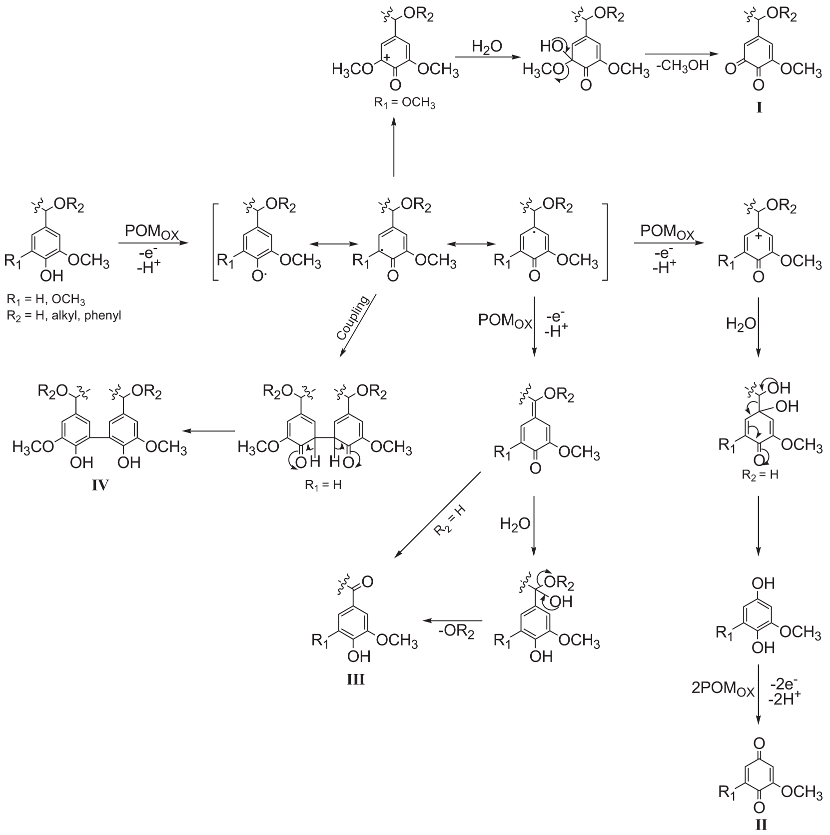


Figure 1. Quantitative ^{1}H NMR spectra for a) acetylated MWL and b) acetylated POM-MWL. *Unknown signals or impurities.



Scheme 1. Possible reaction mechanisms for the POM ($SiVW_{11}O_{40}^{5-}$) oxidation of lignin-based moieties.[8]

Figure 2). For the estimation of the amounts of inter-unit linkages and functional groups, the aromatic region from 162 to 103 ppm was set equal to an integration of 6.12.[15,19] This value represents the six aromatic carbons plus a contribution of 0.12 per 100 aromatic units from the side chain of coniferyl alcohol and coniferaldehyde structures.[20]

Functional Groups (Methoxyl, Hydroxyl, and Carbonyl Groups)

The estimated amount of inter-unit linkages and functional groups determined for the MWL and POM-MWL via quantitative ^{13}C NMR are listed in Tables 2 and 3. The methoxyl content of the acetylated MWL and acetylated POM-MWL was determined by integrating the methoxyl peak region at 58–54 ppm to be 106 and 97 per 100 aromatic rings, respectively, (Table 3).

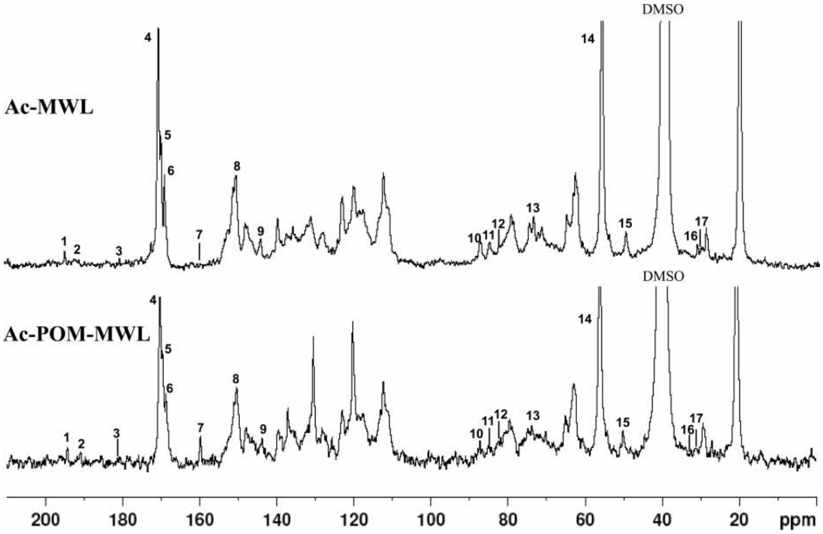


Figure 2. Quantitative ^{13}C NMR spectra for acetylated MWL and acetylated POM-MWL. (See Table 2 for peak label assignments).

These values are comparable to that obtained from ^{1}H NMR (100 and 94, respectively). The small decrease in methoxyl content between the two lignins is consistent with the demethoxylation products detected from the lignin model compound reactions.[8] In the reaction of 1-(4-hydroxyl-3,5-dimethoxylphenyl)-ethanol, demethoxylation and 1,2-benzoquinone formation was observed.[8] The detected ortho-quinone products (I in Scheme 1) indicate the initially formed phenoxy radical intermediates undergo a second electron transfer with POM followed by nucleophilic attack of water and subsequent hydrolysis of the intermediate.

^{13}C NMR analysis of the acetylated MWL and acetylated POM-MWL was also used to determine the amount of aliphatic (OH_{aliph}) and phenolic (OH_{phen}) hydroxyl groups. The aliphatic hydroxyl group content was 104 and 98 per 100 aromatic rings for the acetylated MWL and acetylated POM-MWL, respectively. These values are comparable to those determined by quantitative ^{1}H NMR, 101 and 99 per 100 aromatic rings, respectively. Similarly, the phenolic hydroxyl group content was 21 and 25 (^{13}C NMR) and 17 and 23 (^{1}H NMR) per 100 aromatic rings for the acetylated MWL and acetylated POM-MWL, respectively. The increase in phenolic hydroxyl content after POM oxidation was not anticipated, as lignin model compound studies showed the phenolic moieties react quickly with POM, the relative rate depending on the substituted groups on the aromatic ring.[8] However, in the reaction of the β-O-4 model compound 4-[2-hydroxyl-2-(4-hydroxyl-3,5-dimethoxylphenyl)ethoxyl]-3,5-dimethoxyl-benzoic acid, β-O-4 ether cleavage products 4-acetyl-2,6-dimethoxylphenol, 2,6-dimethoxyl-4-vinyl-

Table 2. Signal assignment in the ^{13}C NMR spectrum of acetylated MWL and POM-MWL.[15,16,19,23]

Peak label	Chemical shift range (ppm)	Spectral region assignment	MWL (per 100 Ar)	POM-MWL (per 100 Ar)
1	196–193	CO in α-CO/β-O-4(**D**), **L**	3	6
2	193–191	Ar-CHO(**M**)	1	2
3	182–180	C-4 in **I**	1	1
4	171.3–170.1	Primary aliphatic OH	73	69
5	170.1–169.3	Secondary aliphatic OH	31	29
6	169.3–168	Phenolic OH, conjugated COOR	21	25
7	162–160	Unknown	—	8
8	162–148.5	All C-3 (except **E** and *p*-hydroxyphenyl-units), C-5 in **S**, C-α in **L**, C-5 in **I**, C-4 in conjugated CO/COOR etherified and *p*-hydroxyphenyl-units	106	93
9	144.5–142.5	C-3 in **E**, C-4 in conjugated $\mathbf{S_I}$, unknown	8	7
10	87.8–86	C-α in **E**	10	9
11	85.3–84.7	C-α in **F**, **G**	10	8
12	83.2–81.5	C-β in **G**	4	4
13	77–72.5	C-α in **A**, **H**, **P**, carbohydrates	42	30
14	58–54	OMe, C-1 and C-β in **I**	108	98
15	50.7–49	C-β in **H**, **E**	12	10
16	34–33.4	C-α in **J**	1	1
17	32.5–31.5	C-α in **Q**	1	1
Clusters				
	125–103	$C_{Ar\text{-}H}$	261	255
	90–58	Alk-O-	215	196
	90–77	Alk-O-Ar, α-O-Alk	69	64
	77–65	γ -OAlk, OH_{sec}	63	58
	65–58	OH_{prim}	80	74

—Absent or too small for interpretation (see Figure 3 for substructure identity).

phenol and 4-hydroxyl-3,5-dimethoxyl-benzoic acid were observed.[8] Moreover, the reaction rate of the α-CO guaiacyl-type model compound 4-acetyl-2-methoxylphenol was the slowest among all the guaiacyl-type model compounds investigated. Therefore, the observed increase in phenolic hydroxyl content after POM oxidation may be a result of the formation of phenolic moieties containing α-carbonyl groups. In addition, the heterogeneous

Table 3. Quantification of inter-unit linkages and so on in MWL and POM-MWL via quantitative ^{13}C NMR[15]

Structure	Calculation	MWL (per 100 Ar)	POM-MWL (per 100 Ar)
β-O-4/α-OH (**A**)[a]	(77–72.5 ppm)-**H**-**P**-3(sugar)	40	29
Spirodienone (**I**)	(182–180 ppm)	1	1
Phenylcoumaran (**E**)	(87.8–86 ppm)	10	9
Dibenzodioxocin (**G**)[b]	(85.3–84.7 ppm)-**F***	10	8
β-1 (**H**)	(50.7–49 ppm)-**E**	2	1
Methoxyl groups	(58–54 ppm)-**H**	106	97
Phenolic hydroxyl groups	Quantitative ^{1}H NMR	17	23
Degree of condensation	3-(125–103 ppm)	39	46

[a] Overestimated because **P** + 3 (sugar) were not included.

[b] Overestimated because **F** was not included (see Figure 3 for substructure identity).

nature of the reaction system may further affect the reactivity of the MWL as compared to the model compound studies.

Comparison of the carbonyl region (196–191 ppm) of the quantitative ^{13}C NMR spectra (Figure 2) for the acetylated MWL and acetylated POM-MWL confirms oxidation of the MWL during the reaction with POM. Integration of this region indicates the number of carbonyl structures doubles from 4 to 8 per 100 aromatic rings (Table 2). Of these, aldehyde groups such as in vanillin (**M**) constitute 1 and 2 per 100 aromatic rings for MWL and POM-MWL, respectively. Similarly, carbonyl groups such as those found in coniferaldehyde (**L**) and α-CO/β-O-4 (**D**) moieties were calculated to be 3 and 6 per 100 aromatic rings for MWL and POM-MWL, respectively (Table 2). The increased levels of oxidized carbon structures in the POM-MWL are supported by the model compound studies.[8] The major reactions of α-hydroxyl or α-alkoxyl monomeric and β-O-4 dimeric lignin model compounds were sequential electron-transfer reactions and carbonyl group formation (Scheme 1). In fact, the predominate degradation product detected from the POM oxidation of (4-[2-hydroxy-2-(4-hydroxy-3,5-dimethoxyphenyl)ethoxy]-3,5-dimethoxy-benzoic acid), an α-OH/β-O-4 model compound was 4-[2-(4-Hydroxy-3,5-dimethoxy-phenyl)-2-oxo-ethoxy]-3,5-dimethoxy-benzoic acid, the corresponding α-CO/β-O-4 compound (III in Scheme 1).[8] In fact, as shown in Figure 2 two strong peaks around 120.3 and 130.6 ppm were observed in the quantitative ^{13}C NMR spectrum of the POM-MWL. The two peaks can be assigned to the aromatic carbons associated with the C2 and C6 position of the aromatic ring in phenolic α-CO moieties. Furthermore, it is likely that the POM

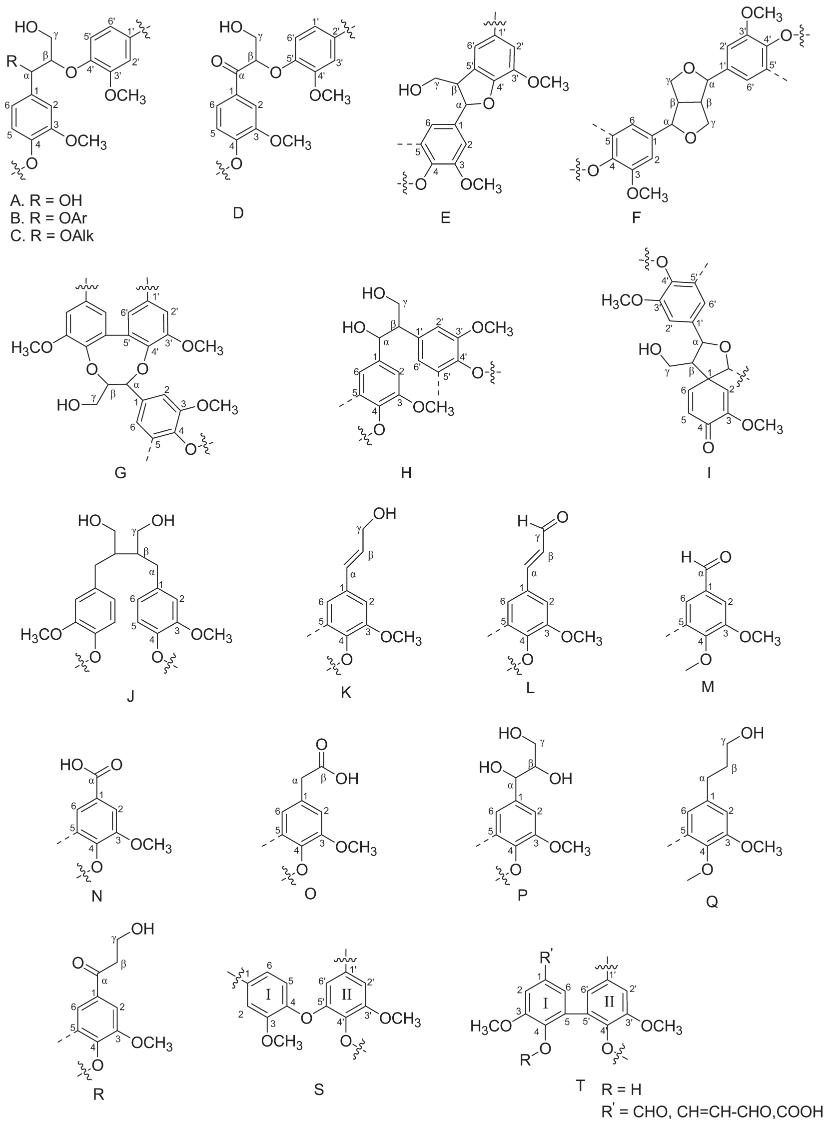


Figure 3. Lignin substructures.[17]

oxidation of MWL involves the degradation of other inter-unit linkages and the formation of smaller lignin moieties with carbonyl groups.

β-O-4 Inter-unit Linkage

The major inter-unit linkage in lignin is the *β*-O-4 bond, which accounts for approximately 48% and 60% of the inter-unit linkages in softwood and hardwood lignins, respectively.[21] ^{13}C NMR analyses determined the total amount of identified β-O-4 moieties (**A**, **D**, and **G**) to be approximately 55 per 100 aromatic rings in the MWL and 44 per 100 aromatic rings in the POM-MWL. The β-O-4/α-OH (**A**) linkages decreased from approximately 40 per 100 aromatic rings in the MWL to 29 per 100 aromatic rings in the POM-MWL. Similarly, the amount of dibenzodioxocin (**G**) units decreased from approximately 10 per 100 aromatic rings in the MWL to 8 per 100 aromatic rings in the POM-MWL. By contrast, the β-O-4/α-CO (**D**) moieties increased from 3 to 6 per 100 aromatic rings after POM oxidation of MWL. Even though the amount of total amount of β-O-4 inter-unit linkages are overestimated (Table 3),[15] the large decrease in the amount of β-O-4/α-OH linkages in the POM-MWL may be due to some of the β-O-4 containing MWL fragments, being less condensed, become soluble in the reaction media; as approximately 10 wt% MWL was lost after POM oxidation.

Aromatic Carbons and Degree of Condensation

The aromatic region of the quantitative ^{13}C NMR spectrum can be divided into oxygenated aromatic carbons (162–141 ppm), condensed aromatic carbons (141–125 ppm), and protonated aromatic carbons (125–103 ppm). The degree of condensation was calculated using the protonated aromatic region (125–103 ppm) due to some ambiguity in the condensed aromatic carbon region (141–125 ppm region), which has overlapping vinylic carbons from coniferyl alcohol (**Q**) moieties and the β-carbon in coniferaldehyde (**M**).[19] The protonated aromatic region consists of methine carbons (C2 and C6) and any protonated C5 carbons, which are not expected to contain overlapping signals. Softwood lignin primarily consists of guaiacyl phenylpropanoid units that contain a methoxyl and a phenolic hydroxyl group at C3 and C4, respectively. Thus, an uncondensed softwood lignin will contain three protonated aromatic carbons per aromatic ring (C2, C5, and C6). The degree of condensation is calculated by subtracting the integral of this region (125–103 ppm) from 3.[17] Integration values obtained for the MWL and POM-MWL indicate a degree of condensation of 39 and 46 per 100 aromatic rings, respectively (Table 3). However, the degree of condensation of the POM-MWL may be slightly overestimated as the signal observed at 120.3 ppm can be assigned to the aromatic carbons at C2 and C6 of α-CO side-chain containing moieties (discussed earlier).

In the reaction of simple model compounds,[8] POM oxidation of cresol and acetovanillone led to primarily dimeric coupling products, however, the reaction of the condensed biphenol-type compound (3,3′-dimethoxyl-5,5′dimethyl-biphenyl-2,2′-diol) was extremely fast toward POM. The increase in the degree of condensation after POM oxidation suggests that the condensed structures are likely less reactive towards POM, either because of their structure (α-carbonyl, etc.) or the heterogeneous nature of reaction system.

Other Lignin Structures

One unknown structure was observed in the MWL after POM oxidation. This chemical shift range has been reported to correspond to the C4 carbon in p-hydroxylphenyl units. However, integration of the acetylated POM-MWL spectrum indicates approximately 8 per 100 aromatic rings. This integral is too high to be an apparent enrichment of p-hydroxylphenyl lignin moieties. In order for the group to be enriched to 8 per 100 aromatic rings, the yield of MWL on oxidation would have to be 25% or lower rather than the 90% as observed. Therefore, peak 7 may be noise, an impurity or another unknown structure.

FTIR Analyses of MWL and POM-MWL

Figure 4 shows the FTIR spectra of the MWL before and after oxidation by POM. Relative differences between the MWL and POM-MWL spectra can be seen in the band envelopes associated with the carbonyl stretching region ($\nu_{C=O} \sim 1650-1850\,\text{cm}^{-1}$). The other major IR absorption bands, for example aromatic C-H out-of-plane deformation (guaiacyl-type) region at $1140-800\,\text{cm}^{-1}$, aromatic C=C bond stretching region at $1600-1500\text{cm}^{-1}$, and hydroxyl stretching region ($\nu_{OH} \sim 3700-3100\,\text{cm}^{-1}$) do not appear to differ significantly between the MWL and POM-MWL.[22] The similarity between the hydroxyl stretching region of the MWL and POM-MWL is consistent with the results determined by quantitative ^{1}H and ^{13}C NMR.

To quantify the differences between the carbonyl stretching region ($1650-1850\,\text{cm}^{-1}$) of the MWL and POM-MWL, deconvolution was performed using Peak Fit software. Analysis of the second derivative spectra for both samples detected 3 band centers. Application of Gaussian peak shape assumptions and full width at half maximum (fwhm) of $30\,\text{cm}^{-1}$, minimized potential overfitting of the data.[13] Figure 5 shows the

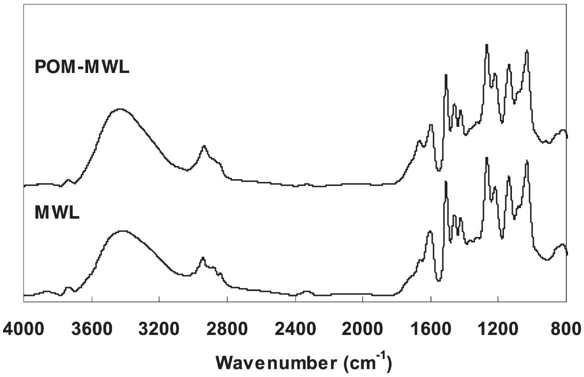


Figure 4. FTIR spectra of MWL and POM-MWL.

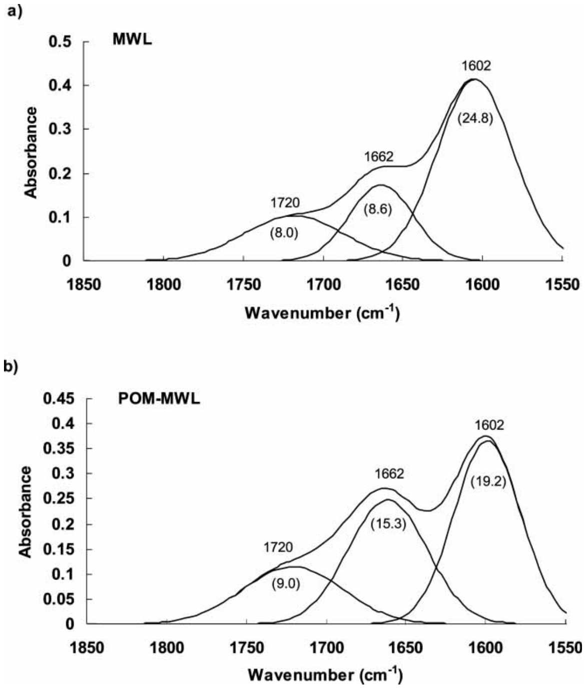


Figure 5. Deconvoluted FTIR spectra of the carbonyl stretching region ($\nu_{C=O}$) of a) MWL and b) POM-MWL. *Value in parenthesis indicates IR band area.

deconvoluted carbonyl stretching region of the MWL and POM-MWL. Three distinct stretching bands were detected at 1720, 1662, and 1602 cm^{-1}, corresponding to unconjugated, conjugated, and aromatic skeletal vibtrations plus carbonyl stretching, respectively.[22] It is clearly evident that the largest change occurs in the band associated with the conjugated carbonyl structures at ~1662 cm^{-1}, where a nearly 78% increase in the absorbance of this band occurs. This is in agreement with ^{13}C NMR analysis and the oxidation of α-OH groups to α-CO groups. In fact, in the reaction of β-O-4 lignin model compounds,[5,8] the major oxidation pathways involved the formation of α-carbonyl groups via sequential electron-transfer reactions (Scheme 1).

Molecular Mass Distributions

The molecular mass distributions for the MWL before and after POM oxidation is shown in Figure 6. The POM-MWL clearly has a slightly broader molecular mass distribution and the presence of higher molecular mass material as compared to the MWL. This is expected based on the change in β-O-4 content and the degree of condensation estimated by

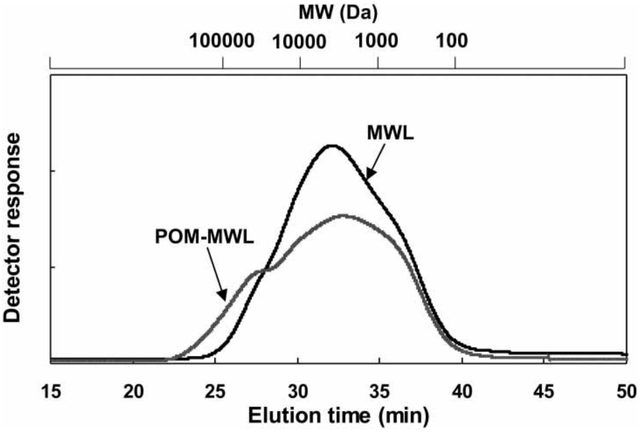


Figure 6. Molecular weight distributions of acetylated MWL and POM-MWL.

quantitative ^{13}C NMR. Thus, in addition to the oxidative degradation of the lignin, some oxidative coupling of the generated phenoxy radical intermediates occurs. However, it is not known if the residual lignin in pulp would undergo the same condensation reactions and molecular mass distribution increases. It is likely that the condensed lignin structures observed during the POM oxidation of MWL may not occur to as significant a degree with pulp, as the generated lignin radicals will be immobilized within the cell wall structure, and potentially precluded from undergoing coupling reactions.

CONCLUSIONS

Changes to the chemical structure of MWL as a result of POM oxidation under heterogeneous conditions were investigated using spectroscopic techniques. Quantitative ^{13}C NMR showed that POM oxidation of lignin results in the degradation of β-O-4 inter-unit linkages. POM oxidation leads to side chain oxidation and/or degradation of dibenzodioxocin and α-OH/β-O-4 inter-unit linkages, as well as increasing carbonyl and phenolic hydroxyl groups. FTIR analysis showed an increase in the carbonyl stretching region ($\nu_{C=O} \sim 1650$–$1850\,\text{cm}^{-1}$) associated with para-substituted aryl ketones, which is consistent with results estimated by quantitative ^{13}C NMR and model compound studies.

In addition to oxidative degradation of inter-unit ether linkages, quantitative ^{13}C NMR analysis showed an increase in the degree of condensation. GPC analysis revealed a change in the relative molecular mass distribution and the presence of higher molecular mass material after POM oxidation. Together, these results support the findings from previous lignin model compounds wherein radical coupling reactions and the formation of dimeric products dominate.

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