Studies of lignin transformation in polyoxometalate (POM) bleaching of kraft pulp

BILJANA BUJANOVIC[1]*, RICHARD S. REINER[2], KOLBY C. HIRTH[2], SALLY A. RALPH[2], RAJAI H. ATALLA[1,2]

[1]Department of Chemical and Biological Engineenng, University of Wisconsin Madison, Madison, WI, USA

[2]USDA Forest Service, Forest Products Laboratory, Madison, WI, USA

*e-mail bujanovic@wisc.edu

ABSTRACT

In order to elucidate changes occurring in lignin during polyoxometalate delignification of kraft pulp, residual lignins of a series of POM-delignified kraft pulps of decreasing kappa number were isolated and characterized. Oxidative treatment of commercial unbleached kraft pulp was performed using complex POM solutions containing the active $[SiVW_{11}O_{40}]^{5-}$ anion. For comparison, oxygen delignification of the same kraft pulp was also performed. It was observed that POM-delignification results in lignin which is more closely associated with carbohydrates/glucose, especially in the early phase of delignification. Residual lignin after POM treatment was characterized by lower phenolic hydroxyl group content than those of kraft and kraft oxygen-delignified pulp, which corroborates the preferential attack of POMs on the phenolic lignin units. The dominant lignin product identified in the POM solution after delignification was vanillin, which is an oxidation product of uncondensed G-units and indicates cleavage of C_α-C_β and/or aryl-ether bonds.

INTRODUCTION

Environmental concerns have driven the pulp and paper industry to examine new chlorine-free bleaching technologies. Our research has focused on polyoxometalates (POMs), after it was found that different mixed-addenda hetero polyanions of the Keggin type are capable of oxidizing lignin while leaving cellulose undamaged. A selective kappa number decrease for unbleached kraft pulp from 30 to <5 has been achieved in bleaching experiments with a variety of POM formulations [27].

The promising results for selective oxidative delignification with POMs prompted interest in elucidating the mechanism of lignin oxidation. The reactivity of phenolic and non-phenolic lignin structural units has been studied using monomeric and dimeric lignin model compounds (LMCs) [14, 28, 29]. These studies imply that phenolic hydroxyl groups in residual lignin are substrates for POM anions. The phenolic lignin dimers, characteristic of both native (β-O-4) and residual (diphenylmethane) lignins, were exposed to $[SiVW_{ii}O_{40}]^{5-}$ attack at room temperature. The observed products, such as *p*- and *o*-quinones and α-carbonyl compounds, suggest that degradation may occur via sequential single-electron oxidation reactions, followed by the hydrolysis of cationic intermediates. By contrast, experiments with non-phenolic lignin model compounds and $Na_{5(+1.9)}[SiV_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ showed that reaction occurs only at elevated temperatures. Oxidation of a benzylic C-H bond to give a benzylic radical was proposed as a rate-determining step in the experiments with non-phenolic LMCs possessing a-hydroxyl groups. It was also proposed that the hydrogen atom on C_β in α-carbonyl structures of lignin polymer may be a critical factor in the oxidative degradation of lignin by POM oxidants.

Phenoxyl radicals, which are initially formed under the attack of POM anions, are reactive in both degradation and coupling (condensation) reactions. Although the observed decrease of kappa number indicates degradation oxidation reactions prevail, the type and extent of degradation and condensation reactions have not been studied for kraft pulp treated with POMs under anaerobic conditions. Lignin oxidation in the presence of POMs under aerobic conditions, however, showed that residual lignin undergoes both degradation and condensation reactions, and the condensation reactions are suggested to occur in the positions C5 of guaiacyl (G-) and C6 of syringyl (S-) units [5].

Results obtained on LMCs represent important information about the lignin reaction pathways. However, LMCs do not reflect the behavior of lignin as a macromolecule in the pulp matrix, especially regarding competition of degradation and condensation reactions. The main goal of this study was to better understand the POM oxidation chemistry in residual lignin of kraft pulp. Residual lignins from a series of kraft POM-bleached pulps of gradually decreasing kappa number were isolated by acid hydrolysis and characterized by analytical and spectroscopic methods. For comparative purposes, residual lignins of kraft and kraft oxygen-bleached pulps were studied using the same methods.

Characterization of the lignin degradation products dissolved during POM delignification

also represents a helpful method in understanding the mechanism of POM-oxidative degradation of lignin. Therefore, some exploratory GC-MS experiments are included to study the solution after the POM delignification of kraft pulp.

EXPERIMENTAL

Materials

Kraft pulp (K) used in these experiments was commercial softwood of 30.5 kappa number (stored at 8°C).

Delignification Experiments: Kraft pulp was delignified by both oxygen and the POM mixture using a 2L horizontal Parr reactor configured with anchor stirrers.

The POM delignification of the kraft pulp was conducted under anaerobic conditions, using an equilibrated POM mixture composed of 0.5M $Na_{5(+1.9)}[SiV_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$, at 12% pulp consistency. The pH range of 5.5-6.5 was controlled by equilibration reactions of the POM [25]. The temperatures (100-140°C) and times (10-240 min) of the reactions were adjusted to produce six kraft POM-bleached pulps of various kappa numbers in the 28.1-10.8 range (KPOM).

The oxygen delignification of kraft pulp was performed using the conditions described previously [1]. Three kraft oxygen-bleached pulps of kappa number in the range of 25.2-16.9 were obtained (KOx).

Residual Lignin Isolation: Before isolation of residual lignin (RL), the pulps were extracted with dichloromethane and acetone (Soxhlet extractor, 8 h).

Acid hydrolysis was conducted following the procedure suggested by Gellerstedt et al. [9]. Slight modification of this original method was performed in the first step after pulp hydrolysis. Before evaporation, the filtrate was neutralized with sodium bicarbonate and filtered [7]. After isolation, residual lignins were extracted in dichloromethane in order to remove any remaining extractives [1].

Lignin Degradation Products Dissolved in POM solution: After POM delignification of kraft pulp, from kappa number 30.5 to kappa number 23.9, the low molecular weight degradation products were extracted from the solution with three organic solvents of decreasing polarity: ether, chloroform, and ethyl acetate. Before extraction, the solution pH was adjusted to 2, stored for 12h at 8°, and filtered (glass filtering crucible, fine (F) porosity).

Methods

Kappa Number, Klason/Acid Soluble Lignin, Carbohydrates: Kappa number and the contents of Klason and acid-soluble lignin in the original kraft and POM- and oxygen-bleached pulps were determined. Residual lignins obtained by acid hydrolysis were analyzed with respect to Klason/acid-soluble lignin and carbohydrates [3,4].

$KMnO_4$ Consumption: To evaluate the level of the oxidizable lignin structures, the consumption of $KMnO_4$ of the isolated lignins was measured [18, 19]. These values were compared to each other and to those obtained for lignin model compounds/lignins selected from the USDA Forest Service, Forest Products Laboratory (FPL) collection.

Phenolic Hydroxyl Groups: PhOH-group content of the residual lignins was measured using the ionization difference UV-spectroscopic method. This method uses three lignin solutions of different pH (pH6, pH12, 0.2M NaOH) and applies the UV-absorbance at 300 and 350nm of these solutions in equations that were developed based on the molar extinction values of typical phenolic lignin model compounds [8]. The UV-absorption measurements were conducted on a Spectronic Genesys 5 spectrophotometer.

FTIR Spectroscopy: The FTIR spectra of residual lignins were recorded using the KBr transmission technique on a Mattson-Galaxy Series FTIR 5000 spectrometer (200 scans at 4 cm^{-1}).

NMR Spectroscopy: 2D NMR spectra were run on a Bruker DPX-250 spectrometer using standard Bruker sequences. A quadranuclear 5-mm probe with a Z-gradient coil was used for all samples. The samples (~50mg) were dissolved in 400 µl of acetone-d_6/D_2O (4:1). The central solvent peak (δ_H 2.04, δ_C 29.83) was used as the internal reference.

GC-MS Analysis: The chloroform extract of the POM solution resulting from kraft pulp delignification from kappa number 30.5 to 23.9 was analyzed by GC-MS without derivatization. The GC-MS analysis was performed using a GCQ ion trap (ThermoElectron Austin, TX). A 30-m ZB-5MS column (0.25mm i.d., 0.25-um film thickness) was used with constant helium flow of 40cm/s. The oven temperature was 40-280°C. ramped at 20°C/min using a splitless injection. The injector temperature was 250°C and the transfer line 275°C. Data were obtained in EI mode at 70eV scanning from 50-450 in 0.46s.

RESULTS AND DISCUSSION

Kappa Number and Lignin Content

Delignification experiments performed in this study resulted in POM- and oxygen-bleached pulps that were characterized by determination of kappa number and the contents of Klason and acid-soluble lignin (Table I).

Table I. – Kappa Number, Klason and Acid-Soluble Lignin Content of Studied Pulps

Pulp	Kappa	Lignin % OD Pulp	
		Klason	AS
Kraft (K)	30.5	4.75	0.67
Kraft-POM (KPOM)	28.1	4.40	0.64
	23.9	4.10	0.58
	20.8	3.60	0.62
	16.2	2.70	0.62
	13.0	2.30	0.58
	10.8	2.00	0.70
Kraft-Oxygen (KOx)	24.2	3.80	0.67
	21.0	3.40	0.65
	16.9	2.65	0.71

Conversion factors (CFs) between kappa number and Klason lignin content were also calculated (Fig. 1). CF was almost constant during oxygen delignification, and only a slight increase of CF was observed for KOx21.

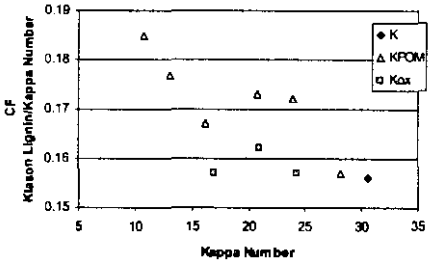

Fig. 1. Conversion Factors Between Kappa Number and Klason Lignin Content for K, KPOM, and KOx pulps

By contrast, CF for KPOM increased as kappa number decreased. This difference indicates that POM delignification resulted in much higher reduction of the total amount of oxidizable structures than oxygen delignification. Hexenuronic acid groups, which are $KMnO_4$ oxidizable structures and are stable toward oxygen delignification, could only partially account for the observed difference due to the softwood origin of pulps [12, 17]. Also, ring cleavage products formed during oxygen delignification, such as muconic acid, undergo oxidation with $KMnO_4$ and contribute to the kappa number value and reduction in CF [19]. The observed difference in CF for KOx and KPOM pulps seems to be result of different lignin structure characteristic of KOx and KPOM pulps.

Although the value chosen for lignin absorptivity represents a critical factor in the calculation of the acid-soluble lignin content [4], the observed increasing ratio of the acid-soluble to Klason-acid-insoluble lignin as kappa number decreased might indicate more oxygenated lignin structure and formation of bonds between lignin and carbohydrates may also increase the filtrate UV-absorption during the Klason lignin procedure [4].

Residual Lignin

Yield, Composition: The residual lignin isolation yield for the KPOM pulps was lower than those for the K and KOx pulps (Table II). The reduction in yield of isolated residual lignin might indicate a closer association of lignin and carbohydrates and/or a more condensed, less soluble lignin in the KPOM pulps. In support of the former, carbohydrate analysis of RL's showed that the total carbohydrate content in RLKPOM was greater than that in both RLK and RLKOx. The highest carbohydrate content was found in RLKPOM23.9 and RL of the KPOM pulps of lower kappa number were characterized by much lower carbohydrate content. This suggests that the association between lignin and carbohydrates was strongest in the initial phase of POM delignification. It seems that glucose plays a dominant role in this association, because it represents the dominant monosaccharide in all the RLKPOM (47-91% of total RL carbohydrates).

Table II. Yield and Composition of RL's

RL	Yield %[1]	% RL				
		Lignin		Carbohydrates		Total
		Kl	AS	Glu	Total[2]	
K30.5	58.5	92.8	0.77	0.53	0.85	94.4
KPOM						
28.1	23.3	87.1	1.34	2.90	3.56	92.0
23.9	27.6	86.3	1.51	4.36	4.78	92.6
20.8	18.4	87.1	1.89	1.57	2.21	91.2
16.2	17.5	81.1	2.92	1.95	3.30	87.3
13.0	25.3	78.5	4.63	1.43	2.54	85.7
10.8	26.8	78.4	5.11	1.05	2.23	85.7
KOx						
24.2	46.7	95.2	1.03	0.70	1.18	97.4
21.0	46.6	93.9	1.34	0.57	1.31	96.6
16.9	48.4	94.5	1.07	0.31	0.98	96.6

[1]yield in % of Klason lignin in pulp
[2]sum of Gal, Glu, Man, Ara, and Glu

The content of acid-soluble lignin in RLKPOM increased, but for the reasons mentioned previously, these values should be verified by determining the absorptivity value for each lignin sample separately. Nevertheless, the sum of the content of total lignin and carbohydrates, which was gradually

reduced as kappa number decreased, may suggest a more intense lignin modification and/or stronger association between lignin and carbohydrates in the later phase of POM delignification (Table 11).

$KMnO_4$ Consumption: POM delignification resulted in an increase of the conversion factor (CF=Klason Lignin/Kappa Number) (Fig. 1). Therefore, level of oxidizable structures was evaluated by measuring $KMnO_4$ consumption for isolated residual lignins [18, 19]. RL's consumption of $KMnO_4$ decreased with decreasing kappa number, and this trend was more pronounced for POM than for oxygen delignification (Fig. 2).

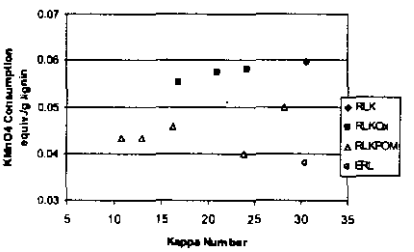

Fig. 2. $KMnO_4$ consumption of RLK, RLKOx, RLKPOM, and ERL vs. pulp kappa number; ERL - residual lignin isolated by enzymatic hydrolysis from loblolly pine kraft pulp of kappa number 30.4 [23]

To further clarify this finding, a series of lignin model compounds was analyzed. Biphenyl model compounds (C5-C5') consumed about 0.071equiv.$KMnO_4$/g, while a diphenylmethane (C5-CH_2-C5') compound consumed 0.0659equiv.$KMnO_4$/g. These values were slightly lower than those found for β-O-4 models in previous studies [18]. These results imply that a more condensed lignin structure would consume a lower amount of $KMnO_4$. (C5-C5' compounds dehydrodipropio vanillone and dehydrodipropyl guaiacol consumed 0.0691 and 0.0720equiv.$KMnO_4$/g, respectively; C5-CH_2-C5' compound was di-(4-allyl-2-methoxyphenol) methane; $KMnO_4$ consumption for β-O-4 compounds 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) ethanone and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) ethanol was 0.0755 and 0.0737equiv.$KMnO_4$/g, respectively [18]).

The slight decrease in $KMnO_4$ consumption for RLKOx would be a combined effect of a more oxidized lignin structure [19] and a greater content of biphenyl structures [1]. The even lower consumption of $KMnO_4$ observed for RLKPOM could be due to either more oxidized or more condensed lignin structure.

Carbohydrates remaining in residual lignin also result in a decrease of the $KMnO_4$ consumption as they are stable toward $KMnO_4$ oxidation. Our studies showed that residual lignin of high carbohydrate content isolated by enzymatic hydrolysis from loblolly pine kraft pulp (ERL) consumed a factor of 1.6 less $KMnO_4$ than residual lignin isolated by acid hydrolysis from commercial kraft pulp (RLK30.5) (Fig. 2; ERL from the FPL collection, kappa number of pulp 30.4, carbohydrate content 8.2% ERL [23], RLK30.5 produced in this study, carbohydrate content 0.85% RL). Therefore, a lower $KMnO_4$ consumption observed for RLKPOM may also be explained by a greater carbohydrate content of these lignins (Table II).

Phenolic Hydroxyl Groups: The content of phenolic hydroxyl groups in the residual lignins was determined using the ionization difference UV-method. This method results in 15-20% lower values than aminolysis due to an incomplete ionization of the compounds with more than one hydroxyl group in proximity, e.g, catechol and phenolic biphenyl structures. Nevertheless, this method is reliable for following trend in PhOH-group content for various lignins [8, 26]. Progressive delignification caused a decrease in the RLPhOH content for both KOx and KPOM (Fig. 3). This was an expected result of oxygen delignification, because oxygen-based reactive species primarily attack phenolic units [1].

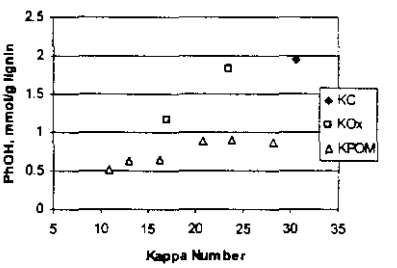

Fig. 3. PhOH-group content of RL vs. kappa number in POM/oxygen-delignification

A decrease in the PhOH-group content was also expected with POM delignification because results obtained with LMCs suggested that phenolic units are readily oxidized with POMs [14, 28]. The initial period of POM delignification was characterized by an intense reduction of the PhOH-group content followed by a period of stabilization, which is indicative of newly formed phenolic hydroxyl groups, i.e., cleavage of aryl-ether bonds (β-O-4, 4-O-

5) leading to the stabilization of the PhOH content.

FTIR-Spectroscopy: The FTIR spectra of all isolated residual lignins contained typical lignin bands (1600, 1510, 1460, 1420, 1365, 1270, 1220, 1140, 1085, 1035cm.$^{-1}$) [6]. The FTIR spectra of RLK30.5, RLKPOM20.8, and RLKOx21.0 are presented in Fig. 4.

The clear presence of a band at 1140cm^{-1}, characteristic only of G-lignins [6], indicates the softwood origin of these lignins. In the carbonyl group area, the spectrum for RLK30.5 indicates the presence of conjugated *p*-substituted aryl ketones by a band at 1685cm^{-1}, and all the RLKPOM and RLKOx spectra of contain a bandshoulder at 1712cm^{-1} that is assigned to unconjugated carbonyl groups. The absorbance ratios of these bands to 1510cm^{-1} increase with progress of both POM and oxygen delignification, which is consistent with the oxidative nature of these two processes. Unfortunately, unconjugated carbonyl groups may also be formed during acid hydrolysis as a result of the β-O-4 cleavage reaction [IO]. Therefore, an observed increase in the content of unconjugated carbonyl groups in kraft and kraft-POM/Oxygen pulps can not be attributed solely to the delignification process.

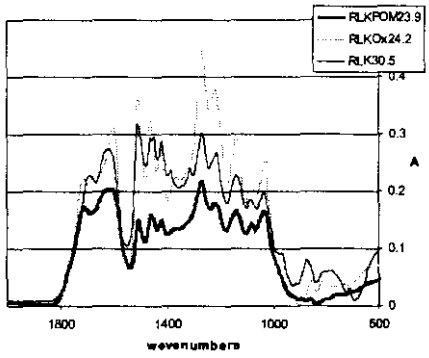

Fig. 4. FTIR-Spectra of RL of kraft (kappa number 30.5). kraft-oxygen (kappa number 21.0), and kraft-POM (kappa number 20.8) pulps

The RLK30.5 spectrum clearly exhibits two bands characteristic of a double bond conjugated with an aromatic ring, i.e., stilbene structure (-C_α=C_β- stretching vibration and =$C_{\alpha,\beta}$-H out-of-plane deformation, 1617 and 967cm^{-1}, respectively [10, 11]). The presence of stilbene structures in RLK30.5 was expected because kraft pulping results in formation of this type of conjugated/chromophoric structure [16]. The absence of both bands in RLKOx spectra confirms the reactivity of stilbene structures during oxygen delignification [13]. Spectra of KPOM pulp residual lignins during initial phase of delignification (RLKPOM28.1-20.8) contain a band at 1620cm.$^{-1}$ but clearly lack a band in the 990-960cm.$^{-1}$ region. Absence of this =$C_{\alpha,\beta}$-H deformation band might indicate either substitution on the conjugated ethylenic bond or very low content of a structure possessing a double bond conjugated with an aromatic ring. As POM delignification progressed, the 1620cm^{-1} band was also absent from the FTIR spectra of RLKPOM16.2-10.8, This corresponds with HSQC data, as noted later in the NMR section.

The increase of the ratios A_i/A_{1510} (i, cm^{-1}-characteristic lignin band; 1510cm^{-1} aromatic skeletal vibration band is usually a reference band in lignin studies [6]) was observed with the progression of both POM and oxygen delignification, and is consistent with aromatic ring cleavage during oxygen delignification [2]. A similar trend observed after the white-rot fungi decomposition of lignin was offered as evidence of a lower content of aromatic nuclei [15]. Notably, the POM delignification of kraft pulp in our experiments resulted in a greater increase of these ratios, which along with a decrease of the PhOH content (Fig. 3), might indicate comparatively more intense ring cleavage.

The A_{1600}/A_{1510} ratio is particularly affected in POM delignitication (Fig.5), which represents the plot of these ratios calculated for the RLK, RLKPOM, and RLKOx vs. kappa number.

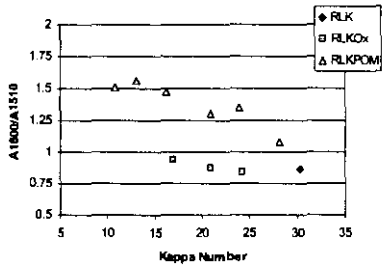

Fig. 5. A_{1600}/A_{1510} ratio of RL's vs. kappa number

The A_{1600}/A_{1510} ratio is dependent on the electronic effects of the ring substituents, i.e., the A_{1600}/A_{1510} ratio is influenced by the ratio of electron-donor and electron-acceptor groups and their position on the aromatic ring. An increase of this ratio was noted previously, e.g. in the (FT)IR spectra of Brauns type lignins, for LMCs with increasing number of C-O bonds, and for fossil wood. This has been interpreted as a consequence of the presence of lignin impurities of phenolic extractives and

carbohydrate nature, and as evidence of lignin oxidation, i.e., high content of carbonyl/carboxyl groups in lignin. The intensification of the 1600cm^{-1} band was also interpreted as a result of progressive substitution of the aromatic ring [10, 11, 22]. Lignin structure rich in carbonyl/carboxyl groups and/or characterized by more substituted aromatic rings would also be consistent with a lower consumption of $KMnO_4$ observed for RLKPOM (Fig. 2).

NMR-Spectroscopy : Changes in the lignin structure during POM delignification were elucidated by observing the HSQC-NMR spectroscopic characteristics (inverse detected short range C-H correlations) of isolated residual lignins and the loblolly pine MWL. The HSQC spectra of MWL, RLK30.5, RLKPOM28.1, RLKOx16.9, and RLKPOM16.2 are presented in Figs. 6-10. Signal assignments were based on published data for lignins/ LMCs [20, 24].

Major structures that characterize MWL lignin were still present in most of the residual lignins isolated in this study (Table III).

Table III. Some important side-chain structures as observed by HSQC in MWL and residual lignins

	Observed $^{13}C/^{1}H$ correlations								
structure	β-O-4 (C_α -OH)			β-5			β-β		
MWL/RL	α	β	γ	α	β	γ	α	β	γ
MWL	+	+	+	+	+	+	+	+	+
RLK30.5	+	+	+	+	+	+	+	+	+
RLKPOM									
28.1	+	+	+	+	+	+	±	+	-
23.9	+	+	+	+	-	+	±	±	-
20.8	+	±	+	-	-	+	-	±	-
16.2	+	+	+	-	+	+	-	±	-
13.0	+	-	+	-	-	+	-	-	-
10.8	+	-	+	-	-	-	-	-	-
RLKOx									
24.2	+	+	+	+	+	+	+	+	+
21.0	+	+	+	+	+	+	+	+	+
16.9	+	+	+	+	+	+	+	+	+

(+ correlation clearly observable; ± only a small correlation observable; - no correlation observed)

Table III does not include the β-O-4 (C_α =O) and trans-dibenzodioxicin Structures as they were detected only in MWL and not in residual lignins, except that the trans-dibenzodioxicin correlations were still detectable in RLK30.5. The correlations observed for β-O-4 (C_α -OH), β-5, and β-β structures in MWL were still quite distinct in RL of kraft oxygen-delignified pulps of decreasing kappa number, but much less intense in RL of KPOM pulps of decreasing

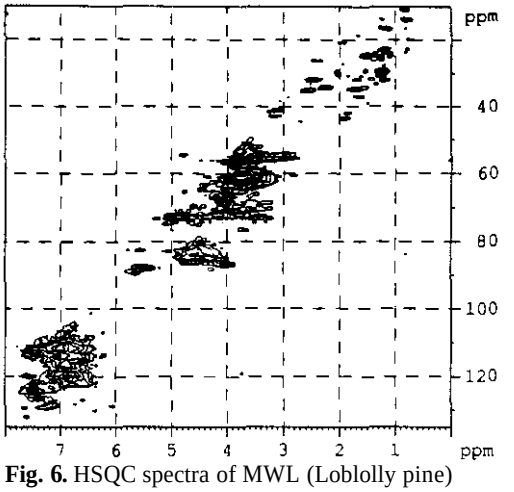

Fig. 6. HSQC spectra of MWL (Loblolly pine)

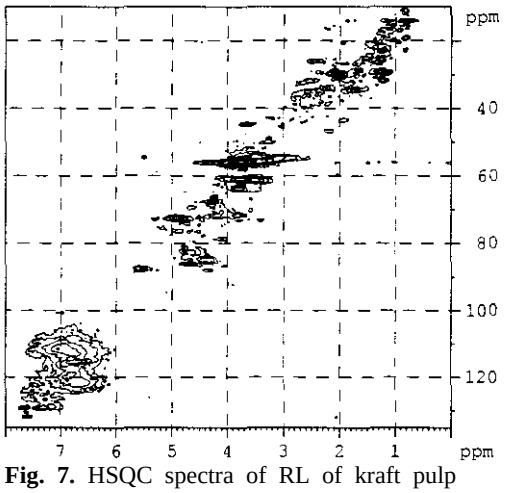

Fig. 7. HSQC spectra of RL of kraft pulp (kappa number 30.5)

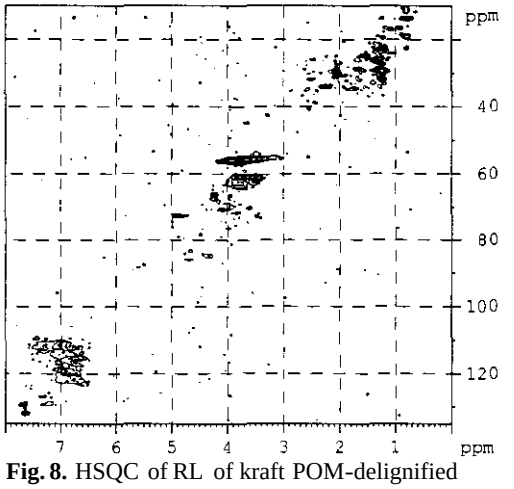

Fig. 8. HSQC of RL of kraft POM-delignified pulp (kappa number 28.1)

kappa number. Furthermore, our results may suggest that the stability of these three lignin linkages during POM delignification decreases in the following order: β-O-4 > β-5 > β-β.

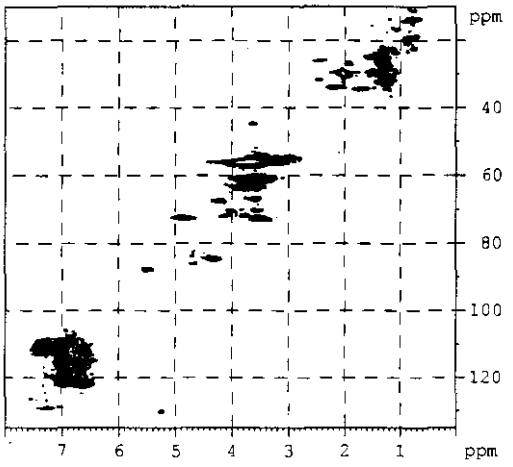

Fig. 9. HSQC of RL of kraft oxygen-delignified pulp (kappa number 16.9)

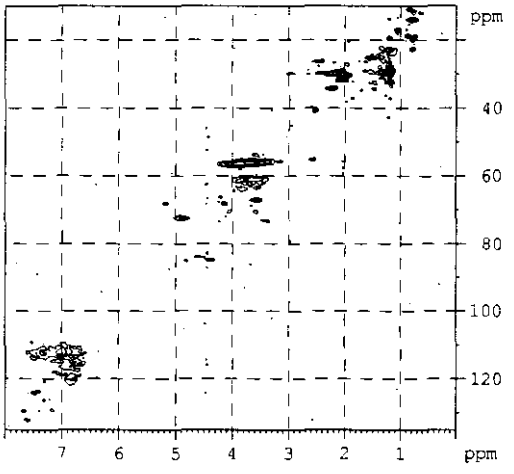

Fig. 10. HSQC of RL of kraft POM-delignified pulp (kappa number 16.2)

Stilbene structures, characteristic of kraft pulp residual lignin [16], which were observed in the FTIR spectra, were also found in the RLK30.5 HSQC spectra based on C_α/H_α and C_β/H_β correlations at 127-129/7.0-7.4 [20]. The characteristic stilbene bands were not discemable in the RLKOx FTIR spectra, which was previously attributed to a fast disappearance of stilbene structures in oxygen delignification [13]. However, our HSQC spectra offered clear evidence of a gradual disappearance of this structure during oxygen delignification, with RLKOx16.9 still containing the signals characteristic of stilbene structure [20]. The HSQC spectra of RLKPOM28.1/23.9 contained weak correlations in the corresponding area, whereas they were totally absent in the spectra of RLKPOM20.8-10.8. These results. combined with the FTIR results. indicate that stilbene structures undergo transformation during POM delignification. To determine the mechanism of this transformation, additional studies are necessary, including those with LMCs.

Alkali-stable vinyl aryl-ether structures formed during kraft pulping from β-O-4 structures [16] were not detected in the HSQC spectra of residual lignins (Ar-C_α H=CH_β -O-Ar, 112.9/6.22 (20]). Absence of this structure in the residual lignin isolated by acid hydrolysis was expected due to its instability under acid conditions [7, 16].

No evidence of diphenylmethane structure (Ar-CH_2-Ar, 29.56/3.94, [24]) was found in the HSQC spectra of residual lignins, even though previous studies on kraft pulping confirmed formation of this condensation product [16].

Weakening of the signals in the aromatic area (C/H 100-130/6.0-7.5) was noticed in the HSQC spectra of RLKPOM of decreasing kappa number. Disappearance of the correlations in the area C/H <110/>6 was immediate, and they were already absent from the RLKPOM28.1 HSQC. This trend might indicate either substitution/condensation or cleavage of the aromatic ring.

Aromatic ring cleavage would most likely cause a shift in the HSQC correlation of the ring methoxyl groups. However, the methoxyl signal of the residual lignins isolated in this study were comparable to the OCH_3 correlation found in the MWL HSQC (56.06/3.75), which corroborates the previous results on LMCs where aromatic ring cleavage was not observed [29]. Our HSQC data is indicative of substitution/ condensation of the aromatic ring during POM delignification. The FTIR data also offer evidence of increased substitution of the aromatic ring (FTIR-Section).

Lignin Degradation Products Dissolved in POM solution

Low molecular weight products of the POM treatment of kraft pulp were extracted from the POM solution as described in the Experimental section. No lignin precipitate was obtained after acidification of the solution to pH2, which may provide evidence of intense lignin depolymerization. Approximately 25% of the total lignin removed during delignification was extracted in the three successive extractions. The low extraction efficiency might suggest that after dissolution, lignin degradation products were further

converted to highly polar compounds and/or carbon dioxide.

GC-MS Analysis: The chloroform extract contained different compounds of MW up to 234. The most abundant compound was identified as vanillin, which is an oxidation product of uncondensed G-units and, being a C_6-C_1 type of compound, may result from cleavage of aryl-ether and/or C_α -C_β bonds.

The GC-MS experiments are in progress, and only the results on dominant degradation product have been obtained.

CONCLUSION

Transformation of lignin upon treatment with polyoxometalates was followed by the characterization of residual lignins from kraft POM-delignified pulps of decreasing kappa number. Characteristics of these lignins were compared with those of both original kraft and kraft oxygen-delignified pulps. Stronger association between lignin and carbohydrates and a higher level of substitution/condensation of the aromatic ring seem to result in the lower yield of lignin isolation from kraft POM-delignified pulp. The large decrease in the PhOH-group content observed in the early phase of POM delignification corroborates the preferential attack of POM on the phenolic lignin units. Preliminary results on the identification of compounds dissolved during POM delignification were obtained. Vanillin, the most abundant compound, indicates that cleavage of the aryl-ether and/or C_α -C_β - bonds takes place during POM delignification.

AKNOWLEDGMENT

We want to sincerely thank Umesh Agarwal, James Beecher, Mark Davis, and Fred Man for their valuable assistance with data acquisition and interpretation.

REFERENCES:

1) Akim, L. G., Colodette, J. L., Argyropoulos, D. S. - *Can. J. Chem.* **79**:201-210(2001).
2) Asgari, F., Argyropoulos, D. S. - *Can. J. Chem.* **76**:1606-1615(1998).
3) Davis. M. W. - *J. Wood Chem. Technol.* **18**(2):235-252(1998).
4) Dence, C. W. - 33-61 **Methods in Lignin Chemistry,** S. Y. Lin, C. W. Dence. eds.: Springer-Verlag (1999).
5) Evtuguin, D. V., Pascoal Neto, C., Rocha, J. - *Holzforschung* **50**(4):381-389(2000).
6) Faix, O. - *Holzforschung* **45**(Suppl.):21-27(1991).
7) Froass, P. M., Ragauskas, A. J., Jiang, J.-e. - *Ind. Eng. Chem. Res.* **37**:3388-3394(1998).
Gärtner, A., Gellerstedt, G., Tamminen, T. - *Nordic Pulp Paper Res. J.* **14**(2):163-170(1999).
9) Gellentedt, G., Pranda, J., Lindfors, E.-L. - *J. Wood Chem. Technol.* **14**(4):467-482 (1994).
10) Hergert, L. H. - *J. Org. Chem.* **25**:405-413 (1960).
11) Hergert, L. H. - 267-297 **Lignins - Occurrence, Formation, Structure and Reactions,** K. V. Sarkanen, C. H. Ludwig, eds.: Wiley-Intersci. (1971).
12) Jiang, Z.-H., Van Lierop, B., Berry, R. - *TAPPI J.* **83**(1):167–174(2000).
13) Johansson, E., Ljunggren, S. - *J. Wood Chem. Technol.* 14(4):507-525(1994).
14) Kang, G., Ni, Y., Van Heiningen, A. - *Appita* **50**(4):313-318 (1997).
15) Kirk, T. K., Chang, H.-m. - *Holzforschung* **29**(2):56–64(1975).
16) Kringstad, K. P., Mörck, R. - *Holzforschung* **37**(5):237–244(1983).
17) Li, J., Gellerstedt, G. - *Carbohydr. Res.* **302:** 213-218 (1997).
18) Li, J., Gellerstedt, G. - *Nordic Pulp Paper Res. J.* **13**(2):153–158(1998).
19) Li, J., Sevastyanova, O., Gellentedt, G. - *JPPS* **28**(8):262-266 (2002).
20) Liitiä, T. M., Maunu, S. L., Hortling, B., Toikka, M., Kilpelainen, I. - *J. Agric. Food Chem.* **51**:2136-2143 (2003).
21) Matsushita, Y., Kakehi, A,. Miyawaki, S., Yasuda, S. - *J Wood Sci.* **50**:136-141(2004).
22) Menchi, G., Matteoli, U., Staccioli, G. - *Wood Sci. Technol.* **31**:391-397(1997).
23) Minor, J. L. - J. Wood Chem. Technol. **6**(2): 185-201(1986).
24) Ralph, S. A., Ralph, J., Landucci, L.L. - http://www.dfrc.wisc.edu/software.html (2005).
25) Reiner, R. S., Weinstock. I. A., Atalla, R. H., Bond, J. S., Sonnen, D. M.. Houtman, C. J., Heintz, R. A., Springer, E. L., Wemple, M., Hill, C. L. - 11th ISWPC Nice, France, Vol. **III**:349–352(2001).
26) Tiainen, E., Drakenberg, T., Tamminen, T., Kataja, K., Hase, A. - *Holzforschung* **53**(5):529-533(1999).
27) Weinstock, I. A., Atalla, R. H., Reiner, R. S., Moen, M. A., Hammel. K. E. - *New J. Chem.* **20**(2):269-275(1996).
28) Weinstack, I. A., Hammel, K. E., Moen, M. A., Landucci, L. L., Ralph, S., Sullivan, C. E., Reiner, R. S. - *Holzforschung* **52**(3):311-315(1998).
29) Yokoyama, T., Chang, H.-m., Reiner, R. S., Atalla, R. H., Weinstock, I. A., Kadla, J. F. - Holzforschung **58**(2):116-121(2004)

Citation: 59th Appita Annual Conference and Exhibition, Auckland, New Zealand, 16-19 May 2005, vol. 3 ISWFPC (International Symposium on Wood, Fibre and Pulping Chemistry) Sessions, Paper 9, pp 49-56 [Carlton, Australia: Appita 2005, CD-Rom, AUD350.00] (C, K, P, S)