Journal of Wood Chemistry and Technology, 31: 121–141, 2011

ISSN 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773813.2010.503980

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Polyoxometalate Delignification of Birch Kraft Pulp and Effect on Residual Lignin

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Abstract: To advance the understanding of delignification with polyoxometalates (POMs) that have been explored for use in bleaching of chemical pulps, the transformation of lignin during anaerobic treatment of birch kraft pulp with an equilibrated POM mixture composed of $Na_{5(+2)}[SiV_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ was investigated. The conversion factor between the Klason lignin and the kappa number corrected for the hexenuronic acid (HexA) contribution gradually increased, indicating loss of lignin oxidizability. Comparative analysis of residual lignins isolated from pulps of decreasing kappa number showed that lignin undergoes changes that include a sharp reduction in the content of PhOH groups, a gradual demethylation, and a high increase in carbonyl groups. The results indicated that the POM treatment of kraft pulps leads to the loss of aromaticity, most likely caused by the conversion of aromatic rings to quinone moieties. The 2D NMR studies revealed the disappearance of the correlations assigned to stilbene structures formed during kraft pulping, and the weakening of those assigned to the native lignin bonds. The GPC studies showed a gradual lignin depolymerization.

Keywords: Polyoxometalates (POMs), birch kraft pulp, residual lignin

INTRODUCTION

To replace environmentally detrimental chlorine-based bleaching technologies, new bleaching technologies are required. The use of different chemical agents and enzymes as alternative delignification agents has been examined and, in some cases, implemented. Polyxometalates (POMs) favorably embrace the advantages of both chemical (active at elevated temperatures) and biological (highly selective) lignin-oxidizing agents. Different mixed-addenda

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heteropolyanions, such as $[SiVW_{11}O_{40}]^{5-}$, $[PV_2Mo_{10}O_{40}]^{5-}$, $[PVMo_{11}O_{40}]^{4-}$, and $[SiV_xMoW_{11-x}O_{40}]^{5-}$, have been successfully applied in the process to facilitate selective removal and mineralization of lignin in the bleaching of chemical pulps. In accordance with one approach for using POMs in bleaching of chemical pulps, the transfer of electrons from lignin to oxygen takes place in two stages. In the first stage, lignin is oxidized by POMs under anaerobic conditions (transfer of electrons from lignin to POMs). In the second stage, reduced POMs are re-oxidized by oxygen at elevated temperatures (transfer of electrons from reduced POMs to oxygen).[1,2] In contrast to this two-stage process,[1] a one-stage aerobic process, in which POMs are used as catalysts in oxygen bleaching, has also been proposed.[3] There are numerous advantages and disadvantages of these two processes, but the presence of oxygen during actual delignification clearly distinguishes one from the other. In the one-stage process, reduced POMs are reoxidized in the same stage and actual delignification takes place under aerobic conditions. In the two-stage process, POMs are reoxidized in a separate stage and delignification takes place under anaerobic conditions. In the current study, we focused on the effect of POMs on lignin in the anaerobic stage of pulp bleaching in the two-stage process. An important aspect of the POM delignification concept is that protons are released during lignin oxidation and there is a need for a buffer to maintain the system pH. A group of POMs described by the formula $Na_{5(+2)}[SiV_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ has been synthesized to develop a self-buffering POM delignification system.[2] This group of POMs has shown a capability to maintain pH in a narrow range, and for this reason was used in this study.

The mechanism of lignin oxidation has been studied to improve our understanding of delignification and facilitate implementation of the POM bleaching. The reactivity of phenolic and non-phenolic lignin structural units has been studied using monomeric and dimeric lignin model compounds (LMCs).[4–6] Model studies, however, do not reflect all the reactions that lignin might undergo as a macromolecule in the pulp matrix. Oxidation of pine milled wood lignin (MWL) with POMs has also been explored.[7] The MWL was insoluble under the conditions used, and oxidative reactions were found to be taking place primarily at the surface of the suspended lignin macromolecules. In our study, the structural transformation of lignin in POM-bleached pulps was evaluated by comparative analysis of the properties of residual lignins isolated from laboratory-made unbleached and POM-bleached birch kraft pulps. Results of these studies, combined with the results obtained using lignin model compounds and MWL, are expected to help us understand the POM delignification reactions, making it possible to avoid the potential undesirable reaction pathways and to optimize the POM-delignification process.

In our previous study,[8] an increase in the ratio of Klason lignin content-to-kappa number was noticed in softwood kraft pulp with the progress of POM delignification. An increase in this ratio, indicating a decrease in lignin oxidizability, was reported during a study of chlorine dioxide and periodate

delignification.[9] In that study, lignin oxidizability was recovered as the lignin/kappa ratio was brought back to the original value after reduction with sodium dithionite. In accordance with this result and the results of model studies on the consumption of permanganate, conversion of lignin aromatic units to quinone moieties was proposed as the main cause of reduced lignin oxidizability. To evaluate the origin of reduced lignin oxidizability, POM-delignified birch pulp was also treated with sodium dithionite in the present study.

Hexenuronic acid groups (HexA) linked to pulp xylans increase pulp permanganate consumption and lead to an increase in kappa number, and hence, to a decrease in the Klason lignin-to-kappa number ratio.[10] This is especially noticeable in hardwood pulps rich in xylans, such as birch kraft pulp. Therefore, analysis of the HexA-group content in pulps was included in the present study, to evaluate the effect of HexA groups on the kappa number of kraft POM-delignified pulps and to gain insight into the stability of HexA groups during the POM delignification. Unbleached birch kraft pulp selected for this study was of kappa number 27.2, which is somewhat higher than the kappa number of conventional bleachable-grade hardwood kraft pulp. This was in accordance with the general intention to stop the kraft process earlier in order to prevent deterioration of the pulp and to provide less condensed, and hence more reactive, lignin to the bleaching process.

Residual lignins isolated by mild acid hydrolysis from unbleached and POM-delignified kraft birch pulps of decreasing kappa number were analyzed by different techniques used in lignin characterization, including analytical, UV-, FTIR-, and NMR-spectral analyses and gel permeation chromatography.

MATERIALS AND METHODS

Pulp

Laboratory-made birch kraft pulp (KB) of kappa number 27.2 was used in these experiments.

Delignification Experiments: Birch kraft pulp was delignified with polyoxometalates under anaerobic conditions using a 2 L horizontal Parr reactor configured with anchor stirrers. An equilibrated POM mixture composed of 0.4 M $Na_{5(+2)}[SiV_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ was used, at 8% pulp consistency. The pH range of 5.5–6.5 was controlled by equilibration reactions of the POM.[2] Temperature and time of the reactions were adjusted to produce kraft POM-bleached pulps of decreasing kappa numbers; KBPOM21.3, kappa number 21.3 (110°C for 10 minutes), KBPOM15.7, kappa number 15.3 (140°C for 12 minutes), and KBPOM10.3, kappa number 10.3 (140°C for 2 hours). The amount of reduced POMs, that is, the reacted POMs, was calculated using UV/Vis. spectroscopy and the reaction between the reduced form of POMs and

$[Co^{III}W_{12}O_{40}]^{5-}$, as explained in detail by Yokoyama et al. ($[Co^{III}W_{12}O_{40}]^{5-}$ + $POM_{red} \rightarrow [Co^{II}W_{12}O_{40}]^{6-} + POM_{ox}$; 625 nm λ_{max} of $[Co^{II}W_{12}O_{40}]^{6-}$).[5]

Residual Lignin Isolation: Residual lignin was isolated from extracted pulps (successive extraction with dichloromethane and acetone; Soxhlet extractor, 8 hours) using a method of mild acid hydrolysis with a slight modification.[8,11]

Methods

Kappa Number/Klason/Acid-Soluble Lignin/HexA-groups: Kappa number and the contents of Klason lignin and hexeneuronic acid groups (HexA) in the original kraft and POM-bleached pulps were determined. Residual lignins obtained by acid hydrolysis were analyzed for the contents of Klason and acid-soluble lignin and carbohydrates, and for permanganate consumption.[12–16]

Pulp Reduction: Sodium dithionite reduction was performed on the extracted (dichloromethane, acetone) POM-delignified birch kraft pulps.[17]

Phenolic Hydroxyl Group Content: The content of free phenolic hydroxyl groups (PhOH) in the lignin was determined directly on pulp using the Folin Ciocalteu reagent.[18] The PhOH content was also determined for the samples of isolated residual lignin by the ionization difference UV-spectroscopic method;[19] the pH6 lignin solution prepared for these measurements was also used in the UV-spectral studies of the lignin samples. The UV-absorption measurements were conducted on a Spectronic Genesys 5 spectrophotometer.

Methoxyl Group Content: The content of methoxyl groups was determined in accordance with the Vieböck and Schwappach procedure as described in detail by Chen (1992).[20] A test substance used to verify the reliability of the procedure was vanillin with measured methoxyl group content of 20.12% (average of three measurements; st. dev. 0.105; theoretical methoxyl group content, 20.40%).

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}). Based on FTIR data, the content of carboxylic acid groups (COOH) and non-conjugated carbonyl groups (C=O groups) in relation to aromatic structures in lignin was determined using the horizontal baseline method.[21] Results are expressed as the ratio between the integrals of the band areas for the C=O groups and aromatic bands (I_{1740}/I_{1510}). The selected integration limits were 1840 ± 15 cm^{-1} and 1680 cm^{-1} for the C=O band, and 1542 ± 5 cm^{-1} and 1483 ± 2 cm^{-1} for the aromatic band. This method is based on the calibration obtained using mixtures of milled wood lignin and tartaric acid. Therefore, the method does provide an opportunity to compare the contents of C=O groups rather than to get the exact number of C=O groups in lignins. The results are expressed as moles of the C=O groups per gram of "aromatic lignin."

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 (∼50 mg) 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.

Gel Permeation Chromatography: Gel permeation chromatography (GPC) profiles of acetylated residual lignin isolated from unbleached and POM-bleached birch kraft pulps were obtained using a Sephacryl-100 column (1.8 × 32.5 cm) at room temperature. Dioxane:water (9:1) was used as the eluant and 1.5-ml fractions were collected (flow rate 0.75ml/min; 60 tubes in 120 minutes). The column was calibrated using acetylated LMC tetramer (#3009 from the FPL collection)[22] and veratraldehyde, as polystyrene standards were only partially soluble in dioxane:water (9:1); lignin was completely soluble in dioxane:water (9:1) but not in solvents (for example, tetrahydrofuran) used in conjunction with polystyrene standards for calibration. The UV-absorbance of the fractions at 280 nm was measured (Spectronic Genesys 5 spectrophotometer), and elution curves were obtained to compare the molecular weight distribution of acetylated residual lignins. Acetylation of lignins was performed in accordance with the procedure described by Lundquist (1992).[24]

RESULTS AND DISCUSSION

In bleaching with POMs, lignin removal is achieved by lignin oxidation and the dissolution of oxidized lignin/lignin fragments. In this process, POMs are reduced and the delignification process may be illustrated as a correlation between the kappa number decrease and the reduction of POMs (Figure 1). The kappa number, however, is related not only to lignin, but also to all permanganate-oxidizable structures, most notably hexenuronic acid groups (HexA) (10 μmol of HexA correspond to 0.85 kappa units).[10] Therefore, in our study the HexA-group content in the pulp was measured to evaluate both the HexA contribution to the kappa number and the stability of HexA groups during POM delignification. The results obtained in the POM delignification of birch kraft pulp are shown in Figure 1.

A gradual decrease in the HexA content was observed during the POM delignification. At about 42% delignification, calculated based on the total lignin decrease, the HexA-group content was reduced by about 73% (Figures 1 and 2). This is more than has been observed in other treatments of hardwood kraft pulps, such as in bleaching with oxygen, oxygen-peroxide, and ozone-peroxide.[24] The reduction of HexA content has been noticed also in oxygen delignification catalyzed by polyoxometalates.[25] The removal of HexA groups correlates with the high temperature and mild acid conditions (pH 5.5–6.5; 110–140°C) of POM treatment, which promote acid degradation of hexenuronic acid to furan derivatives.[26] This is a beneficial effect of

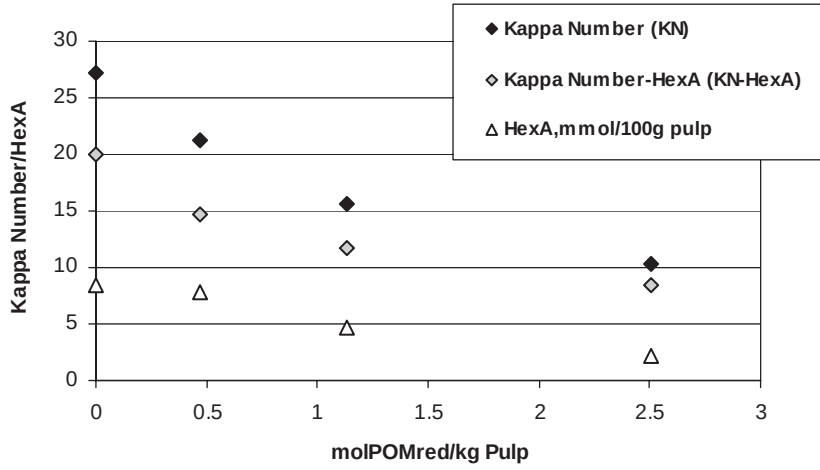


Figure 1. Decrease of kappa number and HexA-group content during POM treatment of birch kraft pulp.

POM delignification because hexenuronic acid groups remaining in the kraft pulp increase consumption of bleaching chemicals, decrease brightness, and may participate in brightness reversion.[27,28] The HexA moieties are also indicated as a site for lignin-carbohydrate linkages[29] and their removal may help enhance pulp bleaching selectivity.

The POM delignification decreased the content of both Klason and acid-soluble lignin with a greater removal of acid-soluble lignin especially in the

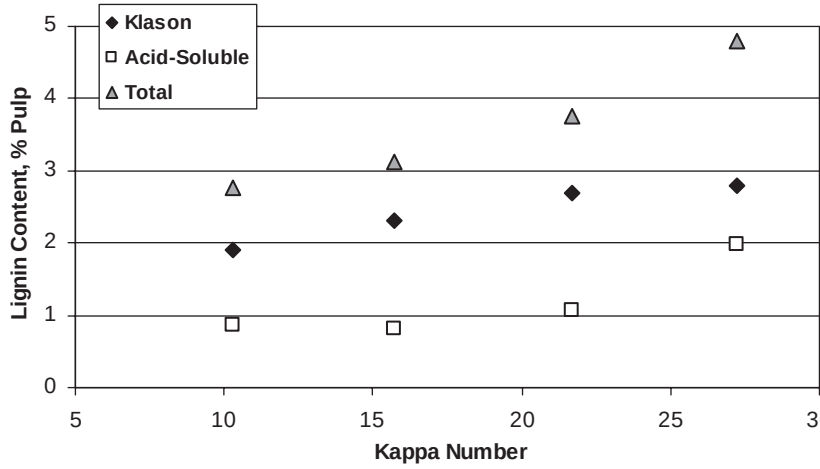


Figure 2. Lignin content decrease in POM treatment of birch kraft pulp.

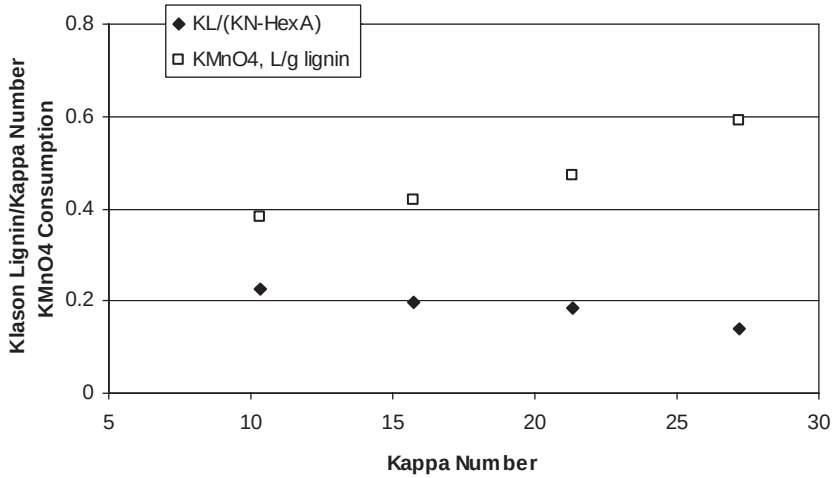


Figure 3. The Klason lignin/kappa number corrected for the HexA contribution ratio (CF = KL/(KN-HexA), permanganate consumption of lignin in pulp ($KMnO_4$,L/g lignin), and permanganate consumption of residual lignin isolated from pulp ($KMnO_4$, L/g RL) during POM-delignification of birch kraft pulp.

initial phase of delignification (Figure 2). Removal of acid-soluble lignin may be due to the cleavage of bonds within the lignin structure as a result of lignin oxidation with POMs[4,6–8] and/or lignin acidolysis.[11,30] It is also consistent with the cleavage of bonds between lignin and carbohydrates, such as acid-labile benzyl ether bonds. Benzyl ether bonds may remain in the pulp and hinder an efficient removal of lignin in the last, residual phase of kraft pulping.[31]

We used the kappa number and the Klason lignin and HexA-group contents to calculate the ratio of Klason lignin content-to-kappa number and the permanganate consumption by lignin in pulps. The Klason lignin (KL) divided by the kappa number (KN) corrected for the HexA-group content (HexA) is referred to here as the conversion factor, KL/(KN-HexA) (Figure 3). The permanganate consumption by residual lignin isolated from pulps was also determined, in accordance with the method used by Li and Gellerstedt.[15] The values of permanganate consumption by lignin in pulps (calculated values) and by corresponding residual lignin (measured values presented in Figure 3) were almost identical, indicating that the oxidizability of the lignin had not been changed during its isolation from pulp. This is a very important result of our study, demonstrating the validity of mild acid hydrolysis as a method of lignin isolation from pulp. In addition, permanganate consumption of both the lignin in unbleached birch kraft pulp and the corresponding residual lignin was very close to the value measured for the residual lignin isolated from birch kraft pulp by Li et al.[16] POM delignification caused a decrease in the permanganate consumption by lignin, indicating diminished lignin oxidizability. Accordingly,

the progress of POM delignification led to a gradual increase in the conversion factor (Figure 3). Our studies included dithionite reduction of the extracted POM-bleached birch kraft pulp of kappa number 15.7, to assess the proposal of the quinone origin of the reduction in lignin oxidizability.[9] Dithionite treatment of the this pulp decreased the conversion factor from 0.197 to 0.185. This is in accordance with the formation of quinone moieties in lignin, as noticed previously in studies of POM treatment of lignin model compounds,[4,6] milled wood lignin,[7] and kraft pulp.[32,33]

As reported recently, mild acid hydrolysis has resulted in a lower yield of residual lignin isolated from POM-delignified softwood kraft pulps than that isolated from both unbleached and oxygen-bleached softwood kraft pulps.[8,34,35] In the present study, residual lignin (RL) from unbleached and POM-delignified birch kraft pulps was isolated using the same method of lignin isolation. Although an increase in the lignin recovery was noticed for unbleached birch kraft pulp of kappa number 27.2 compared with unbleached softwood kraft pulp of kappa number 30.5, a lower lignin recovery was obtained for POM-delignified birch kraft pulps (Table 1). Therefore, it is important to point out that the results discussed in this paper are based on the properties of lignins representing less than one fifth of the total lignin remaining in pulp, as only an average of 17.5% of lignin was recovered from POM-delignified birch kraft pulps. This yield was lower than the average yield of lignin isolated from POM-bleached softwood kraft pulps (23%).[8] The contents of Klason and acid-soluble lignin, along with carbohydrate content and composition in the residual lignins, are presented in Table 1.

The lignins isolated from the pulps of decreasing kappa number were characterized by an increasing amount of remaining carbohydrates. Acid-catalyzed cleavage of lignin-carbohydrate linkages is considered to be the main factor in releasing lignin during isolation using the mild-acid hydrolysis method.[11] Therefore, the reduced yield of lignin isolation in our study may indicate formation of acid-stable lignin-carbohydrate linkages in POM-treated pulps. The presence of carbohydrates in isolated residual lignins may also be attributed to the chemical linkages between lignin and polysaccharides: cellulose and hemicelluloses.[31] Xylose as the dominant carbohydrate in residual lignin of unbleached birch kraft pulp indicates a close association between lignin and xylans in this pulp (Xyl-63.83%, Glu-27.66% of total carbohydrates). Even though the xylose content in residual lignins gradually increases with the progress of delignification, the glucose content increases faster; thus, glucose becomes the dominant carbohydrate in the residual lignin of POM-bleached birch kraft pulp of kappa number 10.3 (Xyl-42.35%, Glu-55.88% of total carbohydrates). In our earlier study,[35] glucose-based carbohydrates remaining in residual lignin from POM-bleached softwood kraft pulp were removed by mild alkali treatment. It seems that POM treatment of kraft pulps results in the formation of acid-stable, alkali-labile bonds between lignin and glucose-based carbohydrates.

Table 1. Chemical composition of residual lignins (- indicates below the detection level)

		% OD RL									
		Lignin			Carbohydrates						
Residual Lignin	Yield% Klason lignin in pulp	Klason	Acid-Sol.	Total	Ara	Gal	Glu	Xyl	Man	Total	Total
KB27.2	73.3	93.4	1.70	95.10	-	0.04	0.13	0.30	-	0.47	95.57
KBPOM21.3	21.9	89.7	1.95	91.75	-	0.03	0.27	0.39	-	0.69	92.34
KBPOM15.7	15.5	91.3	2.05	93.35	0.02	0.03	0.67	0.55	-	1.27	94.62
KBPOM10.3	15.1	89.3	2.15	91.45	-	0.03	0.95	0.72	-	1.70	93.15

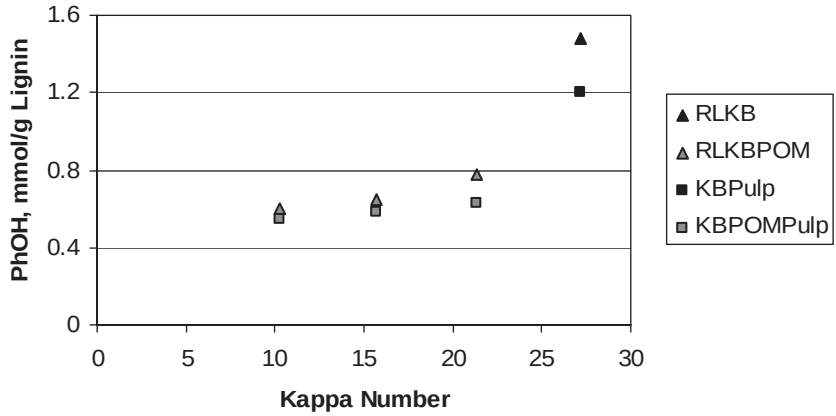


Figure 4. PhOH content in unbleached (KBPulp) and POM-bleached birch kraft (KBPOMPulp) pulps and in corresponding residual lignins (KBRL, KBPOMRL).

The PhOH content in the lignin was determined using the Folin-Ciocalteu method on the pulps[18] and these results were compared with the results obtained by using the ionization difference method[19] on the residual lignins (Figure 4). The RLs were of higher phenolic hydroxyl content than the corresponding lignins in pulps. The difference between the results was higher for the samples of higher kappa numbers (difference of $\sim$23% at kappa numbers $>$20), but lessened at lower kappa numbers (difference of $\sim$10% at kappa numbers $<$16). The higher PhOH content determined for residual lignins is related to the cleavage of aryl ether bonds in lignin; this is recognized as an unavoidable disadvantage of mild acid hydrolysis.[11] An observed diminished difference between PhOH values measured for lignin in pulp and corresponding residual lignin at lower kappa numbers may indicate a diminished amount of aryl ether bonds in POM-treated pulps, i.e. cleavage of aryl ether bonds during POM delignification.[4,7] Cleavage of aryl ether bonds results in an increase of the PhOH content, as has been observed in the POM treatment of pine MWL.[7] In our study, however, a sharp reduction in the PhOH content was observed in both lignin in pulp and corresponding residual lignin at an early phase of POM delignification. These results suggest that POMs readily oxidize non-etherified lignin units and instantly consume available PhOH groups as well as the PhOH groups resulting from a proposed cleavage of aryl ether bonds. Since POM oxidation of phenols yields quinones,[4,6] it is expected that the quinone content in pulps will increase with the progress of POM delignification. This is in accordance with our results on permanganate oxidizability of pulps before and after sodium dithionite reduction. The results of a number of studies of the effect of POMs on lignin have indicated quinone formation.[2,4–7,33,36] In addition, *o*-quinone formation in lignin is consistent with loss of methoxyl

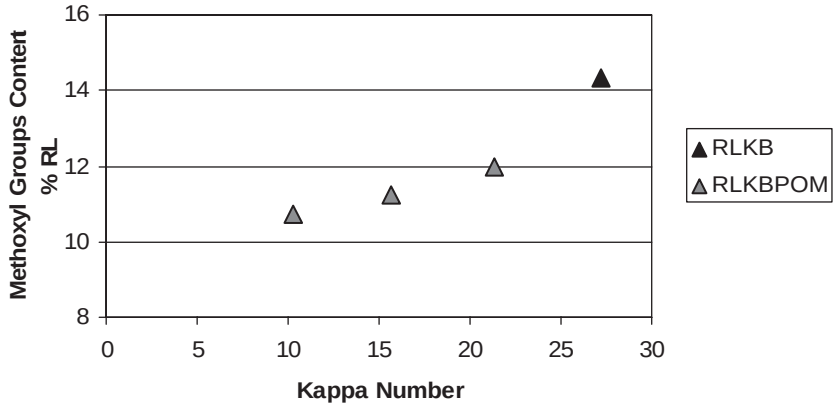


Figure 5. Methoxyl group content in residual lignins from unbleached and POM-bleached birch kraft pulps.

groups.[4–7] In our study, we observed a decrease in methoxyl-group content in residual lignins with the progress of POM delignification (Figure 5). At the end of POM delignification, the residual lignin of POM-bleached birch kraft pulp of kappa number 10.3 was ~25% lower in the content of methoxyl groups than the residual lignin of unbleached birch kraft pulp.

A low content of PhOH groups registered in the decayed lignins has been discussed as an indication of the degradation of aromatic rings caused by white-rot fungi attack.[36] A UV/Vis. spectral analysis of the pH6 lignin solutions (Experimental) was performed in order to test this hypothesis. Figure 6 compares the absorption spectra of the residual lignin from unbleached and POM-delignified birch kraft pulps. Milled wood lignin of aspen (FPL collection of MWLs) was analyzed under the same conditions for comparative purposes. The diagram clearly illustrates a greatly enhanced absorptivity of kraft lignin compared to MWL[37] and indicates that during POM treatment, absorptivity of lignin continues to increase.

Gradual disappearance of the B band of lignin at ~280 nm[37] can be observed in the absorption spectra of the residual lignins of POM-delignified pulps of decreasing kappa number (Figure 6). The difference spectra obtained after subtraction of the absorption spectra of residual lignin of kraft pulp (RLKB27.2) from the spectra of early (RLKBPOM21.3) and more progressed (RLKBPOM10.3) stages of POM delignification reveal this effect (Figure 7).

The difference spectra are characterized by the minimum at 282 nm and maxima at 261 and 302 nm, indicating that POM delignification forms structures with the absorption maxima at 261 and 302 nm at the expense of the syringyl and/or guaiacyl units. The minimum at 282 nm may be indicative of a greater alteration of the guaiacyl units, because the UV-spectra of G-lignins

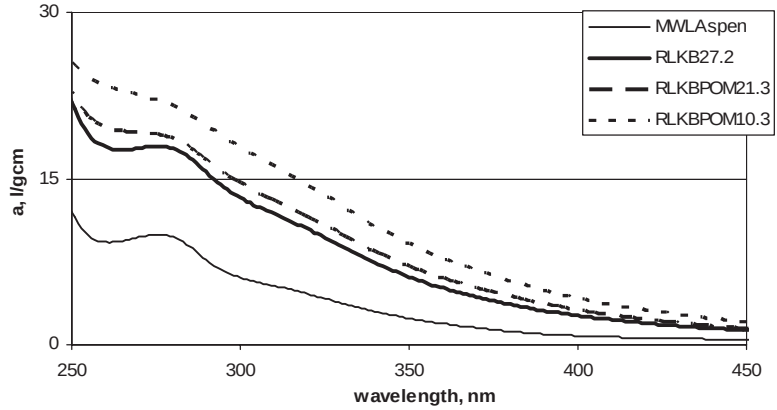


Figure 6. UV/Vis. spectra of aspen MWL and residual lignins of unbleached and POM-delignified birch kraft pulps (RLKB27.2, RLKBPOM21.7, RLKBPOM10.3) (lignin solution in 50% dioxane/50% 0.2 M NaOH buffered at pH6).

consist of a maximum at 280 nm, whereas SG-lignins exhibit the B-bands at shorter wavelengths, in the 268–277 nm range.[37] A greater alteration of G- compared to S-units would be a rather surprising result of POM treatment, as the syringyl compounds have lower oxidation potentials than the guaiacyl compounds; that is, S-units should be oxidized faster than G-units.[38] Based on the observed maxima, the newly formed structures consisted of different

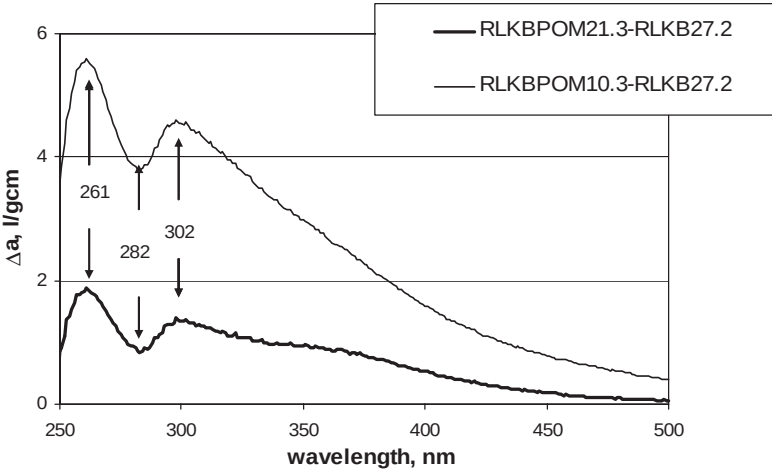


Figure 7. Difference spectra of residual lignins resulting from the POM-delignification of birch kraft pulp—early phase of POM delignification: $a_{RLKBPOM21.3} - a_{RLKB27.2}$; more progressed POM delignification: $a_{RLKBPOM10.3} - a_{RLKB27.2}$.

functionalities, including carbonyl, carboxyl, and quinone groups. No apparent evidence of quinone groups was obtained by UV-spectral analysis. This may be attributable to the inherent instability, particularly in aqueous media, but also to the wide range of the absorption maxima, that quinones may exhibit. Nonetheless, all quinones are recognized as strong UV-light absorbers with high absorptivity values.[39] Thus, quinone formation would be consistent with the observed increase in residual lignin absorptivity during POM treatment of pulp.

The FTIR spectra of residual lignins revealed that POMs caused a decrease in the aromatic skeletal vibration band at 1510 cm^{-1} in comparison with other characteristic lignin bands. The A_i/A_{1510} ratios in the spectra gradually increased with the progress of POM; i (cm^{-1}) is a characteristic lignin band, and 1510 cm^{-1} is an aromatic skeletal vibration band which usually serves as a reference band in lignin studies.[40] A similar effect, a lower intensity of the aromatic band relative to other bands in the white-rot fungi-degraded lignins, has been discussed as an indication of a decreased content of aromatic rings.[37] The FTIR spectra normalized to the aromatic skeletal vibration band at around 1510 cm^{-1} are shown in Figure 8. The most significant differences between the lignin spectra can be seen in the band region associated with the carbonyl stretching region ($\nu_{C=O}$ ~1620–1780 cm^{-1}).[40] POM delignification increased the content of carboxyl acid structures or unconjugated carbonyl structures in ketones and aldehydes (maximum at ~1712 cm^{-1}) and the content of conjugated carbonyl groups such as quinones (maximum at ~1640 cm^{-1}).

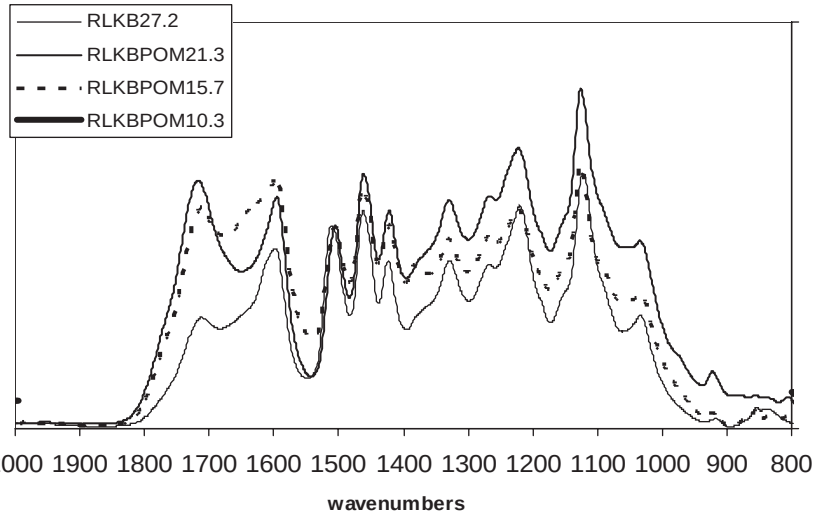


Figure 8. FTIR spectra of RL of unbleached birch kraft pulp, kappa 27.2 (RLKB) and of POM-delignified birch kraft pulps, kappa 21.3, 15.7, and 10.3 (RLKBPOM21.3, RLKBPOM 5.7; RLKBPOM10.3).

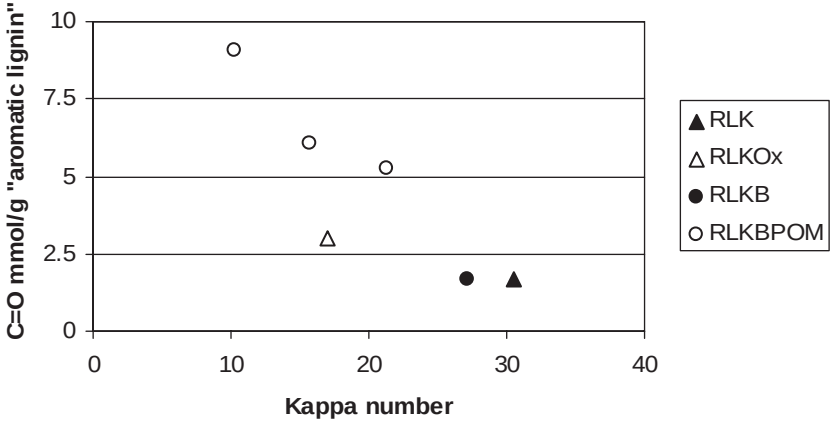


Figure 9. The content of C=O groups (carboxyl + non-conjugated carbonyl) in the residual lignins with the progress of delignification; residual lignin of unbleached (RLK) and oxygen-bleached (RLKOx) softwood pulp shown for comparison.

The content of carboxyl and non-conjugated carbonyl groups (C=O groups) in residual lignins was determined in relation to the aromatic structures in lignins (Experimental). Results obtained for the residual lignins of unbleached and POM-bleached kraft pulps show that the C=O group content increases with the progress of POM delignification (Figure 9).

Although the residual lignins of unbleached birch and softwood kraft pulp were characterized by approximately the same content of carbonyl groups, residual lignins of POM- and oxygen-delignified kraft pulps were of significantly different carbonyl group contents (Figure 9): 3.02 and 6.06 mmol/g "aromatic lignin" for lignin from oxygen-bleached pulp of kappa number 17 and lignin from POM-bleached birch pulp of kappa number 15.7, respectively. This is in accordance with a lower redox potential of dioxygen (O_2; alkaline solution) compared to that of typical POMs ($O_2 + 1e^- \rightarrow O_2^{\cdot -}$, $E^\circ = -0.33$ V vs. NHE; $[SiV^VW_{11}O_{40}]^{5-} + 1e^- \rightarrow [SiV^{IV}W_{11}O_{40}]^{6-}$, pH 2–8; $E^\circ = 0.69$ V vs. NHE).[41] In addition, Fu and Lucia[42] showed that in oxidation under alkali oxygen conditions, lignin maintains most of its C_6-C_3 units, which would lead to the lower values of carbonyl groups per gram of "aromatic lignin" found in the present study. Therefore, the high content of C=O groups (expressed on the basis of "aromatic lignin") in residual lignins of POM-bleached birch kraft pulps might also indicate a lower aromaticity of these lignin compared with residual lignin of oxygen-bleached softwood kraft pulp.

The 2D HSQC spectra of isolated lignins are shown in Figures 10, 11, and 12. The side chain region of the HSQC spectrum of residual lignin of birch kraft pulp still contains the correlations of the main structures of the native lignin (β-O-4, β-β, and β-5) (Figure 10).[22] The intensity of these correlations in the

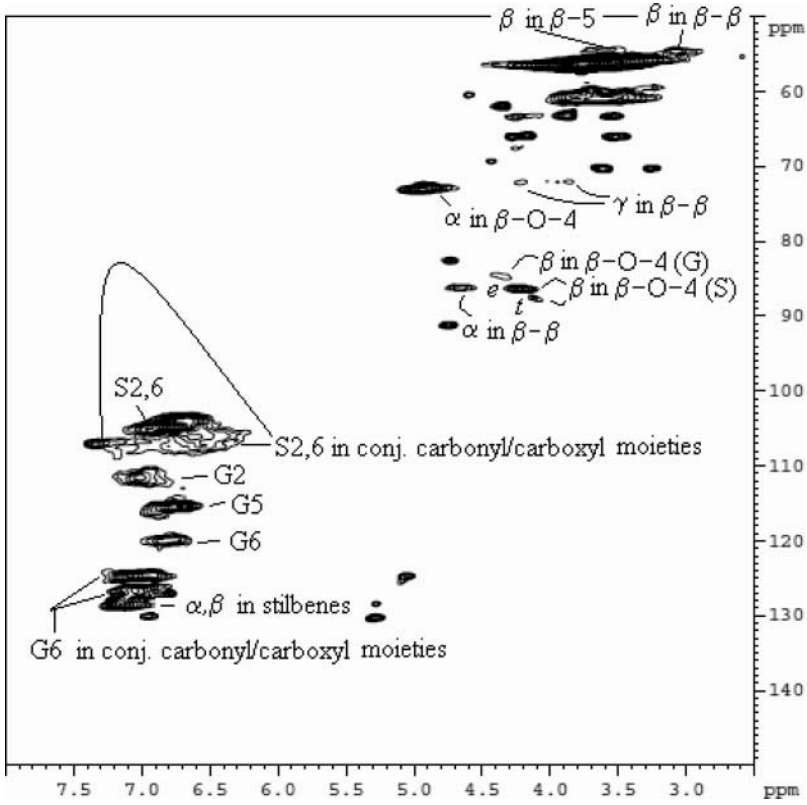


Figure 10. The HSQC spectrum of RLKB.

spectra of residual lignins of POM-treated birch kraft pulps diminishes with the extent of delignification (Figures 11 and 12). This is consistent with the cleavage of these bonds reported earlier in the studies of the POM effect on lignin model compounds.[4] The aryl ether bond cleavage (β-O-4), in particular, is in accordance with the results of the PhOH measurements on pulp and residual lignin obtained in this study. In addition, the C_β-H_β correlation corresponding to the *threo* form of the S type of β-O-4 structure is absent from the HSQC spectrum of residual lignin of POM-bleached birch kraft pulp of kappa number 10.3, indicating its preferential oxidation over the *erythro* isomer (Figures 10 (*t*,*e*), 11 and 12). Recently, Bohlin et al.[43] showed that outer-sphere oxidants analogous to POMs[44] exhibit the preferential degradation of the *threo* forms of the β-O-4 lignin model compounds. The stilbene structures represented by C_α/H_α and C_β/H_β correlations in the HSQC spectra are absent from the spectrum of residual lignin of pulp of kappa number 21.3, which represents the residual lignin of an early phase of POM delignification (Figures 10 and 11).

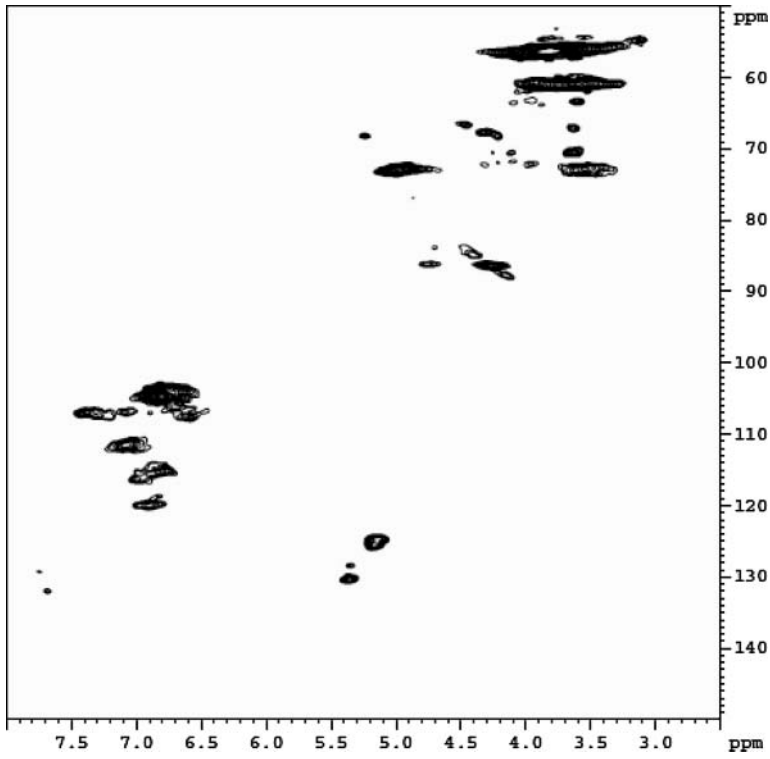


Figure 11. The HSQC spectrum of RLKBPOM21.3.

It is apparent that stilbene structures are readily modified during the POM oxidation of both softwood and hardwood (birch) kraft pulp.[8,35] Oxidative cleavage of *cis*- and *trans*-stilbenes has been reported in the oxidation by the oxo Cr(V) polyoxometalates and has resulted mainly in benzaldehydes and minute amounts of *cis*- and *trans*-stilbene oxides.[45] Based on the absence of epoxide ring C_α/H_α and C_β/H_β correlations[46] from the HSQC spectra in our study, it is more likely that stilbene structures undergo oxidative cleavage and yield benzaldehydes. In contrast to the results of the UV and FTIR measurements that show an increase in the carbonyl group content, the HSQC data demonstrate that the POM treatment leads to an instant removal of C_6-H_6 correlations assigned to conjugated carbonyl and carboxyl guaiacyl units (Figures 10 and 11). This result may be a consequence of condensation reactions, as condensation reactions have been detected in investigations of POM effect on lignin model compounds and MWL.[4,7] Nevertheless, the $S_{2,6}$ and $G_{2,5,6}$ correlations are still present in the spectra of residual lignins isolated from the POM-treated birch kraft pulps with the progress of delignification demonstrating the presence of aromatic uncondensed rings (Figures 11 and 12). It should be noted that the

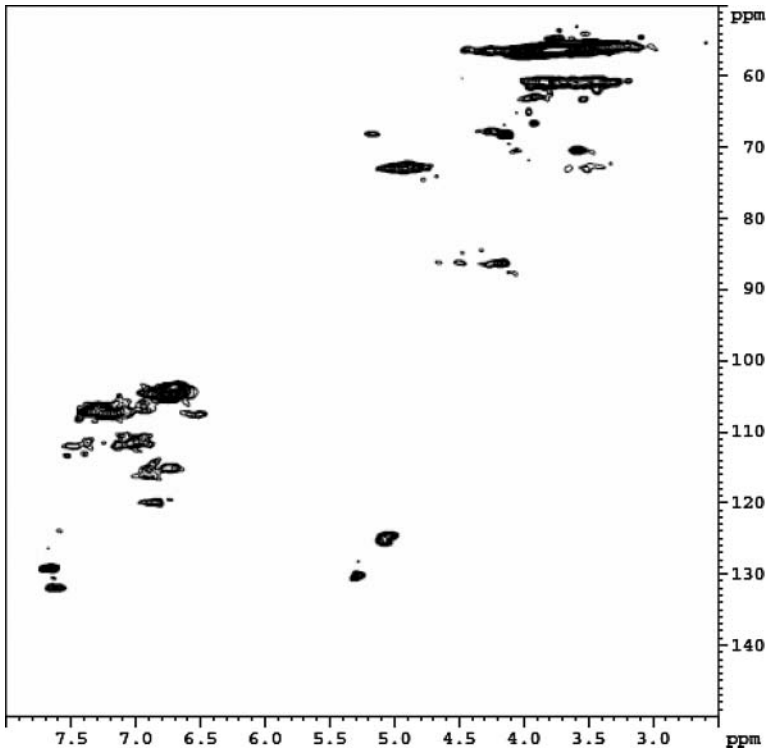


Figure 12. The HSQC of RLKBPOM10.3.

$C_{2,6}$-$H_{2,6}$ correlations assigned to conjugated carbonyl and carboxyl syringyl units are still present in the residual lignin of POM-bleached birch kraft pulp of low kappa number of 10.3, a late phase of POM-delignification (Figure 12). It seems that these units are mostly etherified aldehydes, because they were reported to stay relatively stable in POM oxidation.[5]

The GPC data presented in Figure 13 illustrate that POM delignification leads primarily to lignin depolymerization with minor repolymerization in an early phase of delignification (RLKBPOM21.7 vs. RLKB, ↓ Figure 13).

The GPC results imply that while an instant removal of C_6-H_6 correlations assigned to conjugated carbonyl and carboxyl guaiacyl units from the HSQC spectra (Figures 10 and 11) may be related to condensation reactions, the molecular weight of residual lignin increases only in an initial phase of POM delignification (decrease of kappa number from 27.2 to 21.3). It seems that any detrimental effect of condensation reactions on molecular weight of lignin in more progressed POM delignification is suppressed by reactions that promote lignin depolymerization, such as cleavage of aryl ether bonds indicated by the

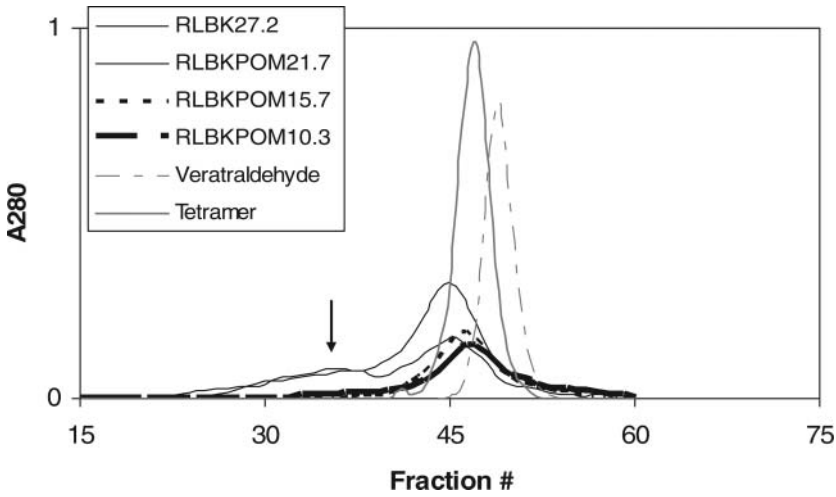


Figure 13. Gel permeation chromatography of residual lignins and model compounds.

results of HSQC experiments in this study and in earlier experiments on lignin model compounds and MWL.[4,7]

This study offers numerous indications of quinone formation and increase in the content of carbonyl groups during POM treatment of pulp. In acid conditions, *o*-quinones may undergo self-condensation reactions leading to their reduced solubility,[47] and hence, to the lower recovery yield observed in this study during lignin isolation by mild-acid hydrolysis. Conversely, *o*-quinones are readily oxidized to muconic acid derivatives by alkaline hydrogen peroxide providing for the dramatic increase in brightness and decrease in the amount of lignin.[32] Thus, a bleaching sequence consisting of POM treatment followed by hydrogen peroxide in alkaline conditions seems to be a realistic alternative to chlorine-based bleaching processes.

CONCLUSIONS

POM treatment of unbleached kraft pulp is efficient in the removal of HexA groups and leads to a decrease in lignin oxidizability, most likely due to quinone formation. The low yield of lignin isolation and carbohydrates remaining in isolated lignins suggests the presence of acid-stable bonds between lignin and glucose-based carbohydrates in POM-bleached pulps. The results obtained in the characterization of lignins isolated from unbleached and birch kraft pulp delignified with POMs show that lignin undergoes changes that include a sharp reduction of the content of phenolic hydroxyl groups, a gradual decrease in methoxyl groups, and a high increase in carbonyl groups. These findings are

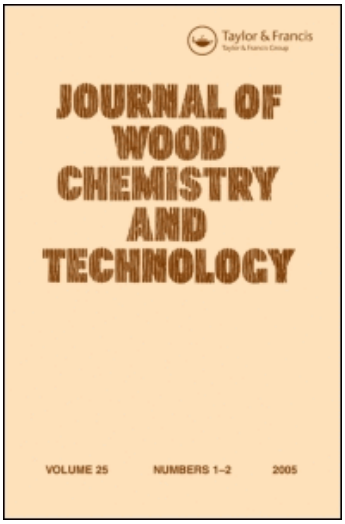
consistent with the proposed conversion of aromatic units to quinone moieties during POM delignification. Stilbene structures characteristic of kraft pulp residual lignin are modified during POM delignification. The HSQC correlations assigned to the dominant native lignin structures, which are still present in residual lignin of unbleached birch kraft pulp, diminish with the progress of POM delignification; this is in accordance with the finding of a gradual depolymerization of lignin demonstrated by the GPC experiments of this study.

REFERENCES

1. Weinstock, I.A.; Atalla, R.H.; Reiner, R.S.; Moen, M.A.; Hammel, K.E.; Houtman, C.J.; Hill, C.L. A new environmentally benign technology and approach to bleaching kraft pulp. Polyoxometalates for selective delignification and waste mineralization. New J. Chem. **1996**, *20*(2), 269–275.
2. 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. Thermodynamically Stable, Self-buffering Polyoxometalate Delignification System, *11th ISWPC Nice, France*, 2001,Vol. III, 349–352.
3. Evtuguin, D.V.; Pascoal Neto, C. New polyoxometalate promoted method of oxygen delignification. Holzforshung **1997**, *51*(4), 338–342.
4. Weinstock, I.A.; Hammel, K.E.; Moen, M.A.; Landucci, L.L.; Ralph, S.; Sullivan, C.E.; Reiner, R.S. Selective transition-metal catalysis of oxygen delignification using water-soluble salts of POM anions. Part. II. Reactions of α-$[SiVW_{11}O_{40}]^{5-}$ with phenolic lignin-model compounds. Holzforschung **1998**, *52*(3), 311–318.
5. Yokoyama, T.; Chang, H.-M.; Reiner, R.S.; Atalla, R.H.; Weinstock, I.A.; Kadla, J.F. Polyoxometalate oxidation of non-phenolic lignin subunits in water: Effect of substrate structure on reaction kinetics. Holzforschung **2004**, *58*(2), 116–121.
6. Kim, Y.S.; Chang, H.-M.; Kadla, J.F. Polyoxometalate (POM) oxidation of lignin model compounds. Holzforschung **2008**, *61*(1), 38–49.
7. Kim, Y.S.; Chang, H.-M.; Kadla, J.F. Polyoxometale (POM) oxidation of milled wood lignin (MWL). J. Wood Chem. Technol. **2007**, *27*(3-4), 225–241.
8. Bujanovic, B.; Reiner, R.S.; Hirth, K.C.; Ralph, S.A.; Atalla, R.H. Studies of Lignin Transformation in Polyoxometalate (POM) Bleaching of Kraft Pulp, *13th ISWFPC Auckland, New Zealand*, May 16–19, 2005, Vol. *3*, 49–56.
9. Brogdon, B.N. Influence of oxidized lignin structures from chlorine dioxide delignified pulps on the kappa number test. J. Pulp Paper Sci. **2001**, *27*(11), 364–369.
10. Li, J.; Gellerstedt, G. The contribution to kappa number from hexeneuronic acid groups in pulp xylem. Carb. Res. **1997**, *302*, 213–218.
11. Gellerstedt, G.; Pranda, J.; Lindfors, E.L. Structural and molecular properties of residual birch kraft lignin. J. Wood Chem. Technol. **1994**, *14*(4), 467–482.
12. Davis, M.W. A rapid modified method for compositional carbohydrate analysis of lignocellulosics by high pH anion-exchange chromatography with pulsed amperometric detection (HPAEC/PAD). J. Wood Chem. Technol. **1998**, *18*(2), 235–252.
13. Dence, C.W. The Determination of Lignin. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin Heidelberg, 1992, 33–61.

14. Chai, X.-S.; Zhu, J.Y.; Li, J. A simple and rapid method to determine hexeneuronic acid groups in chemical pulps. J. Pulp Paper Sci. **2001**, *27*(5), 165–170.
15. Li, J.; Gellerstedt, G. On the structural significance of kappa number measurement. Nordic Pulp Paper Res. J. **1998**, *13*(2), 153–158.
16. Li, J.; Sevastyanova, O.; Gellerstedt, G. The relationship between kappa number and oxidizable structures in bleached kraft pulps. J. Pulp Paper Sci. **2002**, *28*(8), 262–266.
17. Agarwal, U.P.; Landucci, L.L. FT-Raman investigation of bleaching of spruce thermomechanical pulp. J. Pulp Paper Sci. **2004**, *30*(10), 269–274.
18. de Sousa, F.; Reimann, A.; Björklund Jansson, M.; Nilberbrant, N.-O. Estimating the Amount of Phenolic Hydroxyl Groups in Lignin, *11th ISWPC, Nice, France*, **2001**; Vol. III, 649–653.
19. Gärtner, A.; Gellerstedt, G.; Tamminen, T. Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method. Nordic Pulp Paper Res. J. **1999**, *14*(2), 163–170.
20. Chen, C.-L. Determination of Methoxyl Groups. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, 1992, 465–472.
21. Hortling, B.; Tamminen, T.; Kenttä, E. Determination of carboxyl and non-conjugated carbonyl groups in dissolved and residual lignins by IR spectroscopy. Holzforschung **1997**, *51*(5), 405–410.
22. Ralph, S.A.; Ralph, J.; Landucci, L.L. NMR database of lignin and cell wall model compounds. 2006, available at http://www.arc.usda.gov/software.html
23. Lundquist, K. Proton (^{1}H) NMR Spectroscopy. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, 1992, 242–249.
24. Koshijima, T.; Watanabe, T. *Association Between Lignin and Carbohydrates in Wood and Other Plant Tissues*; Springer-Verlag: Berlin, 2003.
25. Gaspar, A.R.; Evtuguin, D.V.; Pascoal Neto, C. Polyoxometalate-catalyzed oxygen delignification of kraft pulp: A pilot-plant experience. Ind. Eng. Chem. Res. **2004**, *43*, 7754–7761.
26. Teleman, A.; Hausalo, T.; Tenkanen, M.; Vuorinen, T. Identification of the acidic degradation products of hexenuronic acid and characterization of hexenuronic acid-substituted xylooligosaccharides by NMR spectroscopy. Carb. Res. **1996**, *280*, 197–208.
27. Buchert, J.; Bergnor, E.; Lindblad, G.; Viikari, L.; Ek, M. Significance of xylan and glucomannan in the brightness reversion of kraft pulps. TAPPI J. **1997**, *80*(6), 165–171.
28. Jiang, Z.H.; Van Lierop, B.; Berry, R. Hexenuronic acid groups in pulping and bleaching chemistry. TAPPI J. **2000**, *83*(1), 167–175.
29. Jiang, Z.H.; Bouchard, J.; Berry, R. Evidence for the formation of lignin-hexenuronic acid-xylan complexes during modified kraft pulping processes. Holzforschung **2006**, *60*(2), 137–142.
30. Li, J.; Gellerstedt, G. Improved lignin properties and reactivity by modifications in the autohydrolysis process of aspen wood. Ind. Crops Prod. **2008**, *27*, 175–181.
31. Choi, J.W.; Choi, D.-H.; Faix, O. Characterization of lignin-carbohydrate linkages in the residual lignins isolated from chemical pulps of spruce (*Picea abies*) and beech wood (*Fagus sylvatica*). J. Wood Sci. **2007**, *53*, 309–313.

32. Weinstock, I.A.; Atalla, R.H.; Agarwal, U.P.; Minor, J.L. Fourier transform Raman spectroscopic studies of a novel wood pulp bleaching system. Spectrochimica Acta. **1993**, *49A*(5/6), 819–829.
33. Bujanovic, B.; Hirth, K.C.; Ralph, S.A.; Reiner, R.S.; Atalla, R.H. Composition of the Organic Components in Polyoxometalate (POM) Liquors from Kraft Pulp Bleaching, *14th ISWFPC Durban*, June 25–28, 2007 (Conf. CD).
34. Fu, S.; Lucia, L.A. Investigation of the chemical basis for inefficient lignin removal in softwood kraft pulp during oxygen delignification. Ind. Eng. Chem. Res. **2003**, *42*, 4269–4276.
35. Bujanovic, B.; Ralph, S.A.; Reiner, R.S.; Atalla, R.H. Lignin modification in the initial phase of softwood kraft pulp delignification with polyoxometalates (POMs). Holzforschung **2007**, *61*(5), 492–498.
36. Crestini, C.; Sermanni-Giovannozzi, G.; Argyropoulos, D.S. Structural modifications induced during biodegradation of wheat lignin by *Lentinula edodes*. Bioorg. Med. Chem. **1998**, *6*(7), 967–973.
37. Lin, S.Y. Ultraviolet Spectrophotometry. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, 1992, 217–232.
38. Lahtinen, M.; Kruus, K.; Boer, H.; Kemell, M.; Andberg, M.; Viikari, L.; Sipilä, J. The effect of lignin model compound structure on the rate of oxidation catalyzed by two different fungal laccases. J. Mol. Cat. B: Enzymatic **2009**, *57*, 204–210.
39. Williams, D.H.; Fleming, I. Ulraviolet and Visible Spectra. In *Spectroscopic Methods in Organic Chemistry*; Williams, D.H., Fleming, I., Eds.; McGraw-Hill: London, 5th ed., 1995, 1–27.
40. Faix, O. Fourier Transform Infrared Spectroscopy. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, 1992, 83–109.
41. Weinstock, I.A.; Atalla, R.H.; Reiner, R.S.; Houtman, C.J.; Hill, C.L. Selective transition-metal catalysis of oxygen delignification using water-soluble salts of POM anions. Part. I. Chemical principles and process concepts. Holzforschung **1998**, *52*(3), 303–310.
42. Fu, S.; Lucia, L.A. TMAH-pyrolysis-gas chromatography—mass spectrometry analysis of residual lignin changes in softwood kraft pulp during oxygen delignification. Can. J. Chem. **2004**, *82*, 1197–1202.
43. Bohlin, C.; Andersson, P.-O.; Lundquist, K.; Jönsson, L.J. Differences in stereopreference in the oxidative degradation of diastereomers of the lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol with enzymic and non-enzymic oxidants. J. Mol. Cat. B:Enzymatic **2007**, *45*, 21–26.
44. Weinstock, I.A. Homogeneous–phase electron-transfer reactions of polyoxometalates. Chem. Rev. **1998**, *98*, 113–170.
45. Khenkin, A.M.; Hill, C.L. Oxo transfer from high-valent totally inorganic oxometalloporphyrin analogs, $[X^{n+}W_{11}O_{39}Cr^{V}O]^{(9-n)-}$($X^{n+}$ = P^{5+}, Si^{4+}), to hydrocarbons. J. Am. Chem. Soc. **1993**, *115*, 8178–8186.
46. Lupattelli, P.; D'Auria, M.; Di Blasio, N.; Lenti, F. A novel approach to combrestatins: from *trans*-epoxide to CA04 and its dioxalane derivative. Eur. J. Org. Chem. **2009**, *141–145*; www.eurjoc.org
47. Simson, B.; Ayers, J.; Schwab, G..; Galley, M.; Dence, C. Reactions of *o*-benzoquinones in aqueous media. Tappi **1978**, *61* (7), 41–46.



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Polyoxometalate Delignification of Birch Kraft Pulp and Effect on Residual Lignin

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First published on: 03 May 2011