ORIGINAL ARTICLE

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# Oxidative cleavage of lignin aromatics during chlorine bleaching of kraft pulp

**Abstract** Methanol liberation and methoxyl loss during chlorine bleaching of softwood kraft pulp were quantitatively investigated to estimate the degree of structural modification of lignin aromatics. An increase in the chlorine multiple led to enhanced methoxyl loss from lignin. Our result, using pH-adjusted chlorine water (pH 5.7), by which chlorination under oxidation-favorable conditions was achieved, strongly supported the importance of the oxidation reaction by chlorine during delignification and lignin degradation. It was also suggested that methanol can be produced not only via catalytic hydrolysis by chlorine but via oxidative cleavage of the ether bond as well. The infrared spectrum of chlorolignins suggested that chlorine oxidation can open aromatic rings to muconic acid derivatives without cleaving ether bonding of the methoxyl group. No straight relation between the methoxyl content and the kappa number of chlorinated pulps was shown. The methoxyl content of bleached kraft pulps subjected to successive chlorination and alkali extraction showed a good relation with the kappa number. This means that almost all the portions of the oxidatively modified lignin structure were successfully removed during these treatments, and the aromatic structures of residual lignin in chlorinated and alkali-extracted pulps were thought to remain intact.

## Introduction

In our previous study, which quantitatively estimated the proportion of oxidation and substitution reactions by chlorine, strong emphasis was placed on the important role of the oxidation reaction during chlorine bleaching.[1] In this study the progress of methanol liberation and methoxyl loss during chlorination, alkali extraction, or both were quantitatively measured to determine how chlorine bleaching caused structural modification of lignin aromatics and how the structural modification of lignin is related to delignification.

First, the effect of the oxidation reaction by chlorine on the progress of methoxyl removal is discussed. For this purpose methanol liberated from methoxyl groups into the chlorination liquor was determined, varying the reaction conditions. Next, methoxyl loss during chlorination and the alkali-extraction stages were quantitatively determined and the relation between methoxyl loss and the removal of lignin was analyzed. These analyses make it possible to estimate what kind of lignin is removed during the chlorination and alkali-extraction stages and what kind of lignin remains. The importance of the oxidation reaction for chlorine delignification is discussed.

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## Experimental

### Determination of methanol liberated during chlorination stage

Unbleached softwood kraft pulp (kappa number 24.9; 2.5 g on the oven-dried weight basis) was treated with chlorine water (chlorine multiple 0.01–0.50, pulp consistency 2.78%) under two conditions as follows. The chlorine multiple is

defined as the percent chlorine charge (percent on pulp) divided by the kappa number of unbleached kraft pulp.

Condition 1: treated with chlorine water (pH 1.7 before bleaching) prepared by introducing gaseous chlorine into deionized water without pH adjustment (low pH)

Condition 2: treated with pH-adjusted chlorine water (pH 5.4 before bleaching) prepared by introducing gaseous chlorine into a dilute NaOH solution (high pH)

The chlorination reaction was performed in a vial sealed with a screw cap for 60 min at room temperature. Just after adding chlorine water, each sample was sealed and shaken for 10 s. It was then shaken every 10 min until the end of the reaction. After the reaction, each sample was cooled in an ice bath for 10 min to suppress vaporization of methanol during the pH measurement. After the pH was measured quickly, each sample was sealed and cooled again in an ice bath for 30 min. An excessive amount of reducing agent (10 ml of 1 M $Na_2S_2O_3$ solution) was then added to reduce the residual $Cl_2$, if any, in the sample. Each sample was sealed and stored in a cold room (4°C) until use. An aliquot of the suspension from each sample was transferred to a 1.5-ml conical centrifuge tube, sealed with a stopper, and centrifuged at 12000 rpm (10500 g) for 10 min at 5°C. The supernatant (1 ml) was used to determine the amount of methanol liberated during chlorine bleaching.

The methanol determination was performed using gas chromatography (GC-8A: Shimadzu) with FID as detector. Packed column (2.6 mm × 2.0 m) coated with PEG 6000 (10%) on Shimalite TPA (60–80 mesh) was used. The column temperature was kept constant at 90°C. The injection temperature was 180°C, and the detector temperature was 200°C. Helium was used as both carrier gas (pressure 170 kPa) and makeup gas (pressure 170 kPa). The gas pressures of hydrogen and air were both set at 60 kPa. A calibration curve for the determination was obtained from the relation between the peak area and the methanol injected using aqueous methanol solutions with various methanol concentrations. The injection volume was 20 $\mu$l. The determination for each sample was performed in triplicate.

To determine the kappa number of chlorinated pulps in a separate experiment, chlorination of softwood kraft pulp was performed in the same way except it was done in a plastic bag. The kappa number of the chlorinated pulps was measured according to the TAPPI useful method (UM 246).

Preparation of chlorolignins for measurement of infrared spectrum

Unbleached softwood kraft pulp (kappa number 24.9, 9 g on the oven-dried weight basis) was treated with chlorine water under three conditions as follows. The reaction was performed in a plastic bag at room temperature for 60 min. The chlorine multiple was set at 0.15 at a pulp consistency of 5%.

Condition 1: treated with chlorine water (pH 1.7 before bleaching) prepared by introducing gaseous chlorine into deionized water without pH adjustment (low pH)

Condition 2: treated with pH-adjusted chlorine water (pH 5.3 before bleaching) prepared by adding NaOH to the chlorine water (high pH)

Condition 3: treated with nonaqueous chlorine solution prepared by introducing gaseous chlorine into pure glacial acetic acid

After treatment each chlorinated pulp was washed three times with 180 ml of deionized water each time. Chlorolignin was extracted at room temperature from the chlorinated and water-washed pulp by soaking the pulp three times with 180 ml of aqueous dioxane (53%) according to the procedure by Shintani et al.[2] The extracted chlorolignin was recovered by lyophilization.

Chlorolignin (28 mg) extracted from the chlorinated pulp prepared under condition 1 was treated with 11.2 ml of NaOH solution containing 28 mg NaOH. The treatment was performed in a waterbath at 70°C for 60 min. The whole solution was dialyzed against dilute hydrochloric acid solution for 24 h by use of a cellulose tube (Viskase Sales Corp.: cutoff molecular weight 12000–14000). Then the whole solution was concentrated under reduced pressure and lyophilized to obtain alkali-treated chlorolignin.

The infrared (IR) spectra of chlorolignins were recorded by the KBr pellet method.

Determination of methoxyl content of pulps

Unbleached softwood kraft pulp (kappa number 24, 10 g on the oven-dried weight basis) was treated with chlorine water (chlorine multiple 0.05–0.20, pulp consistency 5%) in a plastic bag for 60 min under the following two conditions.

Condition 1: treated with chlorine water (pH 1.7 before bleaching) prepared by introducing gaseous chlorine into deionized water without pH adjustment (low pH)

Condition 2: treated with pH-adjusted chlorine water (pH 5.7 before bleaching) prepared by introducing gaseous chlorine into dilute NaOH solution (high pH)

After the reaction, chlorinated pulp was separated from the chlorination liquor by filtration and washed three times with 200 ml of deionized water each time. Part of the chlorinated pulp was subjected to warm alkali treatment at 70°C for 60 min at 2.5% NaOH charge on pulp on the weight basis. Chlorinated pulps (CW-NKPs) and successively chlorinated and alkali-treated pulps (CE-NKPs) thus prepared were subjected to a methoxyl content determination.

The methoxyl content of pulps was determined basically according to the procedure by Sporek and Danyi.[3] Pulp (270 mg to 2.0 g on the oven-dried weight basis) and ethyl vanillin (3-ethoxy-4-hydroxybenzaldehyde 10 mg) were placed in a 50-ml round-bottomed flask, and 57% hydrogen iodide solution (10 ml) was added. A condenser was attached to the flask, and the methoxyl group in kraft pulp residual lignin was converted to methyl iodide under reflux at 135°C for 20 min. The sample was cooled in an ice-water bath after the reaction; 10 ml deionized water and 10 ml carbon tetrachloride ($CCl_4$) were sequentially added to the sample. The sample was centrifuged at 4500 rpm (2800 g) at

0°C for 5 min to achieve complete separation of the $CCl_4$ layer from the water layer. Anhydrous sodium sulfate was then added to the $CCl_4$ fraction, and the methyl iodide in the fraction was determined by gas chromatography (GC). Ethyl vanillin was added to generate in situ ethyl iodide, which was used as an internal standard. A calibration curve was obtained from the GC peak of the methyl iodide/ethyl iodide area ratio using varying amounts (0.8–20.0 mg) of vanillin as a lignin model compound. Pulps were weighed so the lignin content (estimated by kappa number) was approximately 10 mg.

The methoxyl content was determined using GC (GC-14B: Shimadzu) with FID as detector. Pola PLOT Q (GL Science: 0.53 mm $\times$ 25 m, df = 20 $\mu$m) was used as the capillary column. The column temperature was kept at 120°C for 12 min, raised at 5°C/min to reach 180°C, then held there for 10 min. The injection temperature was 120°C, and the detector temperature was 180°C. Helium was used as both carrier gas (pressure 75 kPa) and makeup gas (pressure 110 kPa). The gas pressures of hydrogen and air were set at 50 and 70 kPa, respectively. Injection volume was 1.0 $\mu$l. Determination for each sample was performed in duplicate.

## Results and discussion

### Progress of methanol liberation during chlorination stage

It is well known that during chlorine bleaching substantial amounts of methanol are liberated from lignin as a result of cleavage of the ether linkage of methoxyl groups. Hibbert and his research group[4] proposed that introducing chlorine into aromatic nuclei renders aromatic methyl ethers unstable, and that they become susceptible to the oxidative degradation subsequently caused by chlorine. In contrast, Sarkanen and Strauss[5] concluded later that chlorine substitution at the ortho position to the methoxyl group suppresses the demethylation reaction. As a mechanism of the demethylation reaction, Ivancic and Rydholm[6] suggested a kind of acid-catalyzed hydrolysis, and Sarkanen and Strauss[5] proposed a chlorine-catalyzed hydrolysis mechanism. Ni and coworkers[7] assumed that all the methoxyl groups removed from kraft pulp during chlorine treatment are converted to methanol, and they concluded that all dissolved lignin fragments in chlorination liquor are demethylated. Based on this assumption, they implied that it is possible to estimate the degree of methoxyl loss as methanol in the chlorination effluent. They also reported a linear relation between demethylation and delignification during the chlorination stage and suggested that residual lignin in chlorinated and water-washed softwood kraft pulp (CW-NKP) is not demethylated. They proposed the "methanol number" to determine the lignin content of CW-NKP quickly as an alternative to kappa number determination.[8]

To evaluate how chlorination conditions (pH and chlorine multiple) affect methanol liberation, pulp was chlorinated by varying the chlorine multiple under two pH
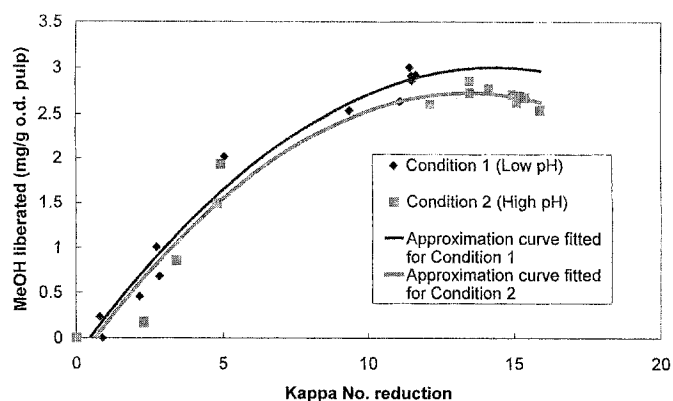


**Fig. 1.** Relation between methanol liberation and kappa number reduction

conditions (condition 1, low pH; condition 2, high pH). Figure 1 shows methanol liberation plotted against the kappa number reduction of CW pulp. Compared to condition 1, condition 2 was intentionally programmed so the oxidation reaction by chlorine (HClO form) is dominant and the substitution reaction is suppressed owing to its higher pH value. No significant difference is observed between conditions 1 and 2, even though methanol formation under condition 2 always appears to be slightly lower than that under condition 1. Methanol liberation seems proportional to the kappa number reduction at low chlorine multiples, but no single straight line is fitted to cover all the data points from low to high chlorine multiples. This does not show good correspondence with the result reported by Ni et al.,[7] who proposed that the decrease in lignin content of CW-NKP can be determined by measuring the methanol liberated during the Chlorination (C) stage. Because the definition of their "chlorine-free lignin" content is different from that measured by the kappa number method we used, we cannot compare their proposal and our present results directly. Our results, however revealed that the kappa number reduction of CW-NKP cannot be simply expressed by the amount of methanol liberated during the C stage. Despite such an inconsistency, their results and ours demonstrate that a certain decrease in kappa number of CW-NKP is accompanied by a certain level of methanol liberation during the C stage regardless of the chlorination condition.

There was an apparent difference in the methanol liberation at a certain dose of chlorine between conditions 1 and 2 (Fig. 2). In both conditions, methanol yields are increased with the chlorine multiple until about 3 mg of methanol is liberated from 1 g of unbleached pulp, which corresponds to approximately 0.5 mol per lignin unit based on the assumption that an equivalent molecular weight (EMW) of 200 is applied. A slight decrease in methanol after the maximum value can be reasonably ascribed to methanol oxidation by excess chlorine.[5] A marked difference is observed between conditions 1 and 2 at chlorine multiples lower than 0.2. When the chlorine multiple ranged from 0.01 to 0.20, methanol formation under condition 2 was higher than that under condition 1. The result apparently indicates that high pH is more favorable to the demethylation reaction than

low pH. This seems contradictory to the previous report by Hibbert and his research group,[4] who found that on the basis of chlorination of soda lignin under wide range of pH the value of methoxyl loss from lignin per consumed chlorine decreases in the order pH 2, 6, and 10. The reason for this discrepancy is unknown at present, but it should be noted that their results were obtained based on the methoxyl content of the recovered lignin after chlorination and that our experiment determined all the methanol liberated from methoxyl groups during chlorination. If recovery of the extensively demethylated part of lignin is quite low, the methoxyl content of recovered lignin cannot give a proper indication of the extent of the demethylation reaction.

Under condition 1 (Fig. 2), it is reasonable to suppose that chlorine is effectively consumed by the aromatic substitution reaction at low chlorine multiples, and thus its contribution to the demethylation reaction is suppressed during the early stage of chlorine bleaching. Our result is in good agreement with an observation by Hosoya[9] and Hosoya et

al.[10] who found that by chlorination of a $\beta$-O-4 type lignin model compound in aqueous dioxane (50%) an aromatic substitution reaction by chlorine occurred exclusively during the early stage of the reaction; and after the chlorine substitution reached a certain level, the demethylation reaction then started.

For methoxyl removal, in addition to the two proposed mechanisms mentioned above, we can point out another possibility: A large part of the chlorine, which is present as hypochlorous acid under condition 2, enhances methoxyl loss as a result of oxidative cleavage of an aromatic moiety. IR spectra of isolated chlorolignins (Fig. 3) seem to confirm this possibility. In all spectra, peaks in the vicinity of 1600, 1505, and 1460cm$^{-1}$ are not seen at all, although usually they are typically found in lignin preparations due to the absorption ascribable to lignin aromatics. This suggests that an aqueous dioxane-extracted part of residual lignin in CW pulp is so greatly modified by oxidation that the aromatic character of lignin is already lost. This result strongly supports our previous report[1] and the study by Shintani and coworkers.[11] Instead of these peaks, strong peaks due to carboxylic acids are observed (1620cm$^{-1}$ for the ionized form carboxylic acids, 1730cm$^{-1}$ for free-form carboxylic acids). Careful attention should be paid to shoulder absorption (1760cm$^{-1}$) characteristically found near a large peak. This shoulder was observed in a sample obtained from the pulp prepared under condition 1 (Fig. 3a) but not in a sample prepared under condition 2 (Fig. 3b). The shoulder can also be clearly seen for the sample prepared by chlorination in glacial acetic acid (condition 3) (Fig. 3c). In this reaction condition, the oxidation reaction by chlorine was intentionally suppressed to a greater degree than under conditions 1 and 2. Therefore, it seems likely that this shoulder appears only in samples where chlorination is carried out under relatively strong acidic conditions. When the chlorolignin underwent warm alkali treatment, the shoulder
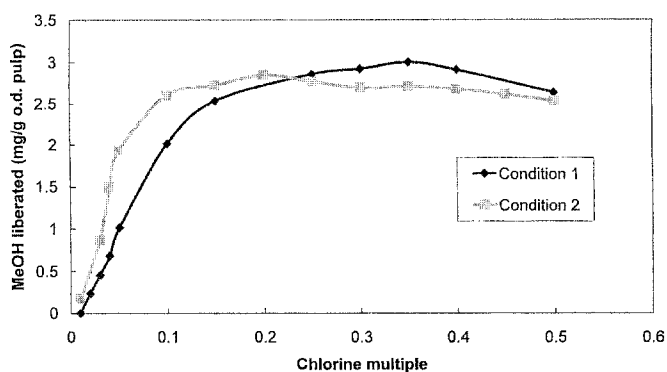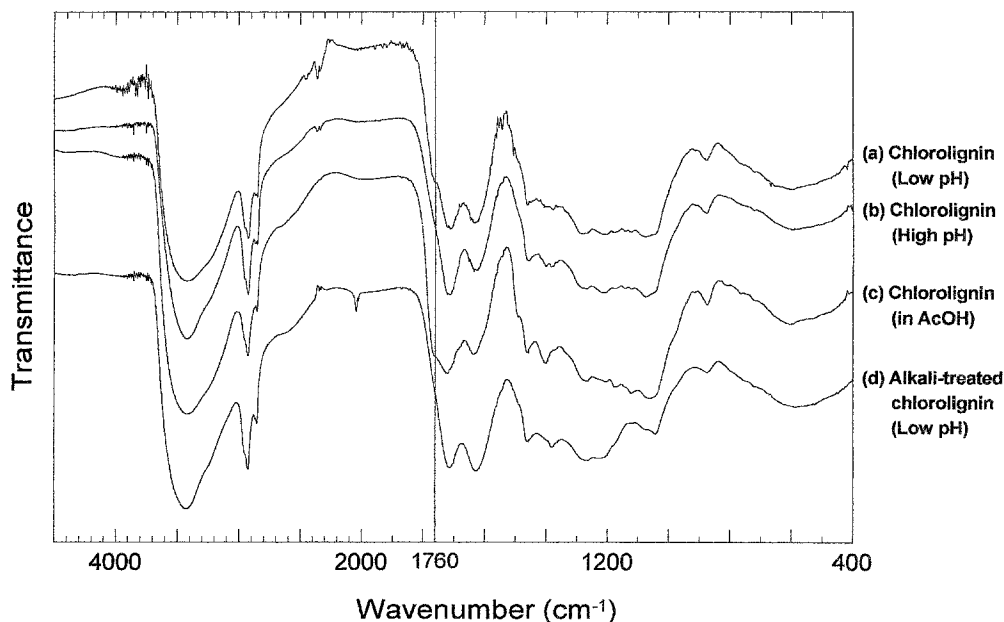


Fig. 2. Methanol liberation at various chlorine multiples



Fig. 3. Infrared spectrum of chlorolignin samples

(a) Chlorolignin (Low pH)

(b) Chlorolignin (High pH)

(c) Chlorolignin (in AcOH)

(d) Alkali-treated chlorolignin (Low pH)

was found to disappear (Fig. 3d) and methanol formation was observed, even though quantitative analysis was not performed. Thus it is thought that the shoulder can be attributed to some esters or lactones, which in general exhibit strong absorption in the range 1700–1800 cm$^{-1}$. This observation suggests that oxidative cleavage of the aromatic part proceeds with release of the methoxyl group as methanol under condition 2 (high pH), whereas oxidative cleavage of the aromatic part proceeds with a part of the methoxyl group remaining in ester form when chlorinated under condition 1 (low pH).

## Methoxyl loss during chlorination stage and alkali-extraction stages

In the previous section it was demonstrated that methanol formation is dependent on the chlorination condition (pH and chlorine multiple). It means that the differences in the chlorination condition affect the extent of modification of lignin aromatics. However, it is still not clear how the chlorination condition affects the progress of delignification. In this section we evaluate quantitatively the role of the oxidation reaction of lignin aromatics in delignification during the C and alkali extraction (E) stages.

When lignin aromatics are oxidized under alkaline conditions, in most cases methanol is released from the methoxyl group. This is also true when an alkali after treatment follows the oxidation. On the other hand, lignin whose aromatics are oxidized to some extent still consumes permanganate although to a lesser extent than unoxidized lignin. Therefore, the methoxyl content/kappa number ratio of a certain pulp can be used as an indication of the degree of oxidation the residual lignin in the pulp underwent. For example, after some oxidative delignification, if this ratio is smaller for delignified pulp than for unoxidized pulp we can reasonably assume that some oxidized lignin remains in the delignified pulp. In contrast, if this ratio is the same as that of unoxidized pulp we can conclude that only unoxidized lignin remains in the pulp after delignification.

In the present study, the same method was applied to evaluate the degree of structural modification of the aromatic part of residual lignin in CW-NKPs and chlorinated/alkali-treated pulps (CE-NKPs). In Fig. 4 (condition 1) and Fig. 5 (condition 2), the methoxyl contents of pulps are plotted against their kappa number. In both conditions the relations between the methoxyl content and kappa number of CW-NKP cannot be expressed by a straight line, which is not in agreement with the report by Ni and coworkers,[7] who proposed a linear relation between methoxyl removal and delignification after chlorination of pulp (CW-NKP). A similar discrepancy was seen for methanol liberation, as discussed in a previous section. It should be noted that the methoxyl content of the pulp does not significantly decrease after the alkali extraction. The methoxyl content/kappa number ratio of CE-NKP is the same as or slightly higher than that of unbleached pulp, suggesting that the lignin remaining in CE-NKP is of a similar nature to that in un-
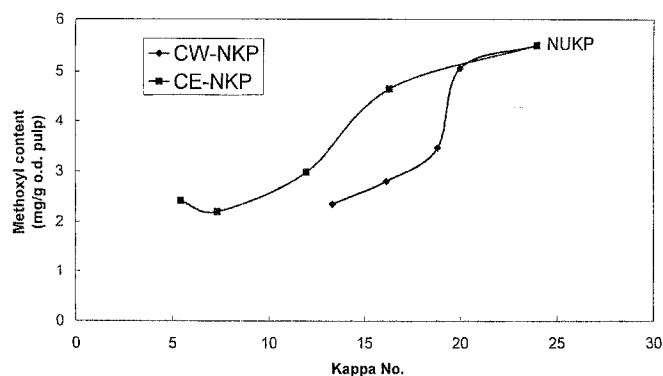


**Fig. 4.** Methoxyl content of chlorinated pulps (*CW-NKP*) and chlorinated/alkali-treated pulps (*CE-NKP*) prepared under condition 1 (low pH). *NUKP*, softwood unbleached kraft pulp
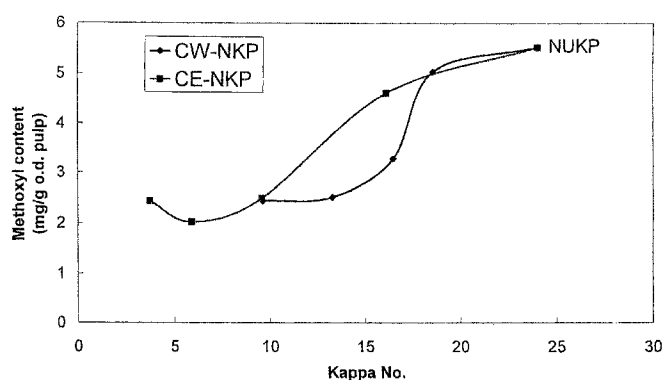


**Fig. 5.** Methoxyl content of CW-NKPs and CE-NKPs prepared under condition 2 (high pH)

bleached pulp. Conversely, this ratio for CW-NKP is always lower than those for CE-NKP and unbleached pulp (Table 1).

Based on these data, we can postulate the process of delignification during the C and E stages as follows. During the C stage there is extensive modification of lignin aromatics, which results in the release of methanol, but most of the modified lignin aromatics remain in the pulp. They are, however, effectively removed by alkali extraction, and only unmodified lignin remains in CE-NKP. A significant difference between condition 1 (low pH) and condition 2 (high pH) is that the methoxyl content/kappa number ratio for CW-NKP prepared under condition 1 is lower than that prepared under condition 2 when compared at the same kappa number. This indicates that structural modification of aromatics, which leads to the release of methanol under condition 2, causes more effective removal of lignin than under condition 1. The kappa number of both CW-NKPs and CE-NKPs prepared under condition 2 with a certain chlorine dose was always lower than that under condition 1 (Table 1). Because condition 2 (high pH) is more favorable to the oxidation reaction, these results again confirm the importance of the oxidation reaction for chlorine delignification.

**Table 1.** Calculated ratio of "methoxyl content/kappa number"

| Sample | Chlorine multiple | Kappa no. | Methoxyl (mg/g pulp) | Methoxyl/kappa |
|---|---|---|---|---|
| NUKP | – | 24.0 | 5.5 | 0.23 |
| Condition 1 | | | | |
| CW-NKP | 0.05 | 20.0 | 5.1 | 0.25 |
| | 0.10 | 18.8 | 3.5 | 0.18 |
| | 0.15 | 16.2 | 2.8 | 0.17 |
| | 0.20 | 13.3 | 2.4 | 0.18 |
| CE-NKP | 0.05 | 16.3 | 4.7 | 0.29 |
| | 0.10 | 12.0 | 3.0 | 0.25 |
| | 0.15 | 7.3 | 2.2 | 0.30 |
| | 0.20 | 5.5 | 2.4 | 0.44 |
| Condition 2 | | | | |
| CW-NKP | 0.05 | 18.6 | 5.0 | 0.27 |
| | 0.10 | 16.5 | 3.3 | 0.20 |
| | 0.15 | 13.3 | 2.5 | 0.19 |
| | 0.20 | 9.6 | 2.4 | 0.25 |
| CE-NKP | 0.05 | 16.1 | 4.6 | 0.29 |
| | 0.10 | 9.6 | 2.5 | 0.26 |
| | 0.15 | 5.9 | 2.0 | 0.34 |
| | 0.20 | 3.7 | 2.4 | 0.65 |
| Ideal[a] | – | 24 | 5.6 | 0.23 |

NUKP, softwood unbleached kraft pulp; CW-NKP, chlorinated softwood kraft pulp; CE-NKP, chlorinated and alkali-extracted softwood kraft pulp
[a] Hypothetically calculated value based on the assumption that 200 g of lignin in pulp (kappa number 24) carries 1 mole of methoxyl group

## Conclusions

The effect of the chlorination condition (pH and chlorine multiple) on the structural modification of lignin aromatics and on the efficiency of delignification was analyzed. Chlorination conducted under higher pH enhances release of the methoxyl group as methanol more effectively and, furthermore, results in more effective delignification. Analysis of the methoxyl content/kappa number ratio for CW-NKPs and CE-NKPs suggests that the aromatic part of the residual lignin remaining in CE-NKP was structurally unmodified. These data strongly support the idea that the oxidation reaction by chlorine is a key to lignin structural modification, which can lead to effective delignification.

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