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Application of the amount of oxygen consumption to the investigation of the oxidation mechanism of lignin during oxygen-alkali treatment

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Abstract The dioxygen consumption by kraft lignin and several lignin model compounds during oxygen-alkali treatments were directly analyzed using a dioxygen flowmeter. The average dioxygen consumption by 200 g of kraft lignin was about 3 moles. Because this value was as much as those obtained for monomeric phenolic lignin model compounds, guaiacol and vanillyl alcohol, it was postulated that not only phenolic but also nonphenolic moieties in kraft lignin are extensively oxidized. The dioxygen consumption by 0.5 moles (one equivalent of aromatic units) of a dimeric lignin model compound, guaiacylglycerol- β -guaiacyl ether (GG), was also similar to that for 1 mole of guaiacol and vanillyl alcohol, regardless of the type of the aromatic moiety, which supports the above postulation. The most plausible mechanism for the oxidation of nonphenolic moieties is the oxidation of side chains of residual β -O-4 substructures by active oxygen species. By this mechanism, nonphenolic moieties in kraft lignin and GG are converted into corresponding phenolic moieties, and the oxidation by dioxygen progresses.

Key words Delignification · Lignin · Oxidation · Oxygen bleaching · Phenolic

Introduction

Oxygen-alkali bleaching plays an important role as prebleaching in elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching sequences, and it is applied worldwide in the pulping industry.¹ The progress of lignin oxidation during the bleaching affects the extent of delignification. Tong and coworkers,^{2,3} for example, tried to establish a correlation between the degree of lignin oxidation and delignification. They applied an indirect method in which the correlation between the extent of lignin oxidation and the change in permanganate consumption by lignin before and after oxygen oxidation was examined. The change actually represents an index for the progress of lignin oxidation and correlates well with the decrease of methoxyl group content in lignin. It was also shown that 200 g of kraft lignin consumes more than 2.2 moles of dioxygen.

Figure 1 shows typical major reaction products obtained by oxygen-alkali treatments of phenolic lignin model compounds.^{4,5} It is possible to calculate the amount of dioxygen consumed in affording 1 mole of these typical products based on the mechanisms for the formation of these products. The results are no more than 1.5 moles of dioxygen as shown in Fig. 1. This value is smaller than that obtained for kraft lignin by Tong and coworkers, although kraft lignin consists of both phenolic and nonphenolic moieties and it has been well established that nonphenolic lignin model compounds do not react with dioxygen under conditions similar to oxygen-alkali bleaching.⁶ Therefore, it was postulated that the oxidation of nonphenolic moieties in kraft lignin is extensive.

In this study, we tried to measure directly the dioxygen consumption by kraft lignin and several lignin model compounds under conditions similar to oxygen-alkali bleaching. In doing so, we designed a device for accurately measuring the amount of dioxygen supplied to a reactor in which a lignin sample was subjected to oxygen-alkali treatment. The experiments determined the number of moles of dioxygen consumed by 200 g of kraft lignin or 1 mole of monomeric phenolic lignin model compounds and whether nonphenolic

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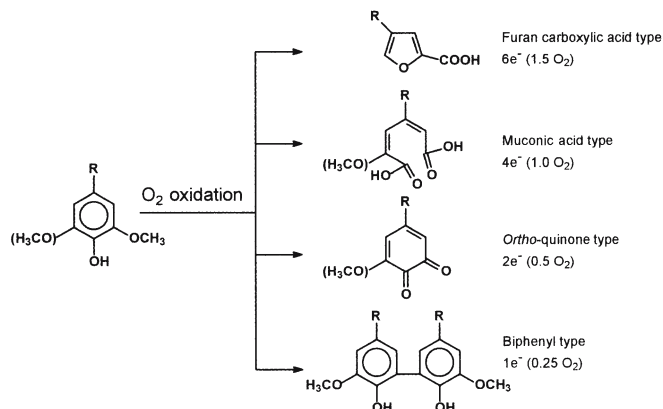


Fig. 1. Major reaction products obtained by oxygen-alkali treatments of phenolic lignin model compounds^{4,5} and the calculated oxygen consumption necessary for their formation

moieties in kraft lignin and lignin model compounds are extensively oxidized.

Materials and methods

Materials

Monomeric lignin model compounds, benzene-1,2,3-triol (pyrogallol), 2-methoxyphenol (guaiacol), 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol), 4-hydroxy-3-methoxybenzaldehyde (vanillin), and 3,4-dimethoxybenzyl alcohol (veratryl alcohol), were purchased from Tokyo Chemical (Tokyo, Japan). Vanillyl alcohol and vanillin were recrystallized from ethanol. Guaiacol and veratryl alcohol were vacuum-distilled. Because pyrogallol is quite sensitive to dioxygen, it was not purified. A dimeric lignin model compound, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (guaiacylglycerol- β -guaiacyl ether, GG), was synthesized according to the method of Li and coworkers.⁷ GG was purified by preparative medium-pressure liquid chromatography (YFLC-540, Yamazen, Osaka, Japan) on a silica gel column (Ultrapack SI-40C, Yamazen) by elution with chloroform/ethanol (10/1). The chemical structures of the compounds used in this study are shown in Fig. 2. Softwood kraft lignin was isolated by acidifying black liquor. The kraft lignin was thoroughly washed by water.

Oxygen-alkali treatment and measurement of dioxygen consumption

Figure 3 shows the scheme of the experimental design. Kraft lignin or a lignin model compound was dissolved into 500 ml of an aqueous solution containing 10 g of NaOH (0.5 mol/l), 10 ml of a 0.1% FeCl₃ solution (0.36 mmol/l). The solution was transferred into a Teflon-coated stainless steel reaction vessel and the vessel was sealed. The vessel was electrically heated to 95°C in 15 min under 0.6 MPa of oxygen pressure. As soon as temperature reached 95°C, the

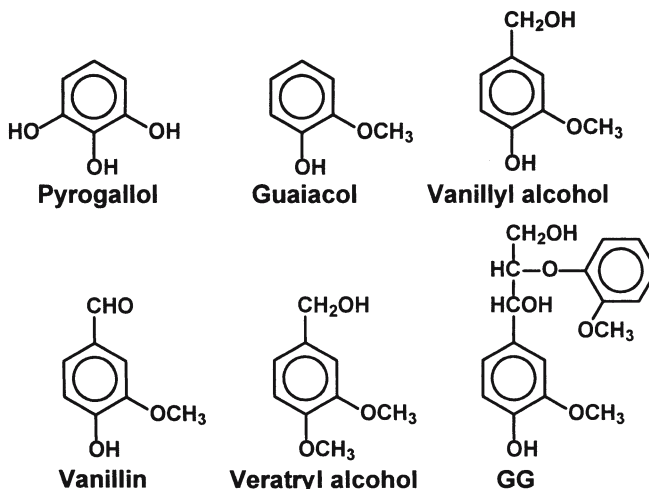


Fig. 2. Chemical structure of the model compounds used in this study. GG, Guaiacylglycerol- β -guaiacyl ether

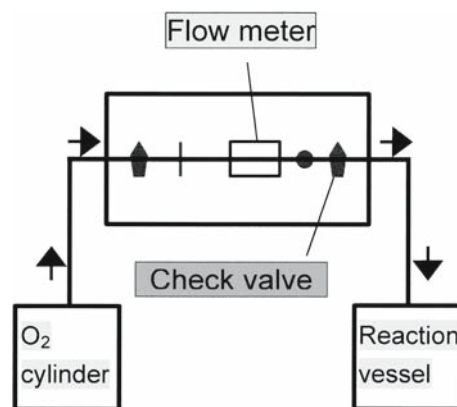


Fig. 3. Diagram of the reaction device developed in this study

oxygen pressure was adjusted to 0.8 MPa and the measurement of the dioxygen flow was begun.

Pyrogallol was also treated under neutral conditions. A control experiment was also conducted without adding any lignin sample.

The amounts of the substrates used were as follows: pyrogallol 0.625 g (9.9 mmol/l), guaiacol 0.625 g (10.1 mmol/l), vanillyl alcohol 0.48 g (6.2 mmol/l), vanillin 0.50 g (6.6 mmol/l), veratryl alcohol 0.48 g (5.7 mmol/l), GG 0.70 g (4.4 mmol/l), and kraft lignin 1.25, 0.625, or 0.313 g.

Results and discussion

In this study, the amount of dioxygen supplied to the reactor, which was measured by the flowmeter shown Fig. 3, was converted into the amount of dioxygen consumed by 1 mole of the monomeric lignin model compounds, 200 g of kraft lignin, or 0.5 moles of GG. These values correspond to the dioxygen consumption by one equivalent of aromatic units. It was assumed in this calculation that all of the oxidation ability of dioxygen (four electron equivalents) was used to

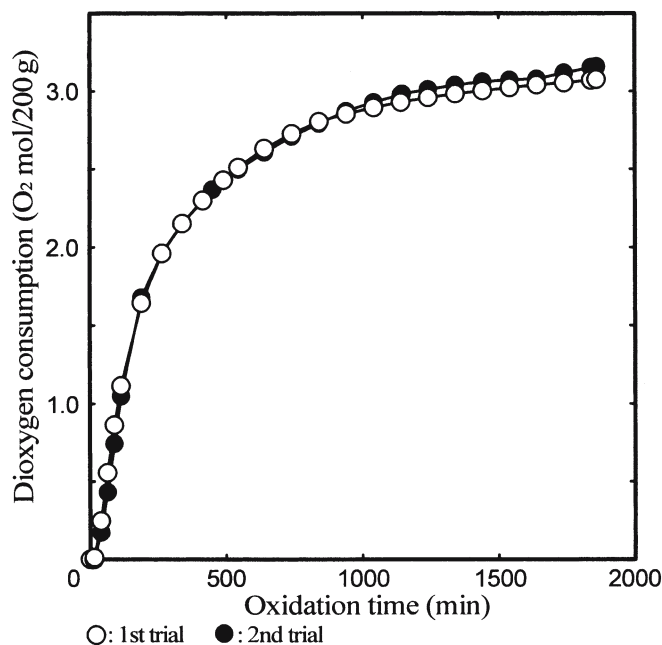


Fig. 4. Dioxigen consumption by kraft lignin measured by the dioxigen flowmeter for an initial amount of kraft lignin of 1.25 g

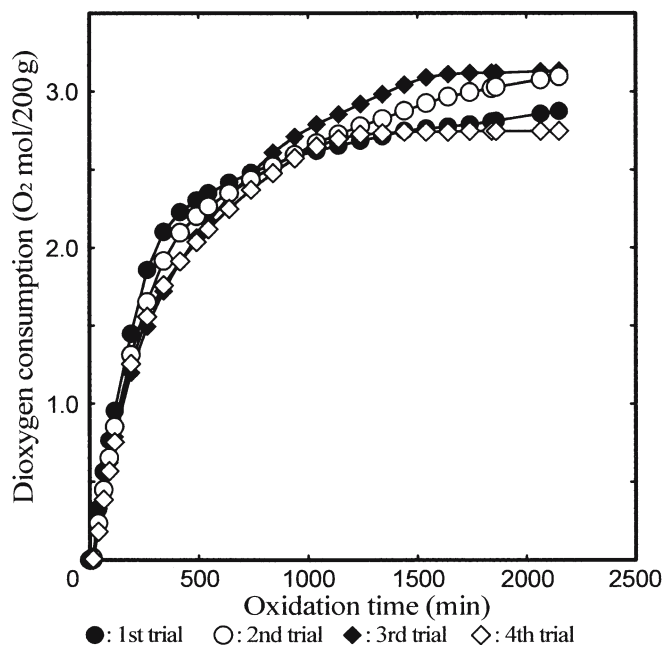


Fig. 5. Dioxigen consumption by kraft lignin measured by the dioxigen flowmeter for an initial amount of kraft lignin of 0.625 g

oxidize organic substances in the reactor. This assumption is incorrect only when peroxides produced in the system are stable enough to accumulate. Because it has been reported that the amount of such peroxides is very small under conditions similar to those in this study,⁸ the assumption can be considered to be always correct. In the case of kraft lignin experiments, because kraft lignin contains some unknown organic substances, sulfur-related compounds, and some structures that are different from common lignin, the amount calculated for 200 g of kraft lignin does not exactly correspond to one equivalent of aromatic units in kraft lignin. However, the experiments for kraft lignin can still be very helpful to discuss the dioxigen consumption by lignin.

Figures 4, 5, and 6 show the amount of dioxigen consumption by 200 g of kraft lignin when the amount of kraft lignin treated was 1.25, 0.625, or 0.313 g, respectively. It is noticed that the variation of the data is greater when the concentration of kraft lignin is lower. When the smallest amount of kraft lignin was subjected to the reaction, the dioxigen supply was the smallest. An amount of dioxigen had already existed in the reactor before the reaction was initiated. When this amount is not significantly smaller than that supplied to the reaction vessel during the reaction, the data variation is significant. As a result, all data used in subsequent analysis were obtained when the dioxigen consumption was considered to be sufficiently high.

Oxygen-alkali treatment of monomeric lignin model compounds

Figure 7 illustrates the amount of dioxigen consumed by 1 mole of the monomeric lignin model compounds. The amount of dioxigen consumed by pyrogallol under alkaline

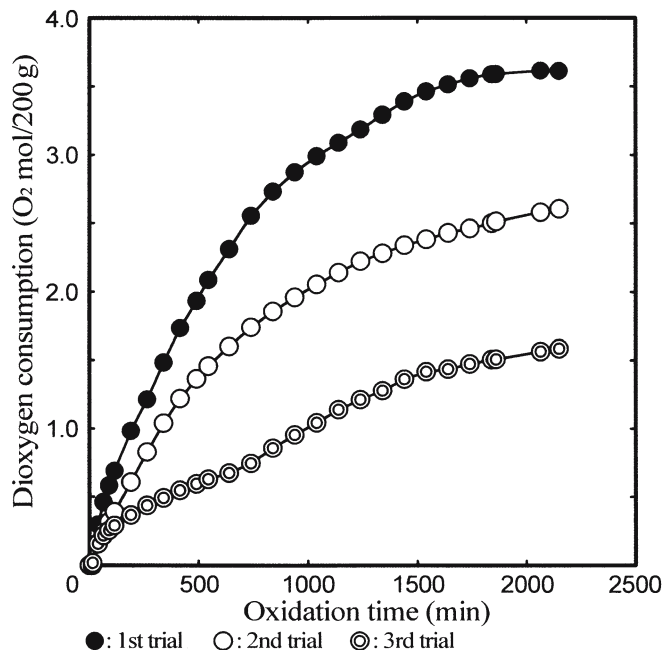


Fig. 6. Dioxigen consumption by kraft lignin measured by the dioxigen flowmeter for an initial amount of kraft lignin of 0.313 g

conditions was 1.7 times that consumed under neutral conditions. Two mechanisms for the pyrogallol oxidation are conceivable: one *via* an *ortho*-quinone derivative and the other *via* a ring-opening step. The *ortho*-quinone derivative is rearomatized by the addition of hydroxide anion and further oxidized by dioxigen. The product of the ring-opening step reacts directly with dioxigen to afford two

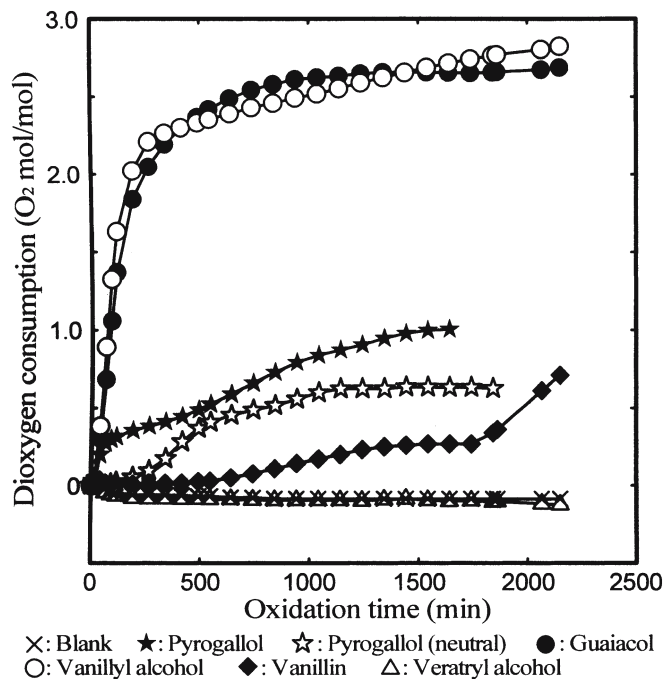


Fig. 7. Dioxxygen consumption by monomeric lignin model compounds measured by the dioxxygen flowmeter

dicarboxylic acids. On the other hand, both primary degradation products are relatively unreactive toward dioxxygen under neutral conditions. Because these possible reaction mechanisms for the degradation of pyrogallol by dioxxygen can be elucidated based on the amount of dioxxygen used, the actual reaction mechanism that occurs can be assigned based on the amount of dioxxygen measured by the flowmeter in the experiment.

One mole of guaiacol or vanillyl alcohol, both of which contain phenolic hydroxyl and methoxyl groups, continuously consumed about 3 moles of dioxxygen (Fig. 7). As mentioned in the Introduction, it is estimated that 1 mole of phenolic lignin model compound consumes no more than 1.5 moles of dioxxygen to give typical degradation products (Fig. 1). This value is smaller than the dioxxygen consumption by guaiacol and vanillyl alcohol obtained in this study. It should also be noted that 1 mole of guaiacol or vanillyl alcohol rapidly consumes more than 2 moles of dioxxygen within 250 min. Based on these results, it is suggested that possible primary degradation products of these model compounds, such as muconic acid derivatives, are continuously oxidized by dioxxygen to give further degradation products under the conditions employed.

It has been well established that vanillin, a monomeric phenolic lignin model compound with an α -carbonyl group, and veratryl alcohol, a monomeric nonphenolic lignin model compound, do not react with dioxxygen without adding any other compound that can react with dioxxygen.⁶ The amounts of dioxxygen consumption by vanillin and veratryl alcohol obtained in this study were also very small.

Oxygen-alkali treatment of kraft lignin

The average dioxxygen consumption per 200 g of kraft lignin was about 3 moles (Fig. 4). This value is approximately the same as that obtained for 1 mole of the monomeric phenolic lignin model compounds, guaiacol and vanillyl alcohol. Aromatic nuclei in kraft lignin consist of phenolic and nonphenolic types. To rationally explain the high dioxxygen consumption by kraft lignin, it is postulated that extensive oxidations occur not only on phenolic but also on nonphenolic moieties in kraft lignin. However, as mentioned in the previous section, it has been well established and also observed in this study that nonphenolic lignin model compounds, such as veratryl alcohol, do not consume dioxxygen without adding any other compound that reacts and consumes dioxxygen. Furthermore, Tong and co-workers² reported that the extent of the oxidation of veratryl alcohol is small when the compound is subjected to oxygen-alkali treatment with a phenolic lignin model compound like vanillyl alcohol. This observation indicates that nonphenolic aromatic moieties are not extensively oxidized by the actions of active oxygen species generated by the reactions between vanillyl alcohol and dioxxygen. Hence, it is necessary to consider mechanisms in which nonphenolic moieties are converted into phenolic ones. Two possible mechanisms are conceivable: (1) hydroxylation of nonphenolic moieties and (2) oxidative degradation of side-chain portions that are connected to aromatic moieties via alkyl-aryl ether bonds. However, the former is not likely, because the extent of veratryl alcohol oxidation is significantly smaller than that of vanillyl alcohol when these compounds are subjected together to an oxygen-alkali treatment as described above.² If the nonphenolic moiety of veratryl alcohol is hydroxylated, the extent of the oxidation of the compound should become similar to that of vanillyl alcohol. Therefore, the oxidative degradation of side-chain portions is more plausible. The most reasonable reaction is the oxidative degradation of side-chain portions of remaining β -O-4 structures to afford new phenolic moieties. If this is the case, veratryl alcohol may be inappropriate as a nonphenolic lignin model compound because the methyl group of veratryl alcohol, which is supposed to be a model for the side-chain portion, is not oxidized and a phenolic compound is not generated from veratryl alcohol.

The oxidative degradation of side chains is probably caused by active oxygen species, such as hydroxyl radical, generated by the oxidation of phenolic moieties by dioxxygen. From this point of view, these active oxygen species play a very important role in the progress of lignin oxidation. This oxidation mechanism is similar to the oxidative degradation of carbohydrate model compounds when subjected to oxygen-alkali treatments together with phenolic compounds.⁹⁻¹¹ Several literatures report that the consumption of dioxxygen by lignin samples is similar to or larger than those obtained in this study.¹²⁻¹⁷

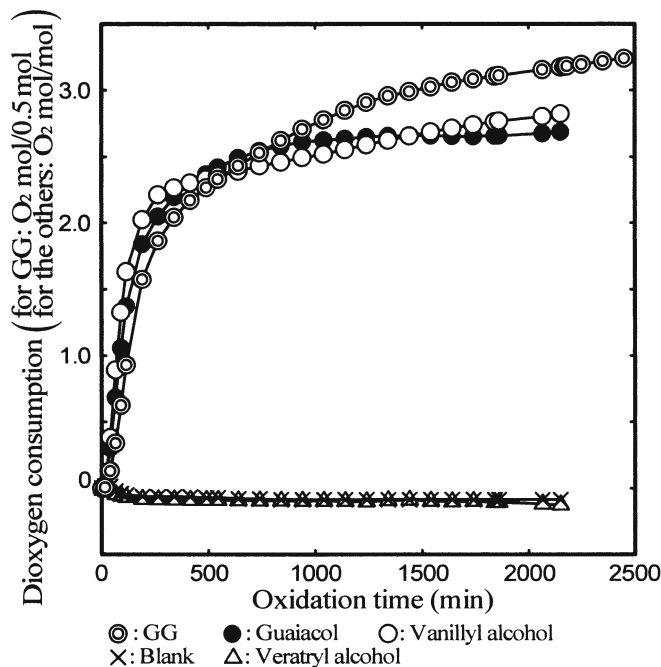


Fig. 8. Dioxxygen consumption by GG and the monomeric phenolic lignin model compounds measured by the dioxxygen flowmeter

Oxygen-alkali treatment of GG

To further examine whether nonphenolic moieties are converted into phenolic moieties during the oxidation by dioxxygen, the amount of dioxxygen consumed by GG was determined. GG is a dimeric β -O-4 lignin model compound and has both phenolic and nonphenolic moieties. It was observed that 3 moles of dioxxygen are consumed by one equivalent of aromatic units (0.5 moles) of GG, regardless of the type of aromatic moieties (Fig. 8). This value is a little greater than those of the monomeric phenolic lignin model compounds, guaiacol and vanillyl alcohol. If the nonphenolic aromatic moiety in GG is supposed not to be extensively oxidized, the phenolic moiety in GG has to consume almost 6 moles of dioxxygen although this moiety resembles guaiacol and vanillyl alcohol. Therefore, it is presumed that the side chain of GG is oxidized by active oxygen species and the nonphenolic moiety is converted into the corresponding phenolic moiety (guaiacol), followed by the oxidative degradation of the new phenolic moiety. The observation that the dioxxygen consumption by 0.5 moles of GG is a little larger than that consumed by 1 mole of guaiacol or vanillyl alcohol may indicate the dioxxygen consumption by the side chain of GG.

The release of guaiacol from GG can also be attained without the action of active oxygen species, when the enol ether, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxyethylene), forms and is oxidized by dioxxygen. The enol ether is produced from the quinone methide derived from GG followed by the release of the γ -carbon as formaldehyde. However, because it is known that the conditions employed in this study are not sufficient to frequently give the quinone methide from GG,¹⁸ the release of guaiacol from GG must result from the action of active oxygen species.

Conclusions

The mechanism of lignin oxidation was confirmed to be elucidated by the amount of dioxxygen consumption, which was measured by a dioxxygen flowmeter in this study. The observation that the dioxxygen consumption by 200 g of kraft lignin and by guaiacol or vanillyl alcohol was similar has led us to postulate that phenolic and nonphenolic moieties in kraft lignin are extensively oxidized. This postulation was supported by the dioxxygen consumption by 0.5 moles of GG (an equivalent of aromatic unit), which was larger than the dioxxygen consumption of 1 mole of guaiacol or vanillyl alcohol. The most plausible mechanism for the extensive oxidation of nonphenolic moieties in kraft lignin and GG is the oxidative cleavage of alkyl-aryl ethers by active oxygen species, a process that converts nonphenolics into phenolic moieties.

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