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INFLUENCE OF NONPROCESS ELEMENTS ON LIGNIN STRUCTURE DURING OXYGEN DELIGNIFICATION

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ABSTRACT

A series of kraft pulps were prepared in which the level of calcium was selectively enriched and depleted. These pulps were then oxygen delignified, and the pulps were characterized according to kappa number and viscosity. The residual lignin samples were isolated via acid-hydrolysis and characterized by NMR techniques. The results indicated that the presence of nonprocess elements could impact not only the extent of delignification but also the types of lignin removed.

INTRODUCTION

Oxygen delignification is widely used in many bleached pulp-grade operations to diminish the levels of residual lignin in kraft pulps (1). The chemistry of oxygen delignification has undergone a renaissance in the last decade. Recent studies have indicated that oxygen delignification occurs primarily via the free phenolics of lignin (2-5). Although the chemical structure and reactivity of residual lignin play a role in its effective removal, a variety of metal ions, frequently referred to as nonprocess elements (NPEs), that are either originated in pulps or introduced are also suggested to strongly affect the oxygen delignification process (6).

Nonprocess elements commonly include magnesium, manganese, barium, calcium, iron, potassium, aluminum, and silicon (7). The incoming wood supply is the principal source of most NPEs for kraft pulps. 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 nonprocess elements, including carboxyl groups, hexenuronic acids, catechols, and phenoxy groups. Werner and Ragauskas have examined the metal binding capacity of kraft lignin (6).

The role of metal ions in oxygen delignification has been a matter of debate for a long time (10,11). It has been demonstrated that peroxides were generated in oxygen delignification from both phenolic lignin structures and carbohydrate components (8,9). In the presence of metal ions, the peroxides formed are decomposed and likely form radical species (8,10). These radical species react with lignin leading to lignin degradation and solubilization, but also with carbohydrates leading to loss of pulp strength. Hydroxyl radical was identified among these to be a strong oxidative species and capable of attacking both lignin and carbohydrate (11). Although the reactions between lignin and hydroxyl radical facilitate lignin degradation, the oxidation of the carbohydrates may lead to the formation of carbonyl group in the C_2 or C_3 position (12,13). The carbonyl group then initiates the cleavage of the cellulose chain through an β–elimination reaction, and this reaction results in a lower pulp viscosity (14).

Results have shown that iron and copper are able to induce the generation of harmful radicals that create a detrimental effect on the pulp viscosity (15). Magnesium is considered to be beneficial for oxygen delignification. The protective nature of magnesium has long been known, and magnesium compounds are the only generally accepted reagents for improving the selectivity of the process. However, the mechanism by which magnesium functions is still not

completely clear. Several hypotheses have been proposed to account for its positive effect: a. formation of stable peroxide complexes (9); b. deactivation of the transition metal ion by absorption or by formation of complexes (16,17); c. formation of complexes with carbonyl group in C_2 or C_3 position of a glucose unit and thus being able to eliminate the further degradation (18). Calcium seems to have attracted little attention in oxygen delignification, although it has distinct solubility profiles that can lead to scaling problems in the bleach plant or recovery cycle. Brown et al. have reported that calcium has a detrimental effect on the selectivity of oxygen delignification (19). In contrast, Yang et al. have found that there is no such effect observed in their study (20).

Although it is well appreciated that nonprocess elements such as manganese, magnesium, calcium, and iron influence oxygen delignification, the impact on the structure of lignin is largely unknown. As part of the work in the study of extended oxygen delignification, this manuscript summarizes our studies directed at determining how nonprocess elements influence the oxidative degradation chemistry of an O-stage on lignin. A series of kraft pulps were prepared in which the level of calcium was selectively enriched and depleted and the effects of calcium on oxygen delignification was examined. Changes in lignin structure were analyzed by characterizing the residual lignin before and after the O-stage via NMR.

EXPERIMENTAL

Materials

All reagents and solvents were commercially purchased and used as received except for *p*-dioxane, which was freshly distilled over $NaBH_4$ prior to usage. A commercial softwood kraft pulp (kappa number 27.6, viscosity 32.6 mPa.s) was employed in this study. The brownstock pulp was extensively washed until the filtrate was pH neutral and colorless prior to usage.

Chelation Treatment

Chelation treatment of the pulps was carried at 10% consistency at 90°C for 1.00 hour according to the procedure (21). Q-Q treatment was performed with addition of 0.6% EDTA for each time of treatment as chelating agent and Ca-Q treatment with addition of 0.2% EDTA and 0.2% CaSO4. The pH of the slurry was adjusted to 5-7 with NaOH solution. Pulp was placed in a sealed polyethylene bag and thoroughly mixed by kneading. After chelation, the pulp was completely washed with deionized water.

Oxygen Delignification

Oxygen delignification was performed in a Parr reactor equipped with a continuous mixing device. The conditions were as follows: pulp consistency 10%, $MgSO_4$ 0.05%, NaOH 1.6%, temperature 104°C, O_2 pressure 100 psig, time 1.00 h. In a typical experiment, the reactor was warmed up to 80°C and charged with a mixture of pulp, water, and reaction agents. The reactor was then sealed and purged with oxygen; the air was driven out. It was pressurized with O_2 and rapidly heated to the desired reaction temperature. Each oxygen delignified pulp was thoroughly washed until the effluent was colorless and pH neutral. The delignified pulps were used for kappa, viscosity analysis, and lignin isolation.

Metals Analysis

Metal ions were analyzed by using the Inductively Coupled Plasma Emission Spectroscopy technique.

Lignin Isolation

Lignins from the brownstock and post-O delignified pulps were isolated by the acid hydrolysis method (22). In general, the pulp was adjusted to 4% consistency in a 2000-mL three-

necked round-bottom flask with 0.1 N HCl solvent solution containing 90% freshly distilled 1,4-dioxane and 10% water (volume percentage). After refluxing for two hours under an argon atmosphere the pulp slurry was cooled and filtered through celite; the filtrate was neutralized to around pH of 6 by using a saturated Na_2CO_3 aqueous solution. The solution was then concentrated under reduced pressure to remove almost all the dioxane. The concentrated lignin solution was then added to acidic water (pH 2-3), frozen, and subsequently thawed. The lignin suspension was centrifuged and the supernatant was decanted. Newly prepared HCl solution at pH 2-3 was used to wash the precipitated lignin three times following the freezing-thawing process. The washed lignin was then freeze dried and stored for use.

NMR Analysis

The isolated lignin samples were analyzed using a 400 MHz Bruker DMX spectrometer. Quantitative ^{13}C NMR spectra were acquired and analyzed in accordance with established literature methods (23). Lignin was dissolved in 500 μL of DMSO-d_6 before being transferred into a 5-mm NMR tube. ^{13}C NMR spectra were recorded with an inverse gated decoupling sequence, 90° pulse angle, 14-s pulse delay, 23,000-Hz sweep, 10-12,000 transients, at 50.0°C. The fourier-transformed spectra were integrated according to reported chemical shifts for lignin functional groups. The integrals were normalized to the aromatic signals, which were assumed to have a value of 6 carbons.

Lignin samples were also derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and analyzed by ^{31}P NMR following literature methods (24,25). ^{31}P NMR spectra were recorded using an inverse gated decoupling sequence, 90° pulse angle, 25-s pulse delay, 13,000-Hz sweep, and 300 transients, at room temperature.

RESULTS AND DISCUSSION

Metal Profiles after Chelation Treatment

Softwood kraft pulps were subjected to EDTA chelation (Q-Q treatment) to remove the metal ions and especially to lower the content of calcium. EDTA&$CaSO_4$ treatment (Q-Ca treatment) was carried out to enrich the calcium content in the pulp. Table 1 summarized the results of metal profiles of the pulp samples before and after chelation treatment.

Table 1. Metal ion contents of pulps before and after chelation and calcium enrichment treatment (mg/kg pulp).

Metal Ion	Non-Q	Q-Q	Q-Ca
Mg	330	174	263
Mn	97.2	0.33	2.63
Ca	1090	106	1360
Cu	<0.5	<0.1	<0.1
Fe	6.03	3.99	4.20
K	45.4	13.2	19.5
Zn	10.5	0.32	0.35
Al	11.4	4.30	7.52
Si	80.7	6.98	20.7
Ba	7.38	7.40	6.08
Sr	4.90	4.33	4.02

After Q-Q treatment the decrease of nonprocess element contents in the pulp was observed. Manganese and zinc in the pulps was drastically reduced by more than 95%, whereas iron was reduced by nearly 30%. The reductions of magnesium, potassium, aluminum, calcium, and silicon are between these two extremes. There was no significant change in barium and strontium contents after chelation. The difference in the chelation efficiency for the ions is probably attributed, in part, to their ability to form complexes with EDTA. As demonstrated by Lapierre,

magnesium ion has a lower tendency to form complexes with EDTA than does ferric ion (26). Judging from the formation constant of iron-EDTA complex (K_{eq}), iron should be removed by EDTA in an efficient manner. However, the data in Table 1 indicate that there are still significant amounts of iron left in the pulp after EDTA treatment. Yang et al. have also observed the same effect and suggested that the failure to completely remove this metal ion may be due to the intimate connection between iron and fiber components, which limits its removal from the pulp during the Q-stage (20).

The reduction of nonprocess element contents in the pulp was also observed after Q-Ca treatment, except calcium with an increase of its content. Since there is a lower charge of EDTA and just a single Q stage in the Q-Ca treatment, the metal removal is a little less effective than Q-Q treatment. The two posttreatment pulps had comparable contents of nonprocess elements, apart from the much higher content of calcium in the Q-Ca treatment pulp.

Influence of Chelation Treatment on Oxygen Delignification

In order to evaluate the effect of the metal ion profile on oxygen delignification, the treated and untreated pulps were subject to oxygen delignification with the addition of magnesium sulfate. The results are summarized in Figure 1 and Table 2. As indicated in Figure 1, the pulp after Q-Q treatment displays lower delignification than that without the pretreatment. The enrichment of calcium after EDTA treatment results in a lower lignin removal than the Q-Q chelated pulp. High pulp viscosity was obtained after the chelation treatment and enrichment of calcium. Oxygen delignification of the pulp after Q-Q and Q-Ca treatment resulted in around 23% reduction in pulp viscosity, whereas in the case of the untreated sample a 30.1% viscosity reduction was found.

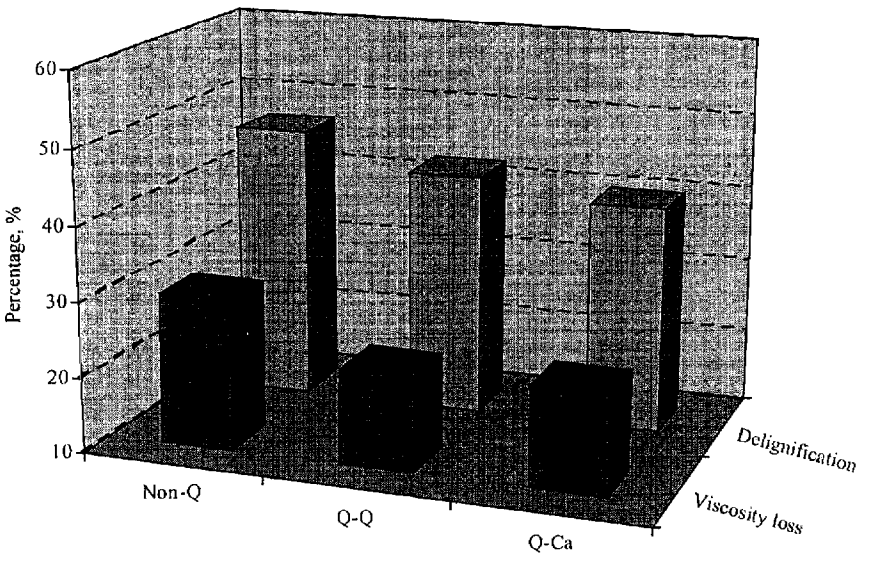

Figure 1. Influence of chelation treatment and enrichment of calcium on pulp delignification and viscosity in oxygen bleaching.

It is evident from these results that the removal of metal ions or the enrichment of calcium can retard carbohydrate degradation. However, the price for the maintenance of pulp viscosity is the reduction in delignification. This observation is in agreement with the basic theory of oxygen delignification. The enrichment of calcium was found to slightly reduce delignification and

maintain similar viscosity of the pulp as compared to the depletion of calcium. Significant removal of calcium can result in higher selectivity of oxygen delignification (Table 2). The amounts and types of metals in the pulp can clearly influence both delignification and carbohydrate degradation.

Table 2. Kappa and viscosity of oxygen delignified nonchelated and chelated pulps.

	Brownstock	Oxygen delignified pulp		
		Non-Q	Q-Q	Q-Ca
Kappa	27.6	14.7	15.9	16.5
Viscosity, mPa.s	32.6	22.8	25.2	25.0
Selectivity*	-	1.32	1.58	1.46

*Δ kappa/Δ viscosity.

NMR Lignin Analysis

The structural changes occurring to lignin during oxygen delignification were analyzed by phosphylating the lignin samples and employing ^{31}P NMR technique to quantify the amounts of hydroxyl groups in the lignin samples (24,25). The results of this analysis are summarized in Figures 2 and 3. As indicated in Figure 2, the residual lignin isolated from post-O delignified pulp which was pretreated with Q-Ca treatment showed a reduction of aliphatic hydroxyl group content, whereas that isolated from Non-Q and Q-Q pulps showed almost unchanged aliphatic OH content. Yang et al. have reported that aliphatic OH group content in residual is enriched after oxygen delignification (27). This result implies that side-chain oxidation occurring to the residual lignin after calcium enrichment is probably more pronounced during oxygen delignification.

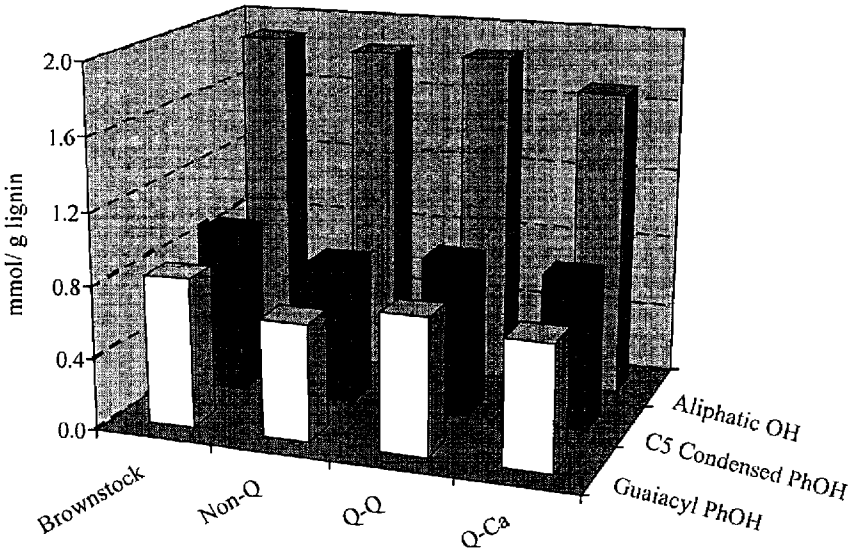

Figure 2. Changes in aliphatic OH, C5 condensed, and guaiacyl phenolic OH content in residual lignins isolated from kraft brownstock and postoxygen delignified pulps.

Figure 2 shows that the guaiacyl and C5 condensed phenolic OH contents decrease after oxygen delignification, and the latter decrease at a relatively reduced rate. Accompanying the

decrease of these phenolic units content was the increase of the carboxylic acid groups content (Fig. 3). These data are consistent with earlier reports that oxygen delignification is accompanied by the elimination of phenolic units and formation of acid groups, with the free phenolic OH groups being the most reactive lignin functionality (2,4,5). The removal amount of phenolic units during the oxygen delignification is in the order Non-Q > Q-Ca > Q-Q. This indicates that depletion of calcium ion of the pulp before O-stage would probably be able to decrease the elimination of the phenolic units of lignin. After oxygen delignification the Q-Q lignin sample has a higher content of guaiacyl phenolic OH group as compared to Non-Q and Q-Ca lignin samples. Interestingly, the amount of acid groups in the residual lignin samples isolated from the postoxygen delignified pulps is in the order Non-Q > Q-Q > Q-Ca, and the Q-Ca lignin sample even showed a slightly lower amount of carboxylic acid groups than the brownstock lignin sample.

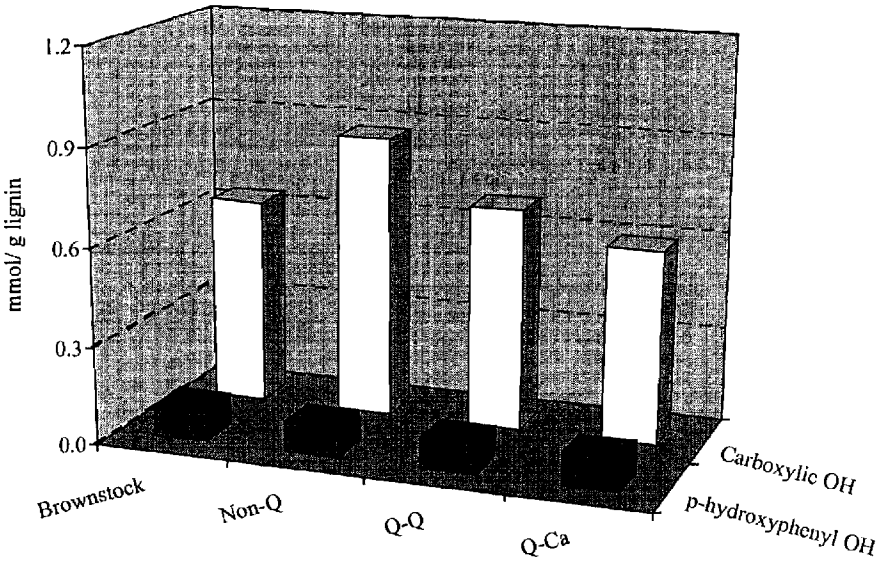

Figure 3. Changes in carboxylic acid and p-hydroxyphenyl group content in residual lignins isolated from kraft brownstock and postoxygen delignified pulps.

The presence of *p*-hydroxyphenyl groups was also quantified, and this analysis indicates that the content of these structures in postoxygen delignified pulps does not vary (Fig. 3). This confirmed the earlier studies that indicate that *p*-hydroxyphenyl group has been shown to be resistant toward oxygen delignification (4,5).

^{13}C NMR analysis (Fig. 4) further showed that the residual lignin sample isolated from the postoxygen delignified pulp has the same order for the carboxyl acid group content, i.e., Non-Q > Q-Q > Q-Ca. Carboxylic acid group content in the Q-Ca lignin sample is slightly lower than in the brownstock lignin sample. This is in good agreement with the study with ^{31}P NMR analysis stated above. Methoxyl group content in Q-Ca lignin from postoxygen delignified pulp is comparable to that in brownstock pulp lignin, which suggests that little demethylation occurred during oxygen delignification as to the pulp with enrichment of calcium ion.

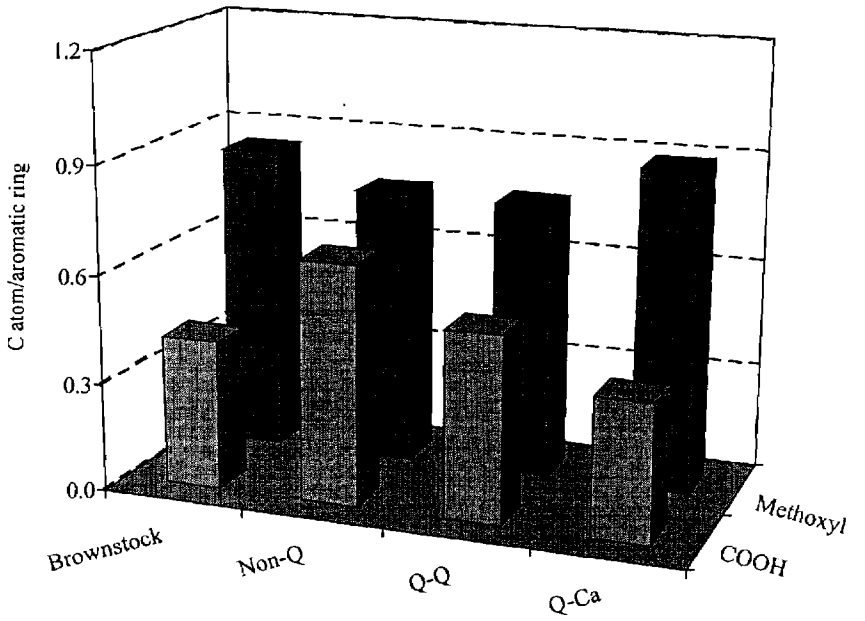

Figure 4. Changes in carboxylic acid and methoxyl group content in residual lignins isolated from kraft brownstock and postoxygen delignified pulps analyzed with ^{13}C NMR.

CONCLUSIONS

The studies described in this report clearly demonstrate that the nonprocess elements present in kraft pulp impact not only the extent of delignification but also the types of lignin removed during oxygen delignification. Removal of nonprocess elements can lower delignification and maintain higher pulp viscosity. The enrichment of calcium after EDTA treatment results in a lower lignin removal and comparable viscosity compared to the depletion of calcium. The calcium ion content in the pulp affects the oxygen delignification process.

Lignin structure analysis suggests that the nonprocess elements profile affects the lignin degradation process. The calcium enrichment in the pulp probably results in more pronounced side-chain oxidation occurring to the residual lignin during oxygen delignification. Removal of nonprocess elements in the pulp would be able to decrease the elimination of the phenolic units of lignin and formation of carboxylic acid. Enrichment of calcium results in a lower amount of carboxylic acid groups formed compared to depletion of calcium. The *p*-hydroxyphenyl group is resistant toward oxygen delignification and not affected by the profile of nonprocess elements in the pulp.

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