

## COMPOSITION OF THE ORGANIC COMPONENTS IN POLYXOMETALATE (POM) LIQUORS FROM KRAFT PULP BLEACHING

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### Abstract

Promising results from the selective oxidative delignification of kraft pulp with polyoxometalates (POMs) prompted interest in elucidating the lignin oxidation mechanism. The degradation of lignin model compounds and residual lignin in kraft pulps, upon treatment with POMs was studied and differences in the reaction mechanisms between guaiacyl (G-) and syringyl (S-) units were found. Our studies are aimed at comparing soluble lignin products resulting from POM treatment of softwood and hardwood kraft pUlps to further explore the behavior of G/GS units of lignin incorporated in the pulp matrix.

Oxidative treatment of unbleached kraft pulps, commercial mixed softwood and laboratory birch, was performed using POM solutions containing the active  $[SiW_{11}O_{40}]^{5-}$  anion. The solutions obtained after POM bleaching were extracted with organic solvents of different polarity, after acidification to pH2 and centrifugation/filtration. Only low-molecular weight lignin fragments were dissolved during POM treatment since acidification did not induce lignin precipitation. The extracts were analyzed by NMR spectroscopy and GC-MS. The majority of degradation compounds were carbonyl and carboxyl aromatic compounds indicating extensive oxidation reactions on lignin. These reactions included  $C_{\alpha}-C_{\beta}$  and alkyl-aryl cleavage.

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### Introduction

New bleaching technologies must be developed to replace environmentally detrimental 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) as selective lignin-oxidizing agents may be used in chlorine-free bleaching as they favorably embrace the advantages of both chemical (active at elevated temperatures) and biological (highly selective) delignification agents<sup>1</sup>. POM's have been examined in a two-step bleaching process; first is the delignification step in which lignin is oxidized with POMs under anaerobic conditions and second is oxidation of both reduced POMs back to fully oxidized POMs, and lignin to  $CO_2$ . POM bleaching does not negatively affect cellulose as the process is free of oxygen-based radicals allowing the cellulose to remain stable and retain its viscosity. The process offers an environmentally benign technology because lignin degradation products, which are dissolved in the POM solution in the first step, are fully oxidized in the second step. The products from lignin model compounds treated with POMs and residual lignin from POM-bleached softwood and hardwood kraft pulps were studied. Results obtained for the etherified lignin monomers showed that the ether-bonded substituent at  $C_4$  of the aromatic ring affects the reaction activation energy and that POMs preferentially attack the phenolic lignin units<sup>2,3</sup>. The yield of lignin isolated by mild acid hydrolysis from kraft POM-treated pulps was two to three times lower than that from kraft pulp. A stronger association between lignin and carbohydrates and lower total aromaticity of lignin were proposed as the main reasons for the lower yield of lignin isolation from kraft POM-delignified pulp. Suggested delignification reactions include alkyl-aryl and  $C_{\alpha}-C_{\beta}$  cleavage<sup>2,4</sup>. Also, some indications of aromatic ring cleavage were found<sup>4</sup>.

We have studied the organic component of the liquor resulting from POM delignification of softwood commercial and birch laboratory kraft pulp to further explore the behavior of guaiacyl and syringyl units when lignin is incorporated in the pulp matrix. The results of our preliminary experiments obtained on underivatized extracts of POM solutions are presented. Our goals were to find an efficient extraction solvent for the lignin degradation products and to make a preliminary

assessment of their structure. The results may provide a basis for the optimization of the POM bleaching technology and evaluation of its potential in production of value added chemicals in the pulp and paper industry.

### Experimental

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

**Delignification Experiments:** Before POM delignification both kraft pulps were Soxhlet extracted with acetone: water (9:1) for 8 hours. The extracted pulps were delignified with a POM mixture under anaerobic conditions using a 2L horizontal Parr reactor configured with anchor stirrers. The details of the POM treatment of kraft pulps were published elsewhere<sup>5,6</sup>. 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 and three birch kraft POM-bleached pulps in the 21.3-10.3 kappa number range.

**Extraction of POM Solutions:** The low-molecular weight compounds dissolved in the spent liquors obtained during POM delignification leading to approximately 40% reduction in the total lignin content (Klason + acid-soluble lignin) were analyzed. The POM solutions of KC pulp delignified to a kappa number of 15.2 and of KB pulp delignified to a kappa number of 10.3 were acidified to pH2 with 0.1 M HCl. The low molecular weight compounds were successively extracted from the solution filtrates with ether and chloroform (solution from softwood kraft pulp, KC delignification) and with chloroform and ethylacetate (solutions from the delignification of softwood and birch kraft pulps, KC and KB). Solvents were removed on a rota-evaporator at 35-40° C and sample weights were taken.

**NMR Spectroscopy:** 20 NMR spectra were run on a Bruker DPX-250 spectrometer using standard Bruker pulse sequences. A quadrupole 5-mm probe with a Z-gradient coil was used for all samples. The samples were dissolved in 400µl of acetone-d<sub>6</sub>. The central solvent peak ( $\delta_H$  2.04,  $\delta_C$  29.83) was used as the internal reference. The assignment of the observed correlations was based on lignin model compound data<sup>8</sup>.

**GC-MS:** GC-MS analysis was performed with a 3800 GC coupled to a 4000 ion trap mass selective detector (Varian, Palo Alto, CA). The MS was operated in internal electron impact (EI) mode using an ionization voltage of 70eV and transfer line, manifold and ion source temperatures of 250° C, 40° C, and 170° C, respectively. The ion trap was operated in full scan mode from  $m/z = 50$  to 350 using a target ion count of 10000 and an emission current of 10 uAmps. Scans were averaged from 3 microscans (0.42 seconds/scan).

The separation was carried out on an Rxi-5ms capillary column (30m x 0.25 mm x 0.25 µm, Restek Corp., Bellefonte, PA) using helium as a carrier gas at constant flow rate of 1.0 ml/min. Injections were made with a Combi-Pal (LEAP technologies, Carrboro, NC) autosampler using a split of 50:1 at 220° C and a Siltek-coated single gooseneck liner (Restek Corp.). The temperature program was: 90° C to 300° C at 8° C /min.

### Results and discussion

#### Some notable properties of POM pulps:

In addition to the decrease in kappa number/Klason lignin the POM treatment of kraft pulps brought about a reduction in the content of HexA-groups (hexeneuronic acid groups). This is not surprising as the POM delignification is conducted at a pH of 5.5-6.5 and temperature of 100-140° C, conditions that promote acid hydrolysis of HexA<sup>7</sup>. In the control experiments KC pulp was treated under the same conditions but without POMs. The HexA content in the resulting pulp was about the same as in the corresponding pulp treated with POMs implying that HexA-groups were removed by acid hydrolysis without involvement of POMs. An underestimation of the lignin content in POM-delignified pulps will occur if the correlation Klason lignin = kappa number x 0.15 is used<sup>9,6</sup>. This error is caused by the change in permanganate consumption by lignin remaining in pulps. The permanganate consumption gradually decreases with the progression of delignification because POM delignification results in gradually more oxidized lignin (containing more carbonyl and carboxyl groups) of lower total aromaticity. The permanganate consumption may also be reduced if lignin is less accessible because it is more condensed, i.e., contains more C<sub>5</sub>-C substituted units<sup>5,6</sup>.

**Composition of POM solutions:** With the progression of POM delignification the Klason lignin content in pulps gradually decreases, i.e.,

lignin is oxidatively modified and dissolved in the POM solution. If the internal lignin bonds were cleaved lignin would be dissolved in higher molecular weight portions and acidification of the POM solutions to pH2 would result in lignin precipitation. After the solution pH was adjusted to 2.3 the higher molecular weight lignin fractions dissolved in the oxygen bleaching liquor, for example, were precipitated, while the lignin-like compounds of lower molecular weight remained in the solution<sup>10</sup>. In contrast, acidification of the solutions obtained in POM delignification of both pulps did not induce lignin precipitation. Lignin dissolution may occur as a result of lower molecular weight lignin fragments, including lignin monomer units from the lignin surface.

Extraction of lower molecular weight lignin-like compounds: After acidification, the POM solutions were filtered and the filtrate from the POM delignification of KC pulp was extracted successively with ether, chloroform and ethylacetate, while the solution from the POM delignification of KB pulp was extracted successively with chloroform and ethylacetate. Combined dry residues after solvent evaporation represented only 15-20% of the total mass of lignin removed during POM delignification. Such a low level of recovery of lignin degradation products may be related to high hydrophilicity and/or volatility. Similar results obtained from a study of lignin degradation in oxygen delignification catalyzed by POM ([ $\text{PMo}_7\text{V}_5\text{O}_{40}$ ] <sup>6-</sup>) were explained by the complete oxidation of low molecular weight compounds to carbon dioxide<sup>11</sup>.

NMR results: The ether and ethylacetate extracts of the solution obtained in POM delignification of KCP were analyzed by NMR

spectroscopy. HSQC spectra which give information about the correlation between <sup>1</sup>H and <sup>13</sup>C using <sup>1</sup>J<sub>C-H</sub> are shown in Figures 1 and 2, respectively. The spectra showed that both extracts contain lignin-like aromatic C-H correlations (aromatic region C/H 100-130/6-8.5 ppm), methoxyl correlations typical for aromatic ring methoxyl shifts (OCH<sub>3</sub> 56-57/3.7-4.2 ppm) and benzaldehyde (Ar-CH(=O) 191-193/9.8-10.2 ppm) groups. The aromatic compounds revealed in the spectra are most likely monomers because the correlations indicative of lignin interunit sidechain bonds were not present in the side chain region C/H 50-90/3-6 ppm). Aromatic moieties appear more abundant than aliphatic moieties in both extracts (aliphatic region C/H 10-40/0-3 ppm). Even though numerous correlations observed in the HSQC spectra could not be assigned by comparison with model data, a few compounds/structures were surmised.

An important correlation found in the spectrum of the ether extract at C/H 49.8/3.30 ppm is consistent with the methyl groups of methanol (CH<sub>3</sub>OH) (this correlation was not observed in the ethylacetate extract spectrum). Methanol identified in the ether extract indicates the occurrence of demethoxylation reactions. Consistent with this result is lignin demethoxylation during POM delignification based on the results of methoxyl analysis of residual lignin isolated from KC and KC POM-treated pulp<sup>4</sup>.

The occurrence of 2-furoic acid in both ether and ethylacetate extract is likely based on the presence of three correlations consistent with its C<sub>3</sub>/H<sub>3</sub>, C<sub>4</sub>/H<sub>4</sub>, and C<sub>5</sub>/H<sub>5</sub> (112.76/6.61, 118.69/7.20, 147.5/7.78, respectively).

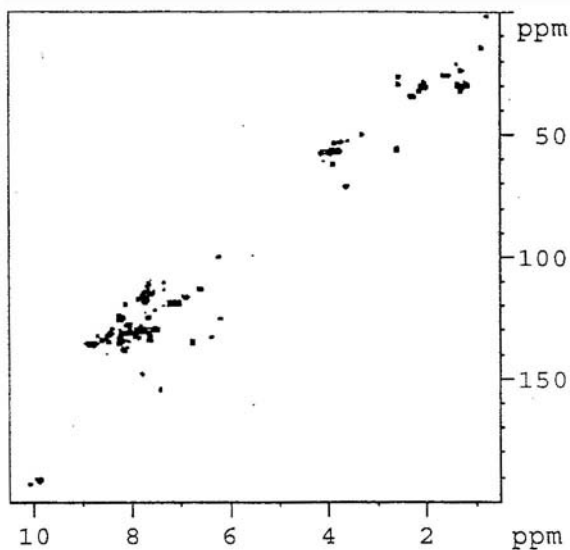


Figure 1 HSQC of the ether extract of softwood kraft pulp POM solution

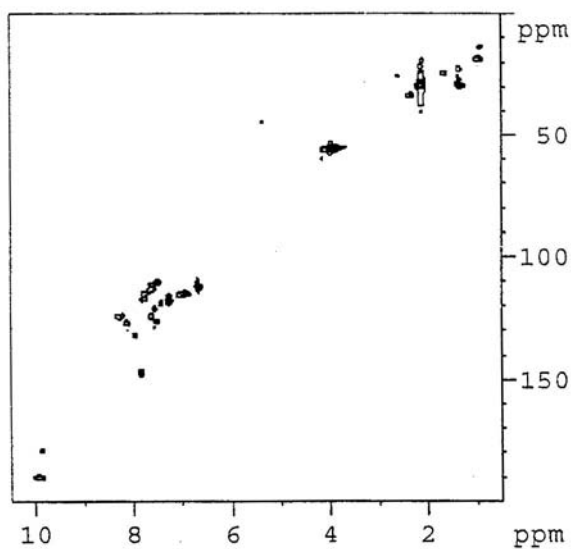


Figure 2 HSQC of the ethylacetate extract of softwood kraft pulp POM solution

Qualitative  $^{13}\text{C}$  NMR spectra (not shown) of the extracts contained signals characteristic of the carboxyl group (158.50 ppm) and  $\text{C}_2$  (144.98 ppm) of 2-furoic acid and provided additional evidence of its presence in the extracts. The presence of 2-furoic acid in the POM solution most likely results from acid hydrolysis of HexA-groups<sup>7</sup>. It is in accordance with the previously reported reduction of HexA-group content in the pulps after POM treatments<sup>6</sup>. It is also important to point out that the organic extracts of the solution resulting from the treatment of lignin

alone with POMs did not contain 2-furoic acid confirming non-lignin origin of 2-furoic acid (results not published; POM treatment of softwood kraft pulp residual lignin).

The spectrum of the ether extract showed correlations at 133.68/7.62 ppm, 130.41/8.03 ppm, and 129.23/7.49, which may be attributed to benzoic acid ( $\text{C}_4/\text{H}_4$ ,  $\text{C}_2/\text{H}_2$  &  $\text{C}_6/\text{H}_6$ , and  $\text{C}_3/\text{H}_3$  &  $\text{C}_5/\text{H}_5$ , respectively). Also, the correlations observed at 26.47/2.57 ppm and 52.84/3.83 ppm may be indicative of Ar-

C(=O)CH<sub>3</sub> and Ar-C(=O)-OCH<sub>3</sub> structures, respectively.

The HSQC spectrum of the ether extract contained a correlation at 132.59/6.37 ppm which is consistent with the presence of maleic acid (COOH-CH=CH-COOH). The occurrence of this acid was also supported by HMBC (heteronuclear mUltiple-bond correlation, long range <sup>3</sup>J<sub>C-H</sub> correlations; 167/6.37 ppm; spectrum not shown). If present this dicarboxylic acid would offer evidence that POM delignification involves ring opening.

**GC-MS results:** A list of the compounds identified in the extracts of both POM solutions from delignification of softwood and birch kraft pulp is shown in Table 1. Table 2 includes compounds identified exclusively in the chloroform extract of the POM solution resulting from the delignification of birch kraft pulp.

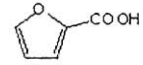

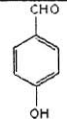
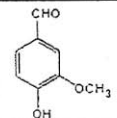
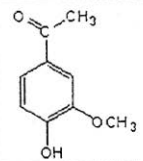
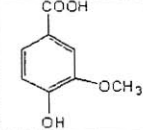
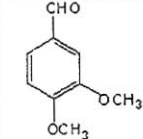
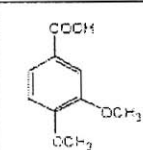
Details on the composition of the POM solution obtained by NMR spectroscopy were mainly confirmed by the results of GC-MS analysis. Benzaldehyde compounds were identified as *p*-hydroxybenzaldehyde, vanillin, veratraldehyde, and syringaldehyde. Vanillin and veratraldehyde were found in the extracts obtained in the delignification of both pulps. Syringaldehyde was identified in the chloroform extract of the KB pulp POM solution as characteristic of syringyl lignin origin (birch lignin is guaiacyl-syringyl or GS lignin), while *p*-hydroxy benzaldehyde was identified only in the ether extract of the KC pulp POM solution.

Three C<sub>α</sub> carboxylic acids were identified as benzoic, vanillic and veratric acid. Benzoic and vanillic acid were found in the extracts of

both POM solutions, while veratric acid was found only in the POM solution of KC pulp. Nevertheless, C<sub>α</sub>-carbonyl and carboxyl compounds identified in this study confirm an earlier conclusion on the C<sub>α</sub>-C<sub>β</sub> cleavage reaction as characteristic of POM delignification<sup>2,4,5</sup>. It is expected that *p*-hydroxybenzaldehyde and benzoic acid identified among the delignification products are also present in the lignin remaining in the pulp (residual lignin). Due to their oxidative resistance these types of compounds would slow down delignification<sup>12</sup>.

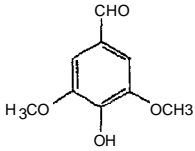
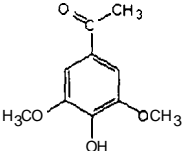
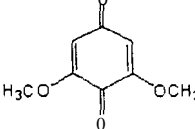
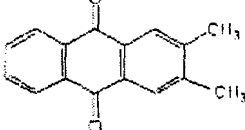
Acetovanillone was identified in the POM solutions of KC and KB pulp, whereas its syringyl analog was identified in the POM solution of KB pulp. These compounds confirmed the presence of Ar-C(=O)CH<sub>3</sub> type structures which were revealed by NMR spectroscopy. This result is in accordance with the results obtained with the lignin model compounds showing that the POM delignification includes oxidation of C<sub>α</sub> in the β-O-4 structure<sup>1</sup>. In contrast to this finding, our recent NMR spectral studies did not indicate the presence of the C<sub>α</sub>-keto structures in the residual lignin isolated from kraft POM-treated pulps.<sup>4</sup> This may be explained by high acid stability of residual lignin enriched in C<sub>α</sub>-keto groups, which was not dissolved during mild acid hydrolysis lignin isolation and decreased the yield of lignin isolation<sup>4,5</sup>. Therefore, an enrichment in lignin of structures bearing C<sub>α</sub>-keto groups during POM treatment of kraft pulps may be the main reason for the low yield of lignin isolated from POM-treated kraft pulps.

Table I: GC-MS results: compounds identified in both softwood and birch kraft pulp POM solution

Compound	Structure	POM solution delignification of kraft pulp				
		Softwood			Birch	
		Extract in				
		ether	CHCl <sub>3</sub>	EtOAc	CHCl <sub>3</sub>	EtOAc
2-furoic acid		w	w	vs	w	vs
benzoic acid		m	m	w	w	
p-hydroxy benzaldehyde		w				
Vanillin		w	s	w	m	
acetovanillone		w	w		w	
vanillic acid				w	w	
veratraldehyde		w	w		w	
veratric acid		w	w			

Signal intensity w-weak; m-medlum; s-strong; vs-very strong

Table II GC-MS results: compounds identified in the birch kraft pulp POM solution

Compound	Structure	Extract in CHCl <sub>3</sub>
syringaldehyde		w
acetosyringone		w
2,6-dimethoxy benzoquinone		vs
2,3-dimethyl-anthraquinone		vs

Consistent with this explanation are the results of NIR, FT-Raman and UV/vis spectral studies of Weinstock et al. (1993)<sup>9</sup>, which indicated a high level of C<sub>α</sub>-keto structures in lignin from POM-treated kraft pulps. Our current results show, however, that this type of structure may dissolve from pulp during pulp POM treatment as acetovanillone (G,GS-lignin) and acetosyringone (GS-lignin). Acetovanillone and acetosyringone were identified among the products of oxidative degradation of lignin model compounds representing the β-O-4 aryl ether structure in the studies of the aerobic oxidation promoted by POMs ([PMo<sub>7</sub>V<sub>5</sub>O<sub>40</sub>]<sup>8-13</sup>). Even though this mechanism is plausible in the case of anaerobic POM delignification, additional studies are needed to clarify the reaction paths leading to the Ar-C(=O)CH<sub>3</sub> type of products.

Quinones were detected in the solution from POM treatment of birch kraft pulp (Table 2). 2,6-dimethoxy-*p*-quinone was observed among the products of POM treatment of the β-O-4 aryl ether lignin model compounds in the study of Weinstock et al. 1998<sup>2</sup>. It was suggested that the alkyl-aryl cleavage takes place during oxidative

degradation of lignin model compounds upon POM attack. Consistent with this conclusion are Our results on the lignin degradation compounds dissolved during POM treatment of birch kraft pulp. Absence of the corresponding guaiacyl compound in the solution of POM treatment of softwood kraft pulp may be related to its higher reactivity compared to its syringyl analog. Even though 2,3-dimethyl-anthraquinone in birch kraft pulp POM solution may originate from birch extractives it is unlikely because pulps were extracted in acetone/ater (9/1) before POM treatment. The origin of this compound will be studied in detail in the continuation of our studies.

The lignin degradation products detected in Our studies did not include C<sub>5</sub>-C substituted aromatic compounds. Even though more studies are needed to completely exclude the production of condensed lignin units during POM delignification, the results of our previous and ongoing studies indicating gradual depolymerization of lignin are consistent with the absence of condensed lignin units in the POM solution. Therefore, the aforementioned reduced

oxidizability of residual lignin leading to erroneous kappa number results is unlikely to be caused by a more condensed lignin structure but 2-furoic acid was found in all extracts. While it was only a minor compound in the ether and chloroform extracts, it was the most prevalent compound in the ethylacetate extracts of both studied POM solutions most probably due to the order of polarity of the compounds resulting from POM treatment of kraft pulp.

### Conclusion

Polyoxometalates (POMs) are effective in oxidizing lignin and aromatic aldehydes, ketones and carboxylic acids are dissolved from pulps during POM delignification. These  $C_{\alpha}$ -carbonyl and carboxyl aromatic compounds are most likely products of the  $C_{\alpha}C_{\beta}$  cleavage taking place during POM treatment of kraft pulps. Identification of 2,6-dimethoxy-*p*-quinone among the dissolved compounds during POM treatment of birch kraft pulp offers evidence of the alkyl-aryl cleavage in lignin upon POM attack.

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