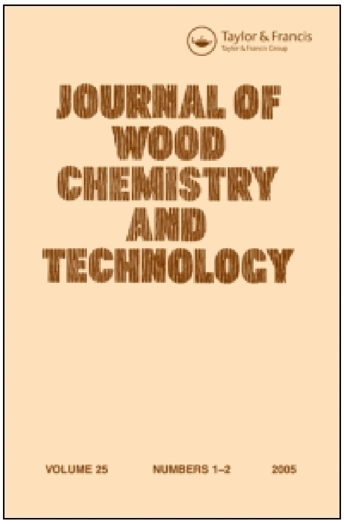

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
VOLUME 25 NUMBERS 1–2 2005

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Werner, John , Ragauskas, Arthur J. and Jiang, Jian E.(2000) 'Intrinsic Metal Binding Capacity of Kraft Lignins', Journal of Wood Chemistry and Technology, 20: 2, 133 — 145

To link to this Article: DOI: 10.1080/02773810009349629

URL: http://dx.doi.org/10.1080/02773810009349629

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 20(2), 133–145 (2000)

INTRINSIC METAL BINDING CAPACITY OF KRAFT LIGNINS

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ABSTRACT

The metal removal properties of kraft lignins were examined for a series of SW kraft pulps. The addition of purified kraft lignins to pulp fibers was shown to result in the removal of 20 to 40% of nonprocess elements, such as Mn, Mg, and Ca, in pulp. The effects of concentration and type and amount of kraft lignin applied were explored. These studies illustrate that structural differences in the kraft lignin affect the metal removal from pulp. Factors such as extent of delignification and cooking technology influence metal removal properties. In addition, we have demonstrated that a correlation exists between metal removal and the content of carboxylic acids and condensed phenolics in the kraft lignin applied.

INTRODUCTION

As modern kraft pulping and bleaching operations are developed it is becoming increasingly apparent that these technologies need to have minimal impact on their surrounding environment. One of the key technologies being developed to address this concern reduces the fresh water usage in kraft pulping, bleaching, and papermaking operations.[1] Minimization of mill water usage is critically dependent on controlling organic and inorganic materials that accumulate in process streams during the production of pulp and paper. Process control of inorganic materials that are not pulping or bleaching chemicals – frequently referred to as nonprocess elements (NPEs), is a rapidly developing field of research. Nonprocess elements commonly include aluminum, barium, calcium, chloride, iron, potassium, magnesium, manganese, and silicon.[2, 3] Mill control of NPEs requires several control strategies; for example, chloride and potassium are very water soluble and difficult to purge from aqueous process streams.[4] Other elements such as calcium and barium have distinct solubility profiles that can lead to scaling in the bleach plant or recovery cycle.[5] Finally, other elements like iron and manganese can detrimentally impact the performance of oxygen-based bleaching agents.[6] In summary, the control of NPEs is an important component of modern pulp manufacturing facilities and additional fundamental studies are needed to provide a sound basis from which new technologies can be developed.

The incoming wood supply is the principal source of most NPEs for kraft pulping operations. Throughout the pulping, bleaching, and papermaking operations NPEs are constantly being partitioned between the fiber and surrounding water. Clearly, the kraft pulping process serves as the first point at which NPEs can be fractionated from the fiber. Under the hot alkaline conditions of pulping, the fiber is able to act as a metal complexing reagent, retaining certain metals and exchanging others for sodium. It is generally believed that a variety of functional groups in the pulp can bind NPEs, including carboxyl groups from lignin, hexenuronic acids and other polysaccharide acids, catechols, and phenoxy groups. Several research groups have begun to make significant advances in modeling this process.[7, 8] Recently, we examined the metal binding capacity for a series of well-characterized kraft lignins.[9] These studies suggested that there was a correlation between the amounts of carboxyl and condensed phenolics present in conventional kraft lignins and their metal binding capacity. These results were tentatively attributed to the potential bidente metal binding capacity of these two functional groups, as shown in Figure 1. This paper further extends our fundamental investigations into the metal binding capacity of kraft lignins.

RESULTS AND DISCUSSION

Based on literature results and general chemical considerations, it is clear that kraft pulp fibers retain a series of NPEs during kraft pulping due to metal complexation with lignin and carbohydrate functional groups. Although many lignin functional groups may be involved in this process, our previous studies had suggested that carboxylic acid groups and condensed phenolics in lignin might play an important role in the overall NPE binding process. To further examine the ability of lignin to complex and remove NPEs from kraft pulp fibers, we examined the intrinsic metal binding capacity of assorted kraft lignins. The kraft lignins were isolated from a series of conventional and extended modified continuous kraft cooks. Table 1 summarizes some of the basic pulp properties and cooking parameters used to generate these lignin samples. The kraft lignins were isolated from the liquors by acid precipitation and subsequently purified to remove all NPEs.

The metal binding capacity of kraft lignin was initially evaluated by preparing a 2% consistency softwood kraft pulp slurry using a 0.010 N NaOH solution. To this solution was added a 5% charge of isolated kraft lignin, and the resulting mixture was stirred for 4 hours at 25° and 80°C. Two kraft lignin samples were employed for these studies. The first lignin sample was isolated from a conventional softwood 21 kappa kraft black liquor. The second lignin sample was isolated from an extended modified continuous softwood 21 kappa kraft black liquor.

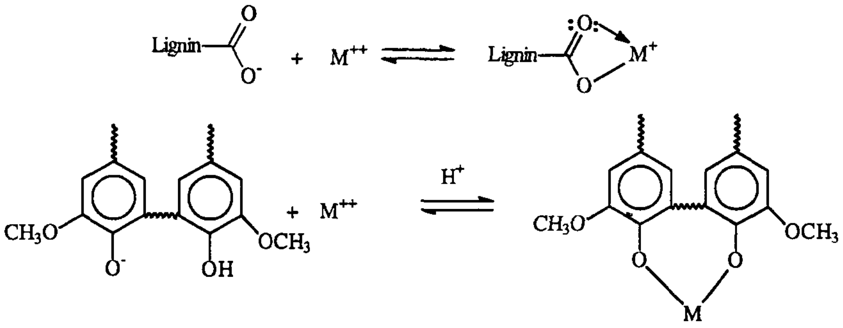

FIGURE 1. Proposed NPE binding scheme involving carboxyl and condensed phenoxy groups.

TABLE 1

Summary of Kraft Pulping Parameters and Pulp Properties.

Cook Type	Kappa #	Viscosity (mPa · s)	Max Cook Temp. (°C)	H-factor	EA Charge During Impreg. (% NaOH on wood)	Sulfidity (%AA)	Total EA Consumed (% NaOH on wood)
Conv.	33	33	168.0	1200	21	30	15
Conv.	21	23	170.0	2000	21	30	15
Conv.	14	13	171.0	4000	21	30	17
Extended Modified	29	43	160.3	2000	10	30	14
Extended Modified	26	36	162.6	2400	10	30	15
Extended Modified	21	37	163.0	2500	10	30	18
Extended Modified	19	26	166.3	3400	10	30	15
Extended Modified	17	21	169.0	4100	10	30	16
Extended Modified	16	19	170.0	4500	10	30	17

As a control, the same experiments were repeated without the addition of kraft lignin. The concentrations of Mn, Mg, and Ca were monitored before and after the metal removal stage. Table 2 summarizes the initial concentration of these metals in the pulp prior to exposure to the 0.010 N NaOH solution.

Figure 2 summarizes the results of metals analysis of the pulp fibers after exposure to caustic with and without lignin at 25°. The results of these studies clearly demonstrate the ability of dissolved lignin to act as a "natural" metal complexing agent to remove metals from kraft pulps. Furthermore, these results indicate that the differences in pulping technology can influence the metal binding efficiency of kraft lignins. Repeating the studies summarized in Figure 2 at 80°C resulted in comparable metal removal properties. This latter result suggests that the observed metal binding properties were obtained at equilibrium.

The metal binding properties of kraft lignins were shown to be charge dependent. As shown in Figure 3, varying the charge of kraft lignin from 2.5% to 10% at 25°C for 4 hours resulted in improved removal of metals from a kappa 30 softwood kraft pulp.

To further explore the metal binding capacity of kraft lignins, a series of different kraft lignin samples were evaluated for their metal binding capacity at 80°C using a softwood kraft pulp and the same procedures as described above. The results of these studies are summarized in Table 3. The results of this analysis suggest to two possible metal binding trends. First, in general, the kraft lignin samples from low kappa kraft pulps appear to be more efficient at removing lignin from pulp fibers than the lignin samples generated from higher kappa pulps. Secondly, it appears that the lignin samples from conventional versus extended modified continuous kraft cooks exhibit differences in metal binding properties. Further studies will be needed to confirm this latter suggestion. Another aspect of lignin as a metal removal reagent is the comparison of its performance with commercial metal-binding chemicals. Currently this research is ongoing in our group. However, preliminary results indicate that lignin performs comparable to DTPA under the alkaline conditions studied.

TABLE 2

Initial Concentration of Metals in Brownstock Kraft Pulp.

Metal	30 kappa softwood kraft pulp	27 kappa softwood kraft pulp
Calcium	2000 ppm	1470 ppm
Magnesium	304 ppm	407 ppm
Manganese	79 ppm	26 ppm

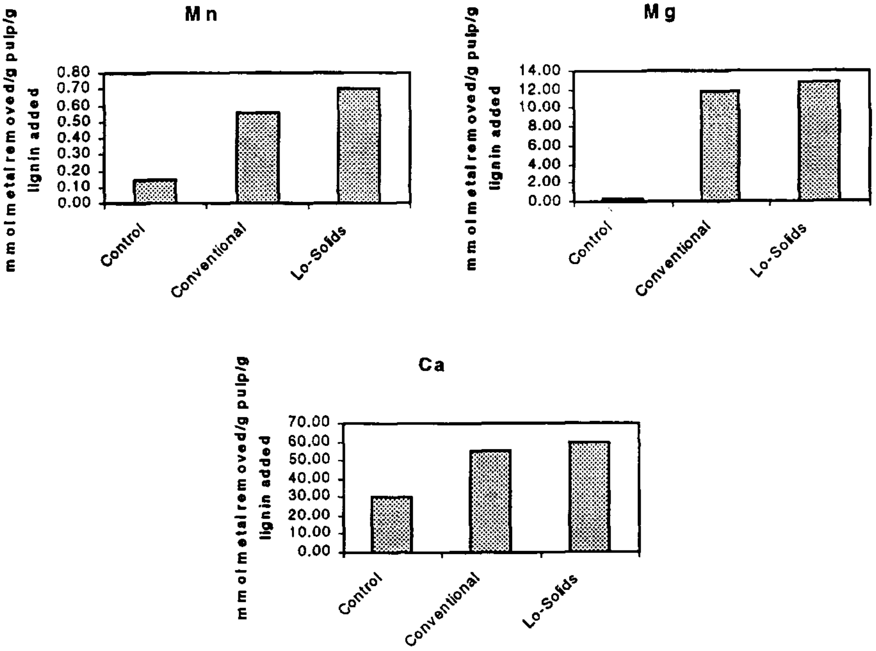

FIGURE 2. Metal removed from 27 kappa softwood kraft pulp at 25°C.

Relationship Between Kraft Lignin Structure and Metal Binding Affinity

To explore the relationship between the structural features of lignin that may govern their metal binding properties we characterized the content of aliphatic hydroxyl groups, condensed and noncondensed phenoxy groups, and carboxylic

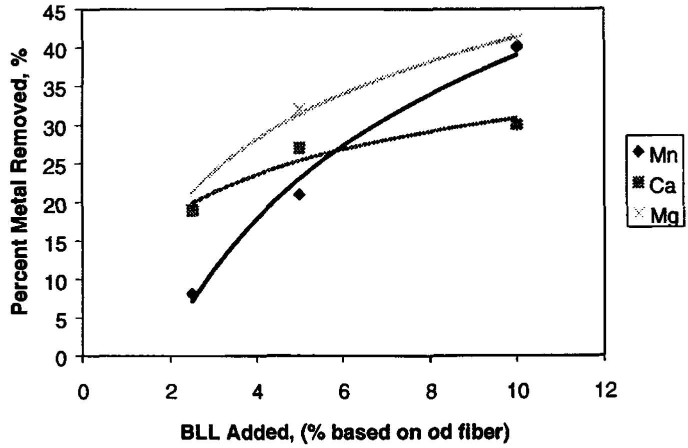

FIGURE 3. Metal removal versus the amount of kraft lignin added to SW kappa 30 kraft pulp at 25°C for 4 hours.

TABLE 3

Metal Removal in Addition to Suspension and Washing and Carboxylic and Condensed Phenolic Content for Various Black Liquor Lignins[1] Applied to SW 27 Kappa Kraft Pulp at 80°C for 4 Hours.

Kraft Cook[2]	Kappa #	% Metal Removal			Total mmol metal removed /kg pulp	Condensed Phenolics[1]	Carboxylic Acids[2]
		Mn	Mg	Ca			
Conv.	33	25.4	21.5	24.6	340	0.7	0.6
"	21	26.3	21.8	27.4	370	0.7	0.6
"	14	35.3	28.9	34.8	476	1.0	1.0
Extend.	29	29.9	23.1	25.5	365	0.7	0.7
"	26	32.6	22.3	27.0	369	0.7	0.6
"	21	31.2	29.7	32.8	457	0.7	0.6
"	19	30.8	22.8	27.7	378	0.7	0.6
"	17	39.3	27.1	31.5	435	0.8	0.7
"	16	35.7	27.6	32.5	447	0.9	0.8
"	11	41.1	24.9	28.5	397	0.8	0.7

[1]kraft lignin was isolated from end of cook; [2]functional group content shown as mmol/g lignin; [2]Conv.:conventional cook, Extend.: Extended modified continuous cook.

acid groups in the kraft lignins using standard NMR methods. Figure 4 illustrates the content of these functional groups in conventional kraft lignin versus the metal removed from a kappa 27 SW kraft pulp.

Based on this analysis the removal of Mn, Ca, and Mg from the SW kraft pulp appears to linearly correlate with the content of carboxylic acids and condensed phenolics. Interestingly, the linear correlation with phenolic and aliphatic hydroxyl group structures had a lower R^2 value. Also, the metal removal was not proportional to the content of free phenolics and aliphatic hydroxyl groups. A comparable analysis for the extended modified lignins did not exhibit a similar relationship between lignin functional groups and NPE removal. Several factors could be contributing to this effect. First, the end-of-cook extended modified lignins are different from the end-of-cook conventional lignins because the latter is a composite sample. In addition, the extended modified lignins represent only a fraction of the lignin released during pulping. Second, the molecular weight distributions of lignins from conventional kraft cooks differ from extended modified kraft cooks.[10] Differences in molecular weight distributions could well influence the NPE binding capacity of kraft lignins.

CONCLUSIONS

In summary, we have demonstrated for the first time, the intrinsic NPE binding capabilities of kraft lignins. We have observed differences in the NPE binding properties both as a function of extent of delignification and cooking technology employed. Furthermore, we have noted a potential correlation between the fundamental structure of kraft lignins and their NPE binding capabilities. The proposed preferential binding of metals by selected lignin functional groups should, in principal, be applicable not only for dissolved lignin samples but also for it for lignin in native wood fibers. Clearly, additional studies will have to be completed to fully define these relationships.

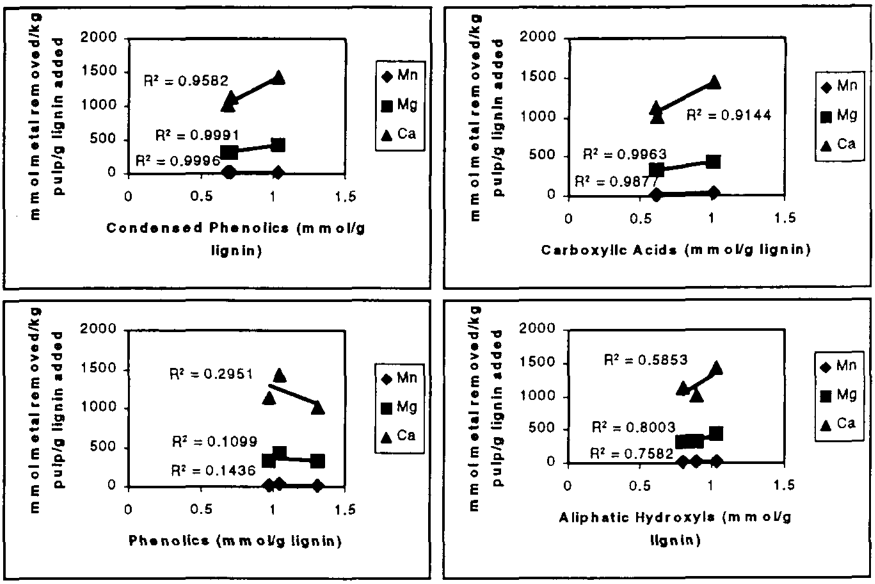

FIGURE 4. Metal removal versus the functional group content of conventional kraft lignins applied to softwood kraft pulp at 80°C for 4 hours.

The results of these studies also suggest that the kraft digester could be employed to maximize NPE removal and simplify closed mill operations. Indeed, once these fundamental principles are fully understood, it may be possible to develop lignin extraction stages in a kraft digester that optimizes the removal of NPEs during a kraft cook. Before this is to be accomplished further metal binding studies will have to be pursued to fully characterize the intrinsic binding capacity of black liquor lignins and carbohydrates.

EXPERIMENTAL

Materials

All chemicals were commercially purchased and used as received except for p-dioxane, which was purified by distillation over sodium borohydride. All pulps were prepared from a single *Pinus taeda* tree grown in the southeastern part of the USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 - 8 mm.

Kraft Pulping

Kraft pulping experiments were performed at Ahlstrom Machinery on a laboratory scale using well-established procedures that simulate conventional and extended modified continuous (i.e., Lo-Solids®) cooking.[11, 12, 13] Table 1 highlights some of the pulping parameters employed and physical pulp properties. All pulps used in this study were extensively washed with Nano-Pure water prior to usage.

Black Liquor Samples

The black liquor samples examined in this study were all end-of-cook samples. Hence, the black liquors from the conventional kraft cooks contain a composite mixture of lignin from throughout the cook. For the extended modified continuous kraft cooks, the end-of-cook black liquors are not a composite of all the lignin dissolved during the cook since the counter-current stage extracts black liquor.

Isolation of Lignin from Black Liquor

The procedure used for the isolation of lignin from black liquor was based upon literature methods.[14] In brief, black liquor (50 mL, ~51 g) was diluted tenfold with distilled water and then treated with diethylenetriamine pentaacetic acid (DTPA, 0.3-0.4 g). This solution was stirred for one hour and then acidified to pH 2 with an aqueous 1.00 N HCl solution. The resulting suspension was frozen, thawed, centrifuged, and the supernatant decanted. The isolated lignin was then dispersed in nanopure water, and the DTPA treatment was repeated. After acidification, the precipitated lignin was washed thoroughly with distilled water and then dissolved with a 9:1 p-dioxane:water solution. The aqueous *p*-dioxane solution was filtered, concentrated under reduced pressure, and resulting precipitate was again treated with DTPA. After acidification to pH 2, the precipitated lignin samples were washed thoroughly with distilled water and then freeze-dried. Finally, the lignin samples were Soxhlet extracted with pentane for 8 h and then dried under vacuum. ICP analysis of these lignins indicated that the metals Mn, Fe, Cu, Ba, Na, Mg, K, and Ca were nondetectable in the final purified form. The limit of detection was approximately 15 ppm for each metal.

Metal Removal Experiments

All of the metal removal experiments were completed using two different temperatures (25°C and 80°C) and/or two different times (2 hours, 4 hours). All experiments were carried out in the same manner so as to reduce variation.

SW kraft pulp (5 g o.d., 30 or 27 kappa) and isolated lignin (250 mg) were added to a 500 mL Erlenmeyer flask. For the control experiments, no isolated lignin was added. A sodium hydroxide solution (0.01 N NaOH) was then preheated to the required temperature and added to the Erlenmeyer flask to make an approximately 5% consistency fiber suspension. The solution was then stirred for 30 seconds to disperse the fibers, and the consistency was further adjusted with 0.01 N NaOH to yield a final consistency of 2%. This flask was placed in a heated shaker at a pre-selected temperature of 25° or 80°C for 2 and 4 h. Upon completion, the pulps were washed with 500 mL 0.1 N NaOH, 500 mL 0.01 N NaOH, and 1000 mL of nanopure water. The pulps were then air dried and acid digested according to standard EPA procedures.[15] The resulting matrix was then analyzed for Mn, Mg, and Ca concentration by inductively coupled plasma (ICP) spectrometry according to standard EPA procedures.[16]

Based on a series of replicate experiments, the experimental error associated with measuring the concentration of Mn, Mg, and Ca were ±1.4 ppm, ±4.8 ppm, and ±23ppm, respectively.

^{31}P NMR Analysis of Kraft Lignins

Kraft lignins (25 mg) were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (65 µL) and analyzed by ^{31}P NMR following literature procedures.[17, 18]

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