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Reactivity of Lignin with Different Composition of Aromatic Syringyl/Guaiacyl Structures and *Erythro*/*Threo* Side Chain Structures in *β*-*O*-4 Type during Alkaline Delignification: As a Basis for the Different Degradability of Hardwood and Softwood Lignin

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ABSTRACT: The reactivity of lignin during alkaline delignification was quantitatively investigated focusing on the effect of the structural differences between syringyl and guaiacyl aromatic nuclei and between *erythro* and *threo* in the side chain of *β*-*O*-4 type lignin substructure on the *β*-*O*-4 bond cleavage rate. It was known that the ratio of this reaction rate of the *erythro* to *threo* isomers of the dimeric *β*-*O*-4 type lignin model compound with two guaiacyl aromatic nuclei was ca. 4. However, the presence of a syringyl nucleus strongly influenced the rate, and the ratio of the syringyl type analogue was in the range between 2.7 and 8.0 depending on the reaction temperature. The effect of syringyl nucleus on the enhancement of the reaction rate appeared to be greater when the syringyl nucleus consists of the cleaving ether bond rather than being a member of the carbon framework.

KEYWORDS: *alkaline hydrolysis, alkyl-aryl ether, cooking, configuration, pulping*

INTRODUCTION

Lignin, together with cellulose and hemicellulose, is one of the major components in the development of a wood cell wall. A unit of lignin consists of an aromatic nucleus and a propane side chain (Figure 1). The lignin in softwood (gymnosperm) contains only a guaiacyl aromatic nucleus, while the lignin in hardwood (angiosperm) is constituted of both guaiacyl and syringyl aromatic nuclei in various proportions depending on the wood species (Figure 1). Furthermore, the chemical reactivity of syringyl lignin should be different from that of guaiacyl lignin, but the difference is not clarified yet quantitatively.

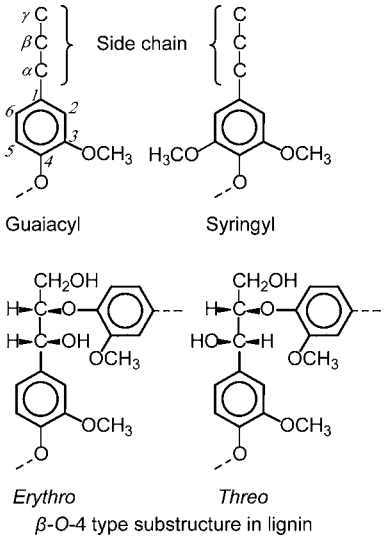

Figure 1. Schematic description of the guaiacyl and syringyl lignin units and the *β*-*O*-4 type lignin substructure.

The most abundant lignin substructure is the *β*-*O*-4 type (see Figure 1 for the nomenclature). There are both *erythro* and *threo* stereostructures in the side chain portion of the *β*-*O*-4 type substructure (Figure 1), and each stereoisomer has a pair of enantiomers. It has been reported that there is a wide variation in the ratios obtained between the syringyl and guaiacyl nuclei present in lignin (syringyl/guaiacyl ratio) and between the *erythro* and *threo* stereostructures present in the side chains of *β*-*O*-4 type substructures (*erythro*/*threo* ratio) depending on the wood species. Furthermore, a positive correlation between these ratios can be determined from the lignin structural analyses of various wood species.[1] In the alkaline delignification, for example, alkaline pulping process, it is empirically well-known that hardwoods containing syringyl aromatic nuclei are delignified more readily than softwoods, and the efficiency of delignification depends on the wood species particularly for hardwoods. Considering the above findings and this empirical information, it becomes clear that a quantitative understanding of the difference in the chemical reactivity between *β*-*O*-4 substructures with various syringyl/guaiacyl and *erythro*/*threo* ratios in alkaline delignification processes is necessary.

The neighboring group participation mechanism is the main reaction mode for the cleavage of the nonphenolic type *β*-*O*-4 linkage (Figure 2) and is accompanied by delignification under alkaline conditions.[2] Miksche[3] and Tsutsumi et al.[4] have reported that the *β*-*O*-4 bonds of the *erythro* isomers of dimeric nonphenolic guaiacyl and syringyl *β*-*O*-4 type model compounds are cleaved faster than those of the *threo* isomers under alkaline conditions. Criss et al. have shown a similar result using a guaiacyl

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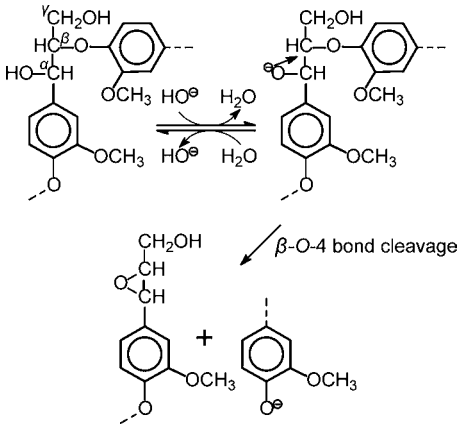

Figure 2. Neighboring group participation mechanism for the *β-O*-4 bond cleavage of nonphenolic lignin substructures.

type analogue.[5] Sugimoto et al. found that *β-O*-4 type lignin substructures with the *erythro* side chain structure are removed more rapidly than those with *threo* side chains during alkaline delignification of wood.[6] It is also empirically known, as described above, that hardwoods are delignified more easily than softwoods in alkaline delignifiation processes. This empirical information suggests that the *β-O*-4 bond of syringyl type lignin is chemically cleaved more easily than that of guaiacyl type lignin.

There are limitations to the application of this existing knowledge for understanding the reactivity of nonphenolic *β-O*-4 structures with different aromatic structures and stereoconfigurations, because the experimental conditions and methods for quantification applied in these literature reports are little varied and inconsistent with one another. In addition, the variety of the model compounds studied in these investigations is not great enough to provide sufficient information. On the basis of these previous studies, however, it is clear that a quantitative examination of the differences in the chemical reactivities of *β-O*-4 type substructures with different syringyl/guaiacyl ratios and *erythro*/*threo* ratios during alkaline delignification is needed. In this study, the difference in the reactivity of different types of nonphenolic *β-O*-4 structures was quantitatively examined under widely varying reaction conditions using dimeric nonphenolic *β-O*-4 type lignin model compounds, each of which has guaiacyl and/or syringyl nuclei and *erythro* or *threo* side chain structure.

MATERIALS AND METHODS

Materials. All chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The dimeric nonphenolic *β-O*-4 type lignin model compounds 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (GG), 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-propane-1,3-diol (GS), 2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol (SG), and 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol (SS) were synthesized according to the method of Adler et al.[7] The structures of these model compounds are shown in Figure 3. The two aromatic nuclei in each model compound are labeled as the A- and B-rings (Figure 3). The abbreviation of the model compounds is based on the type (guaiacyl and syringyl) of A- and B-rings. These compounds were obtained as mixtures of the *erythro* and *threo* isomers, which were separated from each other via anion exchange chromatography after being converted into the boron complexes in an aqueous ethanol solution containing potassium borate.[8−10] Each of the isomers of these model compounds was

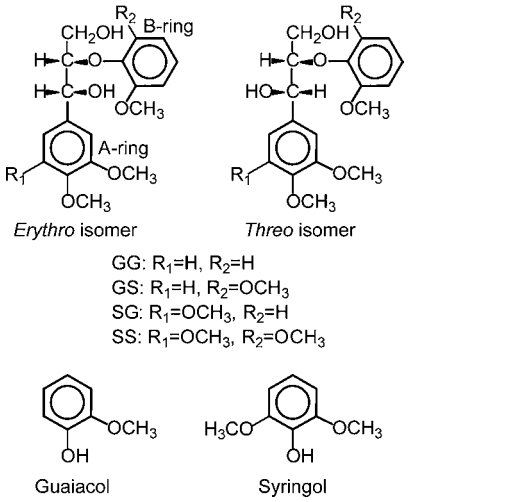

Figure 3. Chemical structures of the model compounds used in this study and the reaction products derived from the B-rings. The definition of the aromatic A- and B-rings is also described.

subjected to ozonation in order to determine the *erythro* or *threo* stereoconfiguration.[11] Erythronic and threonic acids were obtained from ozonation of the *erythro* and *threo* isomers of the model compounds, respectively. The ^{1}H and ^{13}C NMR spectra (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) of all model compounds were recorded using acetone-d_6 and aliquots of D_2O as the solvents. The *erythro* isomer of GG is as follows: ^{1}H NMR δ 3.68 (dd, 1H, J = 3.8, J = 12.0, Cγ-H_a), 3.74, 3.75, 3.78 (s, 9H, −OCH_3), 3.81 (dd, 1H, J = 5.5, J = 12.0, Cγ-H_b), 4.33 (m, 1H, Cβ-H), 4.89 (d, 1H, J = 5.5, Cα-H), 6.77−7.09 (m, 7H, aromatic); ^{13}C NMR δ 55.9, 56.0, 56.2 (−OCH_3), 61.4 (Cγ), 73.3 (Cα), 85.7 (Cβ), 111.7, 112.0, 113.3, 118.5, 112.0, 121.8, 122.9, 135.3, 148.7, 149.3, 149.7, 151.4 (aromatic). The *threo* isomer of GG is as follows: ^{1}H NMR δ 3.47 (dd, 1H, J = 5.5, J = 11.5, Cγ-H_a), 3.71 (dd, 1H, J = 4.5, J = 11.5, Cγ-H_b), 3.73, 3.74, 3.82 (s, 9H, −OCH_3), 4.30 (m, 1H, Cβ-H), 4.92 (d, 1H, J = 5.0, Cα-H), 6.78−7.09 (m, 7H, aromatic); ^{13}C NMR δ 55.8, 55.9, 56.1 (−OCH_3), 61.2 (Cγ), 73.0 (Cα), 86.4 (Cβ), 111.4, 111.9, 113.1, 118.0, 119.8, 121.8, 122.8, 134.8, 149.0, 149.2, 149.6, 150.9 (aromatic). The *erythro* isomer of GS is as follows: ^{1}H NMR δ 3.42 (dd, 1H, J = 3.5, J = 12.0, Cγ-H_a), 3.74, 3.76 (s, 6H, −OCH_3), 3.78 (dd, 1H, J = 5.5, J = 12.0, Cγ-H_b), 3.79 (s, 6H, −OCH_3), 4.17 (m, 1H, Cβ-H), 4.95 (d, 1H, J = 5.0, Cα-H), 6.67−7.02 (m, 6H, aromatic); ^{13}C NMR δ 55.9, 55.9, 56.4 (−OCH_3), 60.6 (Cγ), 72.9 (Cα), 87.1 (Cβ), 106.4, 111.2, 112.0, 119.7, 124.8, 134.8, 136.3, 149.1, 149.6, 154.1 (aromatic). The *threo* isomer of GS is as follows: ^{1}H NMR δ 3.26 (dd, 1H, J = 3.3, J = 12.3, Cγ-H_a), 3.65 (dd, 1H, J = 3.8, J = 12.3, Cγ-H_b), 3.75, 3.75, 3.84 (s, 12H, −OCH_3), 3.96 (m, 1H, Cβ-H), 5.00 (d, 1H, J = 7.0, Cα-H), 6.86−7.05 (m, 6H, aromatic); ^{13}C NMR δ 55.9, 55.9, 56.4 (−OCH_3), 61.0 (Cγ), 73.5 (Cα), 89.0 (Cβ), 106.3, 111.6, 112.1, 120.1, 124.9, 134.6, 136.9, 149.4, 149.7, 153.9 (aromatic). The *erythro* isomer of SG is as follows: ^{1}H NMR δ 3.64 (s, 3H, −OCH_3), 3.72 (dd, 1H, J = 3.8, J = 12.0, Cγ-H_a), 3.75, 3.77 (s, 9H, −OCH_3), 3.83 (dd, 1H, J = 5.5, J = 12.0, Cγ-H_b), 4.36 (m, 1H, Cβ-H), 4.88 (d, 1H, J = 5.0, Cα-H), 6.76−6.93 (m, 6H, aromatic); ^{13}C NMR δ 56.1, 56.2, 60.4 (−OCH_3), 61.4 (Cγ), 73.4 (Cα), 84.9 (Cβ), 105.1, 113.1, 117.8, 121.7, 122.7, 137.8, 138.3, 148.5, 151.0, 153.6 (aromatic). The *threo* isomer of SG is as follows: ^{1}H NMR δ 3.52 (dd, 1H, J = 5.5, J = 12.0, Cγ-H_a), 3.69 (s, 3H, −OCH_3), 3.72 (dd, 1H, J = 4.0, J = 12.0, Cγ-H_b), 3.80, 3.86 (s, 9H, −OCH_3), 4.26 (m, 1H, Cβ-H), 4.92 (d, 1H, J = 5.5, Cα-H), 6.80−7.15 (m, 6H, aromatic); ^{13}C NMR δ 56.1, 56.2, 60.4 (−OCH_3), 61.3 (Cγ), 73.1 (Cα), 86.0 (Cβ), 104.9, 113.1, 117.9, 121.8, 122.7, 137.9, 138.1, 149.0, 150.9, 153.7 (aromatic). The *erythro* isomer of SS is as follows: ^{1}H NMR δ 3.43 (dd, 1H, J = 3.8, J = 11.6, Cγ-H_a), 3.67, 3.78, 3.81 (s, 15H, −OCH_3), 3.85 (dd, 1H, J = 5.5, J = 11.6, Cγ-H_b), 4.18 (m, 1H, Cβ-H), 4.96 (d, 1H, J = 4.5, Cα-H), 6.68−7.01 (m, 5H, aromatic); ^{13}C NMR δ 56.2, 56.4, 60.5 (−OCH_3), 60.6 (Cγ), 73.2 (Cα), 87.0 (Cβ), 104.7, 106.3, 124.8, 136.2, 137.7, 138.0, 153.6, 154.1 (aromatic). The *threo* isomer of SS is as

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follows: ^{1}H NMR δ 3.34 (dd, 1H, J = 3.8, J = 12.0, Cγ-H_a), 3.66 (s, 3H, $-OCH_3$), 3.69 (dd, 1H, J = 4.3, J = 12.0, Cγ-H_b), 3.77, 3.84 (s, 12H, $-OCH_3$), 4.06 (m, 1H, Cβ-H), 4.99 (d, 1H, J = 6.5, Cα-H), 6.67−6.99 (m, 5H, aromatic); ^{13}C NMR δ 56.2, 56.4, 60.4 ($-OCH_3$), 61.2 (Cγ), 73.5 (Cα), 88.4 (Cβ), 104.9, 106.3, 124.8, 136.7, 137.8, 137.8, 153.6, 153.8 (aromatic).

Reaction under Alkaline Conditions. One of the *erythro* or *threo* isomers of GG, GS, SG, or SS was dissolved in a sodium hydroxide solution (1.0 mol L^{-1}) at 40−70 °C for 3−7 h. The concentration of the model compounds was adjusted to 3.0 mmol L^{-1}, except for the *threo* isomer of GS, whose concentration was 1.0 mmol L^{-1} because of its low solubility. All of the water used in this study was deionized and degassed before use.

The prepared reaction solution (5.0 mL) was transferred into a stainless steal vessel (10 mL, Taiatsu Techno Corp., Tokyo, Japan), and nitrogen was bubbled through it. After the vessel was covered with a lid, it was immersed in an oil bath at 130 °C, 140 °C, 150 °C, 160 °C, or 170 °C, and reacted. After the reaction was complete, the vessel was immediately immersed in an ice/water bath, the lid was removed, and acetic acid was added to neutralize the solution.

Six vessels were prepared for conducting the reaction of each model compound at a prescribed temperature for six different reaction periods, and all the vessels were immersed together in an oil bath in order to perform the reactions together at the temperature. The reaction of each compound was conducted at 3 or 4 different temperatures. All of the reactions were repeated at least three times to confirm reproducibility.

Quantification of the Model Compounds and the Reaction Products. A methanol solution of an internal standard compound was added to the neutralized reaction mixture followed by filtration, and the resulting mixture was analyzed by HPLC (LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (280 nm, Shimadzu Co.) to quantify the residual model compound and the reaction product that originated from the B-ring of the model compound (2-methoxyphenol (guaiacol) from GG and SG, or 2,6-dimethoxyphenol (syringol) from GS and SS) (Figure 3).

The conditions for the HPLC analysis were as follows: column, Luna 5u C18(2) 100 A (150 mm × 4.6 mm, Phenomenex, Inc., Torrance, CA, USA); oven temperature, 40 °C; flow rate, 1.4 mL min^{-1} (1.3 mL min^{-1} for the *threo* isomer of SG); solvent system for the *erythro* isomer of GG, gradient CH_3OH/H_2O (v/v) from 10/90 to 28/72 for 7 min, gradient to 17/83 immediately, gradient to 28/72 for 13 min, gradient to 25/75 immediately, gradient to 75/25 for 25 min, gradient to 10/90 for 5 min and maintained for 10 min, total time 60 min; solvent system for the *threo* isomer of GG, gradient from 10/90 to 28/72 for 7 min, gradient to 17/83 immediately, gradient to 28/72 for 13 min, gradient to 25/75 immediately, gradient to 50/50 for 25 min, gradient to 75/25 immediately and maintained for 5 min, total time 60 min; solvent system for the *erythro* and *threo* isomers of GS, gradient from 15/85 to 25/75 for 7.5 min, gradient to 44/56 for 27.5 min and maintained for 5 min, total time 40 min; solvent system for the *erythro* isomer of SG, gradient from 3/97 to 23/77 for 20 min, gradient to 50/50 for 20 min and maintained for 10 min, total time 50 min; solvent system for the *threo* isomer of SG: maintained 25/75 for 7.5 min, gradient to 50/50 for 12.5 min and maintained for 10 min, total time 30 min; solvent system for the *erythro* and *threo* isomers of SS, gradient from 15/85 to 25/75 for 6.5 min, gradient to 48/52 for 28.5 min and maintained for 5 min, total time 40 min.

RESULTS AND DISCUSSION

General Description. In all previous literature reports regarding the investigation of alkaline delignification, organic cosolvents were used to completely dissolve nonphenolic lignin model compounds. It has been suggested, however, that organic cosolvents affect the β-*O*-4 bond cleavage rate of these types of model compounds under alkaline delignification conditions.[12] In this study, all model compounds were completely dissolved in the alkaline solution without the use of an organic cosolvent, as described above. Furthermore, it was confirmed that the model compounds were not structurally altered during dissolution and the solubilization was complete, when the HPLC chromatograms of the alkaline solutions were compared to those of the corresponding methanol solutions that were prepared using the same concentration of each model compound and internal standard compound. These efforts made it possible to examine the reactivity of all of the model compounds without any influence of organic cosolvents.

The behavior of the alkaline hydrolysis products under the reaction conditions was also studied. When a sodium hydroxide solution (1 mol L^{-1}) of guaiacol or syringol (3 mmol L^{-1}) was heated at 170 °C for 90 min, the residual yield obtained was 99% and 90%, respectively, if the air was displaced by bubbling nitrogen through the solution before heating. If the reaction was performed without displacing the air, the residual yield obtained was approximately 40% and 10%, respectively, suggesting that the guaiacol and syringol are oxidized by oxygen. These results indicate that the guaiacol and syringol produced in the reactions of the model compounds are not degraded by alkaline-induced reactions, and that their degradations by oxygen oxidation can be prevented if the air is replaced with nitrogen.

It is important to note that, because it took several minutes for the reaction solution to reach the target temperature after the reaction vessel was immersed in the oil bath, the logarithmic plots for the disappearance of the model compounds deviated from a straight line in the initial phase, as illustrated in Figure 4, which shows the plot of the disappearance of one of the model compounds. However, these deviations did not influence the calculation of the appropriate pseudo-first-order reaction rate constants, which were determined from the slopes of the straight lines.

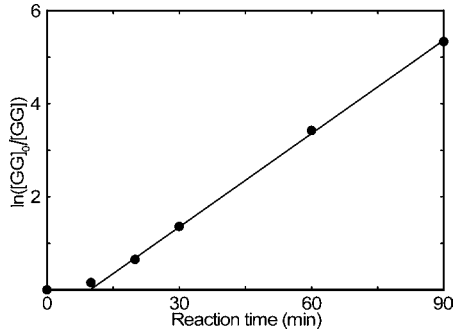

Figure 4. Logarithmic plot of the disappearance of the *erythro* isomer of GG at 160 °C as a function of time.

The disappearance of all compounds was approximated by pseudo-first-order kinetics, as representatively shown in Figure 4. Table 1 lists the following: the pseudo-first-order reaction rate constants, k_{obs}, the Arrhenius activation energies, E_a, and the Arrhenius frequency factors, A, for all compounds. Figure 5 illustrates the Arrhenius plots for all compounds, which afforded the values for E_a and A. Because the reactions were conducted at different temperatures depending on the reactivity of each model compound, it was not easy to compare the reactivities of the model compounds with each other. Therefore, the rate constants, k, at 130 °C, 140 °C, 150 °C, 160 °C, and 170 °C were calculated for each model compound based on the values of E_a and A (Table 2).

Effect of *Erythro* and *Threo* Structures on the Reactivity. The *erythro* isomers degraded faster than the corresponding *threo* isomers in all compounds, which is in accordance with the

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Table 1. Observed Pseudo-First-Order Rate Constants, k_{obs}, Arrhenius Activation Energies, E_a, and Arrhenius Frequency Factors, A

	GG		GS		SG		SS	
	erythro	*threo*	*erythro*	*threo*	*erythro*	*threo*	*erythro*	*threo*
k_{obs}[a]	140 °C, 11.5	150 °C, 6.97	130 °C, 20.6	140 °C, 8.40	140 °C, 16.4	140 °C, 3.30	130 °C, 32.3	140 °C, 11.1
	150 °C, 30.2	160 °C, 16.7	140 °C, 47.3	150 °C, 19.5	150 °C, 37.2	150 °C, 7.86	140 °C, 72.1	150 °C, 36.6
	160 °C, 65.7	170 °C, 38.4	150 °C, 95.0	160 °C, 42.7	160 °C, 83.2	160 °C, 18.2	150 °C, 126	160 °C, 62.8
						170 °C, 40.6	160 °C, 205	
E_a[b]	130	133	108	121	121	129	88.6	129
A[c]	294	166	233	1.64	30.2	60.5	0.0108	217

[a]Units: $\times 10^{-3}$ min^{-1}. [b]Units: kJ mol^{-1}. [c]Units: $\times 10^{12}$ min^{-1}.

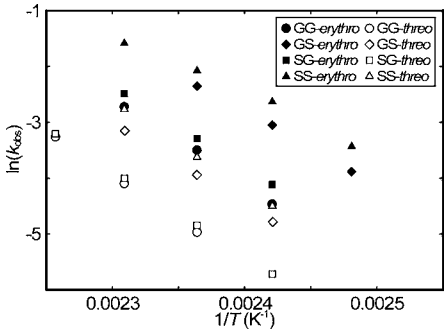

Figure 5. Arrhenius plots for all of the compounds used in this study.

existing knowledge,[3−5] although the difference between the *erythro* and *threo* isomers was dependent on the model compound. The ratio of the k value of the *erythro* isomer to that of the *threo* isomer ($k_{erythro}/k_{threo}$) is 4.0−4.3 for GG, 4.3−6.0 for GS, 4.3−5.4 for SG, and 2.7−8.0 for SS, depending on the temperature. The ratios always decreased with an increase in the reaction temperature for all compounds. These results indicate that the difference in the reactivity between the *erythro* and *threo* isomers is dependent not only on the aromatic nucleus structure (guaiacyl or syringyl) but also on the temperature. The ratio for GG has been reported to be 3.7 and 4.1 by Miksche[3] and Criss et al.,[5] respectively. On the basis of these values, the approximate value, 4, has generally been accepted as the ratio for $k_{erythro}/k_{threo}$. The ratio for GG observed in this study is close to this generally accepted value, and seems to be rather independent of the temperature. It can be observed from these results, however, that the presence of the syringyl nucleus affects the ratio and makes the ratio susceptible to temperature variation. It should particularly be noted that the ratios for SS are 8.0 and 2.7 at 130 and 170 °C, respectively, which are rather different from the generally accepted value and vary widely with temperature.

Effect of Aromatic Nucleus Structure on the Reactivity. The presence of the syringyl nucleus enhanced the *β-O*-4 bond cleavage regardless of which nucleus, the A- and/or B-ring, was syringyl because GG always degraded more slowly than GS, SG, or SS for both the *erythro* and *threo* isomers. Both isomers of GS degraded rapidly and to a relatively greater extent than the corresponding isomers of GG at all temperatures, while both isomers of SG degraded only slightly faster than the corresponding isomers of GG. These results indicate that the effect of the presence of syringyl nucleus appears more strongly in the B-ring than in the A-ring. To investigate the effect of the presence of the syringyl nucleus in the B-ring position on the reaction rate, the k values for the reactions of the *erythro* isomers of GG and GS ($k_{GS\text{-}erythro}/k_{GG\text{-}erythro}$), and for the reactions of these *threo* isomers ($k_{GS\text{-}threo}/k_{GG\text{-}threo}$), were compared, and the ratios obtained are 2.6−4.5 and 2.4−3.3, respectively, depending on the temperature. For the reactions of the *erythro* and *threo* isomers of GG and SG, the ratios obtained are as follows: 1.2−1.5 and 1.1−1.2, respectively ($k_{SG\text{-}erythro}/k_{GG\text{-}erythro}$, $k_{SG\text{-}threo}/k_{GG\text{-}threo}$). For the reactions of the *erythro* and *threo* isomers of GG and SS, the ratios obtained are as follows: 2.5−7.5 and 3.6−4.1, respectively ($k_{SS\text{-}erythro}/k_{GG\text{-}erythro}$, $k_{SS\text{-}threo}/k_{GG\text{-}threo}$). The presence of the syringyl nuclei in both the A- and B-ring positions might not result in synergistic effects at most temperatures. The ratios always decrease with an increase in the temperature for all of the compounds and are larger for reactions of the *erythro* isomers compared to those for reactions of the *threo* isomers, except for SS and GG, where the values of $k_{SS\text{-}erythro}/k_{GG\text{-}erythro}$ are smaller than the values of $k_{SS\text{-}threo}/k_{GG\text{-}threo}$ at 160 and 170 °C. This result suggests that, in these cases, the presence of the syringyl nucleus enhances the reactions of the *erythro* isomers more strongly than those of the *threo* isomers. The above-mentioned result cannot be currently explained.

The difference in values of k obtained for the reactions of the *erythro* isomers of GS and SS decreases with an increase in the temperature. The value of k obtained for the reaction of the *erythro* GS finally exceeds that for the reaction of the *erythro* SS at 170 °C, which lies within the range of temperatures used in common alkaline delignification. Similarly, the difference in the rate constants for the reactions of the *erythro* and *threo* isomers of SS decreases with an increase in the temperature. These

Table 2. Rate Constants, k,[a] That Are Calculated Based on the Arrhenius Parameters

	GG		GS		SG		SS	
	erythro	*threo*	*erythro*	*threo*	*erythro*	*threo*	*erythro*	*threo*
130 °C	4.63	1.07	20.9	3.51	6.80	1.31	34.7	4.37
140 °C	11.8	2.79	45.8	8.42	16.3	3.29	65.8	11.1
150 °C	28.8	6.96	96.7	19.4	37.5	7.90	121	26.9
160 °C	67.4	16.7	197	42.8	82.9	18.2	217	62.6
170 °C	152	38.4	389	91.5	177	40.5	378	140

[a]Units: $\times 10^{-3}$ min^{-1}.

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phenomena result from the extremely small values of E_a and A that are obtained for the reaction of the *erythro* SS. Furthermore these results suggest that temperature is potentially a more important process factor than generally considered.

On the Arrhenius Parameters. The presence of the syringyl nucleus in the *erythro* isomers seems to reduce the value of E_a, while the values of E_a for the *threo* isomers are similar in all model compounds. The presence of the syringyl nucleus in the B-ring position in comparison with the A-ring position seems to have a stronger effect on the reduction of the value of E_a. In addition, the value of E_a for the reaction of the *erythro* SS is rather small. These results suggest that the *erythro* isomers with syringyl nucleus are relatively unsusceptible to temperature variation and their degradations are already rapid at low temperature, because the E_a shows temperature dependence of reaction. No explanation for this phenomenon can currently be proposed. The values of E_a are rather similar to that reported by Ljunggren except those of the *erythro* GS and *erythro* SS.[13]

The presence of the syringyl nucleus in the *erythro* isomers also seems to decrease the value of A for the reactions that involve these compounds, while no obvious trend was observed in the values of A for the *threo* isomers. The value of A for the reaction of the *erythro* SS is significantly smaller than that of the others. Hence, there is no explanation for this behavior at this time.

Possible Mechanistic Considerations. It has been believed that the main reaction mode for nonphenolic β-*O*-4 bond cleavage under alkaline conditions is the neighboring group participation mechanism shown in Figure 2. The results obtained in this study suggest that the model compounds with a syringyl nucleus and/or the *erythro* type of side chain are relatively labile under alkaline conditions. Attempts to discuss the results in light of the mechanism shown in Figure 2 are described in this section, although it must be noted that there are other possible mechanisms that can also lead to these results.

An increase in the acidity of the α-hydroxyl group can change the lability of β-*O*-4 bond and result in an increase in the number of molecules carrying the α-alkoxide group. In this context, an additionally substituted methoxyl group at the position meta to the side chain in a syringyl type A-ring may increase the acidity of the α-hydroxyl group due to the positive σ value (+0.115, substituent constant in the Hammett equation) of the meta-substituted methoxyl group. This increase in acidity is a possible reason for the high lability of the model compounds with syringyl type A-rings (cf. GG vs SG). Schultz and Fisher have also suggested a similar explanation for the high lability of the model compounds with syringyl type A-rings in alkaline delignification.[14] No explanation has currently been proposed for the increase in the acidity of the α-hydroxyl group caused by the presence of a syringyl type B-ring or an *erythro* type side chain, although the additional methoxyl group might possibly play a role.

The lability of the model compounds under alkaline conditions can also be affected by the intramolecular substitution reaction of the α-alkoxide and the β-phenoxide (Figure 2) that occurs in the second step. It is generally known that the leaving ability of a leaving group increases with an increase in the acidity of the conjugate acid of the leaving group (decreasing pK_a value of the conjugate acid). In this context, there is no reasonable explanation for the rather high lability of the model compounds with syringyl type B-rings (cf. GG vs GS), because the pK_a values of syringol and guaiacol, the conjugate acids of the leaving groups, which are 9.98 and 9.93,[15] respectively, do not seem to be different from each other enough to result in the observed difference between the labilities of GG and GS. Increased steric interactions because of the presence of the additional methoxyl group in the syringyl type B-ring might possibly result in the high lability of the β-*O*-4 bond of GS. It is generally considered that the higher lability of the *erythro* isomers compared to the *threo* isomers results from the ease of the *erythro* isomer to reach conformations where the relationship between the α-alkoxide and β-phenoxide are antiperiplanar, and the intramolecular substitution reaction can progress, as shown in Figure 6.[16] An increase in the steric factor because of the presence of the additional methoxyl group in the syringyl type A-ring might

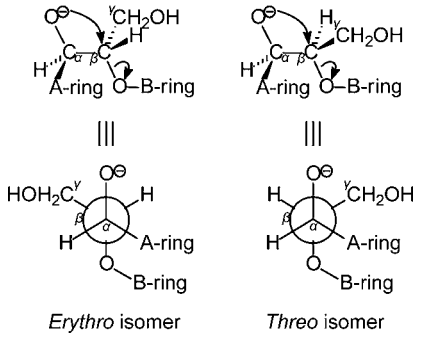

Figure 6. Display of the antiperiplanar conformation of the *erythro* and *threo* isomers, where the α-alkoxide group can intramolecularly attack the β-carbon from the direction opposite to the leaving phenoxide group that contains the B-ring. The lower drawings show the Newman projections for the antiperiplanar conformation.

increase the potential energy of the antiperiplanar conformation and consequently decrease the lability of the model compounds under alkaline pulping conditions; however, this effect is not in accordance with the obtained results (cf. GG vs SG).

It has also been suggested that the intramolecular substitution reaction of the γ-alkoxide and the β-phenoxide contributes to the β-*O*-4 bond cleavage[17] and this reaction mode is more frequent in the *erythro* than the *threo* isomers,[5] although this suggestion has not yet been confirmed and the contribution of the γ-hydroxyl group has been reported to be negligible.[3,18] It might be possible, however, that the model compounds that have an *erythro* isomer side chain with an α-alkoxide group can attain the relatively low energy cyclohexagonal chair conformation shown in Figure 7, where both the A-ring and the ether bond linked with the B-ring are in the equatorial position. In this conformation, the γ-alkoxide afforded by proton abstraction from the α-alkoxide

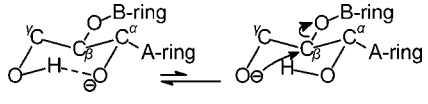

Figure 7. Depiction of the possible chair conformation for the *erythro* isomer, where the α-alkoxide group can abstract the γ-hydroxyl proton, followed by attack of the produced γ-alkoxide on the β-carbon from the direction opposite to the leaving phenoxide group that includes the B-ring.

can attack the β-carbon from the direction opposite to that of the B-ring phenoxide leaving group without any rearrangement of the conformation. Moreover, the formation of α- and γ-alkoxides via this cyclohexagonal conformation can possibly lower the acidities of these hydroxyl groups and can contribute to the faster β-*O*-4 bond cleavage in the *erythro* than the *threo* isomers.

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Finally, it is conclusively emphasized that the presence of syringyl nucleus significantly influences the delignification rate under alkaline conditions and the higher the content of syringyl nucleus and the *erythro* side chain structure in *β*-*O*-4 substructure in lignin, the easier the delignification under alkaline conditions. Incidentally, there is clearly a positively linear correlation between the contents of syringyl nucleus and the *erythro* side chain structure in *β*-*O*-4 substructure in lignin.[1]

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Notes

The authors declare no competing financial interest.

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