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ORIGINAL ARTICLE

Synergistic contribution of hydrosulfide and carbonate anions to the *β-O*-4 bond cleavage of lignin model compounds in a green liquor pretreatment for enzymatic hydrolysis of lignocellulosic materials

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Abstract To examine why green liquor (GL) pretreatment of lignocellulosic materials effectively facilitates enzymatic saccharification under conditions milder than those of a common alkaline cooking process, dimeric *β-O*-4 type lignin model compounds with and without free phenolic hydroxyl group were reacted in several alkaline solutions including a model solution of GL, which mainly contains Na_2CO_3 and Na_2S. The *β-O*-4 bond of the phenolic model compound was cleaved with a sufficient rate in the model solution of GL. The *β-O*-4 bond cleavage of the non-phenolic model compound was more frequent in the model solution of GL than in other alkaline solutions. These results suggest that *β-O*-4 bonds present in lignocellulosic materials are effectively cleaved in a GL pretreatment. It was also suggested that HS^- and CO_3^{2-} synergistically contribute to the *β-O*-4 bond cleavage of the non-phenolic model compound under GL pretreatment conditions.

Keywords Alkyl-aryl ether · Delignification · Kraft pulping

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Introduction

Green liquor (GL) is a solution derived from chemical recovery system in a kraft cooking process. GL mainly contains Na_2CO_3 and Na_2S (NaOH+NaSH) as chemical reagents and is converted to white liquor in a causticizing system by reacting Na_2CO_3 with $Ca(OH)_2$ to generate NaOH and sedimentary $CaCO_3$.

GL pretreatment was developed for semi-chemical and kraft cookings in 1970s. It was reported that southern pine is cooked by GL containing about 29 % total alkali charge to give a pulp with a yield of about 70 % [1]. After the concept of extended delignification was developed [2], GL pretreatment was reported to improve its selectivity and pulp quality [3, 4]. Later, GL pretreatment of wood chip for bioethanol production was developed and reported that enzymatic saccharification of wood chip pretreated with GL is much more efficient than that pretreated with kraft cooking when compared at the same lignin content [5, 6]. Because lots of kraft pulp mills have recently been closed, it has become attractive to repurpose the mills into bioethanol plants [5, 6]. It is the special advantage in this repurposing that the mills already have equipments sufficient and proper as bioethanol plants [5, 6]. Moreover, an enzymatic hydrolysis subsequent to a GL pretreatment was reported to saccharify more efficiently and be freer from inhibitive substances than that subsequent to an acid pretreatment [5–8].

It is well known that cleavage of *β-O*-4 bond connecting non-phenolic units is responsible for delignification not only in kraft but also in alkaline-based cookings [9]. Conditions of GL pretreatment (initial pH around 12, temperature 140 ∼ 160 °C) are milder than those of common kraft cooking (initial pH >13, temperature 150 ∼ 170 °C). Because majority of *β-O*-4 bond cleaves

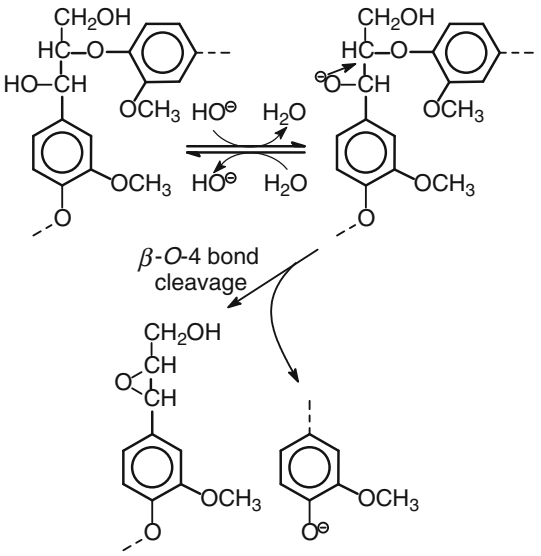

Fig. 1 The neighboring group participation mechanism for the *β-O*-4 bond cleavage of non-phenolic lignin substructures

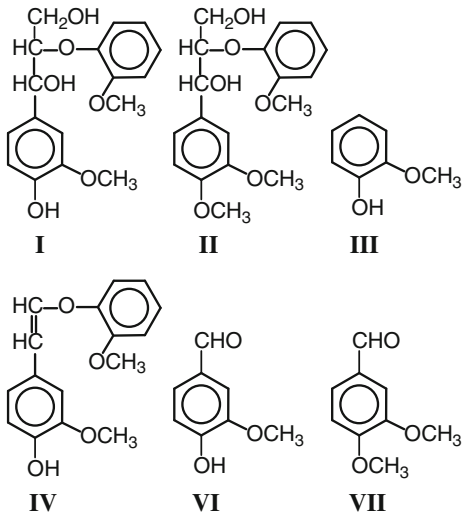

Fig. 2 Chemical structure of the lignin model compounds employed as starting materials (**I** and **II**) and the identified degradation products (**III**, **IV**, **VI**, and **VII**)

via the mechanism shown in Fig. 1 only at high temperature close to the maximum of kraft cooking process, it does not seem to be plausible that this cleavage reaction sufficiently occurs under the conditions of GL pretreatment. It was reported, however, that a GL pretreatment removes about 35, 32, or 50 % of lignin from mixed oak and sweet gum [5], loblolly pine [6], or corn stover [7], respectively.

On the basis of these backgrounds, it is necessary to examine what chemical reactions contribute to the delignification in a GL pretreatment. In this study, a dimeric *β-O*-4 type lignin model compound with or without phenolic hydroxyl group, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (**I**, Fig. 2) or 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (**II**, Fig. 2), was treated with several alkaline solutions including a model solution of GL. It was examined whether or not the *β-O*-4 bonds of compounds **I** and **II** were cleaved in the model solution, and chemical reactions occurring in the model solution were compared with those in other alkaline solutions.

Materials and methods

Materials

All the chemicals used were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Water was deionized and degassed before use. Compounds **I** and **II** were synthesized in according to the method of Landucci et al. [10]. The structures and purities of compounds **I** and **II** were confirmed by ^{1}H-NMR (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) using acetone-d_6 and aliquots of D_2O as solvents. The chemical shift of the acetone peak (δ 2.05) was used as the internal reference in their ^{1}H-NMR spectra.

^{1}H-NMR of compound **I** [mixture of the *erythro* and *threo* isomers (about 5*e*/4*t*)]: δ 3.44 $\sim$ 3.49 (dd, 1H, $J = 5.5$, $J = 12.0$, Cγ-H$_a$ of the *threo* isomer), 3.66 $\sim$ 3.70 (m, 2H, Cγ-H$_a$ of the *erythro* isomer and Cγ-H$_b$ of the *threo* isomer), 3.76 $\sim$ 3.84 (s, 6H, -OCH$_3$ of the *erythro* and *threo* isomers), 3.80 $\sim$ 3.86 (m, 1H, Cγ-H$_b$ of the *erythro* isomer), 4.21 $\sim$ 4.25 (m, 1H, Cβ-H of the *threo* isomer), 4.27 $\sim$ 4.32 (m, 1H, Cβ-H of the *erythro* isomer), 4.86 $\sim$ 4.89 (d, 1H, $J = 6.0$, Cα-H of the *erythro* and *threo* isomers), 6.72 $\sim$ 7.14 (m, 7H, aromatic of both isomers). ^{1}H-NMR of compound **II** [mixture of the *erythro* and *threo* isomers (about 6*e*/4*t*)]: δ 3.45 $\sim$ 3.49 (dd, 1H, $J = 5.5$, $J = 12.0$, Cγ-H$_a$ of the *threo* isomer), 3.66 $\sim$ 3.72 (m, 2H, Cγ-H$_a$ of the *erythro* isomer and Cγ-H$_b$ of the *threo* isomer), 3.74 $\sim$ 3.84 (s, 9H, -OCH$_3$ of the *erythro* and *threo* isomers), 3.78 $\sim$ 3.83 (m, 1H, Cγ-H$_b$ of the *erythro* isomer), 4.23 $\sim$ 4.28 (m, 1H, Cβ-H of the *threo* isomer), 4.30 $\sim$ 4.34 (m, 1H, Cβ-H of the *erythro* isomer), 4.88 $\sim$ 4.90 (d, 1H, $J = 5.0$, Cα-H of the *erythro* isomer), 4.90 $\sim$ 4.92 (d, 1H, $J = 5.5$, Cα-H of the *threo* isomer), 6.78 $\sim$ 6.99, 7.08 $\sim$ 7.13 (m, 7H, aromatic of both isomers).

The activity of a purchased reagent, NaSH, was confirmed by reacting it with I_2 under acidic conditions followed by titration with $Na_2S_2O_3$ under acidic conditions. This reagent was directly used for preparing reaction solutions containing HS^-.

Table 1 List of prepared reaction solutions in this study

Solutioan[a]	Concentration (mol/L)[b]			Initial pH
	Na_2CO_3	NaOH	NaSH	
1	0.215	0	0	11.4
2	0.172	0.0430	0	12.7
3	0.172	0.0430	0.0430	12.7
4	0	0.00631	0	11.8
5	0	0	0.430	11.8
6	0.172	0	0.0860	11.4
7	0	0	0	5.9

[a] Solutions **1**, **2**, and **3** contained the same titratable alkali, while the pH values were similar in solutions **1**, **4**, **5**, and **6**. Solution **7** was a blank run

[b] These are not the actual concentrations but those calculated from the amount of the reagents added

Reaction in alkaline solutions

A series of the following 3 solutions was prepared to contain the constant titratable alkali. **1** 0.215 mol/L Na_2CO_3, **2** 0.172 mol/L Na_2CO_3 + 43.0 mmol/L NaOH, and **3** 0.172 mol/L Na_2CO_3 + 43.0 mmol/L NaOH + 43.0 mmol/L NaSH. These concentrations were not the actual but those which were based on the amounts of these reagents added. Solution **3** was a model solution of GL. The initial pH values of these solutions were 11.4, 12.7, and 12.7, respectively, at room temperature. To examine the reaction at similar initial pH values, the following 3 as well as blank solutions were subsequently prepared. **4** 6.31 mmol/L NaOH, **5** 0.430 mol/L NaSH, **6** 0.172 mol/L Na_2CO_3 + 86.0 mmol/L NaSH and **7** just H_2O. These concentrations were the same type as those shown above. The initial pH values of these solutions were 11.8, 11.8, 11.4, and 5.9, respectively, at room temperature. Solutions **1**, **4**, **5**, and **6** were treated as the other series. Solution **7** was for a blank run. These prepared solutions are listed in Table 1.

Compound **I** was dissolved in solution **1**, **2**, or **3** (3.0 mmol/L). Compound **II** was dissolved in each of all the reaction solutions (3.0 mmol/L) at 50 °C for 180 min without any noticeable decomposition. This prepared reaction solution (5.0 mL) was poured into a stainless steel vessel (10 mL), and the vessel was immersed in an oil bath at a target temperature. The reactions of compound **I** were conducted at 120, 130, or 140 °C. On the other hand, the reactions of compound **II** were run at 140, 150, or 160 °C in solutions **1**, **2**, and **3**, but only at 160 °C in solutions **4**, **5**, **6**, and **7**. Six vessels were prepared for conducting the reaction at a temperature for 10, 20, 40, 60, 90, and 120 min. After the reaction, the vessel was immediately immersed in an ice water bath, and then, the lid was opened. Acetic acid was added to neutralize the solution followed by addition of a CH_3OH solution of an internal standard compound, 4-chlorophenol. The lid was closed for thorough shaking.

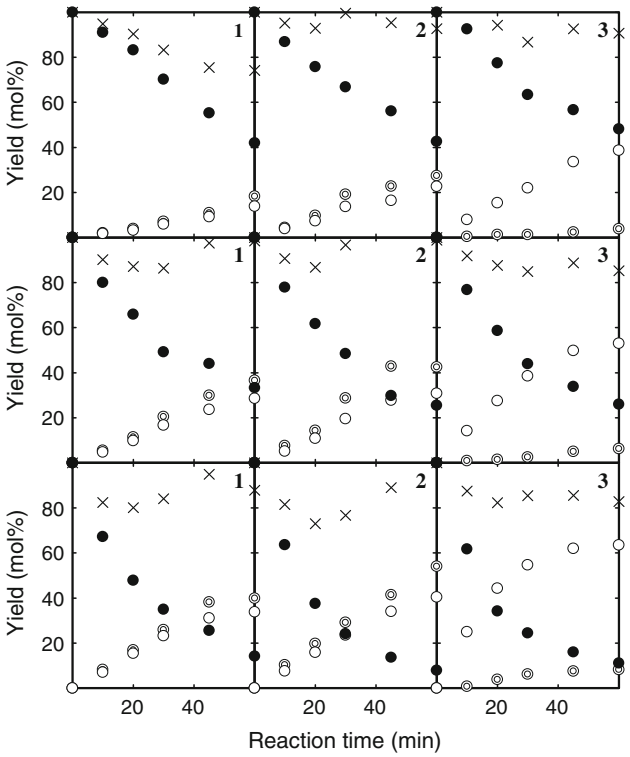

Fig. 3 Change in the yields of compounds **I**: *filled circle*, **III**: *open circle*, and **IV**: *double circle*, and the total yields of these 3 compounds: *multi symbol* on the basis of the initial amount of compound **I**, when compound **I** was treated in solutions **1**, **2**, and **3** at 120 °C: 3 figures in the *upper line*, 130 °C: 3 figures in the *middle line*, and 140 °C: 3 figures in the *lower line*

Quantification of starting compounds and reaction products

After filtration, the resulting mixture was analyzed by HPLC (LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (280 nm, Shimadzu Co.). The conditions of 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 1.0 mL/min; solvent system CH_3OH/H_2O (v/v) from 15/85 gradient to 25/75 for 7 min, gradient to 44/56 for 28 min, and maintained for 2 min, total time 37 min.

Results and discussion

Reaction of phenolic *β-O*-4 type model compound **I**

Figure 3 shows the disappearance of compound **I**, the formations of 2-methoxyphenol (**III**, Fig. 2) and 1-(4-

hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxyl)ethene (**IV**, Fig. 2) and the total yield of these 3 compounds, when compound **I** was treated in solution **1**, **2**, or **3**. The formation of compound **III** indicates the *β-O*-4 bond cleavage of compound **I**. The disappearances of compound **I** were not very different in these 3 solutions, although the initial pH value of solution **1** was fairly lower than those of the other solutions. The formation of compound **III** was more significant in solution **3**, a model solution of GL, than in the other solutions. Instead, the formation of compound **IV** was significant in solutions **1** and **2**. The total amount of compounds **I**, **III**, and **IV** was smaller than 100 %, suggesting that some reactions progress affording unidentified products. However, the oxidation of compound **IV** by molecular oxygen possibly present in the system may partly contribute to the above deviation from 100 % owing to the significant lability of compound **IV** to oxygen oxidation under alkaline conditions. This oxidation is probably accompanied by formation of compound **III**, which overestimates the extent of the alkaline-induced *β-O*-4 bond cleavage. Condensation reaction can be excluded owing to the low initial concentration of compound **I**.

Figure 4 illustrates the general reaction mechanism of compound **I** in an alkaline-based cooking medium. This mechanism explains the significant formations of compound **III** in solution **3** and of compound **IV** in solutions **1** and **2**. A quinone methide structure (**V**, Fig. 4) is primarily generated from compound **I**. Compound **III** is fairly liberated in solution **3** owing to the *β-O*-4 bond cleavage resulting from the attack of HS^- on the α-position of structure **V** and the consecutive intramolecular S_N2 type attack of the α-thiolate on the *β*-carbon. On the other hand, the formation of compound **IV** is preferable for structure **V** in solutions **1** and **2** owing to the absence of HS^-. These two types of reaction about structure **V** as well as the others shown in Fig. 4 are competitive.

It was suggested, therefore, that the *β-O*-4 bond connecting a phenolic lignin unit can be cleaved under conditions of GL pretreatment. All of these results do not contradict the general knowledge [11].

Reaction of non-phenolic *β-O*-4 type model compound **II**

Figure 5 shows the disappearance of compound **II**, the formation of compound **III**, and the total yield of these 2 compounds, when compound **II** was treated in solution **1**, **2** or **3**. Table 2 lists the pseudo-first-order reaction rate constants, Arrhenius activation energies, and Arrhenius frequency factors of the disappearances of compound **II**. The disappearance rates of compound **II** are in the decreasing order of solution **3** (a model solution of GL) > solution **2** > solution **1** at any temperature applied.

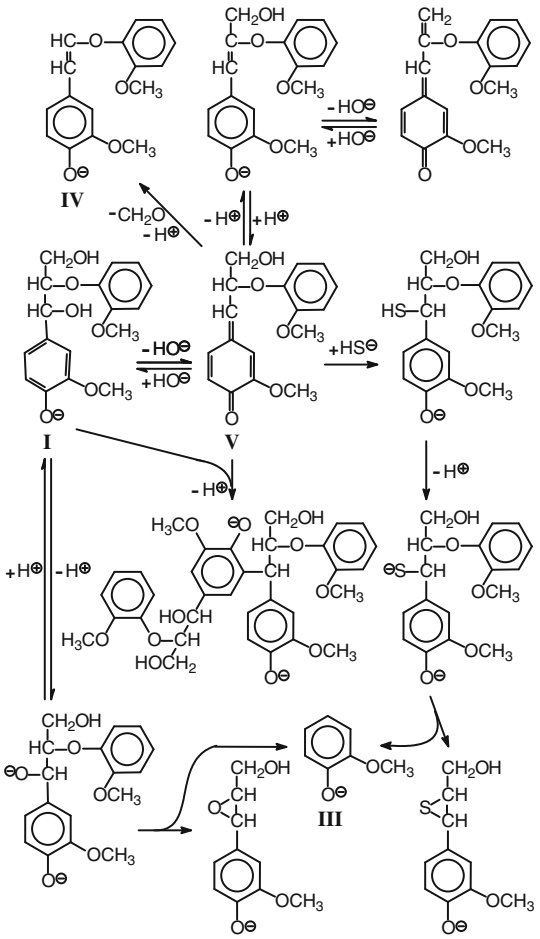

Fig. 4 The general reaction mechanism of compound **I** in an alkaline-based cooking process

It may be stated, however, that the disappearance of compound **II** in these solutions is not very different from one another and that it is fair even in solution **1** where the pH value seems to be too low to attain sufficient delignification. The Arrhenius activation energies are in the decreasing order of solution **1** > solution **2** > solution **3**. This order is the reverse of the rate constants, indicating that the difference in the rate constants between these solutions becomes small with increasing temperature. The Arrhenius frequency factors are the same decreasing order as the Arrhenius activation energies. It seems that increase of pH and addition of HS^- decrease these parameters. The amount of compound **III** liberated was very small in solution **1** (Fig. 5), which indicates that the disappearance of compound **II** is rarely accompanied by the liberation of compound **III** in solution **1**. It is currently unclear what reaction occurs. Compound **III** fairly formed in solution **2**, but the amount was rather smaller than the quantitative yield on the basis of the disappearance of compound **II**. It is considered that the disappearance of compound **II**

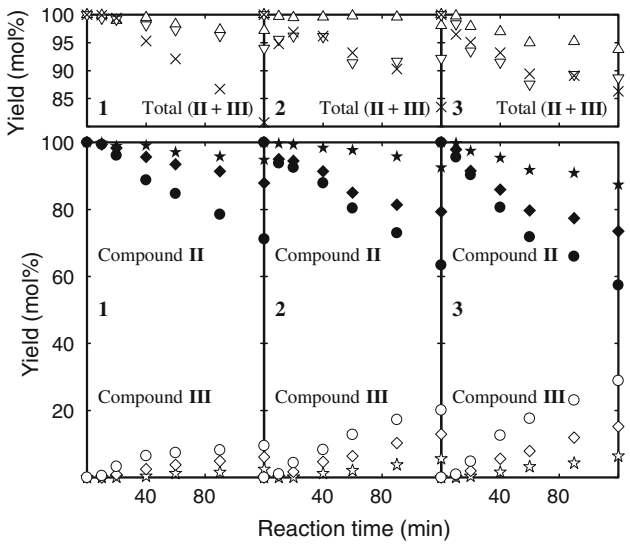

Fig. 5 Change in the yields of compounds **II** and **III**, and the total yields of these compounds on the basis of the initial amount of compound **II**, when compound **II** was treated in solutions **1**, **2**, and **3** at 140 °C: *filled star open star open triangle*, 150 °C: *filled diamond open diamond open inverted triangle*, and 160 °C: *filled circle open circle multi symbol*

becomes to be accompanied by the formation of compound **III** with increasing pH. The amount of compound **III** liberated was sufficiently large but still smaller than the quantitative yield in solution **3**. It is recognized that the general mechanism shown in Fig. 1 becomes more contributable to the disappearance of compound **II** with the addition of HS^-.

It should be emphasized that the disappearance of compound **II** in solution **3**, a model solution of GL, was more rapid than that in solution **2** and that the formation of compound **III** in solution **3** was greater than that in solution **2** in spite of their same initial pH value, 12.7. These phenomena should result from the presence of HS^- in solution **3** and suggest that HS^- not only contributes to the disappearance of compound **II** but also to the *β-O*-4 bond cleavage. This suggestion contradicts the general knowledge that degree of non-phenolic *β-O*-4 bond cleavage is not dependent on the concentration of HS^- but only on that of HO^- in kraft as well as alkaline-based cookings [9].

Action of HS^- in reaction of compound **II**

Because of the above contradiction, the effect of the presence of HS^- was examined in detail by applying the other series of solutions **1**, **4**, **5** and **6**. The initial pH values of these solutions were similar, 11.4, 11.8, 11.8 and 11.4, respectively. Figure 6 shows the disappearance of compound **II**, the formation of compound **III**, and the total yield of these 2 compounds, when compound **II** was treated in solution **1**, **4**, **5**, or **6**. Table 2 lists the pseudo-first-order reaction rate constants for the disappearances of compound **II**. First of all, it should be noted that compound **III** was certainly detected in the blank solution **7** but the amount was negligible and significantly smaller than those in the other solutions (about 0.1 ∼ 0.3 % yield at a reaction time of 120 min).

The disappearances of compound **II** were similar in solutions **1** and **6** as well as in solutions **4** and **5**, and much faster in the former 2 solutions than in the latter 2, where the amounts were small even at a reaction time of 120 min. The formation of compound **III** was greater in solution **6** than in all the other solutions. The amounts of compound **III** liberated were about 30 and 70 % at a reaction time of 120 min in solutions **1** and **6**, respectively, on the basis of the amount of disappearing compound **II**. These results suggest that the existence of CO_3^{2-} accelerates the disappearance of compound **II** without enhancing the *β-O*-4 bond cleavage, while the co-existence of CO_3^{2-} and HS^- accelerates not only the disappearance but also the *β-O*-4 bond cleavage. Because the degrees of the *β-O*-4 bond cleavages occurring in solutions **4** and **5** are similar, HS^- does not solely contribute to the *β-O*-4 bond cleavage. When HS^- exists together with CO_3^{2-}, however, these anions synergistically contribute to the *β-O*-4 bond

Table 2 List of pseudo-first-order reaction rate constants (k) of the disappearance of compound **II** in solutions **1**, **2**, **3**, **4**, **5**, and **6** as well as Arrhenius activation energies (E_a) and Arrhenius frequency factors (A) of the disappearance of compound **II** in solutions **1**, **2**, and **3**

Solution	**1**	**2**	**3**[a]	**4**	**5**	**6**
k[b]						
140 °C	4.88	6.51	11.40	–	–	–
150 °C	10.90	18.10	24.60	–	–	–
160 °C	29.60	35.90	45.50	3.74	6.47	28.30
E_a (kJ/mol)	135	128	104	–	–	–
A (per min)	4.02×10^{14}	8.39×10^{12}	1.06×10^{10}	–	–	–

[a] Solution **3** was a model solution of GL

[b] Unit: $\times 10^{-4}$/min

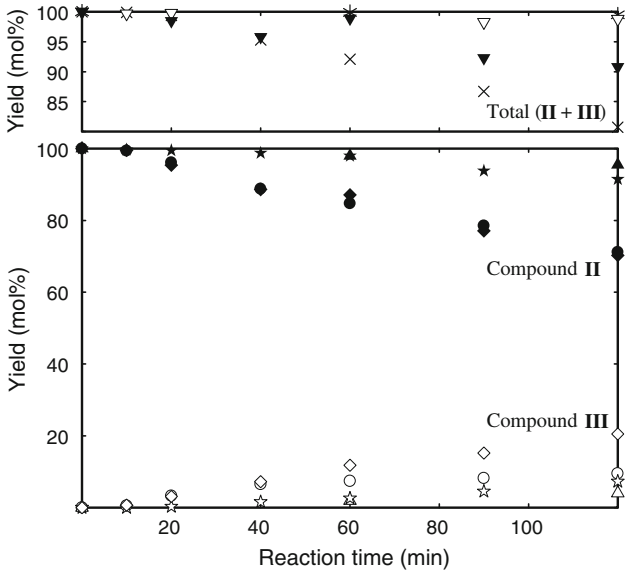

Fig. 6 Change in the yields of compounds **II** and **III**, and the total yields of these compounds on the basis of the initial amount of compound **II**, when compound **II** was treated in solution **1**: *filled circle open circle multi symbol*, solution **4**: *filled triangle open triangle asterisk*, solution **5**: *filled star open star open inverted triangle*, and solution **6**: *filled diamond open diamond filled inverted triangle* at 160 °C

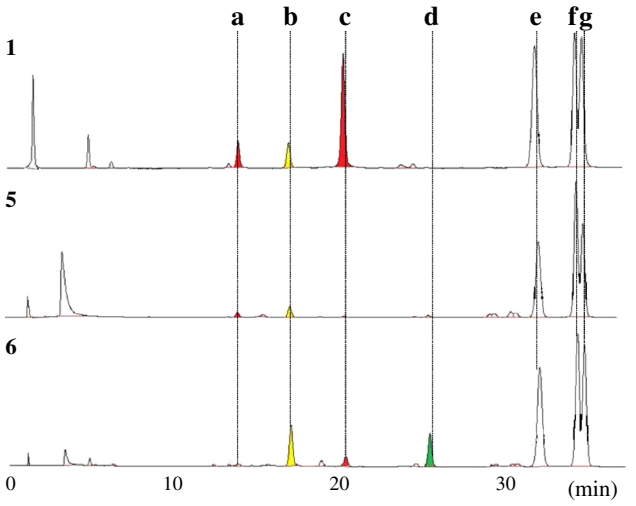

Fig. 7 HPLC chromatograms of solutions **1**, **5**, and **6** after subjecting to the reaction for 120 min at 160 °C

cleavage. This finding is very surprising, because it is generally believed, as described above, that degree of non-phenolic *β-O*-4 bond cleavage is dependent only on concentration of HO^-. It is our future topic to examine the mechanism of this synergistic effect and whether or not the synergistic effect appears under conditions different from those employed in this study.

It was suggested, therefore, that *β-O*-4 bonds connecting non-phenolic lignin units can fairly be cleaved under conditions similar to those of GL pretreatment (solution **6**, co-existence of CO_3^{2-} and HS^-). Moreover, GL pretreatment is considered to be fairly effective to cleave *β-O*-4 bond, although the conditions are milder than those of a common alkaline-based cooking. On the basis of these results, it can be discussed why GL-pretreated wood chip results in better enzymatic saccharification than kraft-cooked wood chip when compared at the same lignin content [5–7]. As demonstrated here, it is considered that both phenolic and non-phenolic *β-O*-4 bonds in lignin are fairly cleaved in GL pretreatment in spite of the mild alkaline conditions. These degraded lignins may not dissolve in the solution but remain in wood chip owing to the low alkalinity of GL pretreatment. It may be the case that wood chips pretreated with GL contain lignin fractions more degraded than those pretreated with kraft cooking resulting in the more efficient saccharification.

Identification of reaction products of compound II

Figure 7 shows the HPLC chromatograms of solutions **1**, **5**, and **6** in the reaction of compound **II** at 160 °C for 120 min. The period before retention time of 10 min is excluded from the discussion here. Peaks **b**, **e**, **f**, and **g** were confirmed to correspond to compound **III**, the internal standard compound, the *erythro* isomer of compound **II**, and the *threo* isomer of compound **II**, respectively. There appear 2 major peaks **a** and **c** in the chromatogram of solution **1**. These peaks were confirmed to correspond to 4-hydroxy-3-methoxybenzaldehyde (vanillin, **VI**, Fig. 1) and 3,4-dimethoxybenzaldehyde (veratrylaldehyde, **VII**, Fig. 1). The yields were 1.9 and 8.5 %, respectively, on the basis of the initial amount of compound **II**, when compounds **II** and **III** were yielded with 71.2 and 9.5 %, respectively. Peaks **a** and **c** are very small in solutions **5** and **6**. In solution **5**, the yields of compounds **VI** and **VII** were 0.7 and 0.1 %, respectively, when compounds **II** and **III** were yielded with 91.5 and 7.3 %, respectively. In solution **6**, the yields of compounds **VI** and **VII** were 0.2 and 0.9 %, respectively, when compounds **II** and **III** were yielded with 70.3 and 20.5 %, respectively. Compound **VII** is considered to originate from the 3,4-dimethoxyphenyl nucleus in compound **II**, although the mechanism is not clear. Compound **VI** was confirmed to be produced by the reaction of compound **VII** in solutions **1** and **4** at 160 °C for 120 min. The yields were 15.7 and 1.7 %, respectively, on the basis of the initial amount of compound **VII**. This result suggests that the presence of CO_3^{2-} contributes to the formation of compound **VI** from compound **VII**, although the S_NAr type substitution reaction of HO^- with

the $-OCH_3$ group located at the *para*-position of the –CHO group is the most plausible mechanism and this reaction should be dependent on the HO^- concentration. In spite of the relatively slow formation of compound **VI** from compound **VII**, the yield of compound **VI** was greater than that of compound **VII** in solution **5**, suggesting a different formation route of compound **VI**.

The other major peak **d** appears in the chromatogram of solution **6**, where the relatively large amounts of compounds **II** and **III** disappeared and formed, respectively, and the very small amounts of compounds **VI** and **VII** were generated. The compound corresponding to peak **d** could not be identified but is considered to originate from the 3,4-dimethoxyphenyl nucleus in compound **II**.

Conclusions

The *β-O*-4 bonds of compounds **I** and **II** were confirmed to be cleaved in solution **3**, a model solution of GL, which can result in the effective delignification in a GL pretreatment previously reported. The *β-O*-4 bond of compound **II** was cleaved most efficiently in solution **6**, which consisted of the reagents similar to those in GL, when compound **II** was treated in several alkaline solutions with the similar pH values. This result surprisingly suggests that HS^- contributes to the non-phenolic *β-O*-4 bond cleavage of compound **II** synergistically with CO_3^{2-} under GL pretreatment conditions.

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