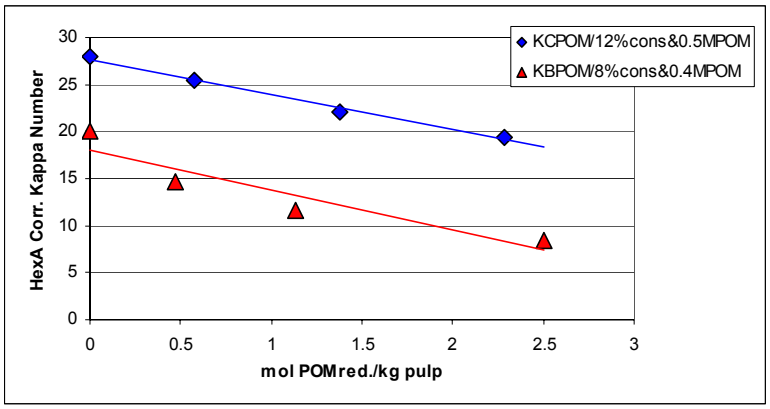


Fig. 2. HexA-Corrected Kappa Number vs. POM reduction

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].

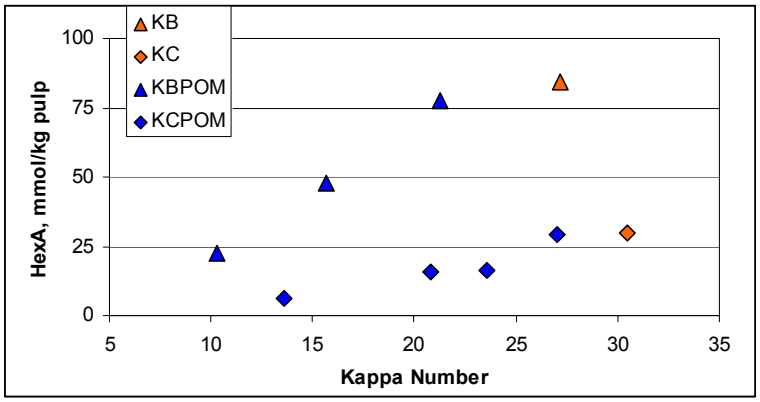


Fig. 3. HexA – Group Content in Unbleached and POM-Bleached Kraft Pulps

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, t°C, N_2) 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.

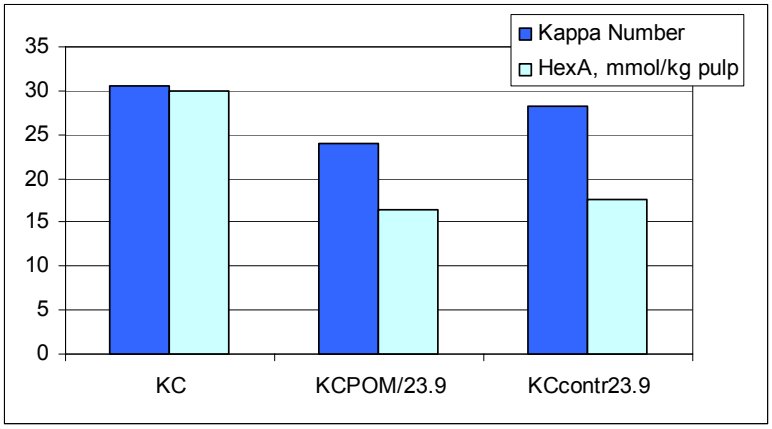


Fig.4. Kappa Number and HexA Content in Unbleached (KC), POM-Bleached (KCPOM) and Control (KCcontr) Softwood Kraft Pulp

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% $Na_2S_2O_4$/OD pulp, CF 0.182; 5% $Na_2S_2O_4$/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.

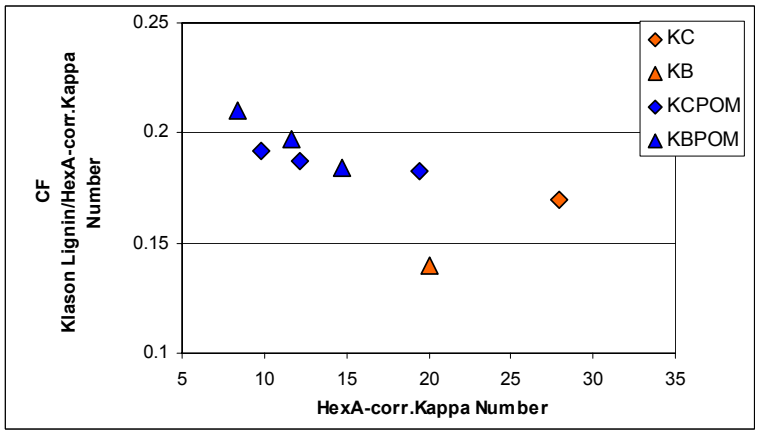


Fig. 5. Increase of Conversion Factor (CF = Klason Lignin Content/HexA-Corr.Kappa Number) in the POM-delignification of Softwood and Birch Kraft Pulps

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).

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

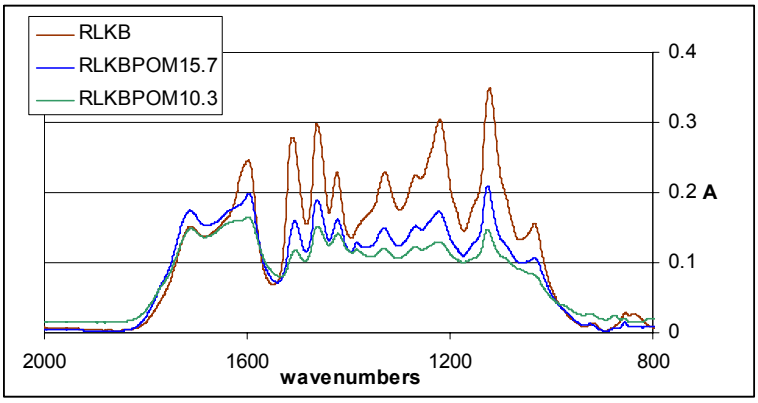


Fig. 11. FTIR Spectra of RL of unbleached birch kraft pulp, kappa 27.2 (RLKB) and of POM-delignified birch kraft pulps, kappa 15.7 and 10.3 (RLKBPOM15.7; RLKBPOM10.3)

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).

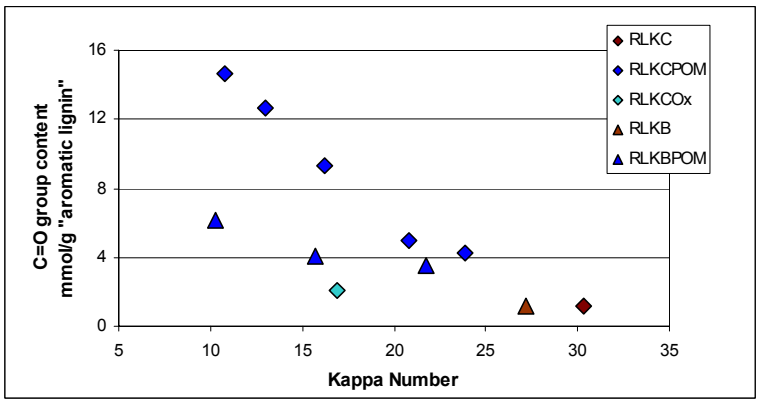


Fig. 12. Contents of C=O groups (carboxyl + non-conjugated carbonyl) in the residual lignins with the progress of delignification

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 ($O_2+1e^- \rightarrow O_2^{\cdot-}$, E°=-0.33V vs. NHE; $[SiV^{V}W_{11}O_{40}]^{5-} + 1e^- \rightarrow [SiV^{IV}W_{11}O_{40}]^{6-}$, pH 2-8; E° = 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_i/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 419cm^{-1} bands. The 1606cm^{-1} band characteristic of RLKC modifies/disappears with the progress of delignification and RLKCPOM10.8 contains a broad band at 1584cm^{-1} with a shoulder at 1606cm^{-1}. Assignments of these bands require additional model studies.

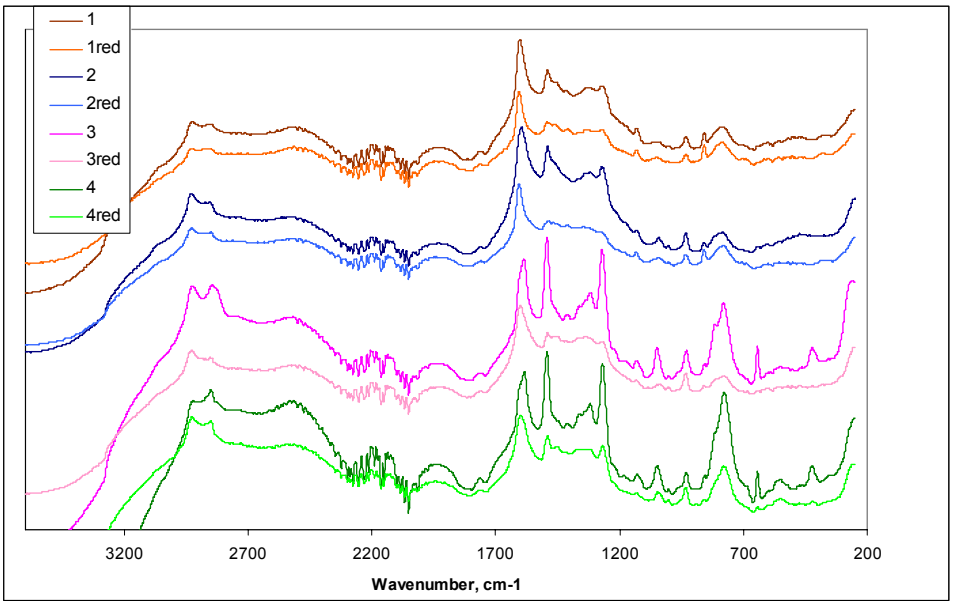
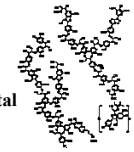


Fig. 13. SER Spectra of Residual Lignins before and after Reduction:
1/1red: RLKC; 2/2red: RLKCPOM28.1; 3/3red: RLKCPOM23.9; 4/4red: RLKCPOM10.8

SER spectra of reduced lignins exhibit a reverse effect compared with POM delignification. For example, the 1494 and 1269cm^{-1} bands were reduced, and instead of the 1584cm^{-1} band, the 1606cm^{-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.

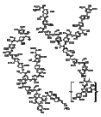
Structural Changes of Residual Lignin of Softwood and Hardwood Kraft Pulp Upon Oxidative Treatment With Polyoxometalates



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



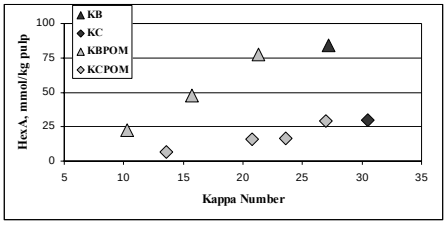
- **Implementation of environmentally friendly bleaching technology based on polyoxometalates (POMs) requires optimization of POM delignification, including reduction of the POM charge/ton pulp**
- **To achieve a maximal delignification effect under optimal process parameters, elucidation of the lignin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

Polyoxometalates - POMs

- Early-transition-metal oxygen-anion clusters
- α-Keggin: $[SiVW_{11}O_{40}]^{5-}$, $[PV_2Mo_{10}O_{40}]^{5-}$, 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

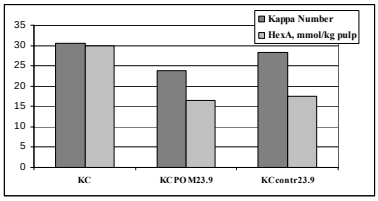
POM treatment of softwood and birch kraft pulps

Hexeneuronic acid groups (HexA) were removed



POM treatment of softwood and birch kraft pulps

POMs are not consumed for the HexA removal

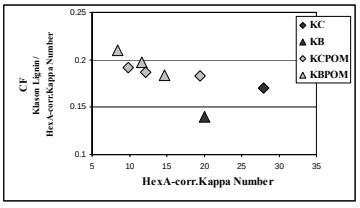


- Approximately the same delignification efficiency of softwood and birch kraft pulps and the HexA removal in control experiment (same conditions as in POM treatment but no POMs) indicate that POMs are not consumed by HexA removal

POM treatment of softwood and birch kraft pulps

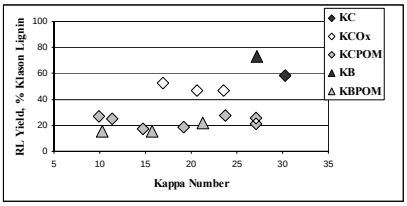
Conversion factor, CF

CF = Klason lignin/Hex-corr.kappa number



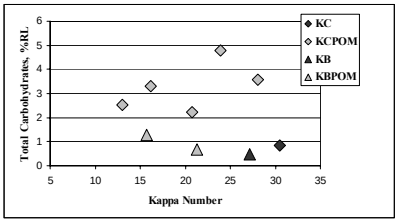
- Permanganate consumption (kappa number test) decreases, i.e., CF increases with the progress of delignification
- POM treatment leads to the reduction of lignin oxidizability (aromaticity loss?)

Residual Lignin Isolation
Yield



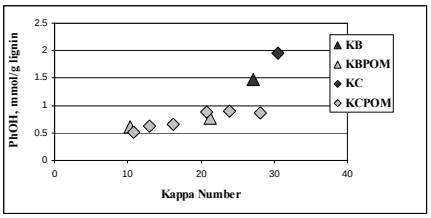
- Acid hydrolysis resulted in a lower yield of RL isolated from POM-delignified softwood and birch kraft pulps than from both corresponding unbleached and oxygen-bleached softwood kraft pulps (KCOx)

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?)