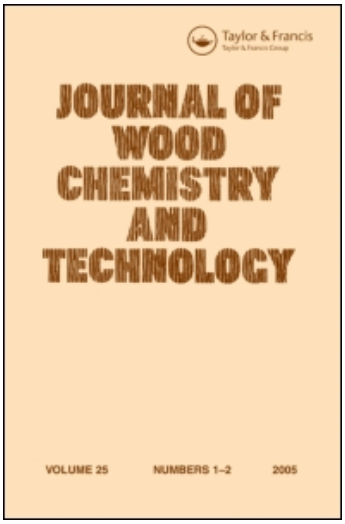


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Delignification Mechanism During High-Boiling Solvent Pulping. V. Reaction of Nonphenolic β-O-4 Model Compounds in the Presence and Absence of Glucose

Takao Kishimoto[a]; Yoshihiro Sano[a]
[a] Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan

Online publication date: 24 November 2003

To cite this Article Kishimoto, Takao and Sano, Yoshihiro(2003) 'Delignification Mechanism During High-Boiling Solvent Pulping. V. Reaction of Nonphenolic β-O-4 Model Compounds in the Presence and Absence of Glucose', Journal of Wood Chemistry and Technology, 23: 3, 279 — 292
To link to this Article: DOI: 10.1081/WCT-120026992
URL: http://dx.doi.org/10.1081/WCT-120026992

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 23, Nos. 3 & 4, pp. 279–292, 2003

Delignification Mechanism During High-Boiling Solvent Pulping. V. Reaction of Nonphenolic β-*O*-4 Model Compounds in the Presence and Absence of Glucose

Takao Kishimoto* and Yoshihiro Sano

Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan

ABSTRACT

Nonphenolic β-aryl ether model compounds, veratrylglycerol-β-guaiacyl ether (**1**) and its α-ethyl ether (**2**) were treated in 70% aqueous 1,4-butanediol solutions at 180°C. The reactivity of compound **2** was higher than that of compound **1**. Benzyl ether formation with 1,4-butanediol was observed. This suggests the high reactivity of lignin–carbohydrate complex with benzyl ether type under HBS pulping conditions. On the other hand, guaiacol was

*Correspondence: Takao Kishimoto, Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan; E-mail: takao@for.agr.hokvdai.ac.jp.

DOI: 10.1081/WCT-120026992 0277-3813 (Print); 1532-2319 (Online)

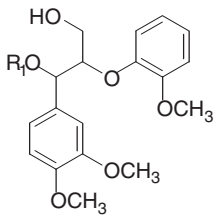
not detected in the reaction mixture. This indicates that β-aryl ether in nonphenolic structures is inert to HBS pulping conditions. Addition of glucose and acetic acid enhanced the benzyl ether formation with 1,4-butanediol, but not cleavage of β-aryl ethers.

INTRODUCTION

Solvent pulping is one of the alternatives to conventional kraft pulping. Lignin and other by-products can be recovered easily and used as raw materials. One of the drawbacks in some solvent pulping processes such as ethanol pulping is that only hardwoods can be used in the processes. However, both softwoods and hardwoods are pulped without any acid catalysts by use of aqueous high boiling solvents (HBS) such as aqueous 1,3-butanediol (b.p. 208°C) and aqueous 1,4-butanediol (b.p. 232°C).[1] The recovered solvent from spent liqor was even better pulping solvent than a fresh solvent even though it contains soluble lignins, sugars, and their modified compounds. The delignification rate of softwood was enhanced by a factor of 1.5 with the recovered solvent.[2] The improved effects by the recovered solvent can be attributed to reducing sugars which exist in the solvent.

In the previous investigations, a phenolic β-aryl ether model compound, guaiacyl glycerol-β-guaiacyl ether was treated with 70 wt% aqueous 1,4-butanediol solutions in the presence and absence of glucose in order to elucidate the effects of reducing sugars on the delignification mechanism during HBS pulping.[3] The model experiments suggest that reducing sugars in the recovered solvents may act as hydrogen donor and stabilize phenoxy radicals formed by homolytic cleavage of phenolic β-aryl ether bonds. The reducing sugar assisted phenolic β-aryl ether bond cleavage may also play a role in addition to homolysis of phenolic β-aryl ether in HBS pulping.

In this study, veratrylglycerol-β-guaiacyl ether (**1**) and its α-ethyl ether (**2**) were treated with 70 wt% aqueous 1,4-butanediol solutions at 180°C in the presence and absence of glucose in order to elucidate the reaction of nonphenolic β-aryl ethers during HBS pulping (Fig. 1). The attention was paid to the reactivity at α- and β-positions of the model compounds. The effects of addition of glucose on the reaction of nonphenolic β-aryl ethers were also investigated in order to understand the role of reducing sugars present in recovered HBS in more detail. Both erythro and threo forms of model compounds were determined separately by high performance liquid chromatography. Reaction products



1: R_1 = H (*erythro*/*threo*)
2: R_1 = CH_2CH_3 (*erythro*/*threo*)
3: R_1 = $CH_2CH_2CH_2CH_2OH$ (*erythro*/*threo*)
4: R_1 = CH_3 (*erythro*/*threo*)

Figure 1. Nonphenolic lignin model compounds.

were isolated and identified by comparison with synthesized model compounds.

EXPERIMENTAL

General

^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AMX500 FT-NMR (500 MHz) spectrometer, or JEOL JNM EX-270 FT-NMR (270 MHz) spectrometer in chloroform-*d* or dimethylsulfoxide-d_6 with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (J) are given in δ-values (ppm) and Hz, respectively. The standard work-up procedure included diluting with an ethyl acetate, washing with aq. $NaHCO_3$, and a brine, drying over Na_2SO_4 and evaporating in vacuo.

Syntheses of Lignin Model Compounds and Authentic Samples

A mixture of erythro and threo forms of veratrylglycerol-β-guaiacyl ether (**1**) was synthesized by the modified method of Adler et al.[4] Compound **2** was synthesized from compound **1**. To a stirred solution of compound **1** (193 mg, 0.58 mmol) in ethanol (3 mL), BF_3 ether complex (220 μL, 1.74 mmol) was added. The reaction mixture was kept at room

temperature over night, and then worked-up by the standard procedure to afford a syrup. The syrup was purified by PTLC (ethyl acetate/*n*-hexane, 2:1, v/v) to yield a mixture of erythro and threo forms of compound **2** (214 mg). Each isomer was separated successfully by PTLC. Assignments of erythro and threo forms were done with similar model compounds.[5]

Compound 2 (*threo*). ^{1}H NMR ($CDCl_3$): δ 1.20 (t, 3H, $J = 7.0$, -$OCH_2C\underline{H}_3$), 3.25 (br. t, 1H, Cγ-Ha), 3.35–3.41 (br. m, 1H, Cγ-Hb), 3.41–3.51 (m, 2H, -$OC\underline{H}_2CH_3$), 3.88 (s, 6H, $OCH_3 \times 2$), 3.89 (s, 3H, OCH_3), 4.19 (m, 1H, Cβ-H), 4.51 (d, 1H, $J = 7.3$, Cα-H), 6.83–7.31 (m, 7H, aromatics). ^{13}C NMR ($CDCl_3$): δ 15.34 (-$OCH_2\underline{C}H_3$), 55.73, 55.80, 55.85 ($OCH_3 \times 3$), 62.04 (Cγ), 64.59 (-$O\underline{C}H_2CH_3$), 82.08 (Cα), 87.72 (Cβ), 109.80, 110.71, 111.72, 119.82, 120.89, 121.28, 123.24, 130.98, 148.51, 148.64, 148.96, 150.80 (aromatics). Acetate: ^{1}H NMR ($CDCl_3$): δ 1.16 (t, 3H, $J = 6.8$, -$OCH_2C\underline{H}_3$), 1.98 (s, 3H, -$OCOC\underline{H}_3$), 3.46 (m, 2H, -$OC\underline{H}_2CH_3$), 3.83 (s, 3H, OCH_3), 3.87 (s, 6H, $OCH_3 \times 2$), 4.01 (dd, 1H, $J = 6.2$, 11.6, Cγ-Ha), 4.24 (dd, 1H, $J = 3.5$, 11.6, Cγ-Hb), 4.50 (br. q, 1H, Cβ-H), 4.57 (d, 1H, $J = 5.7$, Cα-H), 6.80–7.08 (m, 7H, aromatics).

Compound 2 (*erythro*). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 3H, $J = 7.0$, -$OCH_2C\underline{H}_3$), 3.24 (br. t, 1H, Cγ-Ha), 3.40–3.54 (m, 2H, -$OC\underline{H}_2CH_3$), 3.82 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.90–3.96 (br. m, 1H, Cγ-Hb), 4.08 (m, 1H, Cβ-H), 4.54 (d, 1H, $J = 7.5$, Cα-H), 6.50 (dd, 1H, $J = 1.5$, 8.0, aromatic), 6.75 (dt, 1H, $J = 1.6$, 7.8, aromatic), 6.82–6.98 (m, 5H, aromatics). ^{13}C NMR ($CDCl_3$): δ 15.38 (-$OCH_2\underline{C}H_3$), 55.81, 55.92 × 2 (OCH_3), 61.87 (Cγ), 64.72 (-$O\underline{C}H_2CH_3$), 81.10 (Cα), 86.42 (Cβ), 110.20, 110.74, 111.94, 120.06, 120.10, 121.23, 123.35, 132.15, 147.49, 148.51, 148.84, 151.00 (aromatics). Acetate. ^{1}H NMR ($CDCl_3$): δ 1.18 (t, 3H, $J = 6.8$, -$OCH_2C\underline{H}_3$), 2.02 (s, 3H, -$OCOC\underline{H}_3$), 3.43 (m, 2H, -$OC\underline{H}_2CH_3$), 3.75 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.45 (m, 3H, Cβ-H, Cγ-H), 4.54 (d, 1H, $J = 5.9$, Cα-H), 6.60–6.98 (m, 7H, aromatics).

Authentic samples were prepared as reference samples for chromatographic retention time and spectral data. Compound **3** was synthesized from veratrylglycerol-β-guaiacyl ether (**1**). To a stirred solution of compound **1** (111 mg, 0.33 mmol) in chloroform (3 mL), 1,4-butanediol (60 mg, 0.67 mmol) and BF_3 ether complex (85 μL, 0.67 mmol) were added. The reaction mixture was kept at room temperature over night, and then worked-up by the standard procedure to afford a syrup (130 mg). The syrup was purified by PTLC (ethyl acetate/*n*-hexane, 2:1, v/v). Erythro and threo forms were separated by PTLC ($CH_3OH/CHCl_3$, 5/95, v/v).

Compound 3 (*threo*). ^{1}H NMR ($CDCl_3$): δ 1.56–1.73 (br. m, 4H, C2-H, C3-H), 3.34–3.49 (4H, C1-H, C4-H), 3.61 (br. t, 2H, Cγ-H), 3.87 (s, 3H, OCH_3), 3.88 (s, 6H, $OCH_3 \times 2$), 4.19 (m, 1H, Cβ-H), 4.55 (d, 1H, $J = 7.6$, Cα-H), 6.83–7.27 (m, 7H, aromatics). ^{1}H NMR (DMSO-d_6): δ 1.35–1.50 (m, 4H, C2-H, C3-H), 3.25–3.35 (m, 3H, C1, C4, Cγ-Ha), 3.52–3.58 (m, 1H, Cγ-H), 3.72, 3.73, 3.75 (s, 9H, $OCH_3 \times 3$), 4.28–4.33 (m, 2H, Cα-H, OH), 4.48 (d, $J = 4.9$, Cα-H), 4.66 (t, $J = 5.1$, OH), 6.75–7.02 (m, 7H, aromatics). ^{13}C NMR ($CDCl_3$): δ 26.57 (C3), 30.01 (C2), 55.87, 55.90, 55.96 ($OCH_3 \times 3$), 61.58 (Cγ), 62.66 (C1), 69.09 (C4), 82.31 (Cα), 87.46 (Cβ), 109.98, 110.91, 111.93, 120.02, 120.66, 121.45, 123.37, 130.72, 148.22, 148.84, 149.10, 150.99 (aromatics). ^{13}C NMR (DMSO-d_6): δ 26.17 (C3), 29.37 (C2), 55.42, 55.57, 55.73 ($OCH_3 \times 3$), 60.26 (Cγ), 60.62 (C1), 68.71 (C4), 80.21 (Cα), 83.35 (Cβ), 111.01, 111.31, 112.61, 115.64, 119.64, 120.64, 120.96, 131.59, 148.17, 148.41, 148.62, 149.63 (aromatics).

Compound 3 (*erythro*). ^{1}H NMR ($CDCl_3$): δ 1.68 (m, 4H, C2-H, C3-H), 3.45 (m, 2H, C1-H or C4-H), 3.66 (m, 2H, C1-H or C4-H), 3.82 (dd, 1H, $J = 3.8$, 11.9, Cγ-Ha), 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.93 (dd, 1H, $J = 4.3$, 11.9, Cγ-Hb), 4.08 (m, 1H, Cβ-H), 4.55 (d, 1H, $J = 7.3$, Cα-H), 6.52 (dd, 1H, $J = 1.6$, 7.8, aromatic), 6.75 (dt, 1H, $J = 1.6$, 7.3, aromatic), 6.81–6.98 (m, 5H, aromatics). ^{1}H NMR (DMSO-d_6): δ 1.36–1.51 (m, 4H, C2-H, C3-H), 3.26 (br. quint, 2H, $J = 6.2$, C1 or C4), 3.30–3.39 (overlapped, 2H, C1 or C4), 3.51–3.62 (m, 2H, Cγ-H), 3.67, 3.70, 3.71 (s, 9H, $OCH_3 \times 3$), 4.34 (t, 1H, $J = 5.2$, OH), 4.39 (q, 1H, $J = 5.1$, Cβ-H), 4.46 (d, 1H, $J = 5.1$, Cα-H), 4.67 (t, 1H, $J = 5.7$, OH), 6.77–6.99 (m, 7H, aromatics). ^{13}C NMR ($CDCl_3$): δ 26.35 (C3), 29.77 (C2), 55.81, 55.91, 55.95 ($OCH_3 \times 3$), 61.44 (Cγ), 62.63 (C1), 69.05 (C4), 80.91 (Cα), 86.46 (Cβ), 110.25, 110.77, 111.98, 120.12, 120.15, 121.26, 123.45, 131.85, 147.33, 148.56, 148.87, 151.04 (aromatics). ^{13}C NMR (DMSO-d_6): δ 26.16 (C3), 29.42 (C2), 55.41, 55.58, 55.74 ($OCH_3 \times 3$), 59.98 (Cγ), 60.62 (C1), 68.41 (C4), 79.97 (Cα), 82.59 (Cβ), 111.10, 111.47, 112.74, 116.00, 120.24, 120.64, 121.15, 131.20, 147.92, 148.15, 148.29, 149.74 (aromatics).

Reaction of Model Compounds and Determination of Reaction Products

Compounds **1** or **2** (10 mg) was dissolved in 70 wt% aq. 1,4-butanediol solution (3 mL) in a stainless steel autoclave (10 mL) and was heated at 180°C using oil bath in the presence and absence of 10 equiv. of glucose or acetic acid. After the prescribed time, the autoclave was cooled

immediately. An aliquot of the reaction mixture (0.2 mL) was withdrawn, and 2-naphtol (200 μL; 500 mg in 50 mL of dioxane) was added as an internal standard. The mixture diluted with methanol (0.2 mL) was analyzed directly by high performance liquid chromatography (HPLC) on HITACHI Liquid Chromatograph L-7100 with UV detector, L-7405 (280 nm). Discovery C18 column (Supelco) (15 cm × 4.6 mm) was used (CH_3OH, flow-rate: 1.0 mL/min).

RESULTS AND DISCUSSION

Reaction of Nonphenolic β-Aryl Ether Lignin Model Compounds

Homolytic cleavage of phenolic β-*O*-4 substructures in lignin has been considered to be one of the most important reactions in aqueous solvents at elevated temperatures.[6–8] Phenoxy radicals formed from phenolic β-aryl ethers may produce recombination products such as β-5 and β–β structures. On the other hand, a nonphenolic β-aryl ether bond has been reported to be quite stable. Veratrylglycerol-β-guaiacyl ether (**1**) was recovered unchanged after the treatment in dioxane/water at 180°C in the presence or absence of hollocellulose.[9] The reactivity of compound **1** was much lower than that of its phenolic counterpart in our preliminary experiment under HBS pulping conditions. Thus, we concluded that the formation of quinone methide intermediate from phenolic structures was required for homolytic cleavage of β-aryl ether.[6,7]

However, compound **1** was reacted to some extent and unidentified products were detected in the preliminary experiment. The results were different from those in dioxane/water where compound **1** was recovered unchanged.[9] The difference may come from the difference in the solvent used. Thus, compound **1** was treated with 70% aqueous 1,4-butanediol solution at 180°C in order to elucidate the reaction of nonphenolic β-*O*-4 structures in more detail. A mixture of erythro and threo forms (60.5:39.5) of compound **1** was used. The starting material and reaction products were analyzed by high performance liquid chromatography instead of gas chromatography,[6] because erythro and threo isomers can be determined separately. As shown in Fig. 2, compound **1** was reacted, and 62.1% of compound **1** was recovered after 2 h. However, guaiacol was not detected in the reaction mixture, indicating that the cleavage of β-aryl ether bond was negligible in the case of nonphenolic β-aryl ether structures in lignin.

From the reaction mixtures, 4-[1-(3,4-dimethoxy-phenyl)-3-hydroxy-2-(2-methoxy-phenoxy)-propoxy]-butan-1-ol (**3**) was identified.

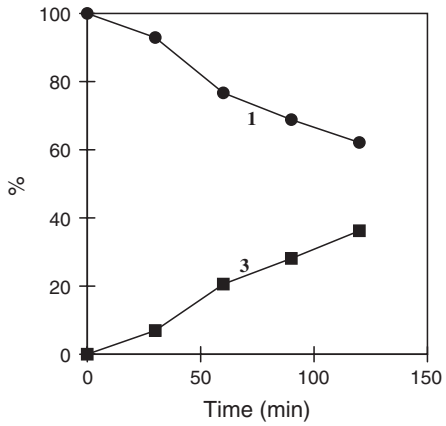


Figure 2. Reaction of compound **1** in 70 wt% aq. 1,4-butanediol at 180°C.

Table 1. ^{1}H NMR spectral data for peracetate derivatives of compounds **2** and **4** (solvent:$CDCl_3$).

	Chemical shifts/ppm (coupling constants/Hz)				
	Cα-H	Cβ-H	Cγ-Ha	Cγ-Hb	OCH_3
2 (*threo*)	4.57 (5.7)	4.50	4.01 (6.2, 11.6)	4.24 (3.5, 11.6)	3.83, 3.87, 3.87
2 (*erythro*)	4.54 (5.9)		4.45		3.75, 3.83, 3.86
4 (*threo*)[a]	4.45 (5.8)	4.52	4.02 (6.0, 11.8)	4.24 (3.8, 11.8)	3.30[b], 3.82, 3.86, 3.87
4 (*erythro*)[a]			4.4–4.5		3.29[b], 3.76, 3.84, 3.87

[a]Data were cited from Lit.[5]
[b]Methoxy protons at α-position.

An assignment of erythro and threo forms of compound **3** was conducted by comparison of ^{1}H NMR spectral data with similar model compounds **2** and **4** as shown in Tables 1 and 2. Compound **2** was synthesized and two isomers were separated as described in the experimental section. The spectral data for both erythro and threo forms of compound **4** (acetate form) were reported.[5] The compounds have been synthesized from corresponding erythro and threo forms of veratrylglycerol-β-guaiacyl ether (**1**). Since the differences in chemical structures

Table 2. ^{1}H NMR spectral data for compounds **2** and **3** (solvent:$CDCl_3$).

	Chemical shifts/ppm (coupling constants/Hz)					
	Cα-H	Cβ-H	Cγ-Ha	Cγ-Hb	OCH_3	Aromatics
2 (*threo*)	4.51 (7.3)	4.19	3.25	3.35–3.41	3.88, 3.88, 3.89	6.83–7.31 6.50
2 (*erythro*)	4.54 (7.5)	4.08	3.24	3.90–3.96	3.82, 3.87, 3.88	(dd, 1.5, 8.0) 6.75 (dt, 1.5, 7.8) 6.82–6.98
3 (*threo*)	4.55 (7.6)	4.19	3.61		3.87, 3.88, 3.88	6.83–7.27 6.52
3 (*erythro*)	4.55 (7.3)	4.08	3.82 (3.8, 11.9)	3.93 (4.3, 11.9)	3.82, 3.86, 3.88	(dd, 1.6, 7.8) 6.75 (dt, 1.6, 7.3) 6.81–6.98

between compounds **2** and **4** are quite small, the spectral data are quite similar to each other. Signals for side chain protons overlapped in the case of erytho form of acetate derivatives of compounds **2** and **4**. An assignment of isomers of compound **3** was conducted by the comparison with compound **2** in unacetylated form as shown in Table 2. Both isomers of compound **3** can be easily distinguished from each other. Characteristic signal separations in aromatic protons are observed with erythro form of both compounds **2** and **3**.

It is important to note that α-ether structures such as compound **3** were formed not only from a phenolic β-aryl ether model compound but also from a nonphenolic counterpart even under neutral conditions. The acid-catalyzed hydrolysis of α-ether model compounds has been reported to follow predominantly S_N1 type mechanism. Hydrolysis of α-ether depends very much on the acidity of the reaction media and no reaction has been assumed to occur under neutral conditions at 30°C.[10] However, it is well known that the pH of water decreases with the increase in temperature. Thus, the S_N1 mechanism might be predominantly involved in the formation of compound **3** under noncatalyzed conditions in HBS pulping as well as acidic conditions. Benzyl cation may be an important intermediate in the formation of compound **3**.

This may be supported by the following results. The ratio of erythro to threo forms of compound **1** decreased gradually from 1.53 to 1.30 in

Table 3. *Erythro* to *threo* ratio of compounds **1** and **3**.

	Reaction time (min)				
Compound	0	30	60	90	120
1 *e*/*t*	1.53	1.49	1.40	1.35	1.30
3 *e*/*t*		1.23	1.22	1.23	1.22

120 min as shown in Table 3. On the other hand, compound **3** is composed of a mixture of erythro and threo forms, and the ratio was almost constant between 1.22 and 1.23 during the treatments. Complicated equibrium reactions should affect the products ratio. However, even at the beginning of the reaction, the amount of erythro form of compound **3** was greater than that of threo form. This suggests the possible formation of erythro form of compound **3** from erythro form of compound **1**. The results support that S_N1 mechanism may be involved in the benzyl ether formation under HBS conditions, although further investigations are needed.

Reaction of Nonphenolic β-Aryl Ether with Benzyl Ether Type Lignin Model Compound

Lignin carbohydrate complexes (LCC) with benzyl ether type are reasonably assumed to be degradable under HBS pulping conditions. A mixture of erythro and threo forms of compound **2** was treated as a LCC model compound with 70% aqueous 1,4-butanediol solutions at 180°C for 2 h. HPLC profile of reaction products from compound **2** is shown in Fig. 3. Compounds **1** and **3** were identified as reaction products. Both erythro and threo forms of compounds **1–3** were determined separately. Cleavage of α-alkyl ether was the only reaction involved, whereas β-aryl ether cleavage products were not detected at all. The disappearance of compound **2** and formation of compounds **1** and **3** are shown in Fig. 4. The amount of formed compounds **1** and **3** increased gradually. The amount of formed compound **3** was always greater than that of compound **1**.

It is shown from Figs. 2 and 4 that the disappearance rate of compound **2** is faster than that of compound **1** under the conditions used. This is probably because bulky ethoxy group is better leaving group than hydroxyl group. These results are quite interesting compared with alkaline pulping conditions. Nonphenolic α-ether model compound **2** is

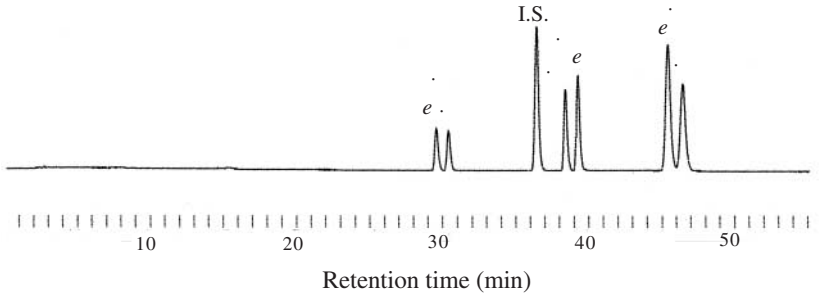


Figure 3. HPLC chromatogram of the reaction mixture obtained from treatment of compound **2** in 70 wt% aq. 1,4-butanediol at 180°C for 90 min.

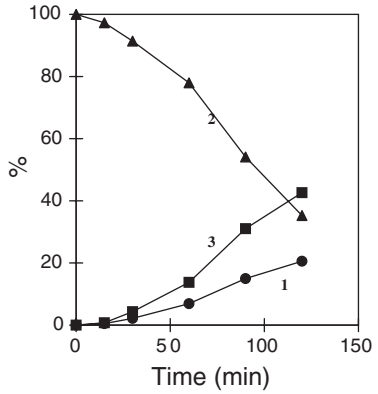


Figure 4. Reaction of compound **2** in 70 wt% aq. 1,4-butanediol at 180°C.

reported to be quite stable and the reactivity is much lower than that of α-hydroxyl counterpart under soda pulping conditions at 160°C.[11] This type of structure is considered to be one of residual lignin structures in alkali pulping. However, LCC linkages with benzyl ether type seem to be cleaved easily in HBS pulping. In fact, recovered HBS lignin obtained from black liqor was not associated with carbohydrates, which was analyzed by ^{13}C NMR spectroscopy.[12] Benzyl ether formation with 1,4-butanediol may prevent undesirable condensation and polymerization, and may contribute to the increase in the solubility of lignin in pulping liqor. The reactivity of α- and β-ether structures under HBS pulping conditions seems to be as the following from our model

experiments: phenolic β-aryl ether > nonphenolic α-alkyl ether ≫ nonphenolic β-aryl ether.

Effect of Glucose on Nonphenolic β-Ether Lignin Model Compounds

In order to elucidate the effect of reducing sugars which exist in recovered solvent, compound **1** was treated in the presence of 10 equiv. of glucose. The disappearance rate of compound **1** in the presence of glucose was much greater than that in the absence of glucose and only 27.4% of the starting material was remained after treatments for 2 h as shown in Fig. 5. The formation of compound **3** was also enhanced by the presence of glucose dramatically. This is probably because the pH of the reaction mixture decreased by the presence of glucose. The pH of the reaction mixture after treatment for 2 h were 3.7 and 4.7 in the presence and absence of glucose, respectively, where the pH was measured at room temperature after the reaction mixture was diluted 10 times with water. The decrease in pH and the increase in the α-ether formation in the presence of glucose have also been observed with a phenolic β-aryl ether model compound.[3]

Compound **2** with benzyl ether type was treated in the presence of 10 equiv. of glucose as shown in Fig. 6. The results were compared with those in the presence of 10 equiv. of acetic acid (0.09 M AcOH) in order to evaluate the effects of slightly acidic conditions. The disappearance of

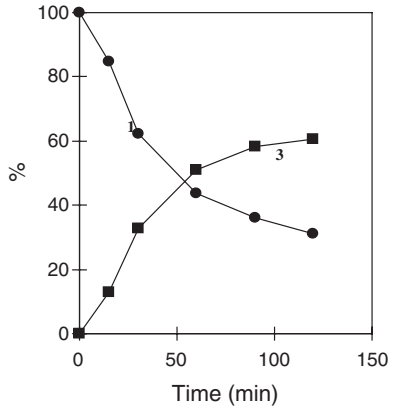


Figure 5. Effect of glucose on the reaction of compound **1** in 70 wt% aq. 1,4-butanediol at 180°C.

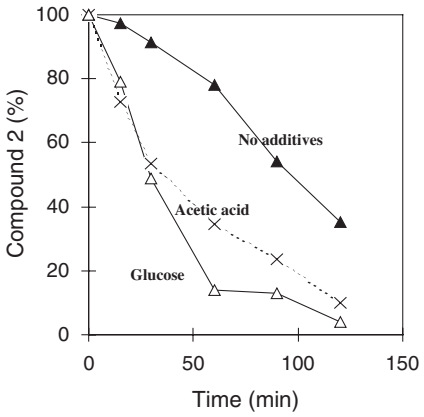


Figure 6. Effect of glucose and acetic acid on the reaction of compound **2** in 70 wt% aq. 1,4-butanediol at 180°C.

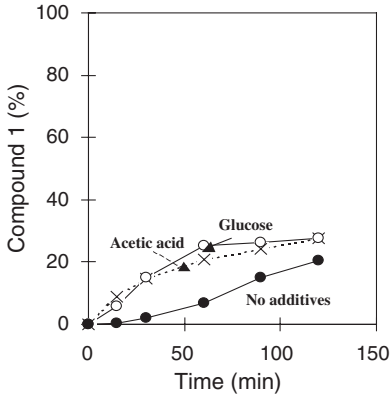


Figure 7. Effect of glucose and acetic acid on the formation of compound **1** during the treatment of compound **2** in 70 wt% aq. 1,4-butanediol at 180°C.

compound **2** was accelerated by the presence of glucose. The effects were almost the same as those with 10 equiv. of acetic acid. The addition of glucose also increased the formation of compounds **1** and **3** as shown in Figs. 7 and 8. The amount of compounds **1** and **3** in the presence of glucose was quite similar to those of acetic acid. Both cleavage of α-alkyl ethers and formation of new α-ether with 1,4-butanediol were enhanced by the presence of glucose. It should be noted that guaiacol was not detected either in the presence of glucose or acetic acid. These

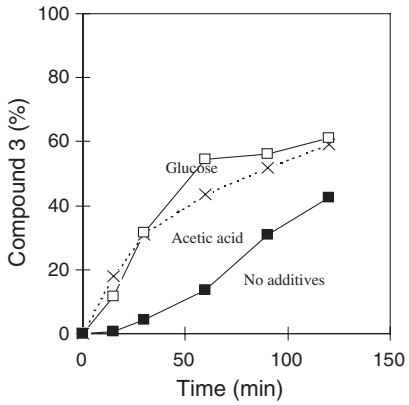


Figure 8. Effect of glucose and acetic acid on the formation of compound **3** during the treatment of compound **2** in 70 wt% aq. 1,4-butanediol at 180°C.

results suggest that acetic acid released from hemicellose during HBS pulping may accelerate hydrolysis of α-aryl and alkyl ethers, but not β-aryl ethers. Reducing sugars present in recovered solvent may reduce pH of pulping liqor and accelerate hydrolysis of α-aryl and alkyl ethers during HBS pulping.

In HBS pulping recovered solvents accelerate the delignification rate dramatically. This was attributed to reducing sugars which exist in the solvents. From our model experiments with phenolic[3] and nonphenolic β-*O*-4 model compounds, effects of reducing sugars may be summarized as following: (1) Reducing sugars may act as hydrogen donor and stabilize phenoxy radicals formed by homolytic cleavage of phenolic β-aryl ether bonds. This may prevent condensation of phenoxy radicals. (2) Sugar-derived endiol assisted phenolic β-aryl ether bond cleavage may cause additional degradation of phenolic β-aryl ether. (3) The relatively low pH caused by the presence of reducing sugars may accelerate hydrolysis of α-aryl and alkyl ethers. The introduction of pulping solvent at α-position may prevent condensation of lignins.

REFERENCES

1. Kajimoto, J.; Sano, Y.; Widodo, W.E.; Kishimoto, T.; Uraki, Y. HBS pulping (1)—pulping of softwood. Japan Tappi **2000**, *54* (9), 1252–1259.

2. Kajimoto, J.; Sano, Y. HBS pulping (3)—accelerated effect of RHBS on delignification. Japan Tappi **2001**, *54* (9), 1470–1479.
3. Kishimoto, T.; Sano, Y. Delignification mechanism during high-boiling solvent pulping. Part 3. Effect of a reducing sugar on the degradation of guaiacylglycerol-β-guaiacyl ether. Journal of Wood Chem. Technol. **2003**, *submitted*.
4. Adler, E.; Lindgren, B.O.; Saedlen, U. The beta-guaiacyl ether of alpha-veratrylglycerol as a lignin model. Sven Papperstidn **1952**, *55*, 245–254.
5. Adler, E.; Brunow, G.; Lundquist, K. Investigation of the acid-catalyzed alkylation of lignins by means of NMR spectroscopic methods. Holzforschung **1987**, *41* (4), 199–207.
6. Kishimoto, T.; Sano, Y. Delignification mechanism during high-boiling solvent pulping. Part 1. Reaction of guaiacylglycerol-β-guaiacyl ether. Holzforschung **2001**, *55* (6), 611–616.
7. Kishimoto, T.; Sano, Y. Delignification mechanism during high-boiling solvent pulping. Part 2. Homolysis of guaiacylglycerol-β-guaiacyl ether. Holzforschung **2002**, *56* (6), 623–631.
8. Li, S.; Lundquist, K.; Westermark, U. Cleavage of arylglycerol β-aryl ethers under neutral and acid conditions. Nordic Pulp and Paper Research Journal **2000**, *15* (4), 292–299.
9. Omori, S.; Aoyama, M.; Sakakibara, A. Hydrolysis of lignin with dioxane-water XIX. Reaction of β-*O*-4 lignin model compounds in the presence of carbohydrates. Holzforschung **1998**, *52*, 391–397.
10. Meshgini, M.; Sarkanen, K.V. Synthesis and kinetics of acid-catalyzed hydrolysis of some α-aryl ether lignin model compounds. Holzforschung **1989**, *43*, 239–243.
11. Taneda, H.; Nakano, J.; Hosoya, S.; Chang, H.-M. Stability of α-ether type compounds during chemical pulping processes. J. Wood Chem. Technol. **1987**, *7* (4), 485–498.
12. Kishimoto, T.; Ueki, A.; Sano, Y. Delignification mechanism during high-boiling solvent pulping. Part 4. Structural changes in lignin analyzed by ^{13}C NMR spectroscopy. Holzforschung, *submitted*.