

ORIGINAL ARTICLE

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Analysis of progress of oxidation reaction during oxygen–alkali treatment of lignin I: method and its application to lignin oxidation

Received: February 12, 1999 / Accepted: April 26, 1999

Abstract A new method is applied to evaluate the progress of the oxidation reaction of lignin during oxygen–alkali treatment. This method employs the difference in permanganate consumption of the sample before and after the oxygen–alkali treatment as an indication for the lignin oxidation. When kraft lignin and residual lignin isolated from unbleached softwood kraft pulp were subjected to oxygen–alkali treatment up to 6000 min, the progress of the oxidation expressed by this method was separated into clearly distinguished three phases. During the first and second phases, the progress of oxidation was well correlated to the loss of methoxyl group and to the decrease in the yield of nitrobenzene oxidation products. The addition of Mn^{2+} to the oxygen–alkali treatment depressed oxidation during the second phase partly and that during the third phase almost completely. Calculations based on the change in the permanganate consumption revealed that the oxidation during the first phase corresponded to 4.2 electrons abstracted from one lignin structural unit on average. The oxidation process by oxygen–alkali treatment was hypothetically attributed to the direct reaction between molecular oxygen and the phenolic unit of lignin, which mainly took place during the first phase, and to the autooxidation-type oxidation during the second and third phases.

Key words: Lignin · Oxygen–alkali treatment · Permanganate consumption · Oxidation · Electron

Introduction

Owing to the environmental and economic benefits, oxygen–alkali bleaching is used commercially for the removal of lignin from kraft pulp. Many studies on oxygen–alkali bleaching have focused on the kinetic analysis of delignification rates on the basis of kappa number reduction.^{1–3} The reactivity of various lignin model compounds with oxygen in aqueous alkali media have also been studied kinetically.^{4–8} In all cases, the studies were based on the rate of degradation of lignin model compounds during oxygen–alkali bleaching. The progress of lignin oxidation is believed to govern the delignification during oxygen–alkali bleaching of kraft pulp. However, there seems to be no clear relations established between the oxidation reaction and delignification. To establish such relations, a method must be developed to determine the progress of oxidation. Because the degradation of carbohydrate must be related to the progress of lignin oxidation,^{9–11} and to the delignification, such a method is indispensable to understand the delignification and carbohydrate degradation as a cooperative reaction.

In the present report a method is proposed to evaluate the progress of lignin oxidation and is applied to analyze the oxidation of lignin during oxygen–alkali treatment. This method is based on the change in permanganate consumption of lignin before and after oxygen–alkali treatment. Lignin is easily oxidized by acidic permanganate. Usually one equivalent molecular weight of lignin consumes about 13 equivalents of permanganate. This value decreases if lignin is already oxidized to some extent by another process such as oxygen–alkali treatment. We assumed that this decrease corresponds to the progress of oxidation during the process. Based on this assumption, the progress of lignin oxidation during oxygen–alkali treatment was analyzed. Samples used were an isolated softwood kraft lignin and a residual lignin isolated from unbleached softwood kraft pulp. Such an analysis will help gain a new insight into the delignification behavior during oxygen–alkali bleaching.

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Part of this paper was presented at the 9th ISWPC, Montreal, June 1997; and at the 42nd Lignin Symposium, Sapporo, October 1997

Experimental

Materials

2,4,6-Trimethylphenol (TMPh), 4-hydroxy-3-methoxybenzyl alcohol [vanillyl alcohol (VaAl)], 3,4-dimethoxybenzyl alcohol [veratryl alcohol (VeAl)], 4-hydroxy-3-methoxyphenylacetic acid [homovanillic acid (HVaA)], and 3,4-dimethoxyphenylacetic acid [homoveratric acid (HVeA)] were commercially available. Kraft lignin was isolated from kraft pulping black liquor by acidification. Residual lignin was isolated from unbleached softwood kraft pulp by hot acidic dioxane–water extraction.¹² The yield was 52% of total Klason lignin in unbleached softwood kraft pulp.

Oxygen-alkali treatment

The reaction vessel is the same as that described by Yokoyama et al.¹¹ A certain amount of sample was dissolved in 300 ml of aqueous sodium hydroxide solution containing 6.0 g of NaOH and 6.0 ml of 1000 ppm Fe³⁺. The mixture was heated to 95°C in 30 min, and kept at the same temperature under 1.0 MPa of oxygen pressure. The amounts of the samples were as follows: TMPh 367.0 mg, VaAl 578.3 mg, VeAl 630.8 mg, HVaA 546.6 mg, HVeA 588.6 mg, and isolated residual lignin or kraft lignin 1500.0 mg, respectively. The treatment of TMPh was carried out under 0.3 MPa of oxygen pressure.

Acidic permanganate consumption

At a prescribed time during the oxygen–alkali treatment a portion of reaction mixture was removed from the reaction vessel and its permanganate consumption was measured by a procedure similar to the kappa number measurement. That is, a portion of reaction mixture was poured to an aqueous solution containing H₂SO₄ 5 mol/l (4 ml) and KMnO₄ 0.02 mol/l (10 ml). The total volume was adjusted to 100 ml. The mixture was kept at 25°C for 30 min with gentle stirring, and immediately 2 ml of potassium iodide solution 1 mol/l was added. The iodine produced was determined by sodium thiosulfate titration. The consumption of permanganate was expressed as the equivalents consumed by 200 g of lignin.

Analysis

The methoxyl content of oxygen–alkali treated lignin was determined basically according to the Zeisel method.¹³ After a prescribed period of oxygen–alkali treatment, 2 ml of the solution was removed, concentrated under reduced pressure, and treated with concentrated hydriodic acid at refluxing temperature. The methyl iodide was titrated with a dilute standard silver nitrite solution using 2% potassium chromate solution as an indicator. The alkali nitrobenzene oxidation was similar to that described by Chen.¹⁴ In

general, 2-ml samples of lignin solution were placed in 10-ml stainless steel autoclaves and were mixed with 0.25 ml nitrobenzene and 2 ml NaOH 3.5 mol/l; they were then heated in an oil bath at 170°C for 2 h. The internal standard solution of 3-ethoxyl-4-hydroxybenzaldehyde was added. The mixture was extracted three times with CH₂Cl₂ (15 ml × 3) to remove any excess nitrobenzene and its reduction products. The mixture of aqueous solution was acidified with 4 M HCl and then extracted twice with CH₂Cl₂ (20 ml × 2) and once with ethyl ether (15 ml). The combined CH₂Cl₂ and ether extract after drying over Na₂SO₄ was evaporated under reduced pressure. The resulting products after silylation with bovine serum albumin (BSA) were analyzed by gas chromatography (GC). GC analyses were conducted on a Shimadzu GC-17 with a flame ionization detector and NB-1 column using helium as carrier gas. The remaining VaAl and VeAl were determined by gas-liquid chromatography (GLC) as acetyl derivatives.

Results

Permanganate consumption by lignin is dependent on the time of permanganate treatment. Under prolonged treatment, not only the easily oxidizable part of lignin but also a part that is relatively resistant to the oxidation are oxidized by this oxidant. In this study, the amount of permanganate consumed by easily oxidizable parts of lignin was estimated because the change in permanganate consumption due to oxygen oxidation must be related to those easily oxidizable parts. Figure 1 shows the time dependence of permanganate consumption by the kraft lignin and by the isolated residual lignin. For both lignins the time course of permanganate consumption seemed to be divided into rapid and slow phases. Here the permanganate consumption during the rapid phase was assumed to indicate the amount of permanganate consumed by the easily oxidizable parts of lignin. This value can be estimated by extrapolating the line approximated from the slow phase into the y-axis. Treatment for 10 min, which is employed in the kappa number determination, did not seem to be enough to obtain the value due to the rapid phase. It was, however, practically difficult to obtain extrapolated values for all samples. Fortunately, the extrapolated value was found to coincide approximately with the value obtained by a single permanganate treatment of about 30 min. Therefore, the 30-min treatment was employed to estimate the permanganate consumption of lignin in this study.

Without oxygen–alkali treatment, one unit of kraft lignin was found to consume 13.9 equivalents of permanganate (an equivalent molecular weight of one unit of kraft lignin, EqMW, was assumed to be 200). When kraft lignin is subjected to oxygen–alkali treatment, permanganate consumption decreased with the progress of the oxygen–alkali treatment and finally, as is shown in Fig. 2, reached the constant level of 4.9 equivalents. The difference between 13.9 and 4.9 (i.e., 9.0 equivalents) is assumed here to indicate the maximum oxidation caused by oxygen–alkali

Fig. 1. Permanganate consumption versus time for permanganate treatment of kraft lignin and isolated residual lignin

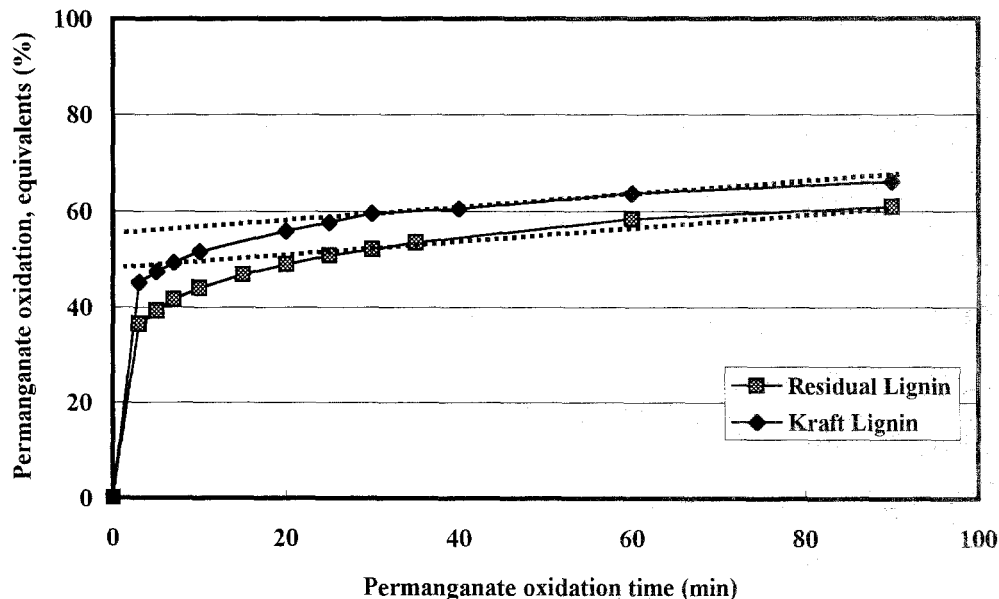
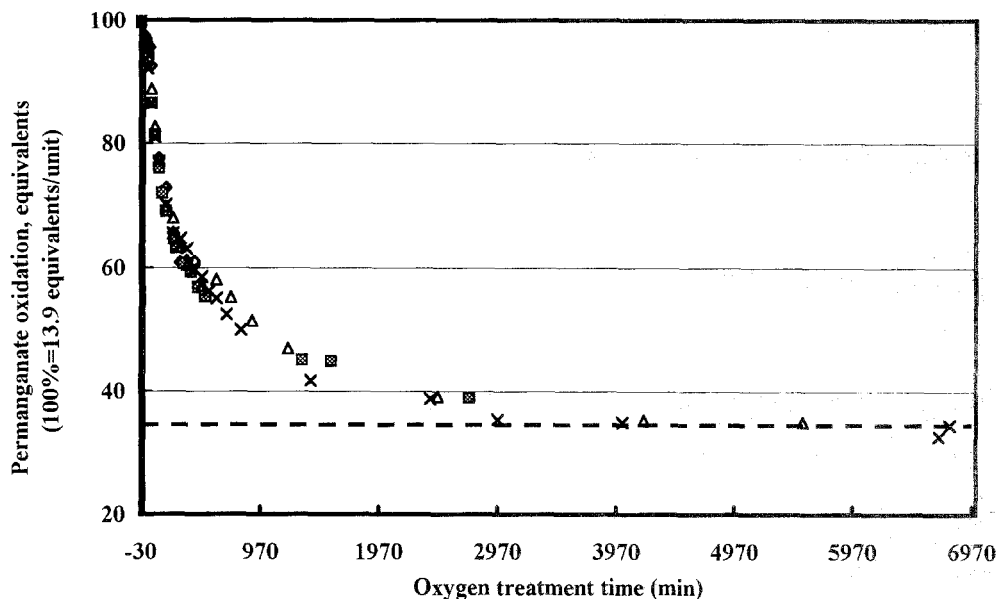


Fig. 2. Progress of oxidation during oxygen-alkali treatment of kraft lignin



oxidation. It is obviously recognized that a "floor level" is present for oxygen-alkali oxidation of kraft lignin. By the same treatment of the isolated residual lignin, the maximum oxidation caused by oxygen-alkali treatment was found to be 9 equivalents (permanganate consumption before oxygen-alkali treatment was 13 equivalents and that at floor level 4 equivalents).

When the change in permanganate consumption of kraft lignin was expressed by logarithm, the time course of permanganate consumption was divided into an initial phase followed by three clearly distinguishable phases (Fig. 3). In this figure the maximum oxidation caused by permanganate oxidation (13.9 equivalents per unit of lignin) is expressed as 100%. The change in the permanganate consumption during the initial phase was negligible;

and those during the first, second, and third phases were 3.8, 2.4, and 2.3 equivalents, respectively. During the first phase the decrease was most significant and rapid. The change in the permanganate consumption during oxygen-alkali treatment of the isolated residual lignin proceeded via similar phases as seen with kraft lignin except for the lack of the initial phase (Fig. 4). The change in the permanganate consumption during the first, second, and third phases were 4.2, 3.1, and 1.7 equivalents per unit of lignin, respectively. Although the reason for the appearance of the initial phase in kraft lignin, is not clearly understood, it might have something to do with the presence of inorganic or organic sulfur compounds in kraft lignin, which may prevent the oxidation due to its reducing characteristics.

Fig. 3. Progress of oxidation during oxygen-alkali treatment of kraft lignin

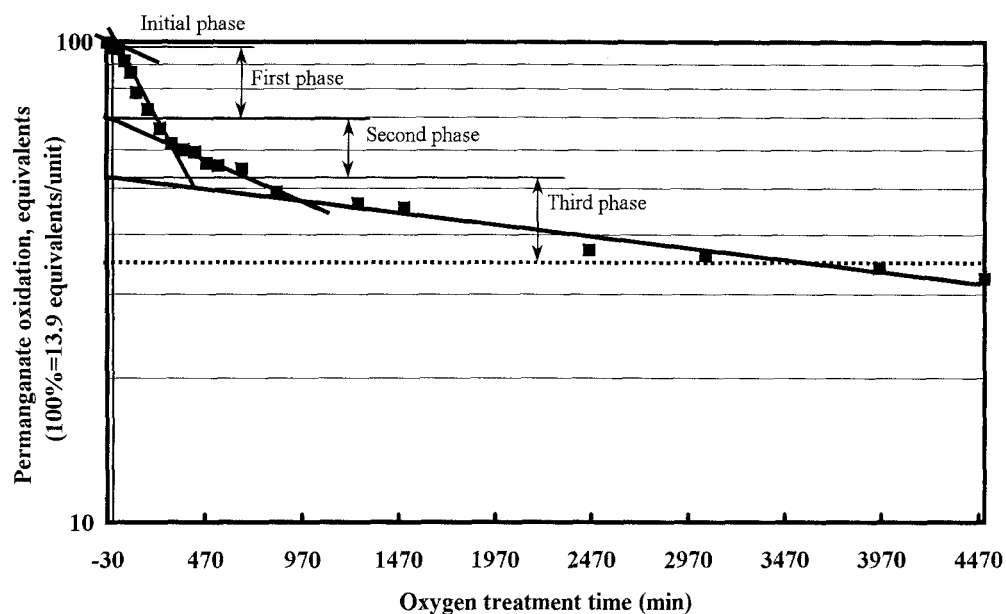
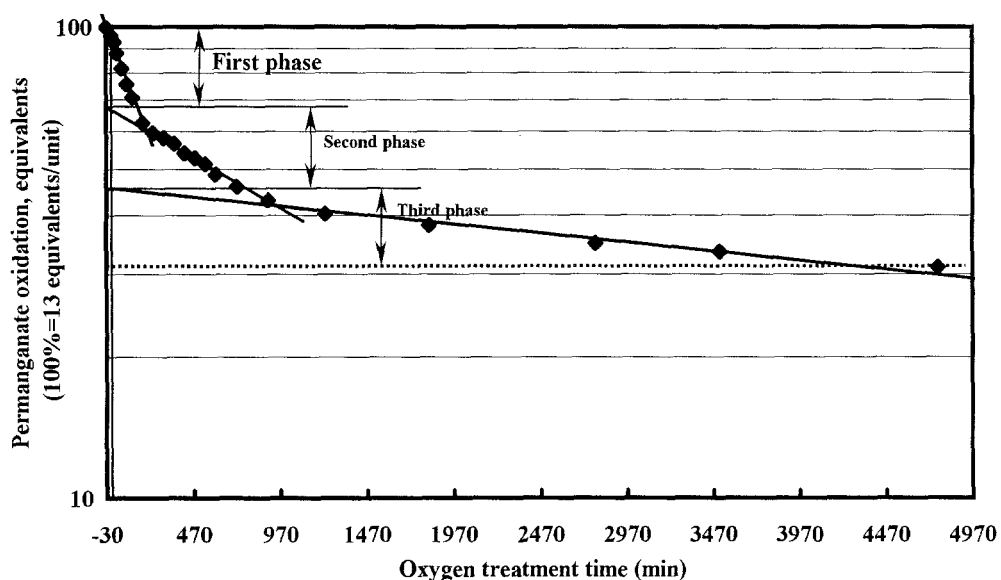


Fig. 4. Progress of oxidation during oxygen-alkali treatment of isolated residual lignin



Oxidation of the isolated residual lignin during oxygen-alkali treatment resulted in a decrease in the methoxyl content and in that of nitrobenzene oxidation products (Fig. 5). Because the number of data points is not enough, a detailed analysis of their time course is not possible. However, their decreasing tendency is similar to that of permanganate consumption. They decreased most rapidly and significantly during the period corresponding to the first phase of permanganate consumption (-30 to 180 min). There are also floor levels present for both methoxyl content and yield of nitrobenzene oxidation products even after prolonged oxygen-alkali treatment. The presence of these floor levels implies the presence of highly resistant structures toward oxygen oxidation in the residual lignin. Although the methoxyl content and the yield of nitrobenzene oxidation products were measured only for isolated residual lignin,

kraft lignin may also contain structures highly resistant to oxidation.

The reaction of phenolic compounds with molecular oxygen produces active oxygen species, and their participation in the reaction accelerates the oxidation of phenolic compounds.¹⁴ On the other hand, the addition of Mn^{2+} to the reaction mixture is proposed to prevent the formation of active oxygen species.¹⁵ Therefore, the addition of Mn^{2+} to the oxygen-alkali treatment of lignin was expected to cause some changes in the oxidation process. As is shown in Fig. 6, when Mn^{2+} was added to the oxygen-alkali treatment of the isolated residual lignin, significant change was observed especially during the second and third phases. The floor level was higher than that without Mn^{2+} addition.

Phenolic model compounds -TPh, HVaA, and VaAl- were subjected to coxygen-alkali treatment, and the

Fig. 5. Progress of oxidation versus methoxyl loss and yield decrease of nitrobenzene oxidation products

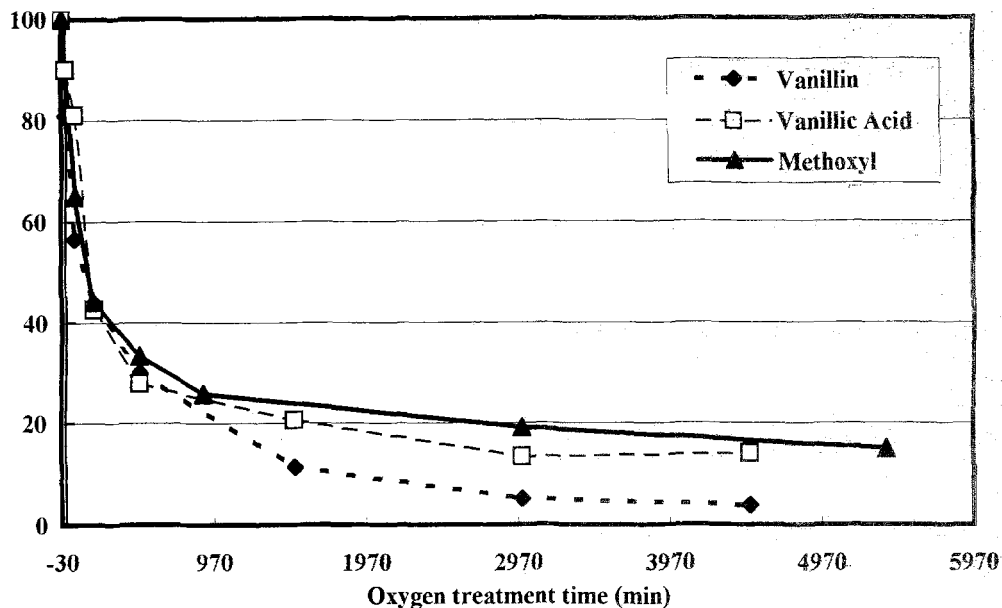
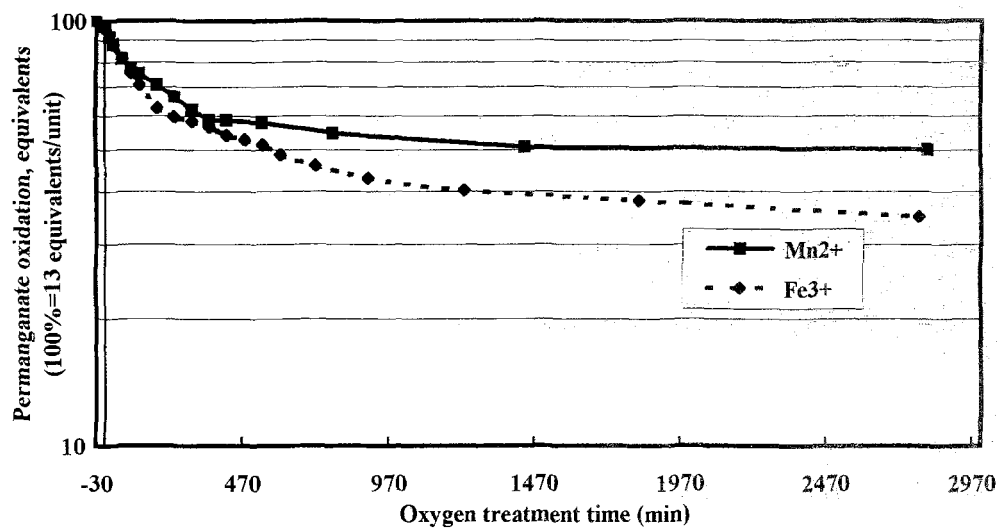


Fig. 6. Depression of oxidation during second and third phases by the addition of Mn^{2+}



changes in the permanganate consumption were measured (Fig. 7). TMPH was found to consume 12 equivalents of permanganate by 30 min of permanganate treatment, a value that decreased with the progress of oxygen-alkali treatment to reach a floor level at 4 equivalents. The difference, 8 equivalents, is assumed to be caused by oxygen oxidation. There seemed to be only two phases present. A nonphenolic model compound, VeAl, was subjected to the oxygen-alkali treatment together with a phenolic model compound, VaAl. The disappearances of these compounds were followed by GC and were compared with the progress of oxidation. When VeAl was treated with oxygen-alkali alone, it was quite stable. In contrast, when VaAl was present, about 20.5% of VeAl disappeared. The disappearance of VeAl came to an end when all the VaAl had degraded. The disappearance of VeAl, however, did not significantly affect the change in permanganate consumption by this mixture. The change in

permanganate consumption of this mixture during the oxygen-alkali treatment can be explained almost only by VaAl.

Discussion

Potassium permanganate, due to its strong oxidizing and electrophilic character, degrades lignin easily. The method employed in the present report was based on the difference in permanganate consumption of lignin before and after oxygen-alkali treatment, which was used to estimate the magnitude of lignin oxidation during oxygen-alkali treatment. The consumption of permanganate was converted to the number of electrons abstracted from one lignin unit (C_6-C_3) during alkali-oxygen treatment by the following formula.

Fig. 7. Progress of oxidation during oxygen-alkali treatment of phenolic model compounds

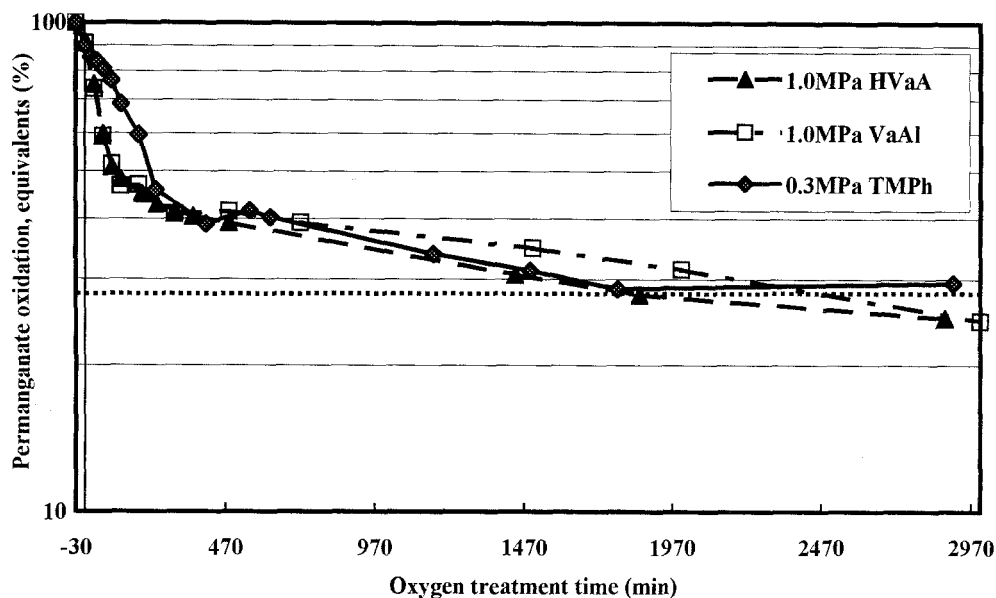


Table 1. Number of electrons abstracted from one lignin unit during oxygen-alkali treatment

Sample	Initial phase	First phase	Second phase	Third phase	Total
Kraft lignin	0.5 e ⁻ (-30 to 30 min)	3.8 e ⁻ (30-300 min)	2.4 e ⁻ (480-1000 min)	2.3 e ⁻ (1000-4500 min)	9.0 e ⁻
Isolated residual lignin	-	4.2 e ⁻ (-30 to 180 min)	3.1 e ⁻ (180-900 min)	1.7 e ⁻ (900-5000 min)	9.0 e ⁻

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

where A is the equivalent of electrons abstracted from one equivalent of C₆-C₃ unit; B is the consumption of permanganate (mole) by one equivalent of C₆-C₃ unit before oxygen oxidation; and C is the consumption of permanganate (mole) by one equivalent of C₆-C₃ unit after oxygen oxidation. The molecular weight of one lignin unit (C₆-C₃) was assumed to be 200.

On the basis of this assumption the number of electrons abstracted from one lignin unit were calculated (Table 1). Number of electrons abstracted during the each phase was obtained by extrapolating the line of the following phase into the y-axis. Until the oxygen oxidation reached the floor level, one unit of kraft lignin and the isolated residual lignin lost approximately nine electrons. The presence of floor levels implied the presence of structure(s) highly resistant to oxygen oxidation in the residual lignin. Such highly resistant structures can be present either as original structure(s) or as secondarily created structure(s) during oxygen-alkali treatment. One of the candidates of such a structure is the α -carbonyl type structure.¹⁵

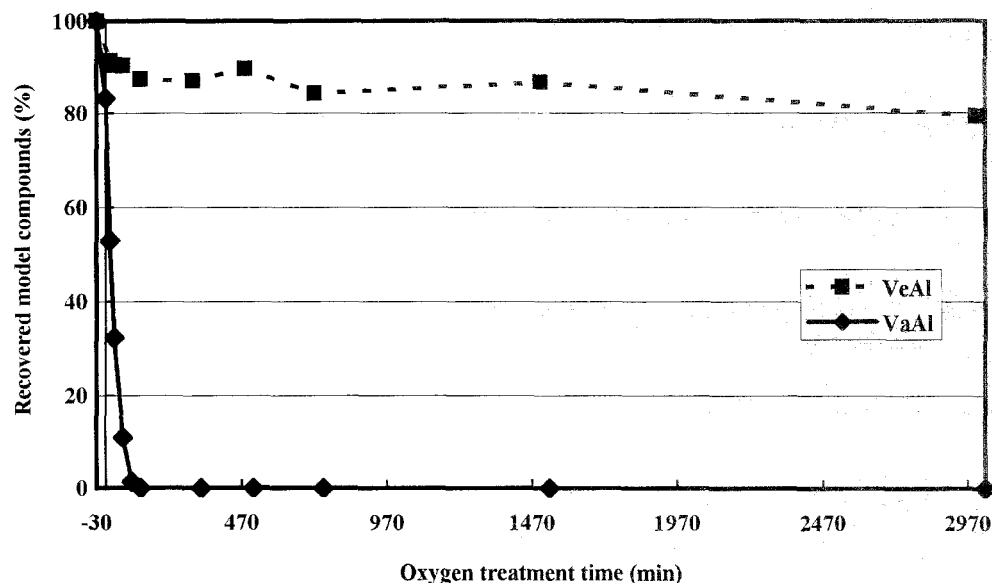
In case of the isolated residual lignin, 4.2 and 3.1 electrons were abstracted during the first and second phases. From these numbers, it is not possible to estimate how many aromatic nuclei were oxidatively degraded by oxygen-alkali treatment. However, data on the decrease in methoxyl content of this sample (Fig. 5) allowed this

estimation. During the first and second phases about 75% of the methoxyl group were removed. Oxidative degradation of aromatic nuclei does not necessarily result in methoxyl loss, but the methoxyl loss must be accompanied by the oxidative cleavage of aromatic nuclei because a simple hydrolysis of methyl-phenyl ether is not possible during the oxygen-alkali treatment. Therefore, one can assume that the value of methoxyl loss (75%) indicated that about 75% of aromatic nuclei were oxidatively cleaved during the first and second phases. It is obvious that this value cannot be achieved only by the oxidation of phenolic units because the content of phenolic units cannot be as high as 75% in the isolated residual lignin. Therefore, the oxidation of nonphenolic units must be taken into account during the first and second phases.

It is well established that nonphenolic aromatic nucleus cannot be oxidized directly by a molecular oxygen under a relatively mild condition such as an oxygen-alkali bleaching. For oxidation of nonphenolic units, the following indirect mechanisms were postulated: (1) co-oxidation with the oxidation of phenolic units; (2) autooxidation; or (3) conversion of nonphenolic units to phenolic units.

The first mechanism, co-oxidation, has been proposed to operate on the oxidation of carbohydrate during oxygen-alkali bleaching.^{10,11,16} With this mechanism, active oxygen species are generated by the decomposition of peroxide species, which are produced by the reaction of phenolic units and molecular oxygen; the active oxygen species thus

Fig. 8. Co-oxidation of phenolic and nonphenolic lignin model compounds



produced are assumed to oxidize nonphenolic units. With the second mechanism (autooxidation), active oxygen species are also anticipated to play a role. This mechanism consists of an initial reaction and successive chain reaction. Peroxide species, which are intermediately produced, are thought to be the origin of these active oxygen species.

To confirm the possibility of these mechanisms by a model experiment, a nonphenolic model compound, VeAl, was subjected to oxygen-alkali treatment together with a phenolic model compound, VaAl. VeAl was quite stable to oxygen-alkali treatment if VaAl was not present. When VaAl was present, as shown in Fig. 8, the disappearance of VeAl was clearly observed; but the disappearance did not continue after all the VaAl had disappeared. What should be noted here is that the disappearance of VeAl did not seem to affect the permanganate consumption seriously. That is, the change in permanganate consumption by this mixture was explained only by the oxidation of the phenolic model compound. Result obtained by this model experiment suggested that during the oxygen-alkali treatment of the lignin samples these two mechanisms are not the direct cause of the oxidation of nonphenolic units in a lignin sample even though these mechanisms surely operate to some extent. Thus, the third mechanism (conversion of nonphenolic units to phenolic units) is most likely among these three mechanisms.

From this point of view, the effect of Mn^{2+} addition is interesting (Fig. 6). Mn^{2+} was added to depress the effect of active oxygen species, as discussed in the previous section. The addition resulted not only in a higher floor level but also in lower rates of oxidation during the first and second phases. When active oxygen species are produced, they can oxidize the side-chain part of lignin, and the side-chain oxidation can create new phenolic units from originally nonphenolic units. This may be the reason the oxidation progress is retarded by addition of Mn^{2+} .

Conclusions

Permanganate consumption can be used to evaluate the progress of the oxidation reaction of lignin during oxygen-alkali treatment. The progress of the lignin oxidation expressed by permanganate consumption was separated into three clearly distinguishable phases. The results show that the phenolic lignin units can be easily oxidized, and partially non-phenolic lignin units can be co-oxidized during the progress of oxygen-alkali oxidation of lignin. There are some significant effects of the degradation of lignin by the addition of various transition metal ions.

References

- Olm L, Teder A (1979) The kinetics of oxygen bleaching. TAPPI J 62(12):43-46
- Hsu CL, Hsieh JS (1988) Reaction kinetics in oxygen bleaching. AIChE J 34(1):116-122
- Iribarne J, Schroeder LR (1997) High-pressure oxygen delignification of kraft pulps. Part 1. Kinetics. TAPPI J 80(10):241-250
- Ljunggren S (1990) The kinetics of lignin reactions during oxygen bleaching. Part 1. The reactivity of p,p'-dihydroxystilbene. Nord Pulp Pap Res J 5(1):38-43
- Ljunggren S, Johansson E (1990) The kinetics of lignin reactions during oxygen bleaching. Part 2. The reactivity of 4,4'-dihydroxy-3,3'-dimethoxy-stilbene and β -aryl ether structures. Nord Pulp Pap Res J 5(3):148-154
- Ljunggren S, Johansson E (1990) The kinetics of lignin reactions during oxygen bleaching. Part 3. The reactivity of 4-n-propylguaiacol and 4,4'-di-n-propyl-6,6'-biguaiacol. Holzforchung 44:291-296
- Johansson E, Ljunggren S (1994) The kinetics of lignin reactions during oxygen bleaching. Part 4. The reactivities of different lignin model compounds and the influence of metal ions on the rate of degradation. J Wood Chem Technol 14:507-525
- Ljunggren S (1986) Kinetic aspects of some lignin reactions in oxygen bleaching. J Pulp Pap Sci 12(2):J54-J57

9. Ericsson B, Lindgren BO, Theander O (1971) Factors influencing the carbohydrate degradation under oxygen-alkali bleaching: *Svensk Papperstidn* 74:757-765
10. Yasumoto M, Matsumoto Y, Ishizu A (1996) The role of peroxide species in carbohydrate degradation during oxygen bleaching. Part 1. Factors influencing the reaction selectivity between carbohydrate and lignin model compounds. *J Wood Chem Technol* 16:95-107
11. Yokoyama T, Matsumoto Y, Yasumoto M, Meshitsuka G (1996) The role of peroxide species in carbohydrate degradation during oxygen bleaching. Part 2. Effect of oxygen pressure on the degradation of lignin and carbohydrate model compounds and on the reaction selectivity. *J Pulp Pap Sci* 22(5):J151-J154
12. Froass P, Ragauskas A, McDonough T, Jiang J (1996) Chemical structure of residual lignin from kraft pulp. *J Wood Chem Technol* 16:347-365
13. Thring RW, Chornet E, Bouchard J, Vidal PF, Overend RP (1990) Characterization of lignin residues deived from the alkali hydrolysis of glycol lignin. *Can J Chem* 68:82-89
14. Chen C-L (1992) Nitrobenzene and cupric oxide oxidations. In: Lin SY, Dence CW (eds) *methods in lignin chemistry*. Springer, Berlin, pp 301-321
15. Matsumoto Y, Minami K, Ishizu A (1993) Studies on chemical structure of lignin by oxidation: erythro and threo ratio of arylglycerol- β -aryl ether structure correlates to low lignin polymerizes. In: *Proceedings of the 7th International Symposium on Wood Pulping Chemistry*, Book 1, pp 98-101
16. Yokoyama T, Matsumoto Y, Meshitsuka G (1999) The role of peroxide species in carbohydrate degradation during oxygen bleaching. Part III. Effect of metal ions on the reaction selectivity between lignin and carbohydrate model compounds. *J Pulp Pap Sci* 25(2):42-46