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Reaction behavior of lignin in supercritical methanol as studied with lignin model compounds

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Abstract The reaction behavior and kinetics of lignin model compounds were studied in supercritical methanol with a batch-type supercritical biomass conversion system. Guaiacol, veratrole, 2,6-dimethoxyphenol, and 1,2,3-trimethoxybenzene were used as model compounds for aromatic rings in lignin. In addition, 5-5, β -1, β -O-4, and α -O-4 types of dimeric lignin model compounds were used as representatives of linkages in lignin. As a result, aromatic rings and 5-5 (biphenyl)-type structures were stable in supercritical methanol, and the β -1 linkage was not cleaved in the β -1-type structure but converted rapidly to stilbene. On the other hand, β -ether and α -ether linkages of β -O-4 and α -O-4 lignin model compounds were cleaved rapidly, and these compounds decomposed to some monomeric compounds. Phenolic compounds were found to be more reactive than nonphenolic compounds. These results indicate that cleavages of ether linkages mainly contribute to the depolymerization of lignin, whereas condensed linkages such as the 5-5 and β -1 types are not cleaved in supercritical methanol. Therefore, it is suggested that the supercritical methanol treatment effectively depolymerizes lignin into the lower-molecular-weight products as a methanol-soluble portion mainly by cleavage of the β -ether structure, which is the dominant linkage in lignin.

Key words Supercritical methanol · Lignin model compound · β -O-4 Linkage · α -O-4 Linkage · β -1 Linkage · 5-5 Linkage

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Introduction

In our laboratory, the supercritical fluid biomass conversion system with a batch-type reaction vessel^{1–5} has been used to study the chemical conversion of woody biomass to obtain useful chemicals and liquid fuels. For example, the supercritical water (>374°C/>22.1 MPa) treatment of cellulosic biomass was studied by Saka and his coworkers.^{2–4} However, the obtained hydrolysis products such as glucose were further decomposed rapidly in supercritical water due to its high critical temperature. Therefore, they also studied the chemical conversion of biomass resources in supercritical methanol (>239°C/>8.09 MPa),^{1,6} which offered milder reaction conditions than supercritical water owing to its lower critical temperature.

Woody biomass is a complex of natural polymer substances: cellulose, hemicelluloses, and lignin. These polymer substances constitute the cell walls of wood and form their fine structures. Especially, lignin is a complex material with dehydrogenatively polymerized structure of phenylpropane (C₆-C₃) units, which have guaiacyl and syringyl nuclei with various ether and condensed linkages. However, the behaviors of natural lignin in supercritical fluid remained unclear.

Yokoyama et al.⁷ thus studied the degradation of organosolv lignin in supercritical water and supercritical methanol, and they reported that the oil and char yields related to the reaction conditions. They also studied the mechanisms of lignin degradation in supercritical methanol using model compounds, including dibenzyl ether, benzaldehyde, benzyl methyl ether,⁸ and benzyl phenyl ether.⁹ However, aromatic rings of these model compounds do not have any substitutional groups such as hydroxyl and methoxyl groups, which are expected to play important roles in the reaction of lignin. In this study, therefore, a series of simple aromatic model compounds and dimeric 5-5 (biphenyl), β -1, β -O-4, and α -O-4 lignin model compounds were studied regarding the reaction behavior of lignin in woody biomass in supercritical methanol.

Materials and methods

Lignin model compounds

Figure 1 shows the lignin model compounds used in this study for supercritical methanol treatment. Guaiacol (**1**) and veratrole (**2**) were used as model compounds for guaiacyl nuclei, and 2,6-dimethoxyphenol (**3**) and 1,2,3-trimethoxybenzene (**4**) were used for syringyl nuclei. They were all purchased from Nakalai Tesque as guaranteed grade agents. 2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**5**) and 2,2',3,3'-tetramethoxy-5,5'-dimethylbiphenyl (**6**) were selected for 5-5 linkages and were prepared according to the method described by Kratzl and Vierhapper.¹⁰ 1,2-(3,4-Dimethoxybenzyl)-1,3-propanediol (**7**) (*erythro* form) was used for the β -1 linkage, prepared by the method of Kristersson and Lundquist.¹¹ For β -O-4 linkages, guaiacylglycerol- β -guaiacyl ether (**8**) (*erythro* form) and veratrylglycerol- β -guaiacyl ether (**9**) (*erythro* form) were prepared according to the method of Nakatsubo et al.¹² For phenolic and nonphenolic α -O-4 linkages, 4-O-(4-hydroxy-3-methoxybenzyl)guaiacol (**10**) and 4-O-(3,4-dimethoxybenzyl)guaiacol (**11**) were prepared, respectively. The former was prepared from 4-benzoyloxy-3-methoxybenzyl bromide obtained by brominating 4-O-benzyl vanillyl alcohol with an excessive amount of guaiacol and potassium carbonate in *N,N*-dimethylformamide. The latter was prepared by similar condensation of 3,4-dimethoxybenzyl bromide with guaiacol.

Supercritical methanol treatment

A batch-type supercritical biomass conversion system¹⁻⁵ was applied for supercritical methanol treatment. In the case of methanol, this system can cover a range of pressures and temperatures up to about 100 MPa and 500°C, respectively, with a constant density of 0.79 g/ml. To start treatment of lignin model compounds in supercritical methanol, the reaction vessel with 10.0 mg lignin model compound dissolved in 5.0 ml of methanol was quickly heated by immersing it in a

molten tin bath preheated at an adequate temperature and maintained under supercritical conditions for 1–30 min. The obtained supercritical conditions of methanol were in the range of 255–350°C temperature and 24–43 MPa pressure, mainly 270°C/27 MPa and 350°C/43 MPa. After an adequate reaction time, the reaction vessel was moved to a water bath to quench the reaction. The detailed profiles of the temperature and pressure in the reaction vessel were described previously.^{1,5}

Analysis of the reaction mixture

The obtained reaction mixture was then directly analyzed by high-performance liquid chromatography (HPLC) carried out with a Shimadzu LC-10A chromatograph under the following conditions: column STR ODS-II; flow rate 0.8 ml/min; eluent (1) CH₃OH/H₂O, 20/80 → 100/0 (0 → 35 min); (2) CH₃OH/H₂O, 20/80 → 60/40 → 100/0 (0 → 40 → 50 min); detector UV₂₈₀; temperature 40°C. Gel permeation chromatography (GPC) was also carried out for the reaction mixture with the Shimadzu LC-10A device under the following conditions: column Shodex KF-801 (exclusion limit: MW 1500 in polystyrene); flow rate 1.0 ml/min; eluent tetrahydrofuran (THF); detector UV₂₈₀; temperature 40°C. Gas chromatography-mass spectrometry (GC-MS) was performed on the Hitachi G-7000M and M-9000 devices. Most products in the reaction mixtures were identified by comparing them with the authentic samples on GC-MS analysis. In addition, some reaction products were separated by preparative thin-layer chromatography (TLC) on a silica gel plate (Kieselgel 60 F₂₅₄; Merck) with ethyl acetate/*n*-hexane (1:1). The isolated compounds were then analyzed by proton nuclear magnetic resonance (¹H-NMR) spectroscopy, in which the spectra were recorded in CDCl₃ with a Varian AC-300 (300 MHz) spectrometer with tetramethylsilane (TMS) as the internal standard.

3,3',4,4'-Tetramethoxystilbene (*trans* form) and 1-guaiacyl-1-veratrylmethane (*o*- and *p*-isomers) were identified by ¹H-NMR analysis.

3,3',4,4'-Tetramethoxystilbene (*trans*): ¹H-NMR (CDCl₃, 300 MHz): δ 3.88 (6H, s, -OCH₃), 3.93 (6H, s, -OCH₃), 6.90 (2H, s, =C-H), 6.83–7.04 (6H, m, aromatic H).

1-Guaiacyl-1-veratrylmethane (*o*- and *p*-isomers): ¹H-NMR (CDCl₃, 300 MHz): (1) δ 3.80 (3H, s, -OCH₃), 3.81 (3H, s, -OCH₃), 3.83 (3H, s, -OCH₃), 3.84 (2H, s, C-H), 5.46 (1H, s, -OH), 6.63–6.83 (6H, m, aromatic H); (2) δ 3.81 (3H, s, -OCH₃), 3.82 (3H, s, -OCH₃), 3.86 (3H, s, -OCH₃), 3.92 (2H, s, C-H), 5.71 (1H, s, -OH), 6.72–6.80 (6H, m, aromatic H).

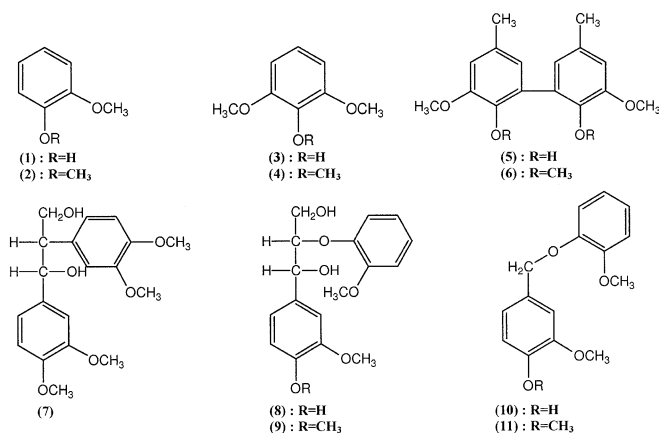


Fig. 1. Lignin model compounds used in this study

Results and discussion

Table 1 shows the types of linkages on 100 phenylpropane (C₆-C₃) units involved in softwood and hardwood lignins.^{13,14} It is apparent that hardwood lignin has more ether linkages than softwood lignin. In this study, therefore, the reactivity of lignin was investigated focusing on the 5-5, β -1, β -O-4,

Table 1. Types of linkages on 100 phenylpropane (C₆-C₃) units involved in softwood and hardwood lignins

Species	Linkages on 100 C ₆ -C ₃ units (no.)						
	Condensed linkage				Ether linkage		
	5-5	β -1	β - β	β -5	β -O-4	α -O-4	5-O-4
Softwood							
Spruce (<i>Picea abies</i>) ¹³	9.5–11.0	7	2	9–12	50	6–8	3.5–4.0
Hardwood							
Birch (<i>Betula verrucosa</i>) ¹³	4.5	7	3	6	62	6–8	6.5
Beech (<i>Fagus crenata</i>) ¹⁴	2.3	15	7.5	6	65		1.5

and α -O-4 linkages, because they are dominant in the lignin structure.

Reactivity of aromatic rings in lignin

The reactivity of the aromatic rings in lignin in supercritical methanol at 270°C/27 MPa has been reported previously by Tsujino et al.¹⁵ In this condition, 98% of guaiacol (**1**), 99% of veratrole (**2**), 91% of 2,6-dimethoxyphenol (**3**), and 97% of 1,2,3-trimethoxybenzene (**4**) were recovered after 10 min of treatment.¹⁵ In addition, under the conditions of 350°C/43 MPa, compounds **1**, **2**, **3**, and **4** were found to be recovered at 73%, 81%, 71%, and 82% yields, respectively, after 10 min of treatment. Although only small amounts of catechol and guaiacol were observed in the reaction mixtures of guaiacol (**1**) and veratrole (**2**), respectively, the aromatic rings themselves are stable in supercritical methanol. Consequently, the aromatic rings of softwood and hardwood lignins consisting, respectively, of a guaiacyl type of nucleus and guaiacyl and syringyl types of nuclei can be stable under conditions of supercritical methanol.

Reactivity of condensed linkages

The reactivity of lignin was then investigated, focusing on the condensed linkages between phenylpropane (C₆-C₃) units in lignin by using the 5-5 and β -1 types of dimeric lignin model compounds **5**–**7**. Adler¹³ reported, as in Table 1, that 9.5–11.0 units of the 5-5 structures exist in 100 C₆-C₃ units in spruce lignin but that this value is smaller (4.5 units) in birch lignin. For the β -1 type structure, 7 units were reported for both spruce and birch lignins and 15 for beech by Nimz.¹⁴ Therefore, these condensed structures are important linkages of lignin.

5-5 Model compounds

Figure 2 shows the HPLC chromatograms of the reaction mixtures obtained from phenolic and nonphenolic 5-5 type model compounds **5** and **6** as treated in supercritical methanol at 350°C/43 MPa. The reactivity of the biphenyl type model compounds in supercritical methanol at 270°C/27 MPa was reported in a previous paper,¹⁵ in which compounds **5** and **6** were found to be recovered at 78% and 91%, respectively, after 10 min of treatment.¹⁵ Figure 2

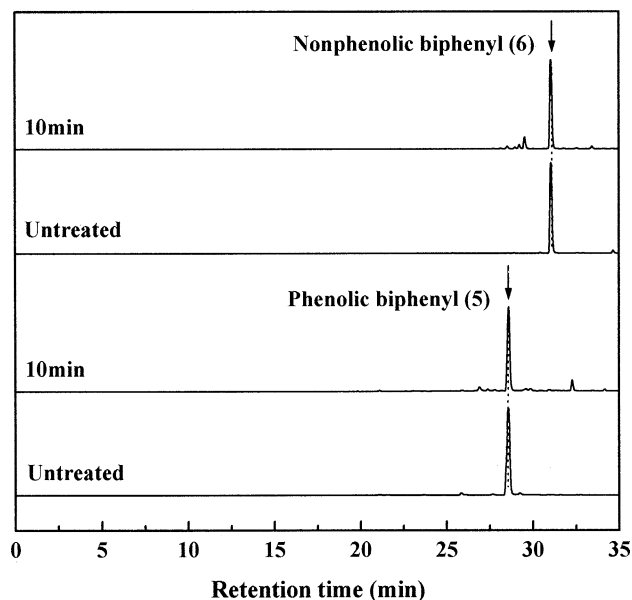


Fig. 2. High-performance liquid chromatography (HPLC) chromatograms of phenolic biphenyl (**5**) and nonphenolic biphenyl (**6**) type lignin model compounds treated in supercritical methanol at 350°C/43 MPa. (Column STR ODS-II; detector UV₂₈₀; eluent MeOH/H₂O, 20/80 → 100/0 (0 → 30 min); flow rate 0.8 ml/min)

shows the results at 350°C/43 MPa, where compounds **5** and **6** are recovered at 71% and 88%, respectively. Although unidentified compounds along with these compounds are observed at the retention times of 32.3 and 29.6 min, they are in small amounts; thus, the biphenyl-type model compounds are stable under treatment with supercritical methanol. If 5-5 linkages of the biphenyl type model compounds are cleaved, 1-methyl-3-methoxyphenol and 1-methyl-3,4-dimethoxybenzene may be expected to be produced. However, these compounds were not the ones unidentified. In addition, GPC analysis indicated that monomeric compounds were not produced from compounds **5** and **6**. Therefore, the 5-5 linkages of the phenolic and nonphenolic biphenyl type model compounds can hardly be cleaved in supercritical methanol.

β -1 Model compound

Figure 3 shows the HPLC chromatograms of the reaction mixtures obtained from nonphenolic β -1-type model com-

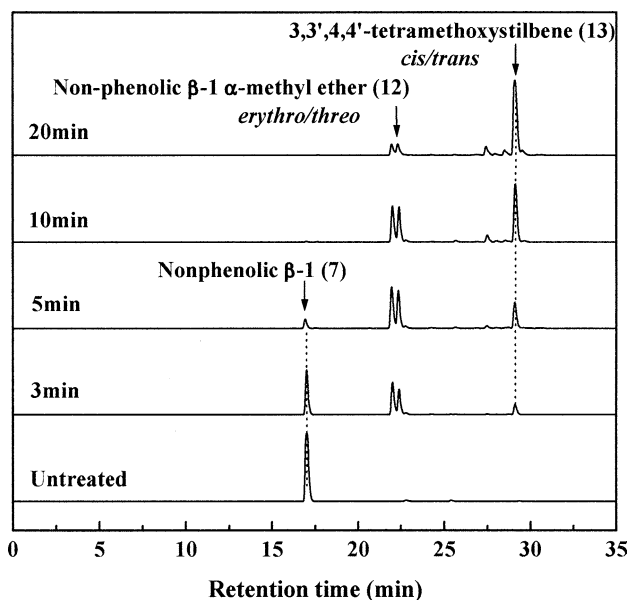


Fig. 3. HPLC chromatograms of nonphenolic β -1 lignin model compound **7** treated in supercritical methanol at 270°C/27 MPa. (Column STR ODS-II; detector UV₂₈₀; eluent MeOH/H₂O, 20/80 → 100/0 (0 → 30 min); flow rate 0.8 ml/min)

compound **7** treated in supercritical methanol at 270°C/27 MPa. The β -1 model compound was found to be reactive in supercritical conditions. As the reaction proceeded, model compound **7** decreased and disappeared completely after 10 min of treatment. The compounds **12** observed at 22.1 and 22.5 min of retention time were identified to be *erythro* and *threo* isomers of the α -methyl ether of compound **7** after comparison with the authentic samples. These compounds increased gradually at an early stage of treatment and decreased after 5 min of treatment. In turn, a peak that consists of two products observed at 29.2 min in the retention time was gradually increased. These newly formed products were identified to be *cis* and *trans* isomers of 3,3',4,4'-tetramethoxystilbene (**13**), determined by ¹H-NMR and GC-MS analysis. Finally, compounds **7** and **12** disappeared completely, and only compound **13** was present with some other small peaks. This compound **13** was converted from the nonphenolic β -1 model compound **7** by eliminating formaldehyde, and its β -1 linkage could not be cleaved. Furthermore, *cis* and *trans* isomers of compound **13** are stable in supercritical methanol. The maximum total yield of *cis* and *trans* isomers of compound **13** was found to be >70 mol% at both 270°C/27 MPa and 350°C/43 MPa.

Finally, the proposed reaction pathway of nonphenolic β -1 model compound **7** is shown in Fig. 4. Conversion of nonphenolic β -1-type model compound **7** to its α -methyl ether is a dominant reaction path due to the acidic character of the supercritical methanol.¹⁶ Acid-labile hydroxyl groups such as the α -hydroxyl group in compound **7** can be eliminated to form a quinonemethide-type intermediate under such an acidic condition, which is easily converted to α -methyl ether and then further converted to tetramethoxystilbene (**13**), which is stable in supercritical methanol.

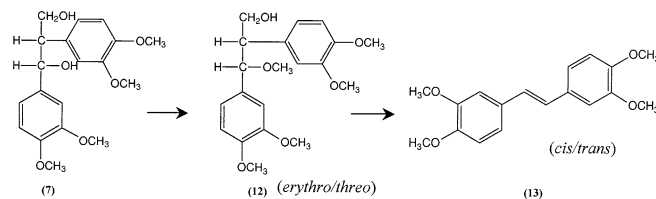


Fig. 4. Major degradation pathway of nonphenolic β -1 lignin model compound **7** treated in supercritical methanol

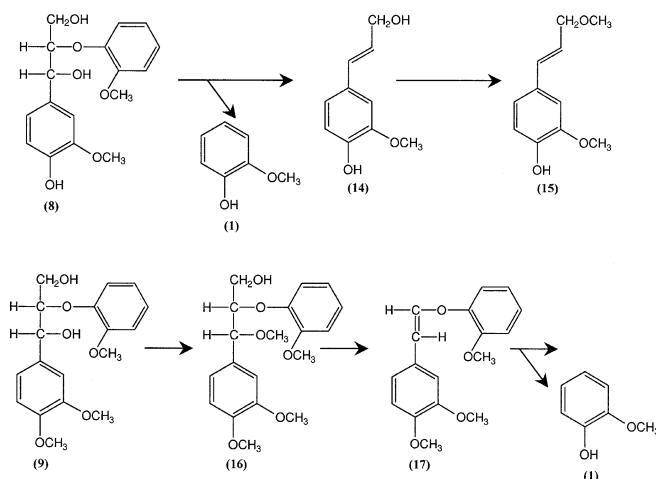


Fig. 5. Degradation pathways of phenolic and nonphenolic β -O-4 model compounds **8** and **9** treated in supercritical methanol¹⁵

Based on these lines of evidence, the quinonemethide-type intermediate must be produced mostly without cleaving the side chain of the phenylpropane unit. Thus, β -1 linkages in lignin must be extremely stable and do not contribute to the depolymerization of lignin during supercritical methanol treatment.

Reactivity of ether linkages

The reactivity of lignin was further investigated, focusing on the ether linkages of lignin. Ether linkages (noncondensed linkages), which are represented by β -O-4 model compounds **8** and **9** and α -O-4 model compounds **10** and **11**, are important linkages of lignin, especially in hardwood, as shown in Table 1.

β -O-4 Model compounds

The reactivity of β -O-4-type model compounds in supercritical methanol at 270°C/27 MPa has been reported previously.¹⁵ The β -O-4 model compounds were found to be highly reactive in supercritical methanol, especially in the phenolic form (**8**). The proposed reaction paths of phenolic and nonphenolic β -O-4 model compounds are shown in Fig. 5. As the reaction proceeded, the model compound **8** decreased and disappeared completely after 20 min of treatment at 270°C/27 MPa. Subsequently, guaiacol (**1**) and coniferyl alcohol (**14**) were produced. Although the amount of guaiacol increased and leveled off after 3 min of treat-

ment, coniferyl alcohol increased up to 10 min of treatment and then decreased somewhat by further treatment. In turn, coniferyl alcohol γ -methyl ether (**15**) was gradually produced. At 20 min of treatment, yields of guaiacol (**1**) and the sum of coniferyl alcohol (**14**) and its γ -methyl ether (**15**) were both 87%. Thus, phenolic β -O-4 model compound **8** was first converted to guaiacol and coniferyl alcohol, and the latter product was further methylated at the γ -position, as shown in Fig. 5. Conversion of coniferyl alcohol to its γ -methyl ether is thought to be due to the acidic character of the supercritical methanol, as discussed for the methylation of nonphenolic β -1 model compound **7**. These lines of evidence indicate that the phenolic β -ether structure is easily cleaved to give the coniferyl alcohol type of structure and this structure is further methylated at the γ -position.

On the other hand, nonphenolic β -O-4-type lignin model compound **9** decreased as the reaction time proceeded and disappeared completely after 5 min of treatment. The initially produced product was found to be an α -methyl ether of compound **9** by $^1\text{H-NMR}$ analysis. Acid-labile α -hydroxyl group is easily methylated via a quinonemethide intermediate, as discussed for the methylation of compound **7**. After supercritical methanol treatment of α -methyl ether of the nonphenolic β -O-4 compound **16**, *cis* and *trans* isomers of 2-(2'-methoxyphenoxy)-1-(3',4'-dimethoxyphenyl) ethene (**17**) appeared and then cleaved off to produce guaiacol (**1**) after 3 min of treatment. Therefore, it can be assumed that guaiacol (**1**) was produced after cleavage of β -ether of these vinyl ether compounds (**17**). The formation of guaiacol, which is evidence of β -ether cleavage, is minimal at the first stage of the reaction. However, later in the reaction (>10 min), guaiacol (**1**) appears to be produced with a decrease in the amount of vinyl ethers (**17**). Thus, nonphenolic β -O-4 model compound **9** must be converted to its α -methyl ether (**16**) and then to vinyl ethers (**12**), followed by the successive cleavage of the β -ether linkage, as shown in Fig. 5.

α -O-4 Model compounds

The α -O-4 model compounds were also found to be highly reactive in supercritical methanol. Especially phenolic α -O-4 model compound **10** was markedly reactive. Figure 6 shows the HPLC chromatograms of reaction mixtures obtained from phenolic α -O-4-type model compound **10** as treated in supercritical methanol at 270°C/27 MPa. Model compound **10** disappeared completely after 1 min of treatment. The products observed at the retention times of 23.1 and 24.1 min were identified to be guaiacol (**1**) and 2-methoxy-4-(methoxymethyl)-phenol (**18**), respectively, after comparing them with the authentic samples. These compounds (**1** and **18**) were stable in supercritical methanol even after 10 min of treatment at 270°C/27 MPa. This reaction occurred at lower temperatures as well. For example, even in methanol at 70°C model compound **10** disappeared completely after 10 min of treatment, and guaiacol (**1**) and 2-methoxy-4-(methoxymethyl)-phenol (**18**) were produced.

Figure 7 shows the HPLC chromatograms of nonphenolic α -O-4-type model compound **11** treated in super-

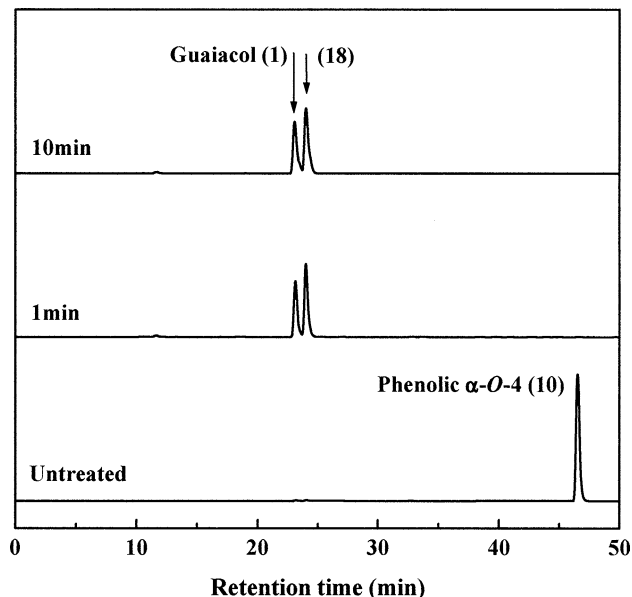


Fig. 6. HPLC chromatograms of phenolic α -O-4 (**10**) lignin model compound treated in supercritical methanol at 270°C/27 MPa. (Column STR ODS-II; detector UV₂₈₀; eluent MeOH/H₂O, 20/80 → 60/40 → 100/0 (0 → 40 → 50 min); flow rate 0.8 ml/min)

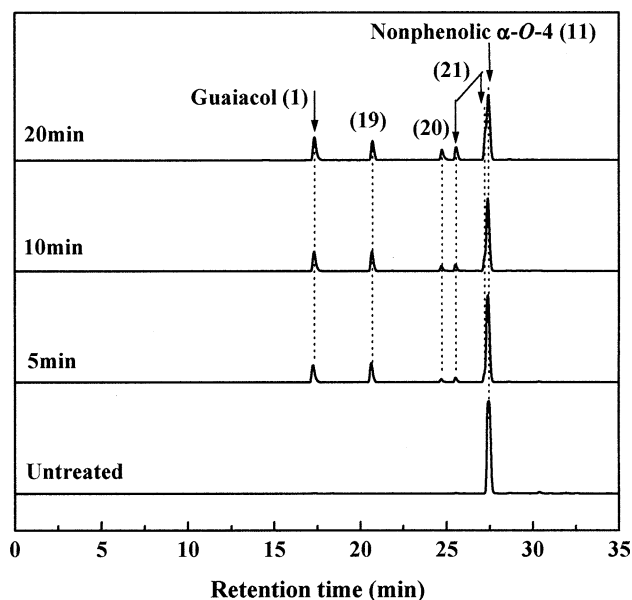


Fig. 7. HPLC chromatograms of nonphenolic α -O-4 (**11**) lignin model compound treated in supercritical methanol at 270°C/27 MPa. (Column STR ODS-II; detector UV₂₈₀; eluent MeOH/H₂O, 20/80 → 100/0 (0 → 30 min); flow rate 0.8 ml/min)

critical methanol at 270°C/27 MPa. As the reaction proceeded, model compound **11** decreased, whereas guaiacol (**1**) and compounds **19**, **20**, and **21** were produced. Compounds **19** and **20** were identified to be 1,2-dimethoxy-4-(methoxymethyl)-benzene and 3,4-dimethoxytoluene, respectively, by comparing them with authentic samples. Other compounds **21** were also identified to be isomers of 1-guaiacyl-1-veratrylmethane by $^1\text{H-NMR}$ analysis.

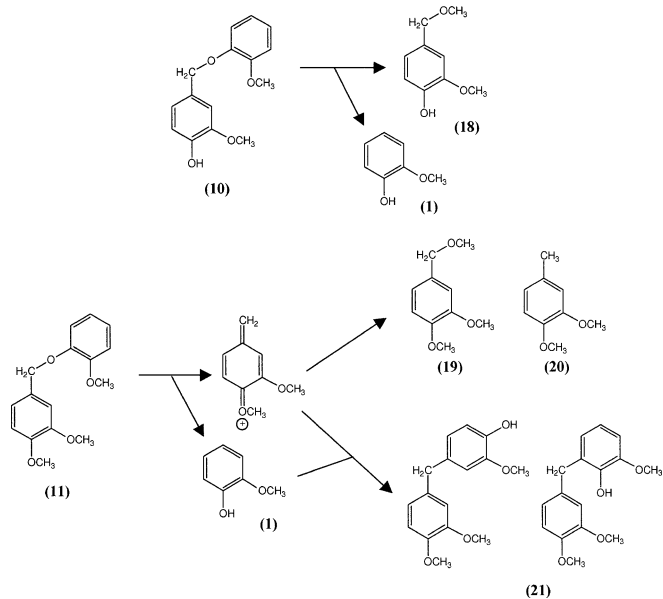


Fig. 8. Degradation pathways of phenolic and nonphenolic α -O-4 model compounds **10** and **11** as treated in supercritical methanol

Consequently, both phenolic and nonphenolic α -O-4 linkages in lignin can be cleaved in supercritical methanol. Finally, the reactions of phenolic and nonphenolic α -O-4 model compounds take place as shown in the proposed reaction pathways in Fig. 8. Phenolic model compound **10** is converted rapidly to guaiacol (**1**) and a quinonemethide-type intermediate by cleavage of the α -ether linkage; 2-methoxy-4-(methoxymethyl)-phenol (**18**) is then produced from the quinonemethide by methanolysis. These compounds (**1** and **18**) are stable in supercritical methanol. On the other hand, nonphenolic model compound **11** is converted to guaiacol (**1**) and the quinonemethide-type intermediate; the quinonemethide is then converted to 1,2-dimethoxy-4-(methoxymethyl)-benzene (**19**) in a manner similar to that described above. Concomitantly, the diphenylmethane-type compounds (**21**) are produced by transformation of nonphenolic α -O-4 model compound **11**. The quinonemethide-type intermediate from nonphenolic compound **11** is supposed to be more reactive than that from phenolic compound **10**; therefore, part of the former intermediate is more likely to react with guaiacol to produce diphenylmethanes.

On the other hand, it was confirmed that 3,4-dimethoxytoluene (**20**) was produced from 1,2-dimethoxy-4-(methoxymethyl)-benzene (**19**) by treating the isolated compound (**19**) in supercritical methanol. Similarly, compound **20** is expected to be directly produced from model compound **11** by cleavage of the α -ether linkage, but this point has not yet been clarified.

Kinetics of cleavage in ether linkages of lignin

Based on the results obtained above, it is concluded that the β -O-4 and α -O-4 linkages of lignin are cleaved in supercritical methanol, whereas the 5-5 and β -1 linkages are

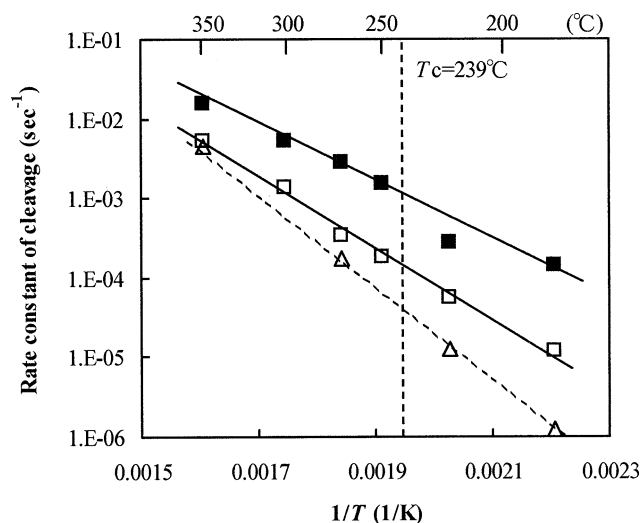


Fig. 9. Arrhenius plots for rate constants of cleavage in β -ether and α -ether linkages. Filled squares, phenolic β -O-4 (**8**); open squares, nonphenolic β -O-4 (**9**); open triangles, nonphenolic α -O-4 (**11**)

stable. In addition, it was found that the cleavages of ether linkages of β -O-4 and α -O-4 structures resulted in the formation of guaiacol. Therefore, the cleavage velocities of these ether linkages were evaluated based on the amount of guaiacol produced by supercritical methanol treatment.

Assuming that the formation of guaiacol was a pseudo-first-order reaction, the rate constant (κ) of cleavage was defined by the following equation:

$$G = [1 - \exp(-\kappa t)] \times 100 \text{ (mol\%)}$$

where G is the amount of guaiacol formed at an early stage of the reaction as a measure of the cleavage of the ether linkages, because guaiacol slightly decreased as the supercritical treatment proceeded.

Figure 9 shows the obtained Arrhenius plots for rate constants of cleavage in various ether linkages. The rate constants of phenolic and nonphenolic β -O-4 linkages were faster than that of the nonphenolic α -O-4 linkage, and the rate constant of the phenolic β -O-4 linkage was faster than that of the nonphenolic β -O-4 linkage at every treatment temperature. Moreover, the rate constant for all linkages continuously and linearly changed on the Arrhenius plot between 180°C and 350°C. Thus, there were no peculiar changes in the rate constant even if the methanol changed to the supercritical state from the subcritical state. On the other hand, activation energies (E_a) for cleavages of phenolic β -O-4, nonphenolic β -O-4, and nonphenolic α -O-4 linkages were 68.9, 85.2, and 113 kJ/mol, respectively. Therefore, the rate constants for the nonphenolic β -O-4 and α -O-4 linkages are closer to that of the phenolic β -O-4 linkage at markedly elevated temperatures.

Reactivity of various linkages of lignin

Table 2 summarizes the lignin model compound study of the various linkages of lignin in supercritical methanol

Table 2. Cleavage rate, rate constant of cleavage, and activation energy in the linkages of the lignin model compounds in supercritical methanol at 270°C/27MPa

Parameter	Condensed linkage			Ether linkage			
	5-5		β -1	β -O-4		α -O-4	
	Ph	Non-Ph	Non-Ph	Ph	Non-Ph	Ph	Non-Ph
Cleavage rate	L	L	L	H	H	ExH	H
κ (10^{-3}s^{-1})	–	–	–	2.8	0.34	NM	0.17
E_a (kJ/mol)	–	–	–	68.9	85.2	NM	113

κ , rate constant of cleavage; E_a , activation energy; L, low; H, high; ExH, extremely high; NM, not measurable because of high reactivity; Ph, phenolic compounds; Non-Ph, nonphenolic compounds

270°C/27MPa. It is apparent that the condensed linkages of the 5-5 and β -1 structures are stable in supercritical methanol, whereas the ether linkages of the β -O-4 and α -O-4 structures are readily cleaved. Therefore, the lignin in wood must be depolymerized in supercritical methanol mainly by cleavage of the ether linkages of lignin.

Reactivity of lignin in wood

The decomposition of lignin in wood has also been studied kinetically in another work,⁶ which estimated the decomposition rate constant of lignin by assuming that the change in the methanol-soluble portion follows pseudo-first-order kinetics. As a result, the decomposition rate constants of lignin in Japanese beech (*buna*, *Fagus crenata*) and Japanese cedar (*sugi*, *Cryptomeria japonica*) were reported to be $5.0 \times 10^{-3}\text{s}^{-1}$ and $0.31 \times 10^{-3}\text{s}^{-1}$, respectively, at 270°C/27MPa.⁶ Thus, the decomposition rate constant for lignin in beech was larger than that in cedar. It was further indicated that the observed differences originated mainly from differences in the intrinsic properties in lignin structures of softwood and hardwood, as shown in Table 1. Hardwood lignin, which has more ether linkages, is more readily depolymerized and liquefied in supercritical methanol than softwood lignin. On the other hand, activation energies for decomposition of lignin in beech and cedar woods were 88.4 and 62.4 kJ/mol, respectively, at relatively low temperatures (180–250°C). These values are close to the rate constants for β -O-4 linkages (Table 2): for phenolic compounds 68.9 kJ/mol and for nonphenolic compounds 85.2 kJ/mol. It is therefore indicated that the β -O-4 linkages, which are the dominant linkages of lignin, mainly contribute to depolymerization of lignin in wood. This finding further suggests that the remaining lower-molecular-weight products of lignin are rich in condensed linkages, as demonstrated by Minami and Saka⁶ with their alkaline nitrobenzene oxidation analysis.

Conclusions

The reactivity of lignin was investigated in this study, focusing on the 5-5, β -1, β -O-4, and α -O-4 linkages of lignin using

some lignin model compounds. The results showed that the 5-5 and β -1 linkages were stable in supercritical methanol, whereas both β -O-4 and α -O-4 linkages were cleaved rapidly. Therefore, it is suggested that supercritical methanol treatment effectively depolymerizes lignin to lower-molecular-weight products by cleaving the ether linkages of lignin.

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