

# Progress of oxidation of non-phenolic lignin moiety in an oxygen bleaching process via the conversion of non-phenolic into phenolic lignin moiety

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**Abstract** To examine whether non-phenolic lignin moiety is converted into the new phenolic counterpart by the participation of active oxygen species (AOS) under oxygen bleaching conditions, a  $\beta$ -O-4 type dimeric lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (I), 2-(3,5-difluorophenoxy)-1-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (III), or 2-(3,5-difluorophenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (IV), was treated under conditions similar to those for oxygen bleaching. A phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol, was added together to generate AOS in the reaction of compound I or IV. The results obtained suggested that AOS attack the side chains of compounds I, III, and IV accompanied by the  $\beta$ -O-4 bond cleavages and the liberations of the corresponding phenolic compounds, 2-methoxyphenol (II), 3,5-difluorophenol (V), and compound V, respectively. However, the rapid liberation of compound V in the oxygen-alkali treatment of compound III may mainly be caused by alkaline-induced reactions and/or some oxidation reactions of the primary degradation product of compound III, a muconic acid derivative.

**Keywords** Alkyl–aryl ether · Bleaching · Lignin · Oxygen · Phenolic

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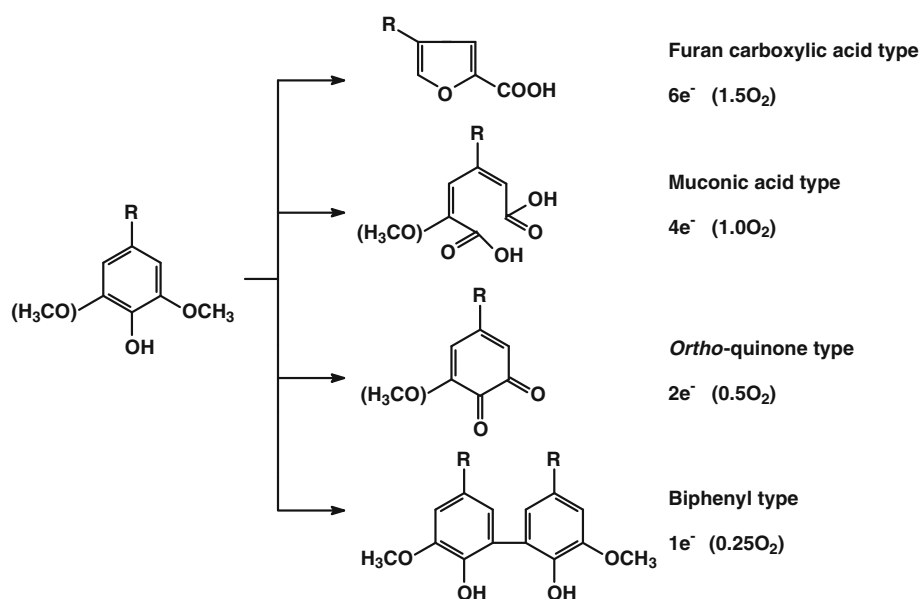
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## Introduction

Owing to its relatively low reactivity, dioxygen reacts only with electron-rich substructures in pulp components, such as dissociated phenolic hydroxyl groups in lignin without  $\alpha$ -carbonyl groups [1, 2] and reducing end groups in carbohydrates [3], under oxygen bleaching conditions. It has been clarified that these reactions generate active oxygen species (AOS) and the AOS attack not only carbohydrates but also lignin portions which are resistant toward dioxygen [3–6].

Gierer et al. [5] and Eckert et al. [7] examined reaction products of phenolic monomeric lignin model compounds when these model compounds were treated under oxygen bleaching conditions (Fig. 1). The number of electrons required for the formation of these reaction products can be calculated as shown in Fig. 1. It is recognized that equal to or <1.5 mol dioxygen is consumed to afford 1.0 mol reaction product. In contrast, Tong et al. [8] indicated that 2.2–3.0 mol dioxygen is consumed by 1.0 M equivalent aromatic ring in kraft lignin and isolated residual lignin when these lignin samples are subjected to oxygen-alkali treatments and the amounts of oxygen consumption are estimated from the differences in the permanganate consumptions by these samples between those before and after the oxygen-alkali treatments. Imai et al. [9] also showed similar results, when kraft lignin and lignin model compounds were subjected to oxygen-alkali treatments and the amounts of oxygen consumption were estimated from the quantities of dioxygen flow into the reactor. These values seemed to be too large when it was assumed that only phenolic lignin moieties were oxidized in the oxygen-alkali treatments, even if primary reaction products such as those shown in Fig. 1 could further be oxidized. Therefore, it was proposed that non-phenolic lignin moieties, which had

**Fig. 1** Reaction products obtained by oxygen-alkali treatment of phenolic monomeric lignin model compounds [5, 7]. The values in the parentheses are the calculated numbers of dioxygen molecules required for the formation of each compound on the basis of the structure of each compound



been considered to be resistant toward oxidation under oxygen bleaching conditions, were also extensively oxidized under the conditions. On the basis of this proposal, we have focused on the possibility that non-phenolic lignin moieties consisting of alkyl-aryl ether, among others, should be converted into the corresponding phenolic counterparts by the cleavage of alkyl-aryl ether bond and consequently extensive oxidation by dioxygen progresses in an oxygen bleaching process.

Substructures shown in Fig. 2 are resistant toward alkaline pulping reactions and, consequently, possibly remain in residual lignin of unbleached pulp [2]. Among these, structures (ii)–(vii), containing phenolic moieties, can be oxidized by dioxygen under oxygen bleaching conditions, although the labilities of these structures toward dioxygen are different from one another. On the other hand, non-phenolic structure (i) is considered to be stable under oxygen bleaching conditions. If the above proposal, the conversion of non-phenolic into phenolic lignin moiety, can occur, structure (i) can also be degraded in an oxygen bleaching process. Examination of this possibility is quite significant in oxygen bleaching chemistry.

On the basis of these backgrounds, we have examined the conversion of non-phenolic aromatic ring of a  $\beta$ -O-4 type dimeric lignin model compound into the corresponding phenolic counterpart, focusing on the participation of AOS. In this study, a common non-phenolic  $\beta$ -O-4 type dimeric lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (I in Fig. 3), was subjected to oxygen-alkali treatments to examine whether the non-phenolic aromatic B-ring (see Fig. 3 for the definition of A- and B-rings) should be converted into the corresponding phenolic compound, 2-methoxyphenol (II in Fig. 3), via the

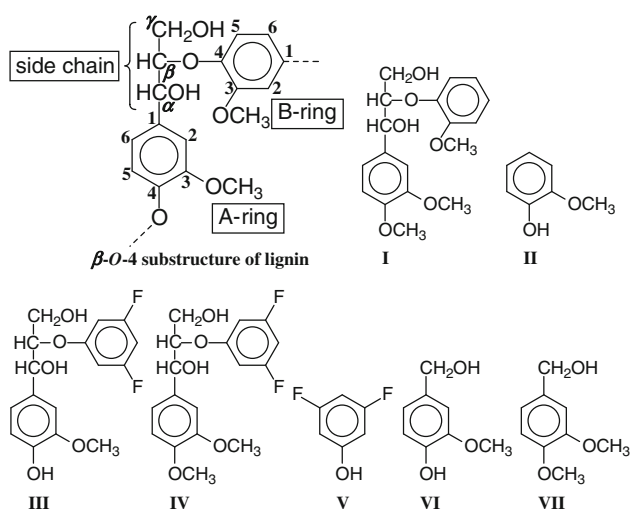
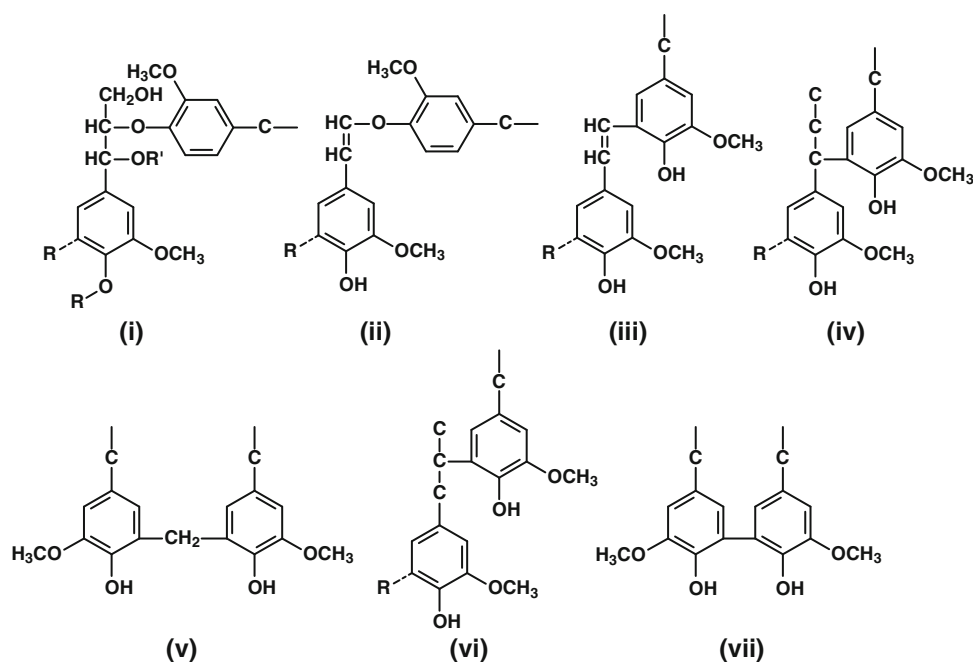
$\beta$ -O-4 bond cleavage caused by some oxidation reactions. Because it was considered that compound II should not quantitatively be detected owing to its lability toward dioxygen under conditions employed in this study even when it is liberated by the  $\beta$ -O-4 bond cleavage, another specially designed  $\beta$ -O-4 type dimeric model compound, 2-(3,5-difluorophenoxy)-1-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (III in Fig. 3) or 2-(3,5-difluorophenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (IV in Fig. 3), was also subjected to oxygen-alkali treatments. When the  $\beta$ -O-4 bond of compound III or IV is cleaved by some oxidation reactions, the corresponding phenolic compound, 3,5-difluorophenol (V in Fig. 3), is liberated. It is expected that compound V should be stable enough to be quantitatively detected in oxygen-alkali treatment and hence the  $\beta$ -O-4 bond cleavages of compounds III and IV should quantitatively be confirmed. Chemical structures of the model compounds used in this paper are shown in Fig. 3.

## Materials and methods

### Materials

Compounds I, III, and IV were synthesized according to the method of Adler et al. [10]. The structures were confirmed by  $^1H$ - and  $^{13}C$ -NMR (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) and GC/MS (GC2010/PARVUM2, Shimadzu Co., Kyoto, Japan). Compound I (mixture of the *erythro* and *threo* isomers):  $^1H$ -NMR ( $(CD_3)_2CO$ )  $\delta$  3.45–3.50 (m, *threo*-C $\gamma$ -H<sub>a</sub>), 3.67–3.86 (m, *threo*-C $\gamma$ -H<sub>b</sub>, *erythro*-C $\gamma$ -H<sub>a</sub>, *erythro*-C $\gamma$ -H<sub>b</sub>, and -OCH<sub>3</sub>), 4.33 (m, *threo*-C $\beta$ -H), 4.34 (m, *erythro*-C $\beta$ -H), 4.91 (d, *erythro*-C $\alpha$ -H),

**Fig. 2** Possible substructures in residual lignin owing to their resistances toward alkaline pulping treatment. (*R* lignin, *R'* lignin or carbohydrates)



**Fig. 3** Chemical structure of model compounds used in this study

4.93 (d, *threo*-C $\alpha$ -H), 6.78–7.10 (m, 7H, aromatic);  $^{13}\text{C}$ -NMR (( $\text{CD}_3$ ) $_2\text{CO}$ )  $\delta$  55.8–56.1 (–OCH $_3$ ), 61.3 (C $\gamma$ ), 73.0 (*threo*-C $\alpha$ ), 73.2 (*erythro*-C $\alpha$ ), 85.6 (*erythro*-C $\beta$ ), 86.6 (*threo*-C $\beta$ ), 111.5 (*threo*-A2), 111.6 (*erythro*-A2), 111.9 (A5), 113.1 (*threo*-B2), 113.2 (*erythro*-B2), 118.3 (B5), 119.8 (*threo*-A6), 119.9 (*erythro*-A6), 121.7 (B6), 122.8 (B1), 134.9 (*threo*-A1), 135.2 (*erythro*-A1), 148.6 (B4), 149.2 (A4), 149.6 (A3), 151.0 (*threo*-B3), 151.3 (*erythro*-B3); MS *m/z* (rel. int.): 334 (M $^+$ , 1), 286 (2), 271 (1), 257 (1), 226 (1), 210 (1), 192 (3), 181 (4), 167 (16), 150 (100), 139 (24), 124 (26), 109 (30), 95 (8), 77 (21), 65 (10), 51 (11). Compound III (mixture of the *erythro* and *threo* isomers):  $^1\text{H}$ -NMR (( $\text{CD}_3$ ) $_2\text{CO}$ )  $\delta$  3.38–3.41 (m, C $\gamma$ -H $_a$ ), 3.52–3.56 (m, C $\gamma$ -H $_b$ ), 3.73–3.84 (m, C $\gamma$ -H $_a$ , C $\gamma$ -H $_b$ , and

–OCH $_3$ ), 4.47–4.49 (m, 1H, C $\beta$ -H), 4.80–4.81 (d, C $\alpha$ -H), 4.87–4.88 (d, C $\alpha$ -H), 6.44–7.05 (m, 6H, aromatic);  $^{13}\text{C}$ -NMR (( $\text{CD}_3$ ) $_2\text{CO}$ )  $\delta$  56.2 (–OCH $_3$ ), 61.7 and 61.9 (C $\gamma$ ), 73.3 and 73.4 (C $\alpha$ ), 84.7 and 85.3 (C $\alpha$ ), 84.7 and 85.3 (C $\beta$ ), 96.2–96.6 (B1), 100.6–100.8 (B3 and B5), 111.4 and 111.6 (A2), 115.3 (A5), 120.3 and 120.6 (A6), 133.8 (A1), 146.8 (A4), 148.1 (A3), 162.3–165.2 (B2, B4 and B6); MS *m/z* (rel. int.): 326 (M $^+$ , 0.1), 308 (0.1), 278 (1), 249 (0.3), 217 (0.4), 189 (0.2), 178 (0.4), 156 (5), 152 (100), 125 (24), 110 (6), 93 (50), 77 (5), 65 (24), 55 (4), 43 (5). Compound IV (mixture of the *erythro* and *threo* isomers):  $^1\text{H}$ -NMR (( $\text{CD}_3$ ) $_2\text{CO}$ )  $\delta$  3.55–3.58 (m, 1H, C $\gamma$ -H $_a$ ), 3.73–3.79 (m, 7H, C $\gamma$ -H $_b$  and –OCH $_3$ ), 4.50–4.53 (m, 1H, C $\beta$ -H), 4.92 and 4.93 (d, 1H, C $\alpha$ -H), 6.47–7.09 (m, 6H, aromatic);  $^{13}\text{C}$ -NMR (( $\text{CD}_3$ ) $_2\text{CO}$ )  $\delta$  56.1 (–OCH $_3$ ), 62.0 (C $\gamma$ ), 73.5 (C $\alpha$ ), 85.4 (C $\beta$ ), 96.3–96.7 (B1), 100.6–100.8 (B3 and B5), 111.7 (A2), 112.4 (A5), 120.0 (A6), 135.1 (A1), 149.8 (A4), 150.2 (A3), 162.9–165.4 (B2, B4 and B6); MS *m/z* (rel. int.): 340 (M $^+$ , 1), 292 (2), 277 (1), 207 (1), 192 (1), 167 (80), 166 (100), 151 (8), 139 (74), 124 (19), 108 (13), 79 (9), 77 (17), 51 (9), 43 (9). (See Fig. 1 for how to number the carbons in the model compounds. A1 shows the number 1 carbon of the A-ring.)

Semiconductor grades (99.99+%) of NaOH and FeCl $_3$  (Sigma-Aldrich Japan K. K., Tokyo, Japan) were used without further purification. All the other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and used without further purification. Ultra-high-purity water produced by reverse osmosis filtration (Puric-Z, Organo Co., Tokyo, Japan) was used in all the experiments.

## Oxygen- or nitrogen-alkali treatment

The reaction solution (300 ml) contained NaOH (0.50 mol/l), FeCl<sub>3</sub> (0.36 mmol/l), a  $\beta$ -O-4 type model compound (1.0 mmol/l), and a phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol (VI in Fig. 3, 0, 1.0, or 10.0 mmol/l). The solution was transferred into a Teflon-coated stainless steel vessel (Taiatsu Techno<sup>®</sup> Co., Tokyo, Japan), and O<sub>2</sub> or N<sub>2</sub> was pressurized to 1.1 MPa. The vessel was heated to 95°C for 10 min, which was maintained for 360 min with stirring. Reaction time was defined as 0 when the temperature reached 95°C. All the reactions conducted in this study are summarized in Table 1.

## Quantification of model compounds

At prescribed times, a portion of the reaction solution (1.0 ml) was withdrawn for the quantification of the model compounds. The reaction solution withdrawn (1.0 ml) was acidified with acetic acid, and 1.0 ml of methanol containing an internal standard compound, 2,3-, 2,5-, or 2,6-dichlorophenol, was added. After filtration, the resulting mixture was injected into HPLC (LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (280 nm for the reaction of compound I or 254 nm for the reactions of compounds III, IV and V, Shimadzu Co.) to determine the concentration of compounds I–VI.

Conditions for HPLC analysis were as follows. Column: Luna 5u C18(2) 100 A (150 mm × 4.6 mm, Phenomenex, Inc.). For the reaction of compound I, oven temperature: 40°C, flow rate: 1.0 ml/min, solvent system: CH<sub>3</sub>OH/H<sub>2</sub>O = 10/90 (v/v) for 10 min; gradient to 80/20 for 20 min and maintained for 10 min, total time: 40 min. For

the reactions of compound III, oven temperature: 40°C, flow rate: 1.2 ml/min, solvent system: CH<sub>3</sub>OH/H<sub>2</sub>O = 20/80 (v/v) for 10 min; gradient to 50/50 for 20 min and maintained for 10 min, total time: 40 min. For the reactions of compounds IV, oven temperature: 40°C, flow rate: 1.2 ml/min, solvent system: CH<sub>3</sub>OH/H<sub>2</sub>O = 40/60 (v/v) for 30 min. For compound V, oven temperature: 40°C, flow rate: 0.8 ml/min, solvent system: CH<sub>3</sub>OH/H<sub>2</sub>O = 45/55 (v/v) for 40 min.

## Results and discussion

It is necessary to generate AOS in situ in the reaction system because AOS are considered to contribute to the cleavage of the  $\beta$ -O-4 bonds of the dimeric model compounds in this study. Compound III has the phenolic aromatic A-ring and the A-ring reacts with dioxygen in the oxygen-alkali treatment of compound III, which generates AOS in situ. On the other hand, AOS are not generated in the oxygen-alkali treatment of compound I or IV, since these compounds do not have any reactive site toward dioxygen. A phenolic compound VI was added together to the reaction systems in these cases and AOS were generated in situ by reactions of compound VI with dioxygen. This method was also applied to our previous studies to generate AOS in situ [4, 6].

There might be a possible mechanism other than the above-mentioned  $\beta$ -O-4 bond cleavage for the conversion of non-phenolic lignin moiety into the corresponding phenolic counterpart. When a non-phenolic aromatic ring is hydroxylated by some oxidation reactions, a corresponding phenolic counterpart is produced. The addition of hydroxyl radical, one of the AOS working in oxygen bleaching process, to a non-phenolic aromatic ring is an instance of this hydroxylation. Because our previous results indicated that a common non-phenolic lignin model compound, 3,4-dimethoxybenzyl alcohol (VII in Fig. 3), is fairly stable under conditions similar to those employed in this study even when AOS are operative [4, 6, 8], non-phenolic aromatic ring of lignin model compounds are estimated to be resistant toward this hydroxylation reaction. Therefore, the conversion of non-phenolic lignin moiety into the corresponding phenolic counterpart by  $\beta$ -O-4 bond cleavage is focused on in this study.

The addition of FeCl<sub>3</sub> plays roles to stably produce AOS and overshadow effects of transition metal ions possibly present in the reaction system. FeCl<sub>3</sub> is commonly known as an oxidizing agent and can oxidize phenolic compounds. It was confirmed, however, that phenolic compound VI is not oxidized at all by FeCl<sub>3</sub>, when it was subjected to a nitrogen-alkali treatment under the conditions employed in this study where the pH was high.

**Table 1** List of all the treatments applied in this study

No.	Substrate	A <sup>a</sup>	B <sup>b</sup>	Gas
1	I	1.0	0.0	N <sub>2</sub>
2	I	1.0	0.0	O <sub>2</sub>
3	I	1.0	1.0	O <sub>2</sub>
4	I	1.0	10.0	O <sub>2</sub>
5	V	1.0	1.0	O <sub>2</sub>
6	V	1.0	10.0	O <sub>2</sub>
7	III	1.0	0.0	N <sub>2</sub>
8	III	1.0	0.0	O <sub>2</sub>
9	IV	1.0	0.0	N <sub>2</sub>
10	IV	1.0	0.0	O <sub>2</sub>
11	IV	1.0	1.0	O <sub>2</sub>
12	IV	1.0	10.0	O <sub>2</sub>

<sup>a</sup> Initial concentration of substrate (mmol/l)

<sup>b</sup> Initial concentration of compound VI (mmol/l)

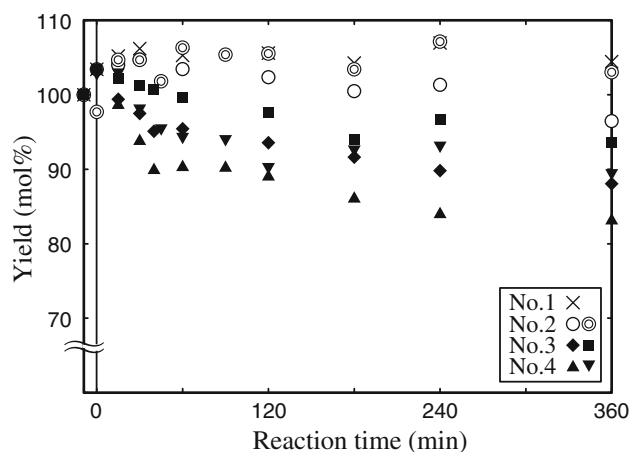
### Conversion of non-phenolic aromatic B-ring into phenolic aromatic ring in compound I

A common non-phenolic  $\beta$ -O-4 type dimeric lignin model compound I was subjected to nitrogen- and oxygen-alkali treatments in the absence and presence of the generator of AOS, compound VI. Figure 4 shows the yields of compound I in the nitrogen- and oxygen-alkali treatments (Nos. 1–4 in Table 1). Compound VI disappeared from the reaction solution at a reaction time of about 60 min. Figure 5 corresponds to the yields of compound II liberated from compound I via the  $\beta$ -O-4 bond cleavage. The degradation of compound I was not clearly observable in the nitrogen- or oxygen-alkali treatment in the absence of compound VI (No. 1 or 2) but a small amount of compound II was detected in the treatment No. 1. These results indicate that compound I is resistant toward both alkaline-induced reactions and oxidation by dioxygen when AOS are absent from the system under the conditions employed. Although a tiny amount of compound II should also have been liberated by alkaline-induced reactions even in the oxygen-alkali treatment (No. 2), the compound II liberated must have been degraded by dioxygen owing to the relative lability of compound II toward dioxygen and consequently compound II was not detected.

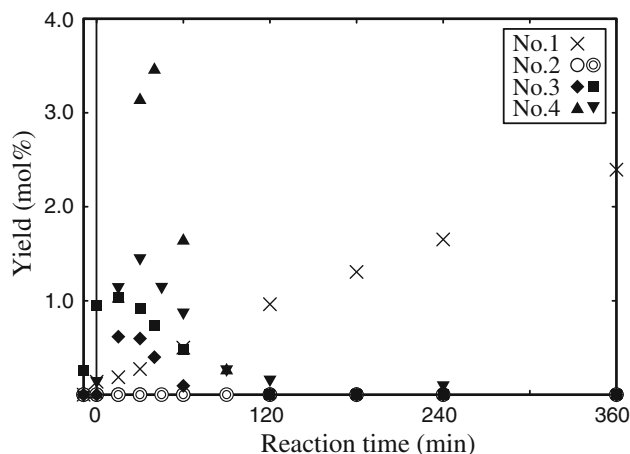
In the presence of compound VI (Nos. 3 and 4), the degradation of compound I and production of compound II in the early stage were clearly observed in the oxygen-alkali treatments of compound I. The formation of compound II in the early stage was probably more rapid than its oxidative degradation by dioxygen, and consequently, compound II was detectable. Since the aromatic A-ring of compound I is considered to be fairly resistant toward oxidation by both dioxygen and AOS, as mentioned above [4, 6, 8], the liberation of compound II from compound I should result from the attack of AOS on the side chain (see Fig. 3 for the definition of side chain) of compound I.

The degradation of compound I seems to be relatively significant in the early stage where compound VI still exists in the reaction solution, and become gradually slow after this time. The degradation of compound I after the disappearance of compound VI is considered to be caused by AOS generated by reactions of degradation products with dioxygen and/or by possible radical chain-type reactions. Although the amount of the generator of AOS, compound VI, added in the treatment No. 4 was as 10 times as that in the treatment No. 3, the difference in the degradations of compound I between these treatments was not significantly great. This result can probably be attributed to the action of compound VI to quench AOS produced from its reactions with dioxygen.

Because the amount of compound II detected must have been much smaller than that actually produced in the



**Fig. 4** Change in the yield of compound I when compound I was treated in the nitrogen- and oxygen-alkali treatments in the absence and presence of compound VI (Nos. 1–4). Reaction was run twice in the treatment Nos. 2, 3, and 4. No. 1: N<sub>2</sub>, No. 2: O<sub>2</sub>, No. 3: O<sub>2</sub> in the presence of compound VI (1 mmol/l), No. 4: O<sub>2</sub> in the presence of compound VI (10 mmol/l) (see Table 1)



**Fig. 5** Change in the yield of compound II when compound I was treated in the nitrogen- and oxygen-alkali treatments in the absence and presence of compound VI (Nos. 1–4). Reaction was run twice in the treatment Nos. 2, 3, and 4. No. 1: N<sub>2</sub>, No. 2: O<sub>2</sub>, No. 3: O<sub>2</sub> in the presence of compound VI (1 mmol/l), No. 4: O<sub>2</sub> in the presence of compound VI (10 mmol/l) (see Table 1)

oxygen-alkali treatments (Nos. 2–4), the contribution of the  $\beta$ -O-4 bond cleavage to the degradation of compound I could not be evaluated from this experiment. As described before, the compound II liberated must have been degraded by dioxygen owing to the relative lability toward dioxygen.

### Confirmation of the stability of compound V in oxygen-alkali treatment

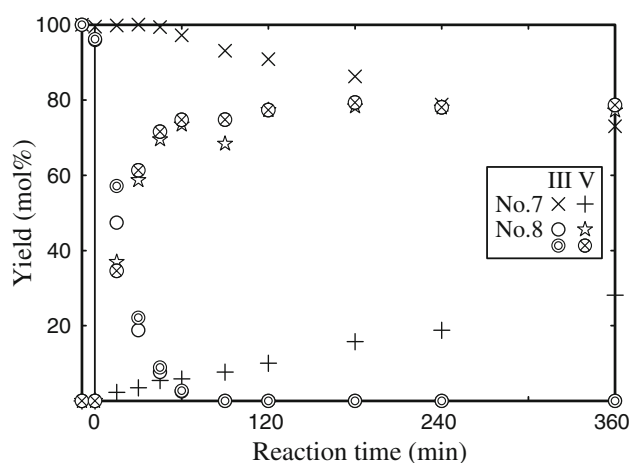
To evaluate the contribution of the  $\beta$ -O-4 bond cleavage to the degradation of a  $\beta$ -O-4 type dimeric lignin model compound in oxygen-alkali treatment, the phenolic

compound liberated from the B-ring of the dimeric model compound must be stable and quantitatively detected under the conditions employed in this study, when the  $\beta$ -O-4 bond of the dimeric model compound is cleaved. A phenolic compound with  $\alpha$ -carbonyl group, such as 4-hydroxy-3-methoxybenzaldehyde (vanillin), satisfies this prerequisite and is suitable for the B-ring of a  $\beta$ -O-4 type dimeric lignin model compound applied to this study. Because it was reported that this type of dimeric lignin model compound is surprisingly labile under alkaline conditions [11, 12], however, a phenolic compound with  $\alpha$ -carbonyl group cannot be utilized as the B-ring of dimeric model compound in this study. In this context,  $\beta$ -O-4 type dimeric model compounds III and IV, carrying two fluorines on their aromatic B-ring, may be utilized to evaluate the contribution. Compound V is liberated accompanying the  $\beta$ -O-4 bond cleavages of compounds III and IV, and hence, should be stable under the conditions employed in this study where AOS are operative. To examine the stability of compound V, it was subjected to oxygen-alkali treatment together with the generator of AOS, compound VI (Nos. 5 and 6 in Table 1). The recoveries of compound V were 95 and 91% at a reaction time of 360 min in the treatment Nos. 5 and 6, respectively. These results confirm that compound V is stable enough to be quantitatively detected when compound V is liberated from compounds III and IV in their oxygen-alkali treatments.

#### Conversion of non-phenolic aromatic B-ring into phenolic aromatic ring in compound III

It is known, as described in “Introduction”, that phenolic lignin moiety without  $\alpha$ -carbonyl group is degraded by dioxygen under oxygen bleaching conditions. It has not yet been clarified, however, whether a non-phenolic aromatic unit in lignin consisting of  $\beta$ -O-4 bond, which is represented by the B-ring of compound III, is converted into the new corresponding phenolic unit via the  $\beta$ -O-4 bond cleavage when the neighboring phenolic unit, which is represented by the A-ring of compound III, is degraded by dioxygen in an oxygen bleaching process. On the basis of this consideration, a phenolic  $\beta$ -O-4 type dimeric model compound III was applied to oxygen-alkali treatment and the liberation of compound V was examined.

Figure 6 shows the yield of compounds III and V in the nitrogen- or oxygen-alkali treatment of compound III (No. 7 or 8 in Table 1). The generator of AOS, compound VI, was not added in these cases because the A-ring of compound III reacts with dioxygen generating AOS. Compound III was degraded both in the nitrogen- and oxygen-alkali treatments, and compound V was liberated accompanying the degradation of compound III. The formation of compound V was quantitative on the basis of the



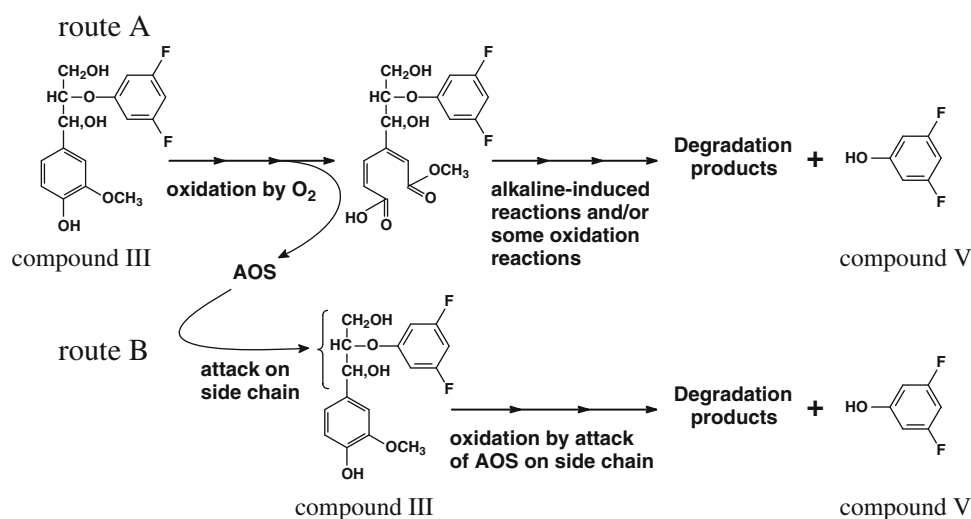
**Fig. 6** Change in the yields of compounds III and V when compound III was treated in the nitrogen- and oxygen-alkali treatments (Nos. 7 and 8). Reaction was run twice in the treatment No. 8. No. 7: N<sub>2</sub>, No. 8: O<sub>2</sub> (see Table 1)

amount of compound III that disappeared and the yield reached about 30% at a reaction time of 360 min in the treatment No. 7, while the yield of compound V was about 80% at the same reaction time in the treatment with oxygen (No. 8) although compound III had been disappeared from the reaction solution. These results suggest that alkaline-induced degradation reactions of compound III are always accompanied by the  $\beta$ -O-4 bond cleavage in the absence of dioxygen while compound III is degraded not only with but also without being accompanied by the  $\beta$ -O-4 bond cleavage in the presence of dioxygen. The relatively high lability of compound III in the absence of dioxygen (No. 7) can be attributed to the higher leaving ability of compound V relative to compound II. The high leaving ability results from the high stability of the conjugate base of compound V as an anion owing to the presence of two fluorines on the aromatic ring.

Both the degradation of compound III and the formation of compound V were significantly greater in the treatment No. 8 than those in the treatment No. 7. This result indicates that the participation of oxidation reactions in the degradation of compound III significantly enhances the  $\beta$ -O-4 bond cleavage although the  $\beta$ -O-4 bond of compound III can also be cleaved only by alkaline-induced reactions. It was confirmed that the non-phenolic aromatic B-ring of compound III is converted into the corresponding phenolic compound V resulting from oxidation reactions of compound III.

There are two possible mechanisms for the liberation of compound V from compound III. These mechanisms are schematically shown in Fig. 7. The primary reaction between compound III and dioxygen is aromatic ring opening of the phenolic aromatic A-ring of compound III affording a muconic acid derivative. The  $\beta$ -O-4 bond of the

**Fig. 7** Schematic description of two possible mechanisms for the conversion of the non-phenolic B-ring of compound III into compound V

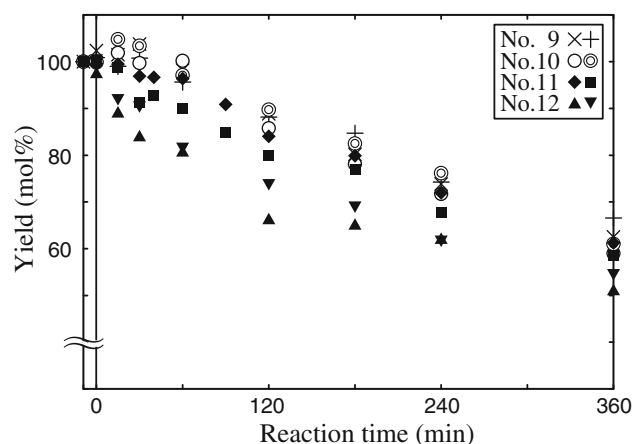


muconic acid derivative is possibly cleaved by alkaline-induced reactions and/or by some oxidation reactions (route A in Fig. 7). This reaction mode progresses only in  $\beta$ -O-4 type lignin structures with phenolic units represented by compound III. Alternatively, the  $\beta$ -O-4 bond may also be cleaved by the attack of AOS on the side chain of compound III before the A-ring of compound III is degraded and ring-opened by dioxygen (route B in Fig. 7). This type of cleavage can progress in any  $\beta$ -O-4 type structure, when AOS are operative in the system.

#### Conversion of non-phenolic aromatic B-ring into phenolic aromatic ring in compound IV

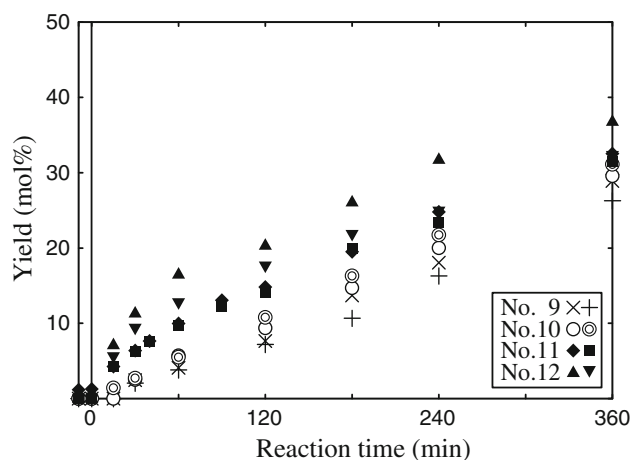
The result obtained above does not necessarily indicate that the  $\beta$ -O-4 bond cleavage of compound III and liberation of compound V result from the attack of AOS on the side chain. To examine whether the attack of AOS on the side chain of  $\beta$ -O-4 type substructure results in the  $\beta$ -O-4 bond cleavage and liberation of the corresponding phenolic counterpart, compound IV was subjected to the nitrogen- or oxygen-alkali treatments in the absence and presence of the generator of AOS, compound VI. Compound IV does not have any reactive site with dioxygen. Reactions between compound VI and dioxygen generate AOS, and the AOS attack compound IV.

Because the aromatic A-ring of compound IV is fairly stable under the conditions employed in this study [4, 6, 8], as mentioned above, the observation of the liberation of compound V should strongly suggest that AOS can attack the side chain of compound IV resulting in the liberation of compound V. Therefore, this type of attack of AOS can be evaluated using compound IV. Compound IV can be dissolved in the alkaline water solution probably owing to the presence of two fluorines in its B-ring.



**Fig. 8** Change in the yield of compound IV when compound IV was treated in the nitrogen- and oxygen-alkali treatments in the absence and presence of compound VI (Nos. 9–12). Reaction was run twice in all the cases. No. 9: N<sub>2</sub>, No. 10: O<sub>2</sub>, No. 11: O<sub>2</sub> in the presence of compound VI (1 mmol/l), No. 12: O<sub>2</sub> in the presence of compound VI (10 mmol/l) (see Table 1)

Figure 8 shows the yield of compound IV in the nitrogen- or oxygen-alkali treatment of compound IV (Nos. 9–12 in Table 1). Figure 9 shows the yield of compound V liberated from compound IV. Compound VI disappeared from the reaction solution at a reaction time of about 60 min. The degradation of compound IV in the nitrogen-alkali treatment (No. 9) was to the same degree as that in the oxygen-alkali treatment in the absence of compound VI (No. 10). The amounts of compound V liberated were slightly smaller than the quantitative yields in both cases. These results indicate that the degradation of compound IV is caused by alkaline-induced reactions without the participation of any oxidation reaction, and that it is resistant toward oxidation by dioxygen. The degradation of compound IV in the oxygen-alkali treatments in the presence of



**Fig. 9** Change in the yield of compound V when compound IV was treated in the nitrogen- and oxygen-alkali treatments in the absence and presence of compound VI (Nos. 9–12). Reaction was run twice in all the cases. No. 9: N<sub>2</sub>, No. 10: O<sub>2</sub>, No. 11: O<sub>2</sub> in the presence of compound VI (1 mmol/l), No. 12: O<sub>2</sub> in the presence of compound VI (10 mmol/l) (see Table 1)

compound VI (Nos. 11 and 12) was greater than that in the absence of compound VI (No. 10). This result suggests that AOS generated from reactions of compound VI with dioxygen attack the side chain of compound IV, and that consequently compound V is liberated. It was confirmed that the non-phenolic aromatic B-ring in compound IV is converted into the corresponding phenolic compound V by the attack of AOS on the side chain of compound IV.

The difference in the degradation of compound IV between the treatment Nos. 10 and 11 (or 12) is considered to correspond to the degradation of compound IV caused by the attack of AOS on the side chain. Its extent is not very large suggesting that the attack of AOS on the side chain is not a significantly frequent reaction mode. This consideration suggests that the liberation of compound V in the oxygen-alkali treatment of compound III (No. 8), described in “[Conversion of non-phenolic aromatic B-ring into phenolic aromatic ring in compound III](#)”, is mainly caused by route A shown in Fig. 7. However, it was clearly suggested that the attack of AOS on the side chain of  $\beta$ -O-4 type lignin substructure results in the  $\beta$ -O-4 bond cleavage and liberation of the new phenolic unit.

Because the extent of the difference in the degradation of compound IV between the treatment Nos. 10 and 11 (or 12) may not seem to be largely different from that observed in the treatments of compound I [between the treatment Nos. 2 and 3 (or 4)], it is suggested that the presence of the fluorines in compound IV does not largely influence its reaction with AOS at the side chain. However, as mentioned above, it is recognized that the presence of the

fluorides significantly affects the progress of alkaline-induced reactions.

## Conclusions

It was suggested that the non-phenolic aromatic rings in compounds I, III, and IV are converted into the corresponding phenolic compounds II, V, and V, respectively, via the attack of AOS on the side chain portions of these dimeric compounds. It is considered that this type of conversion of non-phenolic into the corresponding phenolic lignin moiety contributes to the progress of oxidation toward non-phenolic lignin moiety in an oxygen bleaching process.

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