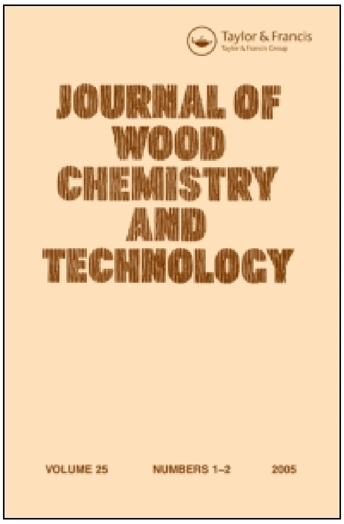

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DEVELOPMENT OF PHENOLIC LIGNIN DURING ClO_2 BLEACHING OF KRAFT PULP

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ABSTRACT

The development of the phenolic lignin content in kraft pulp during ClO_2 bleaching was quantitatively determined by the periodate oxidation method. The effect of hypochlorous acid, an intermediate formed during chlorine dioxide bleaching, was eliminated by addition of sulfamic acid, a scavenger of hypochlorous acid. It was found that the number of free phenolic lignin groups per 100 lignin monomer units decreased from about 29 for unbleached kraft lignin to about 6.5 after 1 minute of ClO_2 bleaching. It was also shown that the *in-situ* generated hypochlorous acid created phenolic hydroxyl groups during chlorine dioxide bleaching. Since it was found that delignification by chlorine dioxide itself was mostly restricted to free phenolic lignin, these findings were used to explain the effect on delignification of addition order of chlorine and chlorine dioxide during bleaching of kraft pulp.

INTRODUCTION

Recent concern regarding the environmental impact of chlorinated organic compounds has lead to the introduction of operational practices which reduce the formation of these chlorinated organics during pulp bleaching. One of these practices, increasing substitution of chlorine by chlorine dioxide in the chlorination stage, has become a common practice in the industry. Practical aspects of ClO_2 substitution, such as the effect of the addition order of chlorine dioxide and chlorine on the degree of delignification have been reported extensively in literature. However, relatively few references deal with the fundamentals of chlorine dioxide bleaching of chemical pulp. Recently, we undertook a project with the aim of obtaining a better fundamental understanding of the delignification process by chlorine dioxide. The objective of the present paper is to study the development of phenolic lignin content during chlorine dioxide bleaching.

EXPERIMENTAL

A 28.7 kappa number black spruce pulp was used. The ClO_2 experiments were performed in a 3-neck round bottom flask. A chlorine dioxide solution was added to 4 g of pulp, which was well dispersed in distilled and deionized water by mechanical stirring. A high ClO_2 concentration was used, so that the addition of the ClO_2 solution could be completed in about 5 seconds. The final pulp consistency was 1% and the kappa factor was 0.22.

The free phenolic hydroxyl content in unbleached and chlorine dioxide treated kraft pulp was determined according to the periodate oxidation method. Its principle is based on the fact that a methoxyl group in the ortho position to a free phenolic hydroxyl group is removed as methanol by the action of periodate, while aliphatic methoxyl groups and etherified aromatic methoxyl groups are stable towards periodate. The method was tested on guaiacol and veratrol. Guaiacol gave a methanol formation of 93.2% of the theoretical value, while only 4.3% of the methoxyl groups in veratrol were converted to methanol. This confirms that the periodate oxidation method is fairly specific for the detection of methoxyl groups adjacent to free phenolic hydroxyl group. Carbohydrates, by far the main component in kraft pulp, are also oxidized by periodate. Therefore, a large excess of periodate must be used to assure complete liberation of methanol. The present experimental procedure is as follows: 0.46 g of sodium meta-periodate ($NaIO_4$) and 1 ml of 4N sulfuric acid were mixed, followed by addition of 2.8 ml of water. The sodium meta-periodate solution was cooled to 4°C before 0.2 g o.d. pulp was charged. The reaction mixture was maintained at 4°C in a refrigerator for 3 days. The pulp suspension was shaken occasionally during this period. Then, the filtrate was separated from the pulp, and the excess amount of periodate was eliminated by addition of sodium thiosulfate. The liquor sample was subsequently analyzed for methanol by gas chromatography (GC). The analytical conditions are as follows:

Column:	Chromosorb 102, mesh size 80/100
Injection temperature (°C):	150
Oven temperature (°C):	107
Detector temperature (°C):	200
Helium flow rate (ml/min):	50
Hydrogen flow rate (ml/min):	22
Air flow rate (ml/min):	250
Sample size (μl):	1.8

Lai et al.[1] found that the number of phenolic hydroxyl groups in wood meal as determined by the periodate oxidation method is approximately the same as that determined by aminolysis. They also showed that the periodate oxidation method is a convenient procedure for estimating the phenolic hydroxyl content of lignin in wood.

The methoxyl content of the pulp samples was determined according to Tappi method T209. The kappa number was determined in accordance with CPPA standard G18.

RESULTS AND DISCUSSION

A 28.7 kappa number unbleached kraft pulp was mixed at 25°C with chlorine dioxide at a consistency of 1% and an initial ClO_2 concentration of 0.237 g/l. These conditions represent an equivalent kappa factor of 0.22. The reaction was stopped at different times, and the pulp samples were washed and air dried. The kappa number, methoxyl content, phenolic methoxyl content were

TABLE 1

Development of the Phenolic Hydroxyl Content During ClO_2 Bleaching

Time (min)	Kappa number	Total OCH_3 in pulp (%)*	OCH_3 converted by $NaIO_4$ (%)*	Phenolic OCH_3 (%)
0	28.7	0.58	0.205	35.3
1	15.9	0.45	0.0364	8.1
10	13.9	0.38	0.0296	7.8
30	12.3	0.34	0.0270	8.2
60	10.7	0.32	0.0255	8.0
112	10.6	0.31	0.0250	8.1
150	10.4	0.28	0.0239	8.5

Initial ClO_2: 0.237 g/l, Initial kappa no.: 28.7, 1% consistency, 25°C

* % on oven dry pulp

then determined. The results are shown in Table 1. It shows that the percentage of methoxyl groups in the ortho position to a phenolic hydroxyl group decreases rapidly to 8% when chlorine dioxide was charged, and that it remained at this value thereafter.

Table 1 also shows that the unbleached kraft pulp contains about 35% of methoxyl groups which are ortho to free phenolic hydroxyl groups. It was shown earlier [2] that the molar ratio of OCH_3/lignin phenylpropane unit of the unbleached kraft pulp is 0.82. Therefore, the phenolic hydroxyl content of kraft pulp at about 48% pulp yield is about 0.29 per C_9 lignin monomer unit. This compares very favourably with a frequency of 0.27 phenolic hydroxyl groups per lignin monomer unit obtained by Gellerstedt and Lindfors [3] using the aminolysis method on a similar kraft pulp. One can also calculate from Table 1 that phenolic lignin units represent only about 6.5% of the residual lignin after the first minute of ClO_2 bleaching.

It has been found [4,5] that about 60% of chlorine dioxide is converted into hypochlorous acid during ClO_2 bleaching of kraft pulp. The reason that hypochlorous acid is normally not detected during ClO_2 bleaching is because it is rapidly consumed in consecutive reactions. In order to determine the effect of *in-situ* generated hypochlorous acid on the development of phenolic lignin content during ClO_2 bleaching, the experiment described in Table 1 was repeated with the addition of sulfamic acid to the pulp suspension prior to ClO_2 bleaching. Sulfamic acid effectively removes hypochlorous acid by the following reaction [4]:

$$H_2NSO_3^- + HOCl \rightarrow HClNSO_3^- + H_2O$$

The sulfamic acid charge was in excess of that of ClO_2 by a 3 to 1 molar ratio.

The development of the phenolic hydroxyl content of kraft pulp during ClO_2 treatment in the presence of sulfamic acid is shown in Table 2. Comparison of Table 2 with Table 1 shows that although the phenolic hydroxyl content also decreases very fast initially, it remains at a lower level of about 5% when the *in-situ* generated hypochlorous acid is captured. This is in agreement with the concept whereby hypochlorous acid reacts with non phenolic lignin units and creates new free phenolic hydroxyl groups so that delignification by ClO_2 can continue. Comparison of the results in Table 1 and Table 2 shows that a significant degree of delignification is obtained both with or without capturing the *in-situ* generated hypochlorous acid. The relatively small decrease in the degree of delignification when hypochlorous acid is eliminated can be explained when it is realized that the capture of about 60% of ClO_2 as hypochlorous acid is equivalent to a kappa factor of 0.025, or 12% of a normal chlorine charge.

The creation of free phenolic hydroxyl groups by hypochlorous acid during ClO_2 bleaching could explain the surprising result of Gianola and Meybeck [6] that chlorine dioxide reacts with etherified phenolics, while acid chlorite does not. In the former case, the generated hypochlorous acid creates phenolic lignin

TABLE 2.
Development of the Phenolic Hydroxyl Content During ClO_2 Bleaching in the Presence of Sulfamic Acid.

Time (min)	Kappa number	Total OCH_3 in pulp (%)*	OCH_3 converted by $NaIO_4$ (%)*	Phenolic OCH_3 (%)
0	28.7	0.58	0.205	35.3
1	17.1	0.452	0.0347	7.7
10	15.1	0.405	0.0216	5.3
30	13.9	0.367	0.0183	5.0
60	13.3	0.333	0.0171	5.1
150	12.8	0.322	0.0156	4.8

Sulfamic acid 10.5 m mol/l, 45°C, Initial ClO_2 conc. 0.237 g/l, 1% consistency, Initial kappa no. 28.7

* % on oven dry pulp

structures which ClO_2 can attack, while in the latter hypochlorous acid reacts preferentially with chlorite rather than the etherified phenolics. An extreme example of the useful effect of *in-situ* generated hypochlorous acid was demonstrated by Rapson and Anderson [7] who found that all lignin could be removed from kraft pulp in a single bleaching stage when applying a large amount of chlorine dioxide for a very long time. ClO_2 was shown to be the only bleaching chemical which has this capacity. The reason that pure chlorine cannot delignify kraft pulp in one bleaching step, even though non-phenolic lignin structures are also attacked by chlorine, is that extensive aromatic substitution of chlorine leads to the formation of stable "blocking groups" which prohibit further delignification [8].

The above results provide an explanation why substitution of chlorine by chlorine dioxide achieves more delignification than that of chlorine or chlorine dioxide alone, and why the DC mode of addition is always favourable in terms of degree of delignification compared to that of the CD or C+D sequence at the same active chlorine charge, as is shown schematically in Figure 1. We have shown earlier [8] that delignification by chlorine can be described by two competing reactions: demethylation and aromatic substitution of chlorine in the lignin monomer units. The aromatic substitution progressively retards delignification until fully chlorinated structures are formed which are stable towards further attack by chlorine. The lignin content remaining after complete chlorination is called "floor level" lignin content. It was also established that "the floor level" lignin content is proportional to the initial lignin content. This suggests that the final kappa number of the bleached pulp can be decreased if the lignin content of the pulp is lower when chlorine is charged.

In the DC mode, by charging ClO_2 first, the available free phenolic lignin is rapidly consumed. When chlorine is subsequently charged, the lignin content of the pulp decreases further since chlorine can attack the non-phenolic lignin. Therefore, more overall delignification is achieved compared to that when only chlorine is charged. As the ClO_2 substitution ratio increases, the phenolic lignin will all be consumed, so that the excess ClO_2 can only react with newly formed free phenolic lignin generated by its reaction intermediate, hypochlorous acid. At very high ClO_2 substitution ratios, delignification by chlorine dioxide is limited to the phenolic lignin available. On the other hand, the supply of chlorine is so small that its contribution to delignification becomes minimal, and as a result the overall delignification is decreased. This explains why there exists an optimum ClO_2 substitution ratio for a DC sequence. In the CD mode, by charging chlorine first, the phenolic lignin content will be lower compared to that in the unbleached kraft pulp at the time when ClO_2 is charged. As a result the supplied ClO_2 is not as completely and efficiently used for delignification as when ClO_2 was added first to the unbleached kraft pulp.

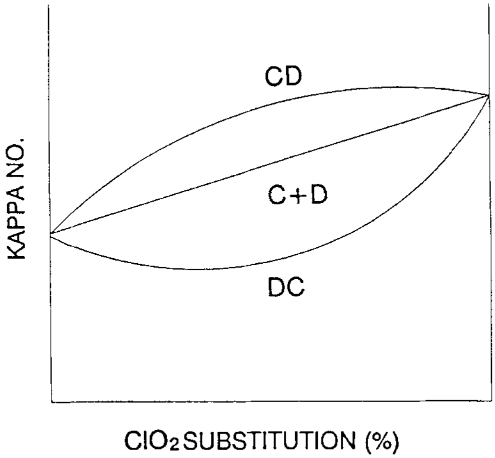

FIGURE 1.

Effect of Addition Mode of Cl_2 and ClO_2 on Delignification During Chlorination

CONCLUSIONS

The development of phenolic lignin content during chlorine dioxide bleaching of kraft pulp was followed by determining the residual methoxyl content and measuring the amount of methanol released by periodate oxidation. It was found that the phenolic lignin content during chlorine dioxide bleaching of kraft pulp decreased from about 29% for unbleached kraft lignin to about 6.5% after 1 minute of reaction. It was also shown that hypochlorous acid, a reaction intermediate formed during chlorine dioxide bleaching, created new phenolic groups. This finding was used to explain the effect of the addition order of chlorine and chlorine dioxide on the degree of delignification during bleaching of kraft pulp.

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