

Structural Changes of Residual Lignin of Softwood and Hardwood Kraft Pulp upon Oxidative Treatment with Polyoxometalates

Biljana Bujanovic¹, Richard S. Reiner², Sally A. Ralph², Umesh P. Agarwal², Rajai H. Atalla^{1,2}

¹Department of Chemical and Biological Engineering, University of Wisconsin – Madison, WI, USA

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

Abstract

Structural transformation of lignin in pulps bleached with polyoxometalates (POMs) should be explored in order to gain insight into the lignin reactions leading to its solubilization during POM treatment of kraft pulp. Our studies include characterization of residual lignin isolated from softwood commercial and birch laboratory kraft pulps delignified with POMs.

Oxidative treatment of unbleached kraft pulps, commercial mixed softwood and laboratory birch, was performed using complex POM solutions containing the active $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$ anion. Kappa number and contents of Klason lignin and hexeneuronic acid groups (HexA) were determined in the pulps before and after POM treatment. It was found that during this treatment the HexA groups were removed from both pulps. The kappa number corrected for the HexA contribution (“HexA-corr. kappa number”) was calculated for the pulps with the progress of POM delignification and the corresponding levels of POM reduction were measured. Based on these data, no difference in the delignification efficiency between softwood and birch kraft pulp was observed. The conversion factor between Klason lignin and “HexA-corr. kappa number,” which is used as a convenient method for estimating the lignin oxidizability level, gradually increased with the progress of POM delignification. This indicates that POM delignification reduces the level of oxidizable structures in lignin. Residual lignins of unbleached kraft and kraft POM-delignified pulps were isolated by mild acid hydrolysis. Analyses of the residual lignins show that during POM delignification lignin undergoes changes that include a sharp reduction in the content of phenolic hydroxyl groups (PhOH groups) and a high increase in carbonyl groups, based on the “aromatic lignin.” Results strongly indicate that POM treatment of kraft pulps results in a loss of aromaticity. Stilbene structures characteristic of kraft pulp residual lignin are modified during POM delignification, and the stability of lignin bonds in this process decreases in the following order: $\beta\text{-O-4} > \beta\text{-5} > \beta\text{-}\beta$. Based on the results of this study it appears that in POM delignification the residual lignins of softwood and birch kraft pulps are removed in a similar manner. The different levels of carbonyl groups in the residual lignins isolated from pulps of approximately the same kappa number suggest, however, that the extent of the corresponding reactions may be different for guaiacyl (G), softwood and syringyl-guaiacyl (SG), birch lignins.

Introduction

New bleaching technologies are needed to replace environmentally unfriendly chlorine-based bleaching technologies. The use of different chemical agents and enzymes as alternative delignification agents has been examined and, in some cases, implemented. Polyoxometalates (POMs) favorably embrace the advantages of both chemical (active at elevated temperatures) and biological (highly selective) lignin-oxidizing agents and have been under investigation for pulp bleaching purposes at the USDA Forest Service, Forest Products Laboratory (FPL), for the past decade [1].

POMs are discrete, nanoscale (0.6-2.5nm), early-transition-metal-oxygen-anion clusters. Different mixed-addenda heteropolyanions such as $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$, $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$, $[\text{PVMo}_{11}\text{O}_{40}]^{4-}$, and $[\text{SiV}_x\text{MoW}_{11-x}\text{O}_{40}]^{5-}$, have been successfully applied for the selective removal and mineralization of lignin in a two-step process [1,2].

To achieve a maximal delignification effect under optimal process parameters, elucidation of the lignin oxidation mechanism is needed. The reactivity of phenolic and non-phenolic lignin structural units has been studied using monomeric and dimeric lignin model compounds (LMCs) [3-5].

Model studies, however, do not reflect all of the reactions that lignin might undergo as a macromolecule in the pulp matrix. Therefore, to obtain better insight into the lignin reactions leading to its solubilization during POM treatment of kraft pulp, the structural transformation of lignin in POM-bleached pulps should be examined. Our studies include characterization of residual lignin isolated from commercial softwood and laboratory birch kraft pulps delignified with POMs. Results of these studies, combined with those obtained in the model studies, should enable us to avoid the potentially undesirable lignin reaction

pathways and lead us to optimization of the POM-delignification process. In this context, the possibility of reducing the amount of POMs needed per ton of pulp will lead to an improved bleaching process.

In our previous studies [6], an increase of the conversion factor, CF between Klason lignin and kappa number from 0.152 to about 0.185 was noticed with the progress of POM delignification of softwood commercial kraft pulp. Chlorine dioxide/periodate delignification also resulted in an increase of CF to a value of 0.18 as observed by Brogdon [7]. This increase was attributed to quinonoid structures formed during ClO₂ bleaching because quinonoid structures consume less permanganate than do most of the aromatic structures, including those resulting from the quinone reduction, and because the CF was shifted back to the usual value of about 0.15 after pulp reduction with sodium dithionite or alkaline extraction. To test the quinone contribution to the CF increase during POM delignification, reduction of the POM-delignified softwood pulp and the corresponding residual lignin was performed in this study.

Although quinone structures lead to the kappa number decrease/CF increase, hexeneuronic acid groups (HexA) linked to pulp xylans have an opposite effect on these values because HexA groups consume permanganate, i.e., increase kappa number [8]. Analysis of the HexA-group content in pulps was included in this study to obtain both information on the HexA effect on the kappa number of kraft POM-delignified pulps and insight into the stability of HexA groups in POM delignification.

UV-, FTIR-, and NMR-spectral analyses of lignin were performed in this study. Also, the SERS (Surface Enhanced Raman Spectroscopy) method, which has been under development at the FPL, was used in the lignin analysis.

Experimental

Materials

Commercial softwood kraft pulp (KC) used in these experiments was of 30.5 kappa number. Birch kraft pulp (KB) was laboratory made of 27.2 kappa number (both stored at 8°C).

Delignification Experiments: Both kraft pulps were delignified with the POM mixture under anaerobic conditions using a 2L horizontal Parr reactor configured with anchor stirrers. This was conducted using an equilibrated POM mixture composed of 0.5M Na₅₍₊₂₎[SiV_{1(-0.1)}MoW_{10(+0.1)}O₄₀], at 12% pulp consistency (12% cons.&0.5MPOM) for KC and 0.4M Na₅₍₊₂₎[SiV_{1(-0.1)}MoW_{10(+0.1)}O₄₀], at 8% pulp consistency (8% cons.&0.4MPOM) for KB. The pH range of 5.5-6.5 was controlled by equilibration reactions of the POM [2]. Temperature (100-140°C) and time (10-240 min) of the reactions were adjusted to produce kraft POM-bleached pulps of various kappa numbers: six softwood kraft POM-bleached pulps in the 28.1-10.8 kappa number range (KCPOM) and three birch kraft POM-bleached pulps in the 21.3-10.3 kappa number range (KBPOM). The amount of reduced, i.e., reacted POMs was monitored using the reaction between reduced form of POMs and [Co^{III}W₁₂O₄₀]⁵⁻: [Co^{III}W₁₂O₄₀]⁵⁻ + POM_{red} → [Co^{II}W₁₂O₄₀]⁶⁻ + POM_{ox}. Then, the concentration of POM_{red} in the solution was calculated based on the absorption at 625nm, which is absorption maximum of [Co^{II}W₁₂O₄₀]⁶⁻, as explained in detail by Yokoyama et al. (2004) [5].

Residual Lignin Isolation: Residual lignin was isolated from extracted (successive Soxhlet extraction with dichloromethane and acetone, 8 hours) pulps using a method of mild acid hydrolysis with a slight modification [9, 6].

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 with respect to Klason/acid-soluble lignin and carbohydrates [10-12].

Pulp/MWL/RL Reduction: Sodium dithionite reduction [13] was performed on the extracted (dichloromethane, acetone) softwood kraft pulp POM-delignified of kappa number 23.9. Kappa number and Klason lignin content were measured on the extracted/reduced pulp. Sodium borohydride reduction of MWL (loblolly pine) and residual lignins isolated from softwood kraft pulp and softwood kraft POM-delignified pulps (kappa number 23.9 and 10.8) was performed according to Browning (1967) [14], with a modification that included precipitation of reduced lignin by acidification of the solution to pH2.

KMnO₄ Consumption: To evaluate the level of the oxidizable lignin structures, the consumption of KMnO₄ by the lignins before and after reduction was measured [15, 16].

Phenolic Hydroxyl Groups/UV/Vis. Spectroscopy: The content of free phenolic hydroxyl groups (PhOH) was determined by the ionization difference UV-spectroscopic method [17]. The pH6 lignin solution prepared in accordance with the method requirements was also used in the UV-spectral studies of

the lignin samples. 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}). 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 suggested by Hortling et al. (1997) [18]. 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 $1840\pm 15\text{ cm}^{-1}$ and 1690 cm^{-1} for the C=O band and $1542\pm 5\text{ cm}^{-1}$ and $1483\pm 2\text{ cm}^{-1}$ for the aromatic band. This method is based on the calibration obtained using mixtures of milled wood lignin and tartaric acid. Therefore, the method provides an opportunity to compare the contents of C=O groups in lignins rather than to get the exact number of C=O groups. The results are expressed as moles of C=O groups per g of “aromatic lignin.”

SERS/Surface Enhanced Raman Spectroscopy: Lignin samples were mixed with 200 times their weight in Ag 2-3.5micron powder (Aldrich 32708-5). A small amount of ethanol was added to make a thick slurry or paste. The ethanol was allowed to evaporate, and the mixing process was repeated a second time. The mixed samples were placed in aluminum powder sample holders and the near-IR FT-Raman spectra were obtained using a Bruker RFS 100 set to 600mW diffuse laser power and 4 cm^{-1} resolution.

NMR Spectroscopy: 2D NMR spectra were run on a Bruker DPX-250 spectrometer using standard Bruker pulse 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 $_2$ O (4:1). The central solvent peak (δ_{H} 2.04, δ_{C} 29.83) was used as the internal reference.

Results and Discussion

Pulp Characterization

Kappa Number/POM Reduction/HexA Content: Lignin removal in POM bleaching is achieved by oxidation of lignin with POMs followed by lignin dissolution in the liquor. The delignification efficiency could be expressed as a correlation between the kappa number decrease and the reduction of POMs. Data obtained in the POM delignification of softwood commercial kraft pulp (KC, kappa number 30.5) and birch laboratory kraft pulp (KB, kappa number 27.2) are presented in Fig. 1.

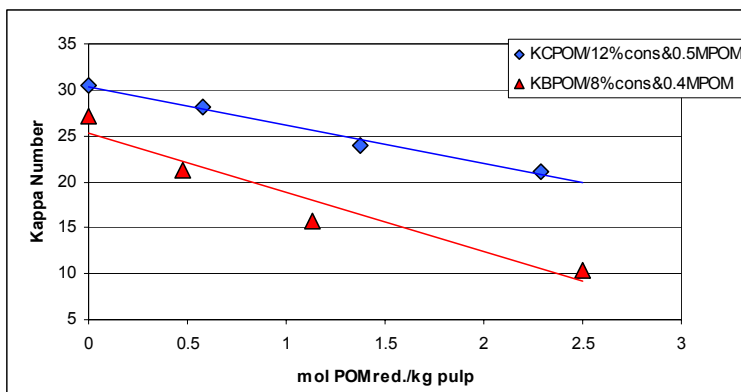


Fig. 1. Kappa Number vs. POM Reduction

Trends presented in Fig.1 indicate a slightly greater chemical efficiency in delignification of birch kraft pulp compared with that of softwood kraft pulp, i.e., less POMs appears to be consumed to achieve a given reduction in kappa number. The hexeneuronic acid group (HexA) content in the pulps, however, should be considered in this analysis because the kappa number corrected for the HexA groups better reflects the Klason lignin content in pulp (10 μmol of HexA correspond to 0.85 kappa units [8]). Data obtained after the kappa number correction for the HexA contribution suggest that the POM delignification of birch and softwood kraft pulp is conducted at approximately the same chemical efficiency (Fig. 2).

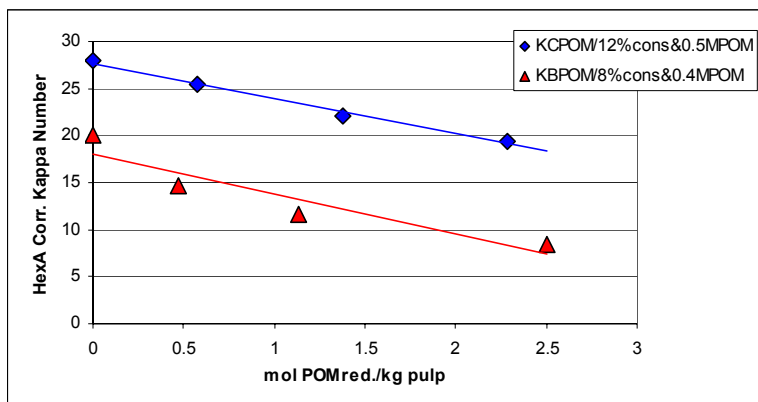


Fig. 2. HexA-Corrected Kappa Number vs. POM reduction

Hexeneuronic acid groups were removed during the course of POM delignification (Fig. 3). This is an important characteristic of the bleaching process because HexA remaining in the traditionally bleached kraft pulp might participate in brightness reversion [19].

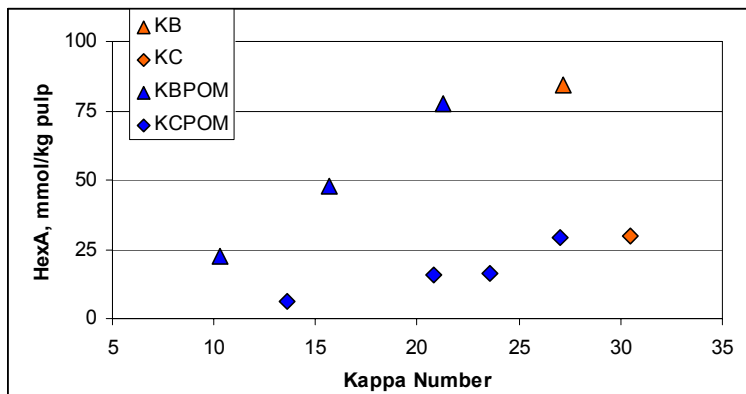


Fig. 3. HexA – Group Content in Unbleached and POM-Bleached Kraft Pulp

A control experiment was conducted to test if the HexA removal was a result of the POM action. Unbleached softwood kraft pulp, kappa number 30.5, was treated under the same conditions as in the POM delignification (pH, °C, N₂) except that POMs were excluded. Cooking time corresponded to the time needed to obtain kappa number 23.9 in the POM experiment. HexA content and kappa number were determined for the resulting pulp (Fig. 4). It was found that the control experiment (KCcontr23.9) resulted in the same level of HexA reduction as did the corresponding experiment of POM delignification (KCPOM23.9). These results imply that the slightly acid conditions/high temperature of the POM delignification provide for the HexA removal. The same efficiency of lignin removal in POM delignification of HexA-enriched birch and softwood kraft pulps (Fig.2), together with this result (Fig. 4) indicate that POMs are most likely not consumed for the HexA removal.

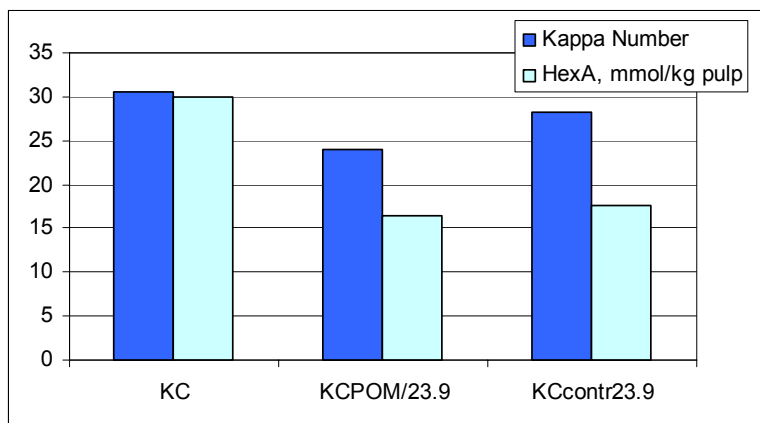


Fig.4. Kappa Number and HexA Content in Unbleached (KC), POM-Bleached (KCPOM) and Control (KCcontr) Softwood Kraft Pulp

CF/Dithionite Reduction: POM-delignification caused an increase in the CF (Klason Lignin Content/Kappa Number) for both softwood [6] and birch kraft pulps. CF data obtained after the correction of kappa number for the HexA-contribution (HexA-corr. kappa number) are presented in Fig. 5. To test the possibility of quinones contributing to this increase [7], a dithionite reduction was performed on the extracted POM- delignified softwood kraft pulp, kappa number 23.9 (CF 0.183 after extraction). Dithionite reduction of the pulp resulted in a slight decrease of CF, but only at higher levels of dithionite (2% $\text{Na}_2\text{S}_2\text{O}_4/\text{OD}$ pulp, CF 0.182; 5% $\text{Na}_2\text{S}_2\text{O}_4/\text{OD}$ pulp, CF 0.177). These results suggest that quinone structures, which may be formed during POM delignification [3, 4, 20], only partially explain the CF increase. Additional studies are needed to identify the primary reason for the CF increase during POM delignification.

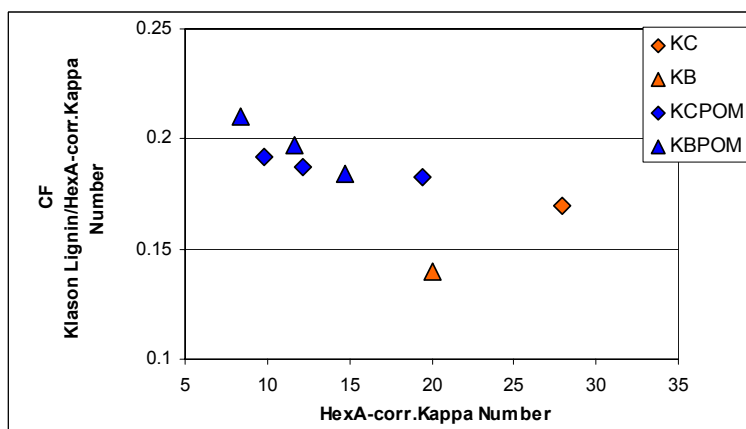


Fig. 5. Increase of Conversion Factor (CF = Klason Lignin Content/HexA-Corr.Kappa Number) in the POM-delignification of Softwood and Birch Kraft Pulps

Residual Lignin Isolation and Characterization

RL Isolation Yield/RL Composition: In our previous studies [6], acid hydrolysis resulted in a lower yield of residual lignin isolated from POM-delignified softwood kraft pulps than from both unbleached and oxygen-bleached softwood kraft pulps. In this study, residual lignin from unbleached and POM-delignified birch kraft pulps was isolated using the same method of lignin isolation (Experimental). Although an increase in the yield (RL yield, % Klason lignin) was noticed for unbleached birch kraft pulp, kappa 27.2 compared with unbleached softwood kraft pulp, kappa 30.5 (RLKC 58.5%, RLKB 73.3 %), the lowest yields were obtained for POM-delignified birch kraft pulps (average yield, RLKCPOM 23.1%, RLKCOx 48.6%, RLKBPOM 17.5%) (Fig. 6).

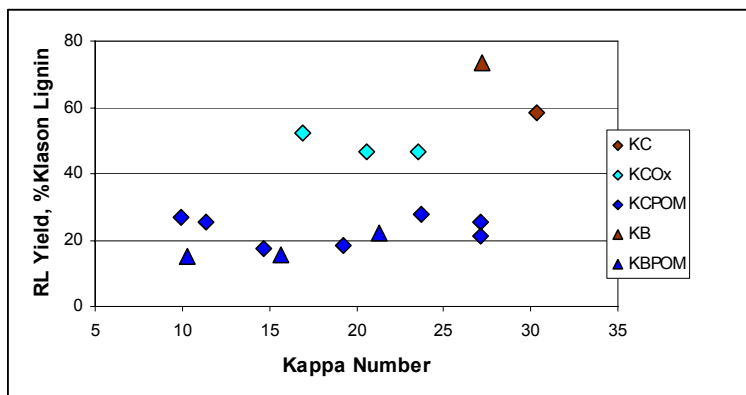


Fig.6. Yield of Isolated Residual Lignin from Unbleached, Oxygen- and POM-delignified Softwood and Birch Kraft Pulps

The reduction in the isolated lignin yield might be associated with an increased level of lignin condensation and/or a closer association between the lignin and carbohydrates. Syringyl-guaiacyl (SG), hardwood lignins are less likely to participate in condensation reactions than are guaiacyl (G), softwood lignins due to the occupied C5 position in the S units. Therefore, a higher yield of RLKB than of RLKC can be partially explained by the less condensed residual lignin of birch kraft pulp.

The carbohydrate content of residual lignin is an indication of the association between lignin and carbohydrates in pulp, especially when comparisons are made for the lignins obtained using the same method from the pulps of gradually decreasing kappa number. The carbohydrate content and composition, along with the contents of Klason and acid-soluble lignin in the residual lignins, are presented in Table I.

Table I: Chemical Composition of Residual Lignins (- indicates below the detection level)

RL of Pulp	Pulp Kappa Number	Lignin, %RL			Carbohydrates, %RL					
		Klason	Acid-Sol.	Total	Ara	Gal	Glu	Xyl	Man	Total
KC	30.5	92.8	0.77	93.6	0.04	0.06	0.53	0.16	0.06	0.85
KPOM #1	28.1	87.1	1.34	88.4	0.06	0.09	2.90	0.32	0.19	3.56
KPOM #3	23.9	86.3	1.51	87.8	0.04	0.06	4.36	0.21	0.11	4.78
KPOM #11	20.8	87.1	1.89	89.0	0.07	0.07	1.57	0.25	0.25	2.21
KPOM #14	16.2	81.1	2.92	84.0	0.10	0.17	1.95	0.64	0.44	3.30
KPOM #12	13.0	78.5	4.63	83.1	0.08	0.10	1.43	0.50	0.43	2.54
KB	27.2	93.4	1.68	95.1	-	0.04	0.13	0.30	-	0.47
KBPOM#1	21.3	89.7	1.95	91.7	-	0.03	0.27	0.39	-	0.69
KBPOM#2	15.7	91.3	2.03	93.3	0.02	0.03	0.67	0.55	-	1.27

The higher carbohydrate content in RLKC compared to RLKB is in accordance with the lower yield of RLKC, indicating that a closer association between lignin and carbohydrates decreases the isolated lignin yield. Also, the carbohydrate content of the residual lignins isolated from POM-delignified pulps with the lower yields is greater than that of the residual lignins isolated from the corresponding unbleached pulps with the higher yields. The average carbohydrate content of the RLKCPOM is approximately three times greater than that of the RLKBPOM, indicating that the lignin-carbohydrate association might be stronger in the POM-delignified softwood than in the birch kraft pulp, even though the average yield of lignin isolated from the KCPOM was greater than that from the KBPOM. Based on these data, the lignin-carbohydrate association is not a major reason for the extremely low yield of lignin isolation from KBPOM pulps. Regarding the composition of carbohydrates remaining in the residual lignins, glucose represents the main carbohydrate in RLKCPOM (aver. 70% of carbohydrates in RL), and glucose and xylose are the main carbohydrates in RLKBPOM (xylose and glucose, aver. 50 and 45% of carbohydrates in RL, respectively).

KMnO₄ Consumption of RL/Reduced RL: Our previous studies showed that the permanganate consumption of the RLKCPOMs was less than that of RLKC, indicating that POM delignification results in reduction of the lignin oxidizability, and consequently, in an increase of the CF [6]. In these studies, the

KMnO₄ consumption of RLKC, RLKCPOM23.9, and RLKCPOM10.8 was measured after reduction of the lignins with sodium borohydride (RLK_{red}, RLKCPOM_{red}). The average KMnO₄ consumptions of RLKC, RLK_{red}, RLKCPOM, and RLKCPOM_{red} were 523, 510, 395, and 435 ml 0.1N KMnO₄/g lignin, respectively. The KMnO₄ consumption by the residual lignin of POM-delignified softwood pulps was increased only ~10% after reduction. This suggests that a greater level of quinones/carbonyl groups in residual lignin is not a major reason for the observed reduction of the lignin oxidizability during POM-delignification; this is consistent with the results of the dithionite reduction of KCPOM23.9.

Phenolic Hydroxyl Groups (PhOH)/UV/Vis. Spectroscopy: The PhOH content in the residual lignins was determined using the ionization difference method [17] (Fig. 7). A sharp reduction in PhOH content in the residual lignins isolated from the pulps at an early phase of POM delignification (kappa number of softwood and birch POM-delignified pulp 28.1 and 21.3, respectively) suggests that POMs readily oxidize non-etherified lignin units [3, 4].

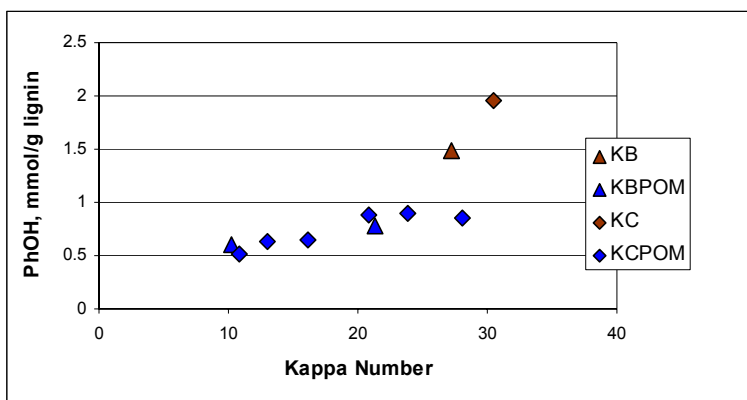


Fig. 7. PhOH Content in Birch and Softwood Kraft Pulps during POM delignification

A significantly low content of PhOH groups in decayed lignins has been discussed as an indication of aromatic ring degradation caused by white-rot fungi attack [21, 22]. UV/Vis. spectral analyses for pH6 lignin solutions (Experimental) were obtained in order to test for concomitant aromatic ring degradation. Fig. 8 compares the absorption spectra of the residual lignin of unbleached and POM-delignified softwood kraft pulps.

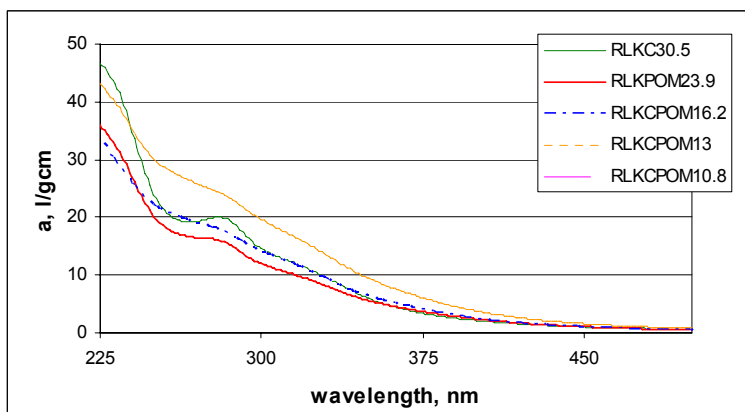


Fig. 8. UV/Vis. Spectra of Residual Lignins of Unbleached and POM-delignified Softwood Kraft Pulps (lignin solution in 50% dioxane/50% 0.2M NaOH buffered at pH6)

Gradual disappearance of the “B band” [23] of lignin at ~280nm can be noticed in the absorption spectra of the residual lignins of POM-delignified pulps of decreasing kappa number (Fig. 8). The difference spectra obtained after subtraction of the absorption spectra of residual lignins of POM-delignified

pulps from those of the corresponding kraft pulps very clearly indicate this effect of POM delignification. Fig. 9 shows the difference spectra obtained for residual lignins of POM-delignified softwood kraft pulps.

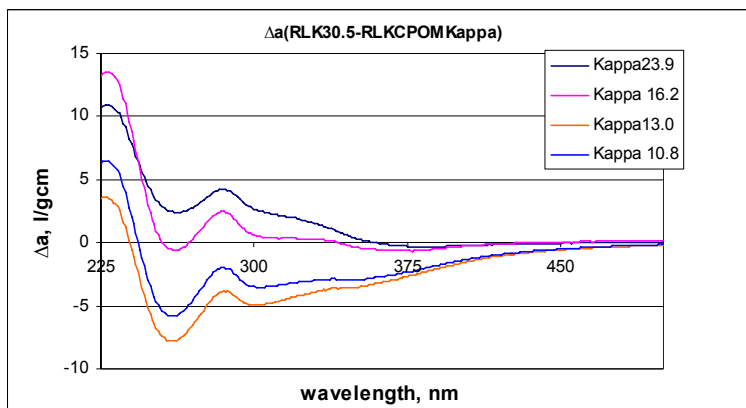


Fig.9. Difference Spectra of Residual Lignins Resulting from the POM-delignification of Softwood Kraft Pulps ($a_{RLKC} - a_{RLKCPOM}$)

All of the difference spectra are characterized by the maxima at 282nm and minima at 262 and 302nm, i.e., the structures exhibiting the absorption maxima at 262 and 302nm and shoulder at ~350nm are newly formed at the expense of the guaiacyl unit alteration in the POM delignification. The structures possessing the corresponding maxima are characterized by different functionalities, including carbonyl, carboxyl, and quinone groups. The negative values in the difference spectra of RLKCPOM13 and RLKCPOM10.8 result from the higher absorption coefficients characteristic of these compounds, especially quinones. Additionally, characteristic absorption maxima of p-benzoquinones are in the same regions as those of the newly formed compounds: bands of strong and medium intensity appear in the 240-300nm and 285-440nm region, respectively [24]. It should be noted that quinone structure formation was also indicated in previous studies of the mechanism of POM delignification using both lignin model compounds and POM-delignified pulps [3, 4, 20].

The difference spectra between the absorption spectra of RLKCPOM13 and RLKCPOM10.8 are characterized by positive values, indicating that towards the end of the POM delignification newly-formed structures are degraded (Figs. 9, 10).

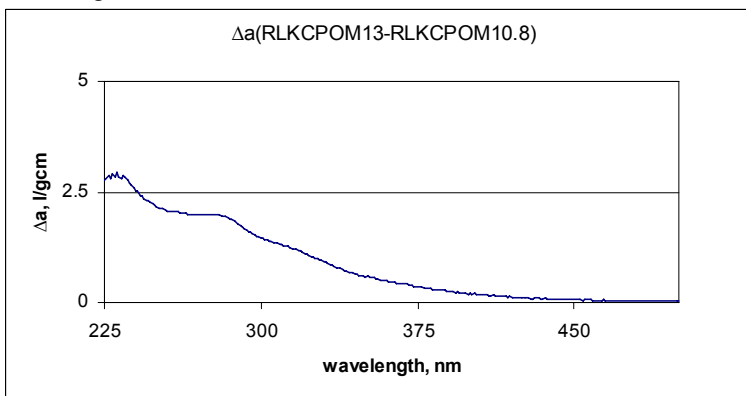


Fig.10. Difference Spectra of Residual Lignins of POM-delignified Pulps KCPOM13 and KCPOM10.8 ($a_{RLKCPOM13} - a_{RLKCPOM10.8}$)

FTIR Spectroscopy/Carbonyl Groups/ReducedRL: Previous FTIR spectral studies of residual lignins from softwood unbleached and POM-delignified kraft pulps showed that the ratios A_i/A_{1510} (i , cm^{-1} -characteristic lignin bands; 1510cm^{-1} aromatic skeletal vibration band usually serves as reference band in lignin studies [26]) increased with the delignification progress. A similar effect (a lower intensity of the aromatic band relative to other bands) in white-rot fungi-degraded lignins was discussed as an indication of

a decreased content of aromatic rings [21]. The FTIR spectra of RLKB and RLKB15.7 and RLKB10.3 are shown in Fig. 11.

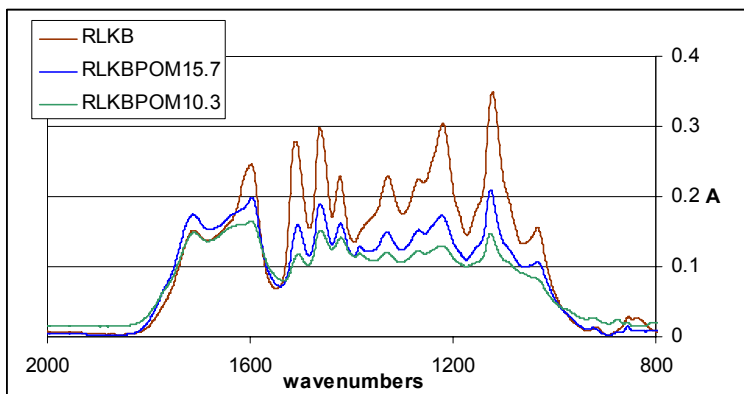


Fig. 11. FTIR Spectra of RL of unbleached birch kraft pulp, kappa 27.2 (RLKB) and of POM-delignified birch kraft pulps, kappa 15.7 and 10.3 (RLKBPOM15.7; RLKBPOM10.3)

Based on FTIR data, the content of carboxyl and non-conjugated carbonyl groups (C=O groups) in residual lignins was determined in relation to aromatic structures (Experimental). Results obtained for the residual lignins of unbleached and POM-bleached kraft pulps indicate that the C=O group content increases with the progress of POM delignification and are consistent with the UV/Vis. spectral results (Fig. 12).

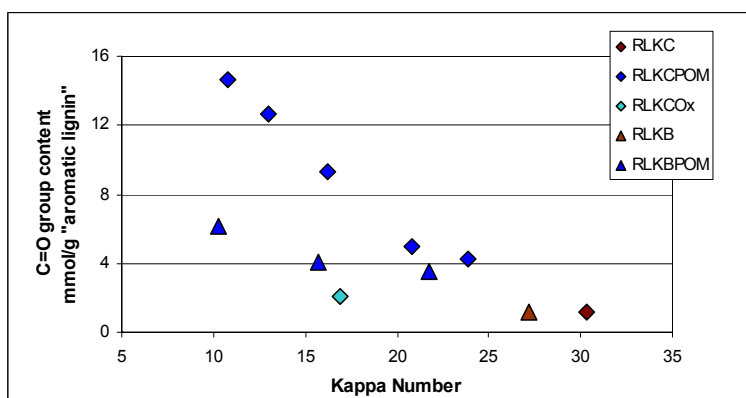


Fig. 12. Contents of C=O groups (carboxyl + non-conjugated carbonyl) in the residual lignins with the progress of delignification

Residual lignins from POM-delignified softwood pulps contain more C=O groups than those from corresponding birch pulps (9 and 4 mmol/g "aromatic lignin" for RLKCPOM16.2 and RLKBPOM15.7, respectively). At a kappa number of about 16, the content of C=O groups in RLKCPOM is approximately four times greater than that in residual lignin of RLKCOx. This is in accordance with a lower reduction potential of dioxygen (O_2 ; alkaline solution) than that of typical POMs ($O_2 + 1e^- \rightarrow O_2^-$, $E^\circ = -0.33V$ vs. NHE; $[Si^V W_{11}O_{40}]^{5-} + 1e^- \rightarrow [Si^{IV} W_{11}O_{40}]^{6-}$, pH 2-8; $E^\circ = 0.69V$ vs. NHE) [27]. In addition, Fu and Lucia (2004) [28] recently showed that, in oxidation under alkali oxygen conditions, lignin maintains most of its C_6-C_3 units that would lead to the lower values of C=O/g "aromatic lignin" found in the study here. Therefore, the high content of C=O groups (expressed on the basis of "aromatic lignin") in RLKCPOM might also indicate a lower aromaticity of RLKCPOM compared with RLKCOx. Also, this would be supported by the results of POM delignification discussed previously: the UV/Vis. difference spectra, a reduction of the PhOH-group content, and FTIR results indicating an increase of the A_7/A_{1510} ratios.

Based on FTIR data, reduction of residual lignins with $NaBH_4$ led to a decrease of both the C=O group content and the A_{1600}/A_{1510} ratio. This confirms that the $1600cm^{-1}$ band results from the aromatic skeletal vibrations and the C=O stretch [26] and implies that an increase of the C=O group content may

account for most of the A_{1600}/A_{1510} ratio increase with the POM delignification. For example, reduction of RLKCPOM23.9 resulted in a decrease of ~40% of the C=O group content and ~30% of the A_{1600}/A_{1510} ratio.

SERS/Surface Enhanced Raman Spectroscopy: Residual lignins isolated in this study were difficult to investigate using conventional Raman spectroscopy due to the presence of chromophores, which make lignins highly fluorescent. Surface-enhanced Raman spectroscopy performed under the conditions outlined in the Experimental showed significant improvement. SERS results for RLKC, RLKCPOM28.1, RLKCPOM23.9, and RLKCPOM10.8 before and after reduction are presented in Fig. 13. Note that the POM delignification resulted in the intensification of the 1494, 1269, 1048, 643, and 419 cm^{-1} bands. The 1606 cm^{-1} band characteristic of RLKC modifies/disappears with the progress of delignification and RLKCPOM10.8 contains a broad band at 1584 cm^{-1} with a shoulder at 1606 cm^{-1} . Assignments of these bands require additional model studies.

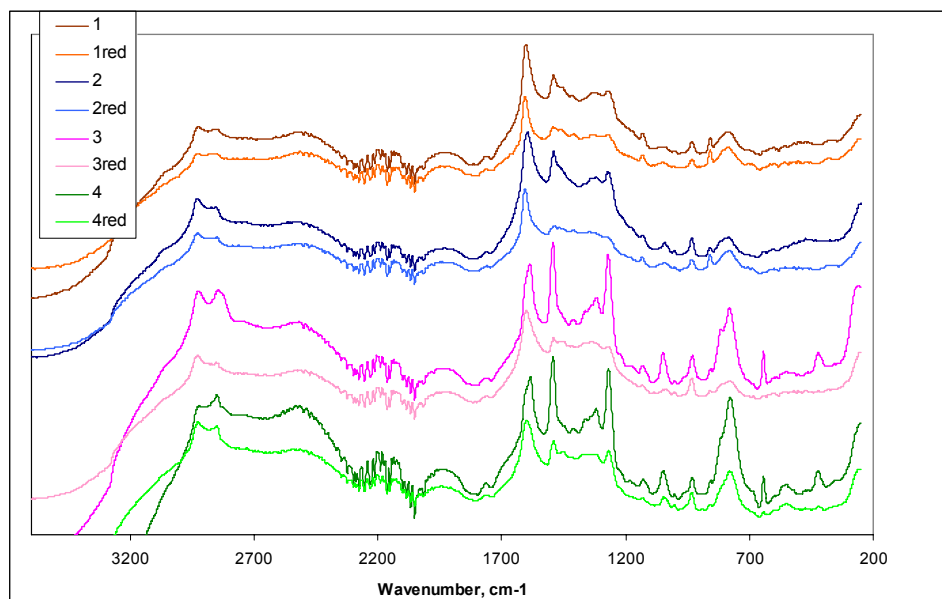


Fig. 13. SER Spectra of Residual Lignins before and after Reduction:

1/1red: RLKC; 2/2red: RLKCPOM28.1; 3/3red: RLKCPOM23.9; 4/4red: RLKCPOM10.8

SER spectra of reduced lignins exhibit a reverse effect compared with POM delignification. For example, the 1494 and 1269 cm^{-1} bands were reduced, and instead of the 1584 cm^{-1} band, the 1606 cm^{-1} band appeared (bands similar to those characteristic of RLKC). SERS analysis of different lignin samples and lignin model compounds is in progress in our laboratory, but the first results confirm the UV/Vis. and FTIR spectral results, which suggest that the POM delignification of kraft pulps results in carbonyl group introduction into the lignin structure.

NMR Spectroscopy: 2D HSQC (inverse detected short range C-H correlations) spectra of RLKB and RLKBPOM15.3 are shown in Figs.14 and 15, respectively.

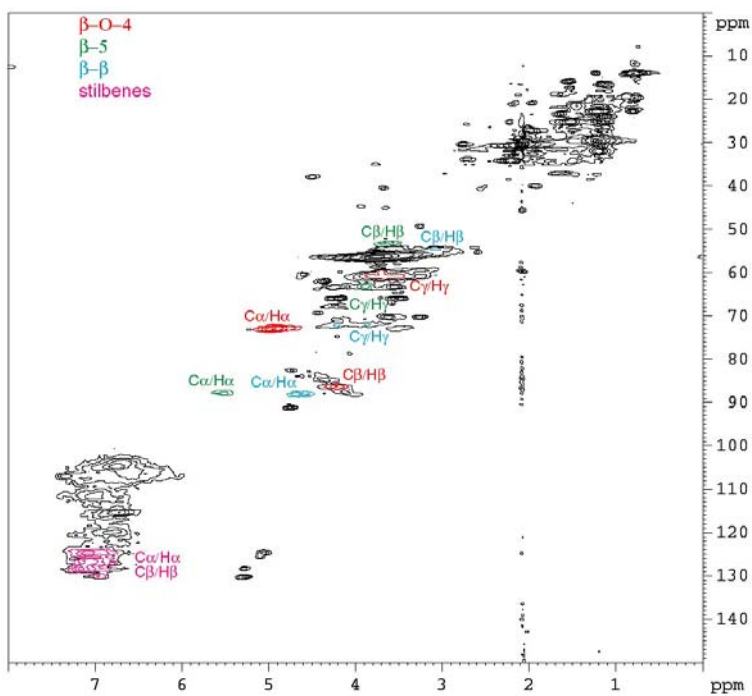


Fig. 14. HSQC Spectra of RLKB (kappa number 27.2)

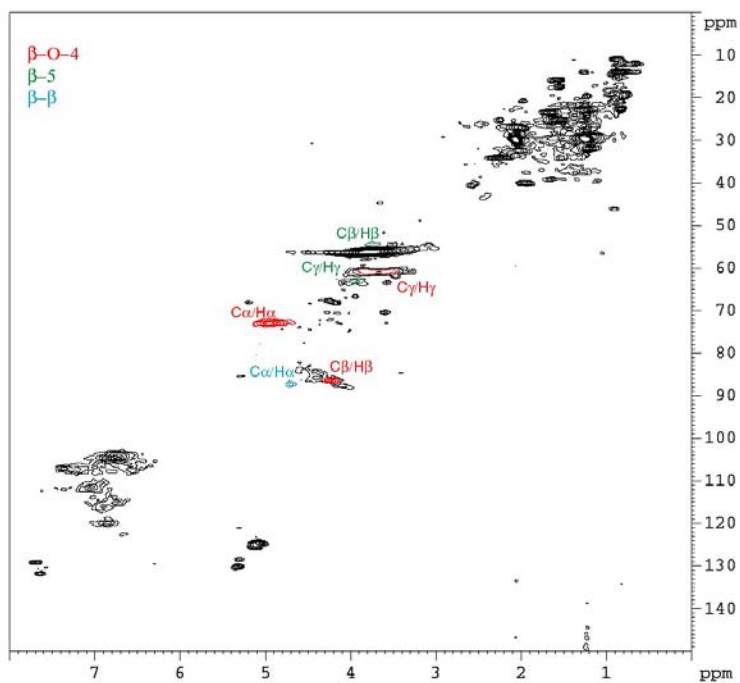


Fig.15. HSQC Spectra of RLKBPOM15.3

Results obtained from the analysis of the HSQC spectra of RLKB and RLKBPOM correspond those results obtained in the analysis of RLKC and RLKCPOM [6]. Stilbene structures characterized by

their C_{α}/H_{α} and C_{β}/H_{β} correlations are absent from the HSQC of RLKBPOM21.3 (the residual lignin from an early phase of POM delignification). Therefore, high reactivity of these structures to POMs is indicated for both softwood and birch kraft pulps. Model studies are planned to explore the mechanism of stilbene reactions in the POM delignification. A gradual disappearance of the correlations that characterize the β -5 and β - β lignin bonds suggests their gradual cleavage. Conversely, all three correlations, the C_{α}/H_{α} , C_{β}/H_{β} , and C_{γ}/H_{γ} , characteristic of the β -O-4 lignin bonds, remain present in the residual lignins resulting from the late delignification phase (RLKCPOM10.8 and RLKBPOM10.3); this implies higher resistance of the β -O-4 bonds to POM attack.

Conclusions

Results obtained in the analyses of the residual lignin isolated from softwood and birch kraft pulp delignified with POMs show that lignin undergoes changes that include a sharp reduction in the content of PhOH groups and a high increase in carbonyl groups, based on the "aromatic lignin." Results strongly indicate that POM treatment of kraft pulps results in a loss of aromaticity. Stilbene structures characteristic of kraft pulp residual lignin are modified during POM delignification, and the stability of lignin bonds in this process decreases in the following order: β -O-4 > β -5 > β - β . Based on the results of this study it appears that in POM delignification the residual lignins of softwood and birch kraft pulps are removed in a similar manner. The different levels of carbonyl groups in the residual lignins isolated from the pulps of approximately the same kappa number suggest, however, that the extent of the corresponding reactions may be different for guaiacyl (G), softwood and syringyl-guaiacyl (SG), birch lignins.

References

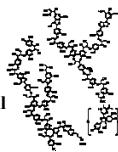
1. Weinstock, I. A., Atalla, R. H., Reiner, R. S., Moen, M. A., Hammel, K. E., Houtman, C. J., Hill, C. L. (1996): "A new environmentally benign technology and approach to bleaching kraft pulp. Polyoxometalates for selective delignification and waste mineralization," *New J. Chem* 20:269-275.
2. Reiner, 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. (2001): "Thermodynamically stable, self-buffering polyoxometalate delignification system," 11th ISWPC Nice, France, Vol. III:349-352.
3. Kang, G., Ni, Y., Van Heiningen, A. (1997): "Polyoxometalate delignification: study of lignin-model compounds," *Appita* 50(4):313-318 (1997).
4. Weinstock, I. A., Hammel, K. E., Moen, M. A., Landucci, L. L., Ralph, S., Sullivan, C. E., Reiner, R. S. (1998): "Selective transition-metal catalysis of oxygen delignification using water-soluble salts of POM anions. Part. II. Reactions of α -[SiVW₁₁O₄₀]⁵⁻ with phenolic lignin-model compounds," *Holzforschung* 52(3):311-318.
5. Yokoyama, T., Chang, H.-m., Reiner, R. S., Atalla, R. H., Weinstock, I. A., Kadla, J. F. (2004): "Polyoxometalate oxidation of non-phenolic lignin subunits in water: Effect of substrate structure on reaction kinetics," *Holzforschung* 58(2):116-121.
6. Bujanovic, B., Reiner, R. S., Hirth, K. C., Ralph, S. A., Atalla, R. H. (2005): "Studies of Lignin Transformation in Polyoxometalate (POM) Bleaching of Kraft Pulp," 13th ISWFPC Auckland, New Zealand, May 16-19, 2005, Proc., Vol.3:49-56 (Poster Pres.).
7. Brogdon, B.N. (2001): "Influence of oxidized lignin structures from chlorine dioxide delignified pulps on the kappa number test," *J. Pulp Paper Sci.* 27(11):364-369.
8. Li, J., Gellerstedt, G. (1997): "The contribution to kappa number from hexeneuronic acid groups in pulp xylem," *Carb. Res.* 302:213-218.
9. Gellerstedt, G., Pranda, J., Lindfors, E.L. (1994): "Structural and molecular properties of residual birch kraft lignin," *J. Wood Chem. Technol.* 14:467-482.
10. Davis, M. W. (1998): "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.* 18(2):235-252.
11. Dence, C. W. (1999): "The determination of lignin," in: *Methods in lignin chemistry*, S. Y. Lin, C. W. Dence, eds.: Springer-Verlag, 33-61.
12. Chai, X.-S., Zhu, J.Y., Li, J. (2001): "A simple and rapid method to determine hexeneuronic acid groups in chemical pulps", *J. Pulp Paper Sci.* 27(5):165-170.

13. Agarwal, U. P., Landucci, L.L. (2004): "FT-Raman investigation of bleaching of spruce thermomechanical pulp," *J. Pulp Paper Sci.* 30(10):269-274.
14. Browning, B. L. (1967): "Investigation of lignin preparations," in: *Methods of wood chemistry*," B. L. Browning ed. Intersci. Publ., Vol.II: 747-783.
15. Li, J., Gellerstedt, G. (1998): "On the structural significance of kappa number measurements," *Nordic Pulp Paper Res. J.* 13(2):153-158.
16. Li, J., Sevastyanova, O., Gellerstedt, G. (2002): "The relationship between kappa number and oxidizable structures in bleached kraft pulps," *J. Pulp Paper Sci.* 28(8):262-266.
17. Gärtner, A., Gellerstedt, G., Tamminen, T. (1999): "Determination of Phenolic Hydroxyl Groups in Residual Lignin Using a Modified UV-method," *Nordic Pulp Paper Res. J.* 14(2):163-170.
18. Hortling, B., Tamminen, T., Kenttä, E. (1997): "Determination of carboxyl and non-conjugated carbonyl groups in dissolved and residual lignins by IR spectroscopy," *Holzforschung* 51(5): 405-410.
19. Buchert, J., Bergnor, E., Lindblad, G., Viikari, L., Ek, M. (1997): "Significance of xylan and glucomannan in the brightness reversion of kraft pulps," *TAPPI J.* 80 (6):165-171.
20. Weinstock, I.A., Minor, J. L., Reiner, R. S., Agarwal, U. P., Atalla, R. H. (1993): "FT Raman and UV visible spectroscopic studies of a highly selective polyoxometalate bleaching system," 1993 Pulping Conf., November 1-3, Atlanta, Ga: Proc., Book 2., TAPPI Press: 519-532.
21. Kirk, T. K., Chang, H.-m. (1975): "Decomposition of lignin by white-rot fungi II. Characterization of heavily degraded lignins from decayed spruce," *Holzforschung* 29(2):56-64(1975).
22. Crestini, C., Sermanni-Giovanozzi, G., Argyropoulos, D. S. (1998): "Structural modifications induced during biodegradation of wheat lignin by *Lentinula edodes*," *Bioorg.Med.Chem.* 6(7): 967-973.
23. Lin, S. Y. (1992): "Ultraviolet spectrophotometry," in: *Methods in lignin chemistry*," S. Y. Lin, C. W. Dence eds., Springer-Verlag, 217-232.
24. Berger, St., Rieker, A. (1974): "Identification and determination of quinones," in "The chemistry of the quinonoid compounds," S. Patai. Ed., John Wiley & Sons, 163-229.
25. Weinstock, I.A., Minor, J. L., Reiner, R. S., Agarwal, U. P., Atalla, R. H. (1993): "FT Raman and UV visible spectroscopic studies of a highly selective polyoxometalate bleaching system," 1993 Pulping Conf., November 1-3, Atlanta, Ga: Proceedings, TAPPI Press, Book 2: 519-532
26. Faix, O. (1992): "Fourier Transform Infrared Spectroscopy," in: *Method in lignin chemistry*," S. Y. Lin, C. W. Dence eds., Springer-Verlag, 83-109.
27. Weinstock, I. A., Atalla, R. H., Reiner, R. S., Houtman, C. J., Hill, C.L. (1998): "Selective transition-metal catalysis of oxygen delignification using water-soluble salts of POM anions. Part. I. Chemical Principles and Process Concepts," *Holzforschung* 52 (3): 303-310.
28. Fu, S., Lucia, L. A. (2004): "TMAH-pyrolysis-gas chromatography – mass spectrometry analysis of residual lignin changes in softwood kraft pulp during oxygen delignification," *Can. J. Chem.* 82: 1197-1202.

Structural Changes of Residual Lignin of Softwood and Hardwood Kraft Pulp Upon Oxidative Treatment With Polyoxometalates

2005 TAPPI Engineering, Pulping & Environmental Conference
August 28-31, Philadelphia, PA: 30-3

Biljana Bujanovic, Richard S. Reiner, Sally A. Ralph, Umesh P. Agarwal, Rajai H. Atalla, University of Wisconsin-Madison/USDA Forest Products Laboratory, Madison, Wisconsin



Objectives

- **Implementation of environmentally friendly bleaching technology based on polyoxometalates (POMs) requires optimization of POM delignification, including reduction of the POM charge/ton pulp**
- **To achieve a maximal delignification effect under optimal process parameters, elucidation of the lignin oxidation mechanism is needed**



Polyoxometalates - POMs

- Early-transition-metal oxygen-anion clusters
- α -Keggin: $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$, $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$, etc.
- Reversible oxidants, capable of undergoing repeated cycles of reduction and re-oxidation, water soluble, easy to prepare
- As delignification agents under investigation at the FPL since 1993
 - development of POMs capable of selectively decreasing kraft pulp kappa number
 - design of the overall POM bleaching process
 - understanding of lignin oxidation: some studies with lignin model compounds (LMCs) have been performed
- Inadequate attention has been dedicated to the lignin reactions in the pulp



Lignin Chemistry

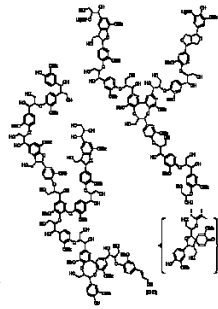
Key factor in understanding and development of POM bleaching

Lignin origin:

- Softwood G-Lignin
- Hardwood GS-lignin

Important parameters:

- G/S ratio
- PhOH-group content
- C-O-C/C-C bonds/condensation level
- Molecular weight
- Level and nature of LCC bonds

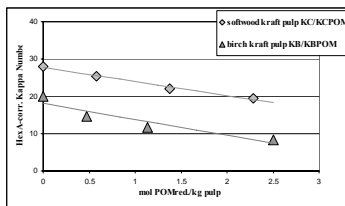


G-lignin scheme
Brunow (1995)

Experimental

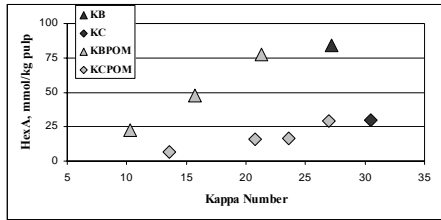
- POM Delignification of Unbleached Kraft Pulps
 - POM: $\text{Na}_{5(+2)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}\text{O}_{40}]$
 - commercial, softwood kraft pulp
 - KC, kappa number 30.5
 - after POM treatment KCPOM, kappa number 28.1-10.8
 - laboratory, birch kraft pulp
 - KB, kappa number 27.2
 - after POM treatment KBPOM, kappa number 21.3-10.3
- Residual Lignin (RL) Isolation
 - acid hydrolysis
- Characterization – Pulps/RL
 - kappa number, Klason lignin/carbohydrate content, HexA, PhOH
 - UV, FTIR, SERS, NMR

POM treatment of softwood and birch kraft pulps
No difference in delignification efficiency was observed

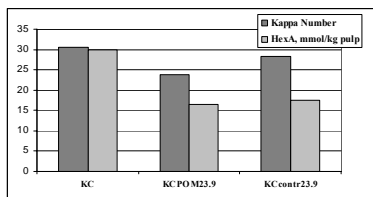


- Delignification efficiency expressed as a correlation between the lignin content decrease and the reduction of POMs
- HexA-corrected kappa number (hexeneuronic acid groups - HexA) reflects Klason lignin content in pulp more accurately than kappa number because HexA groups consume permanganate in kappa number test (10 μ mol of HexA correspond to 0.85 kappa number)

POM treatment of softwood and birch kraft pulps
Hexeneuronic acid groups (HexA) were removed

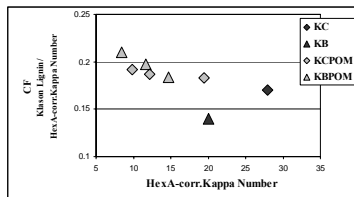


POM treatment of softwood and birch kraft pulps
POMs are not consumed for the HexA removal



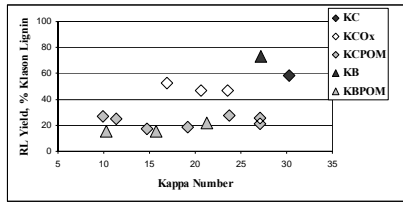
- Approximately the same delignification efficiency of softwood and birch kraft pulps and the HexA removal in control experiment (same conditions as in POM treatment but no POMs) indicate that POMs are not consumed by HexA removal

POM treatment of softwood and birch kraft pulps
Conversion factor, CF
CF = Klason lignin/Hex-corr.kappa number



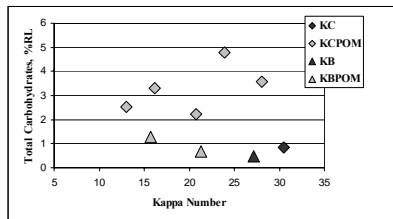
- Permanganate consumption (kappa number test) decreases, i.e., CF increases with the progress of delignification
- POM treatment leads to the reduction of lignin oxidizability (aromaticity loss?)

Residual Lignin Isolation Yield



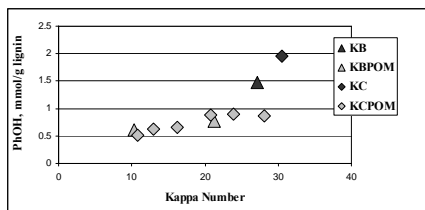
- Acid hydrolysis resulted in a lower yield of RL isolated from POM-delignified softwood and birch kraft pulps than from both corresponding unbleached and oxygen-bleached softwood kraft pulps (KCOx)

Residual Lignin Characterization Carbohydrate Content



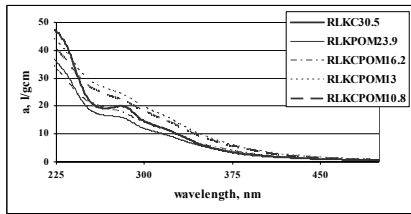
- Even though carbohydrate content is higher in RLKCPOM & RLKBPOM than in RLKC & RLKB, the lignin-carbohydrate association is not a major reason for the low yield of lignin isolation from POM-delignified pulps

Residual Lignin Characterization Phenolic Hydroxyl Group Content - PhOH



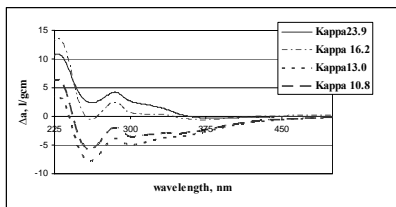
- Sharp reduction in PhOH content in RL's of the pulps of an early phase of POM delignification suggests that POM's readily oxidize non-etherified lignin units (aromaticity loss?)

**Residual Lignin Characterization
UV/Vis. Spectral Analysis**



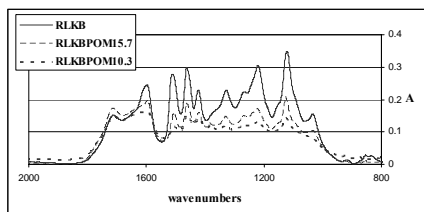
- Gradual disappearance of the lignin band at ~280nm (B band) can be observed in the absorption spectra of the residual lignins of POM-delignified pulps of decreasing kappa number

**Residual Lignin Characterization
UV/Vis. Spectral Analysis – Difference Spectra**
 $\Delta a, l/gcm = a_{RLKC30.5} - a_{RLKPOM}$



- All difference spectra of RLKPOM are characterized by the 282nm maximum, minima at 262 and 302nm, and shoulder at ~350nm; new structures (C=O, COOH, COOR, quinones) are formed at the expense of the guaiacyl unit alteration (aromaticity loss?)

**Residual Lignin Characterization
FTIR Analysis**

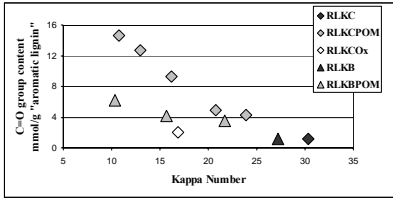


- The ratios A_{1510}/A_{1510} (i, cm^{-1} – characteristic lignin bands; $1510cm^{-1}$ aromatic skeletal vibration band) increased with the delignification progress (aromaticity loss?)

Residual Lignin Characterization

FTIR Analysis

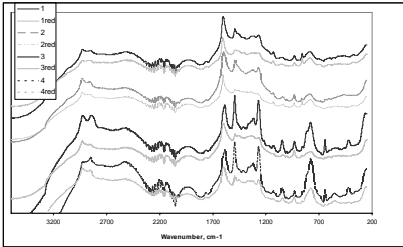
C=O (carboxyl+nonconjugated carbonyl) group content



- C=O-group content based on "aromatic lignin" (I_{1740}/I_{1510}) is higher in RLKPOM than in RLKC/RLKB/RLKCOx (aromaticity loss?)
- RLs of KPOM contain 2-3 times greater amount of C=O-groups than RLs of KBPOM

Residual Lignin Characterization

SERS Analysis

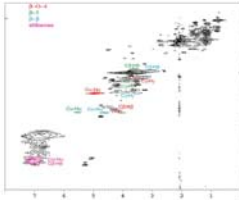


- Surface Enhanced Raman Spectroscopy enables lignin characterization
- The lignin peaks characteristic of RLKPOM are reduced/removed after reduction with NaBH_4 – carbonyl groups
- 1 – RLKC, 2 – RLKPOM28.1, 3 – RLKPOM23.9 4. RLKPOM10.8
- red. – RL reduced with NaBH_4

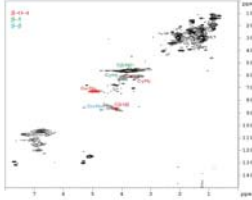
Residual Lignin Characterization

2D NMR - HSQC Analysis

RLKB



RLKBPOM15.3



- Gradual disappearance of the β -5 and β - β correlations suggests their cleavage with the progress of POM delignification
- the β -O-4 correlations remain present in the RL of the late delignification phase
- high reactivity of stilbene structures is observed based on the disappearance of corresponding correlations

Conclusion



- POM delignification is performed with the same efficiency on the softwood and birch kraft pulp
 - POM treatment of kraft pulps leads to the removal of HexA groups
 - Alteration of lignin structure upon POM treatment involves
 - decrease in oxidizability
 - reduction in content of PhOH groups
 - increase in content of C=O-groups
 - stilbene removal
 - gradual decrease in β - β and β -5 lignin bonds
 - potential loss of aromaticity
-

In: Proceedings of the 2005 TAPPI
engineering, pulping & environmental
conference. 2005 August 28-32; Philadelphia,
PA. Norcross, GA; TAPPI press: 13 p. Available
CD Rom; ISBN# 1-59510-095-4.