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Analysis of progress of oxidation reaction during oxygen-alkali treatment of lignin 2: significance of oxidation reaction of lignin during oxygen delignification

Received: June 14, 1999 / Accepted: August 18, 1999

Abstract The progress of lignin oxidation during oxygen-alkali bleaching of pulp was evaluated by the method based on the difference between permanganate consumption of original pulp and that of the mixture of pulp and effluent after oxygen-alkali bleaching. By low-consistency oxygen bleaching of softwood kraft pulp, the permanganate consumption decreased very little. When the kappa number of the pulp was halved (from 25.4 to 13.4), the decrease in permanganate consumption of 1 g pulp was only 1.22 ml of 0.02 mol/l potassium permanganate. This value was smaller than that obtained for the oxygen-alkali treatment of a corresponding amount of isolated residual lignin, 6.40 ml. This was not due to the slow oxidation of lignin in pulp but to the formation of permanganate-consuming substances from carbohydrates. Those newly formed substances cannot be oxidized by oxygen-alkali treatment. Taking these facts into account, lignin originally present in pulp was found to be oxidized well. Reduction of carbonyl groups in carbohydrates prevented the formation of such substances.

Key words Oxygen bleaching · Permanganate consumption · Permanganate-consuming substances · Lignin oxidation

Introduction

There are increasing environmental pressures on the pulp industry to decrease the use of chlorine-containing bleaching agents. These pressures have resulted in increased use of oxygen-based chemicals. Oxygen-alkali bleaching has become important in the commercial pulp industry. It is generally believed that the main reaction of oxygen-alkali bleaching is oxidation, with the residual lignin being degraded to become hydrophilic and removed by solubilization.¹ Hence, it is important to know the role of oxidative degradation of lignin during oxygen-alkali bleaching. In our previous report,² we proposed a method to express and analyze the progress of lignin oxidation during oxygen-alkali treatment of lignin based on the number of electrons abstracted from one lignin unit (C_6-C_3). This method is based on the difference in permanganate consumption of lignin before and after oxygen-alkali treatment. The consumption of permanganate was converted into the number of electrons abstracted from one lignin unit (C_6-C_3) during oxygen-alkali treatment by the following formula.

$$A = 5 \times (B - C) \quad (1)$$

where A is the equivalent of electrons abstracted from one equivalent of C_6-C_3 unit; B is the amount of permanganate (mole) consumed by one equivalent of C_6-C_3 unit before oxygen oxidation; and C is the amount of permanganate (mole) consumed by one equivalent of C_6-C_3 unit after oxygen oxidation.

When an oxygen-alkali treatment of an isolated residual lignin was analyzed by this method, the progress of oxidation was found to be rapid and significant. It is of interest to examine whether extensive lignin oxidation is required for delignification during the actual oxygen bleaching process.

In the present report, the same analysis was performed for low-consistency oxygen bleaching of softwood kraft pulp and for oxygen oxidation of a residual lignin isolated from an unbleached kraft pulp. To determine the effect of degradation of carbohydrate during oxygen bleaching,

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Part of this paper was presented at the 10th ISWPC, Yokohama, June 1999; and at the 43rd Lignin Symposium, Fuchu, October 1998

the holocellulose and hemicellulose were subjected to the same analysis after oxygen-alkali and alkali treatments.

Experimental

Materials

Unbleached softwood kraft pulp (kappa number 25.4) was washed and screened before use. Residual lignin was extracted from this pulp by refluxing in acidic dioxane-water.³ Residual hemicellulose was extracted by 17.5% sodium hydroxide solution from the holocellulose, which was obtained from the pulp by the acidic chlorite method.⁴ The reduction of holocellulose was carried out by sodium borohydride in pH 9 buffer solution.

Low-consistency oxygen-alkali bleaching of softwood kraft pulp

Unbleached softwood kraft pulp was subjected to low-consistency oxygen bleaching by the following condition: pulp consistency 1%, alkali charge 5% on pulp, oven-dried weight of the pulp 3.0 g, and 2 ml of 1000 ppm Fe^{3+} solution. The pulp was heated to 95°C and kept at this temperature under 1.0 MPa of oxygen. At a prescribed time of oxygen-alkali treatment the reaction vessel was cooled, and the pulp was washed completely for measuring the kappa number. The filtrate was collected and adjusted to a certain volume. A portion of pulp and an aliquot of the filtrate were mixed and subjected to permanganate treatment. The degree of delignification was determined by the kappa number method. Permanganate consumption was calculated based on 1 g of pulp.

Oxygen-alkali and alkali treatments of isolated residual lignin and hemicellulose

The sample was dissolved in 300 ml aqueous alkali solution containing 150 mg (6000 mg for the standard condition) sodium hydroxide and 2 ml (6 ml for the standard condition) 1000 ppm Fe^{3+} solution. The sample was heated to 95°C and kept at this temperature under 1.0 MPa of oxygen or nitrogen pressure. Periodically, 20 ml (2 ml for the standard condition) of the solution was taken from the reaction vessel and subjected to permanganate consumption measurement. Based on the data obtained, consumption of potassium permanganate solution (0.02 mol/l) by 38.1 mg of lignin and by 190.5 mg of hemicellulose was calculated. These amounts correspond to the content of lignin and hemicellulose in 1.0 g of pulp, respectively.

Samples and their amounts subjected to treatments are as follows.

Low-consistency condition

Sample A: residual lignin isolated from unbleached kraft pulp, 114.3 mg

Sample B: residual hemicellulose isolated from unbleached kraft pulp, 571.5 mg

Standard condition

Sample: 1500 mg of residual lignin and the data in parentheses, above

Measurement of permanganate consumption

Permanganate consumption of the mixture of bleached pulp and dissolved lignin

After a certain period of oxygen bleaching the mixture of pulp and liquor sample (both are one-tenth the original amount) was put in the aqueous solution containing 4 ml of sulfuric acid solution (5 mol/l) and 10.0 ml of potassium permanganate solution (0.02 mol/l). The total volume was adjusted to 100 ml. The mixture was kept at 25°C for 30 min, and immediately, 2 ml of a potassium iodide solution (1 mol/l) was added. The iodine produced was titrated with standard sodium thiosulfate solution (0.02 mol/l).

Permanganate consumption of isolated residual lignin, hemicellulose

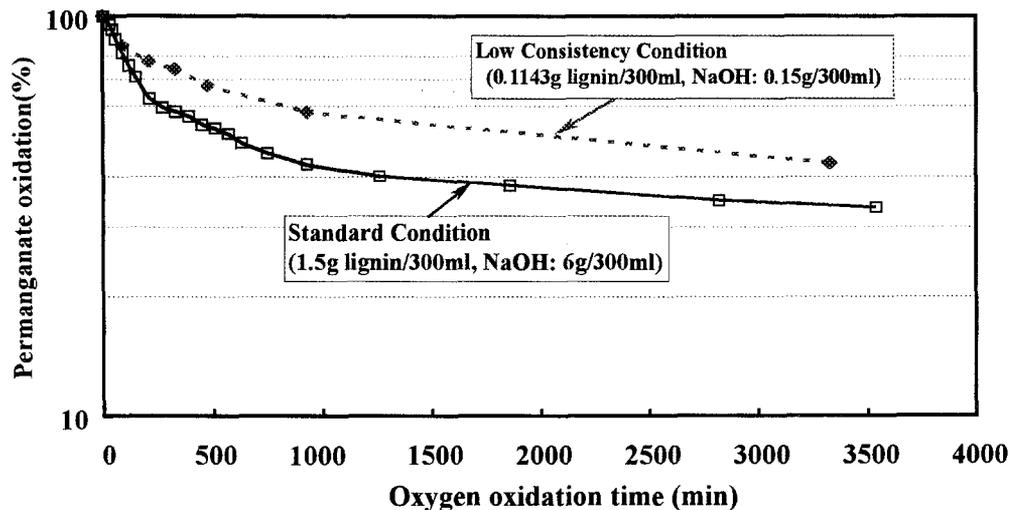
Certain volumes of sample solution periodically removed from the reaction vessel were poured into the aqueous solution containing 4 ml of sulfuric acid solution (5 mol/l) and 10.0 ml of potassium permanganate solution (0.02 mol/l). The total volume was adjusted to 100 ml. The reaction mixture was kept at 25°C for 30 min and immediately 2 ml of potassium iodide solution (1 mol/l) was added; the iodine produced was titrated with standard sodium thiosulfate solution (0.02 mol/l).

Results and discussion

Oxygen-alkali treatment of isolated residual lignin by low-consistency bleaching condition

As seen in Fig. 1, when the isolated residual lignin was oxidized by the standard condition⁵ and by the low-consistency oxygen-alkali bleaching condition, the oxidation proceeded via similar phases, but the progress of lignin oxidation observed under the low-consistency condition was evidently slower than that under the standard condition. At 60 min, which is the usual time for oxygen bleaching, 2.4 electrons were abstracted from one lignin unit of residual lignin under the standard condition. This number seems to indicate that the isolated residual lignin is well oxidized to a level comparable with that seen during the chlorine bleaching process, where lignin is oxidized by 3–4 electrons per unit.⁶ Only 1.9 electrons were abstracted from one lignin unit under the low-consistency condition at 60 min. It is clear that the alkali concentration significantly affects the progress of oxidation even though the alkalinity of low-consistency oxidation was well maintained even at

Fig. 1. Progress of oxidation of isolated residual lignin under different conditions



the end of 180min of oxidation (pH at 180min was 11.4 whereas the initial pH was 11.7). This result indicates a need to examine in more detail the effect of an alkali concentration (not the alkali charge) on the progress of lignin oxidation.

Low-consistency oxygen bleaching of kraft pulp

The results in the previous section suggested that oxidation of lignin in pulp during bleaching is a rather slow process. To obtain evidence for this, low-consistency oxygen bleaching of kraft pulp was performed. To analyze the progress of the oxidation reaction, permanganate consumption of lignin after oxidation was obtained by measuring the permanganate consumption of both the dissolved lignin and the lignin remaining in the pulp.

The results shown in Fig. 2 demonstrate that oxidation of lignin apparently proceeded slowly. The decrease of permanganate consumption by 1.0g pulp at 180min of treatment was only 1.22ml of potassium permanganate (0.02 mol/l). When the decrease in permanganate consumption of the mixture of pulp and liquor was converted to numbers of electrons abstracted from one C₆-C₃ unit of lignin according to Eq. (1), those were only 0.1, 0.6, 1.45, and 1.9 electrons after bleaching for 60, 180, 450, and 900min, respectively. Even when the delignification reached about 50% (reaction time 180min), the number of electrons abstracted from one lignin unit was calculated to be only 0.6 on average.

An explanation for this phenomenon is that new structures are created from carbohydrate during oxygen-alkali bleaching, and these new substances could consume the permanganate but could not be oxidized by oxygen-alkali. If this is the case, even though lignin in pulp is oxidized well, the decrease in permanganate consumption due to lignin oxidation must be compensated for by an increase in permanganate consumption due to the formation of such substances.

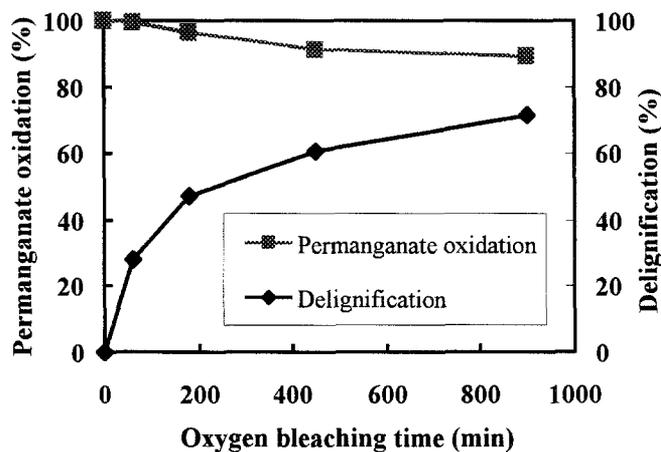


Fig. 2. Delignification and apparent progress of oxidation of lignin during low-consistency oxygen bleaching of kraft pulp

Oxygen-alkali and alkali treatments of hemicellulose and holocellulose

The residual hemicellulose isolated from unbleached softwood kraft pulp was subjected to oxygen-alkali and alkali treatments. Similar results were observed after the two treatments (Fig. 3). Permanganate consumption increased during the treatments: during the first 300 min, permanganate consumption by 190.5mg hemicellulose reached 14.7 ml of the 0.02 mol/l potassium permanganate solution. Therefore, it is confirmed that the hemicellulose creates permanganate-consuming substances during the alkali treatment without regard to the presence of oxygen, and these permanganate-consuming substances cannot be oxidized during oxygen-alkali treatment.

This result explains why the decrease in permanganate consumption during oxygen-alkali bleaching of pulp was slow. It is clear that this phenomenon is not due to the slow oxidation of lignin present in the pulp but to the formation

of permanganate-consuming substances from hemicellulose. It is possible to estimate the amount by obtaining the difference between permanganate consumption of the original pulp and that of the pulp-liquor mixture after certain reaction time of alkali treatment under nitrogen, because hemicellulose creates permanganate-consuming substances during the alkali treatment of pulp, whereas change in the permanganate consumption of lignin is negli-

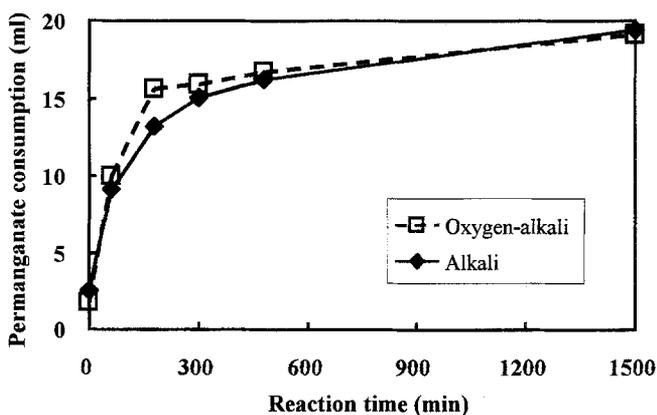


Fig. 3. Oxygen-alkali and alkali treatments of isolated residual hemicellulose

gible under nitrogen. At a reaction time of 180 min, this difference was 4.81 ml of the 0.02 mol/l potassium permanganate solution per 1.0 g of pulp. The overall decrease in permanganate consumption at 180 min during oxygen-alkali treatment was 1.22 ml/1.0 g pulp. Therefore, the sum of these two values, 6.03 ml, could be the decrease in permanganate consumption due to the oxidation of lignin (Table 1). Based on this value, it was calculated that 3.0 electrons were abstracted from one lignin unit at 180 min of oxygen-alkali bleaching of pulp. This value is only slightly lower than the 3.2 electrons obtained for the oxygen-alkali oxidation of isolated residual lignin (Fig. 4). Obviously, it is not reasonable to assume that this result indicates that the reactivity of the residual lignin does not change before and after the isolation from pulp, because the isolated residual lignin used in this study was obtained using a rather strong condition that may have resulted in significant structural modification of lignin and, thus, is not representative of the residual lignin in pulp. However, it should be noted that the number of electrons (3.0) is large, as 4.0-electron oxidation of an aromatic ring corresponds to a ring opening reaction. Therefore, it is concluded that the residual lignin in the unbleached kraft pulp is well oxidized during oxygen bleaching. The progress of lignin oxidation during low-consistency oxygen bleaching is as shown in Fig. 5. The delignification corresponds well with lignin oxidation during oxygen bleaching.

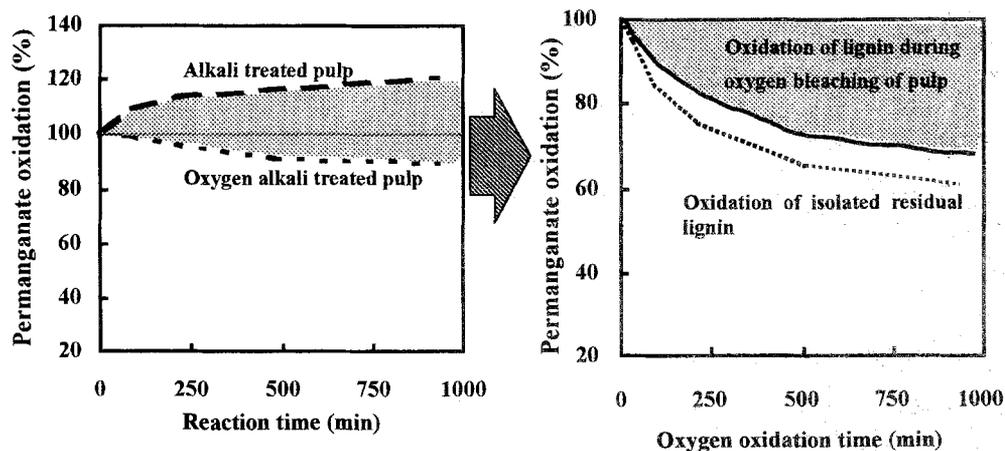
Table 1. Formation of permanganate-consuming substances from kraft pulp and holocellulose during oxygen-alkali and alkali treatments^a

Substance	Before treatment	After oxygen-alkali treatment		After alkali treatment	
		Residue	Filtrate	Residue	Filtrate
Holocellulose (1 g)	1.44	0.65	5.20	0.80	5.80
NaBH ₄ reduced	1.04	0.65	1.64	0.80	1.44
Holocellulose (1 g)					
Kraft pulp (1 g)	33.94		32.72		38.75

Reaction conditions: NaOH 0.5g/l; temperature 95°C; O₂/N₂ pressure 1.0MPa; reaction time 180 min

^a0.02 mol/l permanganate consumption (ml)

Fig. 4. Lignin oxidation during oxygen bleaching of pulp



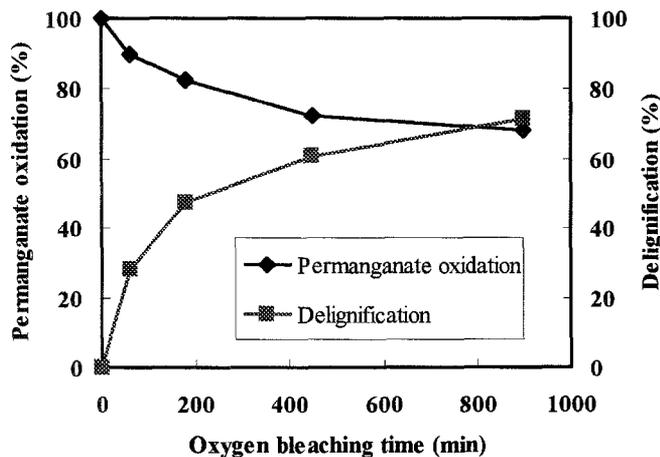


Fig. 5. Delignification and progress of oxidation of lignin during low-consistency oxygen bleaching of kraft pulp

To determine where those newly produced substances are located, the holocellulose prepared from the unbleached softwood kraft pulp was subjected to alkali and oxygen-alkali treatments. After treatment the holocellulose was washed completely, and the filtrate was subjected to permanganate oxidation. The filtrate, which came from the alkali-treated holocellulose, consumed 5.8 ml of the 0.02 mol/l permanganate (Table 1). In contrast, permanganate consumption by the residue (holocellulose) did not change significantly before and after alkali treatment. These results indicate that newly produced permanganate-consuming substances are soluble in aqueous alkaline solution and can be removed from the pulp to the effluent by a washing stage. Thus sufficient washing after oxygen-alkali bleaching becomes important. It can help save the bleaching chemicals at the following stage. When the holocellulose reduced by sodium borohydride was subjected to alkali and oxygen-alkali treatments, the increase in permanganate consumption is much less than for the nonreduced holocellulose (Table 1). Therefore, the permanganate-consuming products may come from the carbonyl groups.

Forsskahl et al. showed that D-xylose and D-glucose can produce aromatic rings and conjugated double bonds after treatment with sodium hydroxide (0.63 mol/l) at 96°C under an atmosphere of nitrogen.⁷ Alkali treatment of hemicellu-

lose and holocellulose in the present investigation also indicated that such compounds could be produced under mild conditions, such as oxygen-alkali bleaching.

Conclusions

Lignin oxidation correlates well with delignification during oxygen bleaching of pulp. Lignin oxidation governs the delignification during oxygen bleaching. When delignification reached about 50%, lignin was oxidized by 3.0 electrons per lignin unit on average. Hemicellulose can create permanganate-consuming structures during the alkali treatment without regard to the presence of oxygen, and these new structures cannot be oxidized by oxygen-alkali. This may be the reason permanganate consumption by the pulp and the bleaching liquor showed only a slight decrease when the pulp was subjected to oxygen bleaching. The new substances, which were produced from hemicellulose, can be removed from the pulp by washing. Lignin itself in the pulp was found to be well oxidized during oxygen-alkali bleaching.

References

- Gellerstedt G, Lindfors EL (1987) Hydrophilic groups in lignin after oxygen bleaching. *TAPPI J* 70(6):119-122
- Tong G, Yokoyama T, Matsumoto Y, Meshitsuka G (2000) Analysis of progress of oxidation reaction during oxygen-alkali treatment of lignin I: method and its application to lignin oxidation. *J Wood Sci* 46:32-39
- Froass P, Ragauskas A, McDonough T, Jiang J (1996) Chemical structure of residual lignin from kraft pulp. *J Wood Chem Technol* 16:347-365
- Timell T (1965) Galactoglucomannans from the wood of gymnosperms. *Methods Carbohydrate Chem* 5:134-137
- Matsumoto Y, Yokoyama T, Tong G, Meshitsuka G (1997) Degradation of non-phenolic lignin unit by co-oxidation mechanism during oxygen bleaching. In: *Proceedings of 9th international symposium on wood and pulping chemistry [poster presentation]*, Montreal, pp 68.1-68.4
- Koda K, Shintani H, Matsumoto Y, Meshitsuka G (1995) Role of oxidation reaction in the chlorine bleaching process [in Japanese]. In: *Proceedings of 40th lignin symposium*, pp 33-36
- Forsskahl I, Popoff T, Theander O (1976) Reactions of D-xylose and D-glucose in alkali aqueous solution. *Carbohydr Res* 48:13-21