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Revisiting the condensation reaction of lignin in alkaline pulping with quantitativity part III: predominant formation of α - β -type over α -5-type condensation product in soda cooking treatments of apocynol and creosol

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Abstract

Progress in the condensation of lignin is believed to interfere with delignification in alkaline pulping processes without any clear evidence, which motivated us to revisit it quantitatively. This study is the 3rd in the series which evaluates the condensation reactions of lignin in model systems of soda cooking processes using 4-(1-hydroxyethyl)-2-methoxyphenol (apocynol, Ap) and 2-methoxy-4-methylphenol (creosol, Cr). Ap was primarily converted to 2-methoxy-4-vinylphenol (vinylguaicol, Vg) via the quinone methide intermediate to establish equilibrium before condensation reactions proceeded. Only the α -5-type condensation product between Ap and Cr (ApCr, 1-(4-hydroxy-3-methoxyphenyl)-1-(2-hydroxy-3-methoxy-5-methylphenyl)ethane) and the α - β -type condensation product between Ap and Vg or two molecules of Vg (ApVg, *trans*-1,3-bis(4-hydroxy-3-methoxyphenyl)but-1-ene) were identified without detecting any self-condensation products of Ap. The α - β -type condensation has not been well known and is an important finding of this study. The formation of ApVg was over 10 times faster than that of ApCr, which demonstrates that the α - β -type condensation is a major mode in soda cooking. However, because origins of α - β -type condensation substructures, such as C₆-C₂-type enol ethers, do not exist in native lignin, the results support our previous conclusion that the condensation reactions of lignin progress less frequently than previously believed.

Keywords: Alkaline cooking, Condensed structure, Delignification, Quione methide

Introduction

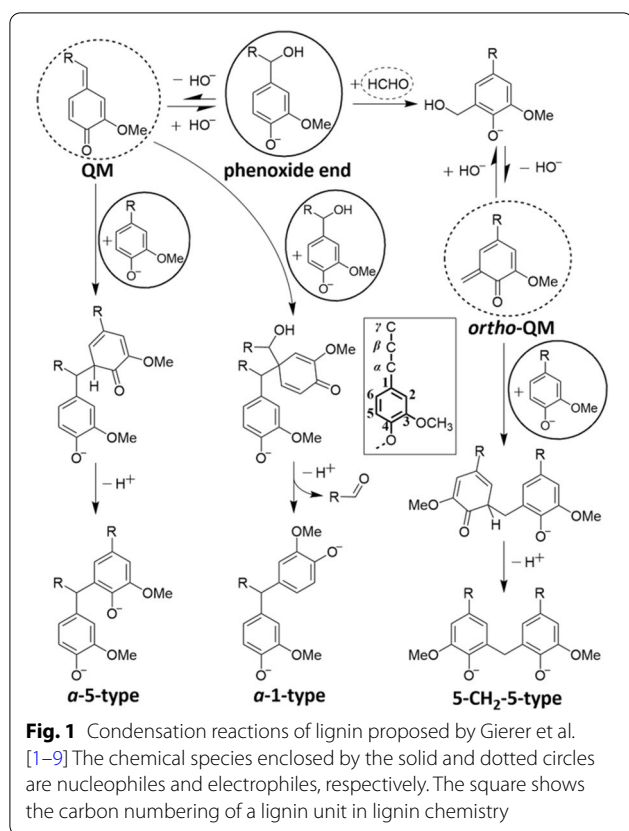
Condensation is a major reaction mode of phenolic substructures in lignin under alkaline pulping conditions. Gierer reviewed the condensation reactions of lignin and showed the formation of α -5-, α -1-, and 5-CH₂-5-type products under these conditions [1] on the basis of the results of Gierer and co-workers in their model experiments, as shown in Fig. 1 [2–9]. The quinone methide

intermediate (QM) is primarily generated as an electrophile by releasing the hydroxide anion (HO[−]) and reacts with a nucleophilic aromatic nucleus during condensation. Other researchers also supported the progress of these condensation reactions [10, 11]. Moreover, the condensation products described above were confirmed to be stable under these conditions [12, 13]. In light of the previous knowledge and the fact that lignin polymerizes during condensation, it is unquestionably believed that condensation of lignin interferes with delignification under alkaline pulping conditions.

However, it was reported that the β -O-4 bond cleavage of a trimeric model compound of condensation

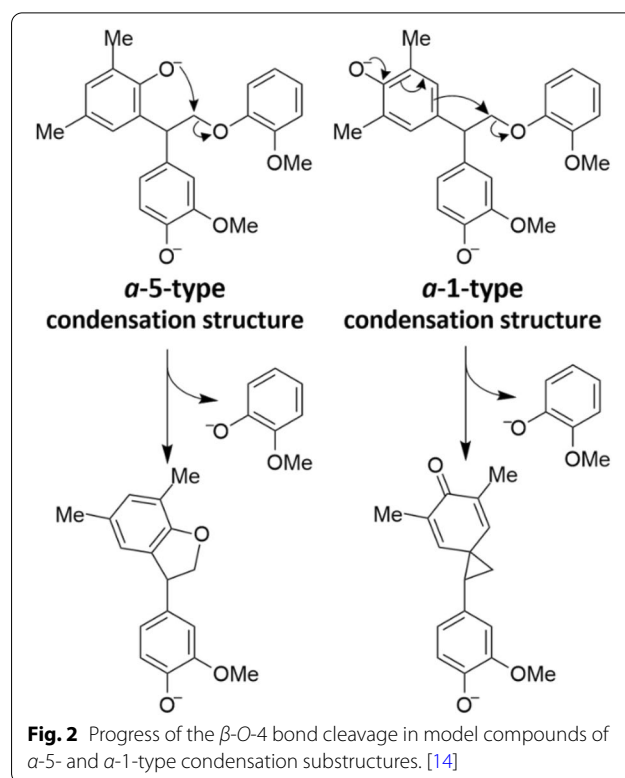
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products of lignin, which consists of both β -O-4 and α -5 interunit bonds, is faster than that of the common β -O-4-type model compound in soda cooking treatment (Fig. 2). [14] Another trimeric model compound carrying both β -O-4 and α -1 interunit bonds also underwent β -O-4 bond cleavage despite the slower rate than that of the common β -O-4-type model compound in the same treatment (Fig. 2) [14]. Various studies showed that the β -O-4 bond cleavage in a soda cooking process of a woody sample progresses more efficiently when *p*-cresol and its analogs are condensed to lignin in an acidic pretreatment before the soda cooking process [15–23]. These observations suggest a possibility that condensation of lignin accelerates the β -O-4 bond cleavage occurring near the α -position at which condensation has previously progressed and hence does not always interfere with delignification. Furthermore, the literatures described in the previous paragraph were not based on the quantitative, but only qualitative analyses. Thus, we have revisited the condensation reactions of lignin under alkaline pulping conditions with quantitatively, in previously published reports [24, 25].

In our previous studies, we employed the simplest system using C_6 - C_1 -type phenolic lignin model compounds, 4-hydroxymethyl-2-methoxyphenol (vanillyl alcohol,



Va, Fig. 3) and 2-methoxy-4-methylphenol (creosol, **Cr**, Fig. 3), under soda cooking conditions [24, 25]. The condensation reactions in this system are as follows: The specific **QM** is primarily generated from **Va** (**QM_{Va}**, Fig. 3) and electrophilically reacts with an aromatic nucleus as a nucleophile to afford a condensation product. Other **QMs** can also be generated from condensation products with a specific aromatic nucleus carrying both phenolic and benzyl hydroxy groups. We successfully identified and quantified the α -5-type condensation product between **Va** and **Cr** (2-(4-hydroxy-3-methoxybenzyl)-6-methoxy-4-methylphenol, **VaCr**, Fig. 3), the α -5-type self-condensation product of **Va** (2-(4-hydroxy-3-methoxybenzyl)-4-hydroxymethyl-6-methoxyphenol, **VaVa**, Fig. 3), the α -1-type self-condensation product of **Va** (bis(4-hydroxy-3-methoxyphenyl)methane, **VaVa'**, Fig. 3) as dimers, and the α -5-/ α -1-type self-condensation product of **Va** (2,4-bis(4-hydroxy-3-methoxybenzyl)-6-methoxyphenol, **VaVaVa'**, Fig. 3) as a trimer. The results were summarized as follows: (i) The formation rates of the dimers are in the order **VaCr** \approx **VaVa** > **VaVa'**, comprehensively showing that **Va** prefers to progress to self-condensation reactions rather than condensation with **Cr** (owing to the existence of two routes in the former); (ii) **VaVaVa'** is generated from **VaVa** rather than **VaVa'** via the reaction of the **QM** derived from **VaVa** (**QM_{VaVa}**, Fig. 3) with **Va**; (iii) The dimers are not good nucleophiles in

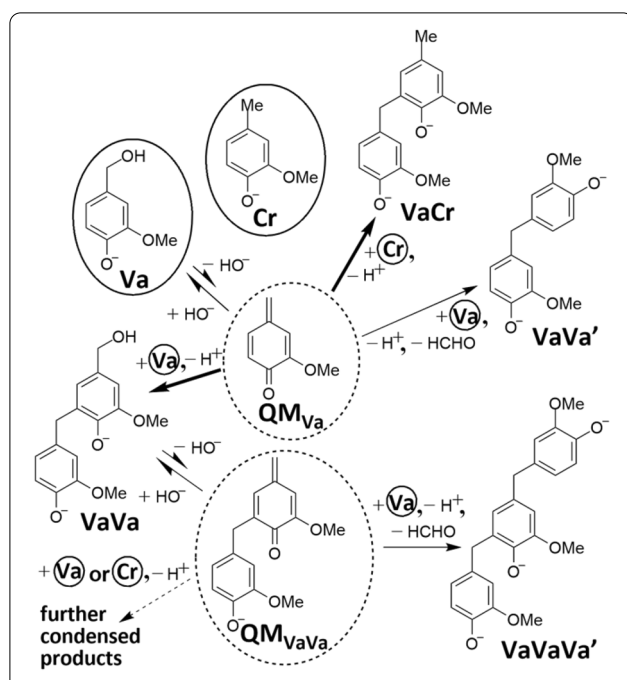


Fig. 3 Summary of the condensation reactions in the soda cooking treatment of **Va** and **Cr** observed in our previous reports. [24, 25] The chemical species enclosed by the solid and dotted circles indicate nucleophiles and electrophiles, respectively

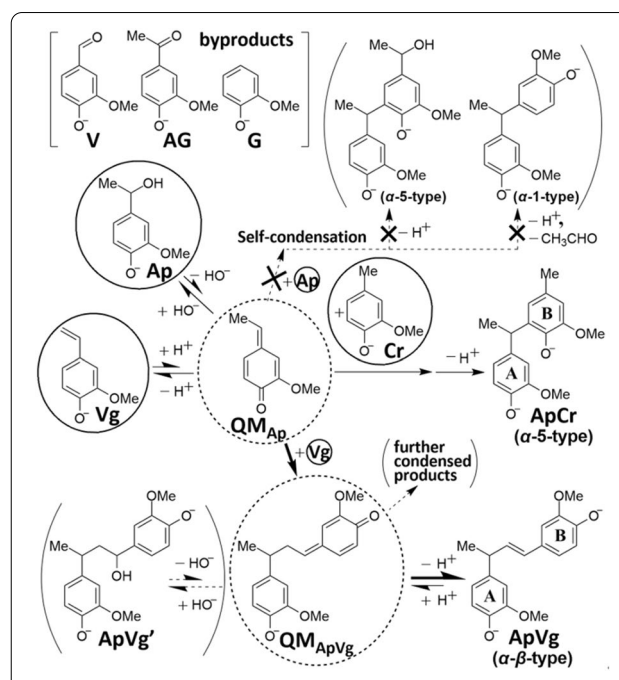


Fig. 4 Summary of the condensation reactions in the soda cooking treatment of **Ap** and **Cr** observed in this report. The chemical species enclosed by the solid and dotted circles indicate nucleophiles and electrophiles, respectively

reactions with **QM_{Va}**, **QM_{VaVa}**, and others; (iv) Because of iii), the condensation reaction of lignin may progress less readily than expected during actual soda cooking processes.

In the present study, a $\text{C}_6\text{-C}_2$ -type phenolic lignin model compound, 4-(1-hydroxyethyl)-2-methoxyphenol (apocynol, **Ap**, Fig. 4), was treated alone or together with **Cr** under soda cooking conditions. The results were compared with those obtained in our previous studies, in which **Va** and **Cr** were used, to examine the effect of increasing the steric factor of the side chain on the condensation reaction [24, 25]. The disappearance of **Ap** and **Cr** was quantitatively examined, and the condensation products were identified and quantified. Although substructures with the same structures as **Ap** or **Cr** do not exist in native lignin, these compounds would undergo condensation reactions much more frequently than any common substructures in native lignin owing to their small steric factors. Thus, these compounds are good model compounds for examining the reactions and mechanisms of lignin condensation in detail.

Materials and methods

Materials

All chemicals, except **Ap**, were purchased from Fuji-film Wako Pure Chemical Industries Co. (Osaka, Japan),

Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), or Sigma-Aldrich Japan K. K. (Tokyo, Japan), and used without further purification. Deionized water (H_2O) used was degassed in advance by sonication under reduced pressure. **Ap** was synthesized from 4-acetyl-2-methoxyphenol (acetoguaiacone, **AG**). It was reduced with sodium borohydride in sodium hydroxide (NaOH) solution. The isolated reduction product, consisting mostly of **Ap**, was recrystallized from a mixture of *n*-hexane ($n\text{-C}_6\text{H}_{14}$) and ethyl acetate (EtOAc) (3/1, v/v). The structure and high purity of **Ap** and **Cr** were confirmed by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$, JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) using acetone- d_6 with a drop of deuterium oxide (D_2O) as the solvent.

Soda cooking for isolation and identification of condensation products

A solution (25 mL) containing NaOH (1.35 mol/L), **Ap** (0.10 mol/L), and **Cr** (0.25 mol/L) was prepared for simulating a soda cooking process. This solution was equally divided into five portions, each of which was transferred into a stainless-steel autoclave (10 mL volume, Taiatsu Techno[®] Co., Tokyo, Japan), and the air present in the headspace was replaced with nitrogen gas. The five autoclaves were immersed in an oil bath at 150°C and left to soak with shaking for 180 min.

All autoclaves were removed, subsequently immersed in an ice/water bath, and content of each was neutralized with acetic acid (AcOH, 0.8 mL). The combined neutralized solution was extracted with dichloromethane three times and then with EtOAc once, followed by washing with H₂O and brine, and drying over anhydrous sodium sulfate (Na₂SO₄). The dried solution was concentrated using an evaporator under reduced pressure to obtain a brown syrup (1.30 g). The syrup was fractionated by flash chromatography (Isolera, Biotage Japan Ltd., Tokyo, Japan) using a mixture of *n*-C₆H₁₄/EtOAc (2/1, v/v) as the eluent. The removal of the eluent from each of the two fractions using an evaporator under reduced pressure afforded a light brown syrup. Each light brown syrup was further purified by preparative thin-layer chromatography (PTLC) using a mixture of *n*-C₆H₁₄/EtOAc (3/1, v/v) as the mobile phase. During the separation of either light brown syrup, an area of the PTLC surface, where condensation products could exist, was extracted with EtOAc and successively evaporated to obtain a colorless syrup (181 mg or 88 mg). Further isolation was performed because the amount of syrup (88 mg) obtained in this procedure was not sufficient for use.

Another reaction solution containing the same additives as the above solution (with slightly different concentrations), except for the absence of **Cr**, was also prepared and reacted in a manner similar to the above solution. The obtained reaction solutions were subjected to procedures similar to those described above to isolate the condensation products. Finally, two colorless syrups were obtained with amounts of 235 and 73 mg from 2.0 g of **Ap**.

Each of the four obtained syrups was dissolved in acetone-*d*₆ with an aliquot of D₂O, and then analyzed by ¹H-NMR, ¹³C-NMR, ¹³C-NMR DEPT135, 2D-NMR ¹H-¹H COSY, 2D-NMR ¹H-¹³C HSQC, 2D-NMR ¹H-¹³C HMBC (JNM-A500), and liquid chromatography/mass spectrometry (LC/MS, LC-2010C_{HT}/LCMS-2020, Shimadzu Co., Kyoto, Japan). Conditions for the LC-2010C_{HT} apparatus were as follows: a column for high-performance liquid chromatography (HPLC), Luna 5 μm C18(2) 100 Å (length: 150 mm, inner diameter: 4.6 mm, particle size: 5.0 μm, Phenomenex, Inc., Torrance, CA, USA), was used at an oven temperature of 40 °C with a solvent flow rate of 0.2 mL/min. The solvent and gradient were methanol (MeOH)/H₂O (v/v) from 15/85 to 45/55 for 5 min, 45/55 to 50/50 for 55 min, 50/50 to 75/25 for 0 min and maintained for 7.5 min, and 75/25 to 15/85 for 0 min and maintained for 7.5 min, giving a total time of 75 min. Electrospray ionization (ESI) was used for MS analysis.

Soda cooking for quantitative analysis

A reaction solution (5.0 mL) containing NaOH, **Ap** (10 mmol/L), and **Cr** was prepared using degassed H₂O and transferred into a stainless-steel autoclave. The initial concentrations of the components and systems employed in this study are listed in Table 1. The system employed in our previous studies was Cr0–Cr75 [24, 25]. The air in the headspace was replaced with nitrogen gas. Seven other autoclaves with the same content were also prepared. All eight autoclaves were immersed in an oil bath with shaking at 150 °C, and each was soaked for 0, 5, 10, 20, 30, 45, 60, or 120 min with shaking. All reactions were conducted thrice to confirm reproducibility.

The same procedure was repeated for another reaction solution containing NaOH (1.01 mol/L) and 2-methoxy-4-vinylphenol (10 mmol/L, vinylguaicol, **Vg**, Fig. 4), as listed in Table 1.

Quantification

The autoclave was removed from the oil bath at each specified reaction time and immediately immersed in an ice/water bath. AcOH (0.6 mL) was added for neutralization, followed by the addition of a MeOH solution (5.0 mL) containing the internal standard compound (IS), 3-ethoxy-4-hydroxybenzaldehyde (ethyl vanillin). After shaking the autoclave thoroughly, a portion of the content was filtered through a membrane filter, and the filtrate was analyzed by HPLC (LC-2010C_{HT}) equipped with a UV–Vis detector for quantification (280 nm). The conditions for HPLC analysis were same as those described above.

Results and discussion

Identification of reaction products

Ap and **Cr** were together or **Ap** was solely treated under conditions similar to system Cr25' or Cr0' for quantitative

Table 1 Reaction systems employed in this work

System ^a	Temp (°C)	Initial concentration			
		Ap ^b	Vg ^b	Cr ^b	NaOH ^c
Cr0'	150	10	0	0	1.010
Cr10'	150	10	0	10	1.020
Cr25'	150	10	0	25	1.035
Cr50'	150	10	0	50	1.060
Cr75'	150	10	0	75	1.085
Vg	150	0	10	0	1.010

^a The system names employed in our previous studies were Cr0–Cr75, in which **Va** with or without **Cr** were used under the same conditions as this study. [24, 25]

^b mmol/L

^c mol/L

analysis, respectively, to isolate and identify reaction products including condensation products, except that the scale was larger than that of Cr25' or Cr0', respectively. As described above, four colorless syrups were isolated with amounts of 181 mg in the co-treatment of **Ap** (420 mg) with **Cr** (864 mg), 88 mg in the co-treatment of **Ap** with **Cr**, 235 mg in the sole treatment of **Ap** (2.0 g), and 73 mg in the sole treatment of **Ap**. These four syrups were identified as 1-(4-hydroxy-3-methoxyphenyl)-1-(2-hydroxy-3-methoxy-5-methylphenyl)ethane (the α -5-type condensation product between **Ap** and **Cr**, **ApCr**, Fig. 4), *trans*-1,3-bis(4-hydroxy-3-methoxyphenyl)but-1-ene (the α - β -type condensation product between **Ap** and **Vg** or between two molecules of **Vg**, **ApVg**, Fig. 4), **ApVg**, and **Vg**, respectively, based on the observed NMR and MS spectra (Additional file 1: Figs. S1, S2, and S3, respectively, in the additional file). Both syrups (88 and 235 mg) corresponded to **ApVg**. The peaks in the ^1H -NMR, ^{13}C -NMR, and MS spectra were assigned below. The letters "Ar_A-" and "Ar_B-" in the spectral data indicate the aromatic nuclei of **ApCr** or **ApVg** labeled as "A" and "B", respectively, in Fig. 3. The MS spectra are described below. When the reaction solution obtained from each of Cr0'-Cr75' at 120 min for quantitative analysis was analyzed by LC/MS (Fig. 5), the MS spectra of the peaks appearing at 21.8, 59.3, and 62.4 min were identical to those of isolated **Vg**, **ApCr**, and **ApVg**, respectively.

^1H -NMR of **Vg**: δ 3.84 (s, 3H, Ar-OCH₃), 5.04 (dd, 1H, J =1.2 & 10.9 Hz, C β -H (*cis* of C α -H)), 5.61 (dd, 1H, J =1.1 & 17.6 Hz, C β -H (*trans* of C α -H)), 6.63 (dd, 1H, J =10.9 & 17.8 Hz, C α -H), 6.79 (d, 1H, J =8.1 Hz, ArC5-H), 6.89 (dd, 1H, J =2.0 & 8.3 Hz, ArC6-H), 7.07 (d, 1H, J =2.0 Hz, ArC2-H). ^{13}C -NMR of **Vg**: δ 56.1 (-OCH₃), 109.9 (ArC2), 111.0 (C β), 115.7 (ArC6), 120.6 (ArC5), 130.5 (ArC1), 137.7 (C α), 147.6 (ArC4), 148.4 (ArC3). MS in positive mode of **Vg** (m/z (detected ion, relative intensity)): 355 ([2 M + MeOH + Na]⁺, 96), 301 ([2 M + H]⁺, 100). MS in negative mode of **Vg** (m/z (detected ion, relative intensity)): 149 ([M - H]⁻, 100).

^1H -NMR of **ApCr**: δ 1.50 (d, 3H, J =7.2 Hz, Ar_AC β -H₃), 2.16 (s, 3H, Ar_BC α -H₃), 3.76 (s, 3H, Ar_A-OCH₃), 3.78 (s, 3H, Ar_B-OCH₃), 4.47 (q, 1H, J =7.2 Hz, Ar_AC α -H), 6.52 (d, 1H, J =1.7 Hz, Ar_BC2-H), 6.58 (d, 1H, J =1.7 Hz, Ar_BC6-H), 6.71 (m, 2H, Ar_AC5-H and Ar_AC6-H), 6.87 (s, 1H, Ar_AC2-H). ^{13}C -NMR of **ApCr**: δ 21.1 (Ar_BC α), 21.2 (Ar_AC β), 37.4 (Ar_AC α), 56.2 (Ar_A-OCH₃), 56.2 (Ar_B-OCH₃), 110.4 (Ar_BC2), 112.5 (Ar_AC2), 115.3 (Ar_AC5), 120.6 (Ar_AC6), 120.6 (Ar_AC6), 128.5 (Ar_BC1), 133.4 (Ar_BC5), 138.5 (Ar_AC1), 141.8 (Ar_BC4), 145.4 (Ar_AC4), 147.6 (Ar_BC3), 147.9 (Ar_AC3). MS in positive mode of **ApCr** (m/z (detected ion, relative intensity)): 599 ([2 M + Na]⁺, 100), 343 [M + MeOH + Na]⁺, 34), 329 ([M + H₂O + Na]⁺, 17), 311 ([M + Na]⁺, 99). MS in

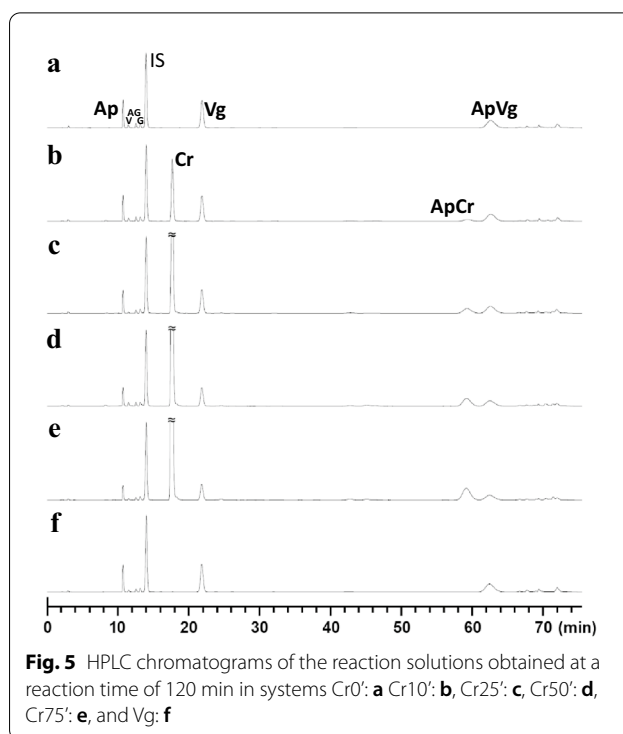


Fig. 5 HPLC chromatograms of the reaction solutions obtained at a reaction time of 120 min in systems Cr0': **a** Cr10': **b**, Cr25': **c**, Cr50': **d**, Cr75': **e**, and Vg: **f**

negative mode of **ApCr** (m/z (detected ion, relative intensity)): 287 ([M - H]⁻, 100).

^1H -NMR of **ApVg**: δ 1.37 (d, 3H, J =7.2 Hz, Ar_AC β -H₃), 3.51 (qu(qd), 1H, J =6.8 Hz, Ar_AC α -H), 3.80 (s, 3H, Ar_A-OCH₃), 3.81 (s, 3H, Ar_B-OCH₃), 6.26 (dd, 1H, J =6.6 & 15.8 Hz, Ar_BC β -H), 6.31 (d, 1H, J =16.1 Hz, Ar_BC α -H), 6.71 (dd, 1H, J =2.0 & 8.2 Hz, Ar_AC6-H), 6.74 (d, 1H, J =8.1 Hz, Ar_BC5-H), 6.76 (d, 1H, J =8.0 Hz, Ar_AC5-H), 6.82 (dd, 1H, J =2.0 & 8.2 Hz, Ar_BC6-H), 6.86 (d, 1H, J =1.7 Hz, Ar_AC2-H), 7.01 (d, 1H, J =2.0 Hz, Ar_BC2-H). ^{13}C -NMR of **ApVg**: δ 22.0 (Ar_AC β), 43.0 (Ar_AC α), 56.1 (Ar_A-OCH₃), 56.2 (Ar_B-OCH₃), 109.9 (Ar_BC2), 111.8 (Ar_AC2), 115.7 (Ar_AC5 or Ar_BC5), 115.7 (Ar_AC5 or Ar_BC5), 120.2 (Ar_AC6), 120.2 (Ar_BC6), 128.7 (Ar_BC β), 130.6 (Ar_BC1), 133.7 (Ar_BC α), 138.3 (Ar_AC1), 145.6 (Ar_AC4), 146.8 (Ar_BC4), 148.2 (Ar_AC3), 148.4 (Ar_BC3). MS in positive mode of **ApVg** (m/z (detected ion, relative intensity)): 623 ([2 M + Na]⁺, 26), 355 ([M + MeOH + Na]⁺, 100), 341 ([M + H₂O + Na]⁺, 37), 323 ([M + Na]⁺, 80). MS in negative mode of **ApVg** (m/z (detected ion, relative intensity)): 299 ([M - H]⁻, 100).

Reaction products appearing at retention times of 11.4, 12.5, and 13.2 min in Fig. 5 were identified as 4-hydroxy-3-methoxybenzaldehyde (vanillin, **V**), **AG**, and 2-methoxyphenol (guaiacol, **G**) by confirming that their authentic compounds appeared at the same retention times in the HPLC analyses and that their MS spectra were the same as those of the peaks appearing

at 11.4, 12.5, and 13.2 min, respectively. The spectral data are presented in the additional file. The formation of these compounds will be explained in detail later.

Reactions progressing in the systems employed in this report

Figure 4 shows the presumed reactions that occur in the systems employed in this study. In systems Cr0'–Cr75', QM_{Ap} is primarily generated from **Ap**. QM_{Ap} is converted to **Vg** via β -proton abstraction. Besides, QM_{Ap} , as an electrophile, reacts at the $C\alpha$ (benzyl) carbon with a nucleophile that is mainly **Cr** at the aromatic C5 carbon or **Vg** at the $C\beta$ carbon of the side chain. Subsequent deprotonation affords **ApCr** or **ApVg**, respectively. In the latter reaction, the QM precursor (QM_{ApVg}) is primarily generated and can react with HO^- to afford the adduct, 1,3-bis(4-hydroxy-3-methoxyphenyl)butan-1-ol (**ApVg'**). The reactions progressing in system Vg are mostly the same as those in system Cr0', except that the starting compound is **Vg** and QM_{Ap} is primarily generated from **Vg**.

Interconversion between **Ap** and **Vg**

Figures 6a–6f show the time course of the disappearance of the starting compound, **Ap** or **Vg**, and the formation of the quantified reaction products, **Ap**, **Vg**, **ApCr**, and **ApVg**, in systems Cr0'–Cr75' and Vg, respectively. The values of all data points are listed in Additional file 1: Table S1 in the additional file. Figures 6g and 6h show the time course of the disappearance and formation of **Ap** and **Vg**, respectively, in all the systems. Figure 6i shows the disappearance of **Cr** in all the systems. Figures 6k and 6l show the formation of **ApCr** and **ApVg**, respectively, in all the systems.

ApVg was formed with a yield of lower than 3 mol% before a reaction time of 20 min in systems Cr0' and Vg. **ApCr** and **ApVg** were formed similarly with yields of lower than 3 mol% before the reaction time in systems Cr10' and Cr25', although the yields of **ApCr** were slightly higher than 3 mol% before the reaction time in the other two systems. The disappearance of **Ap** in system Cr0' or **Vg** in system Vg was much faster than the formation of **ApVg** before the reaction time and was almost quantitatively accompanied by the formation of **Vg** or **Ap**, respectively. These phenomena comprehensively

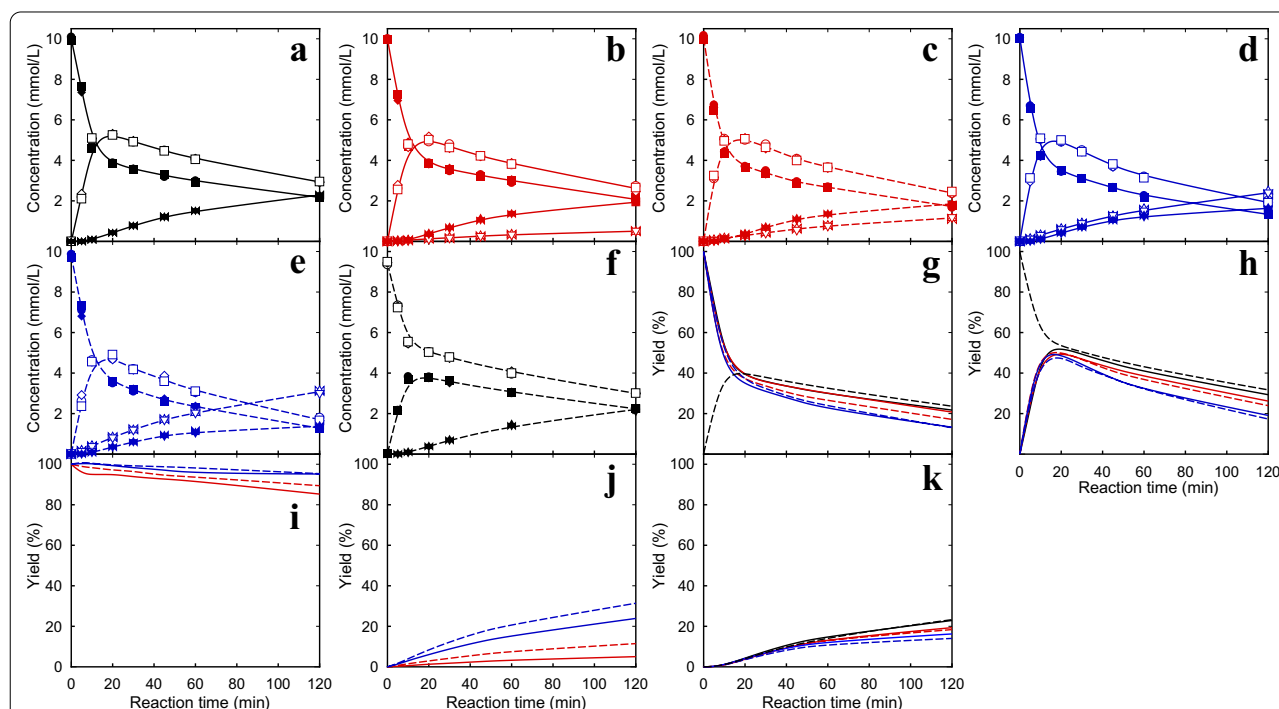


Fig. 6 Time courses of the changes in the concentrations of **Ap** (filled circles, filled diamonds, and filled squares), **Vg** (open circles, open diamonds, and open squares), **ApCr** (open bow-tie-shaped marks, open triangles, and open inverted triangles), and **ApVg** (filled bow-tie-shaped marks, filled triangles, and filled inverted triangles) in systems Cr0': **a** (solid black lines), Cr10': **b** (solid red lines), Cr25': **c** (dotted red lines), Cr50': **d** (solid blue lines), Cr75': **e** (dotted blue lines), and Vg: **f** (dotted black lines), and in the yields of **Ap**: **g**, **Vg**: **h**, **Cr**: **i**, **ApCr**: **j**, and **ApVg**: **k** in all the systems. Filled circles, open circles, open bow-tie-shaped marks, and filled bow-tie-shaped marks show the 1st trials. Filled diamonds, open diamonds, open triangles, and filled triangles show the 2nd trials. Filled squares, open squares, open inverted triangles, and filled inverted triangles show the 3rd trials

show that the chemical reaction that progressed in all the systems before a reaction time of 20 min could be limited to the interconversion between **Ap** and **Vg** via **QM_{Ap}** regardless of the starting compound (**Ap** or **Vg**). The ratio of the amounts of **Vg** to **Ap** remaining after a reaction time of 20 min in each system was almost constant between 1.3 and 1.4, although their absolute amounts gradually decreased owing to the progress of the condensation reactions. Therefore, the interconversion between **Ap** and **Vg** via **QM_{Ap}** represents the pre-equilibrium step of the condensation reactions; hence, it was much more rapid than the condensation reactions in the systems employed in this study. In actual soda cooking processes, this type of equilibrium corresponds to that between a C₆-C₂-type enol ether and C₆-C₂-type β-O-4 substructures. Although the establishment of this equilibrium is not general, a few previous reports supposed or referred to it [26, 27].

This pre-equilibrium is described by formula (1), where k_{Ap} and k_{-Ap} are the rate constants of the conversion of **Ap** to **QM_{Ap}** and the reverse conversion, respectively, and k_{Vg} and k_{-Vg} are the rate constants of the conversion of **Vg** to **QM_{Ap}** and the reverse conversion, respectively.



Ap and **Vg** do not decrease owing to this interconversion, although these compounds disappear owing to the progress of condensation reactions after establishing the pre-equilibrium. Equations (2) and (3) thus work thereafter when [**Ap**], [**QM_{Ap}**], and [**Vg**] show the concentrations of **Ap**, **QM_{Ap}**, and **Vg**, respectively.

$$d[\text{Ap}]/dt = -k_{Ap}[\text{Ap}] + k_{-Ap}[\text{QM}_{Ap}] = 0 \quad (2)$$

$$d[\text{Vg}]/dt = -k_{Vg}[\text{Vg}] + k_{-Vg}[\text{QM}_{Ap}] = 0 \quad (3)$$

By arranging these equations, the following Eq. (4) is obtained because the value of [**Vg**]/[**Ap**] is approximately 1.3.

$$[\text{Vg}]/[\text{Ap}] = (k_{Ap}/k_{Vg})(k_{-Vg}/k_{-Ap}) \approx 1.3 \quad (4)$$

In our previous report, the formation rates of **Ap** and **Vg** from **QM_{Ap}** were examined by generating **QM_{Ap}** from the benzyl methyl ether of **Ap** (2-methoxy-4-(1-methoxyethyl)phenol) and detecting **Ap** and **Vg** as almost exclusive reaction products under conditions using the same concentration of NaOH as in this report (1.0 mol/L) at a temperature of 95 °C [28]. The ratio [**Vg**]/[**Ap**] during this reaction was presumed to be smaller than 0.1, because the yield of **Ap** was always higher than 90% based on the amount of the disappearing starting compound.

Furthermore, the interconversion between **Ap** and **Vg** was slow at 95 °C, which was much lower than the temperature employed in this study (150 °C). Thus, the value of 0.1 is regarded to correspond to that of k_{-Vg}/k_{-Ap} . When 0.1 is used as the value of k_{-Vg}/k_{-Ap} in Eq. (4), despite the different temperatures employed between this and our previous reports, the value of k_{Ap}/k_{Vg} is calculated to be approximately 13. The values of k_{Ap}/k_{-Ap} and k_{-Vg}/k_{-Vg} cannot be calculated only from the above discussion. A schematic of the potential energy diagram for this interconversion is shown in Fig. 7. The formation of **Ap** is kinetically more favorable than that of **Vg** when these compounds are generated from **QM_{Ap}**, which is expressed by the activation energy of the route from **QM_{Ap}** to **Ap** (TS_{Ap}) lower than that from **QM_{Ap}** to **Vg** (TS_{Vg}). **Vg** is thermodynamically more stable than **Ap** in this equilibrium via **QM_{Ap}**, which is expressed by the free energy of **Vg** lower than that of **Ap**.

Condensation reactions and predominant formation of α-β-type condensation product

In order to determine how frequent side reactions including further condensations were, it is necessary to determine what percentage of the whole reaction products, **ApCr** and **ApVg**, they represented. In system Cr0', the starting compound, **Ap**, was converted to **Vg**, **ApVg**, and side products, including further condensation products. In systems Cr10'–Cr75', it was converted to **Vg**,

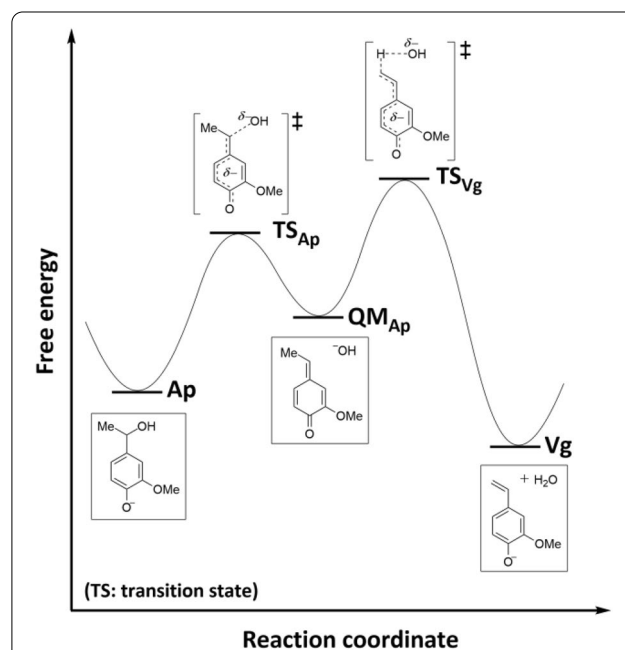


Fig. 7 Schematic potential energy diagram for the interconversion between **Ap** and **Vg** as the pre-equilibrium of condensation reactions in this study

ApCr, **ApVg**, and side products, including them. In system Vg, **Vg** was converted to **Ap**, **ApVg**, and side products, including them. The total molar yield of **Ap**, **Vg**, **ApCr**, and twice the **ApVg** was 97% (± 0.3), 91% (± 3.2), 89% (± 1.4), 89% (± 1.2), 90% (± 2.2), or 102% (± 1.1) (the values in parentheses: standard deviations obtained by three duplications) based on the initial molar amount of the starting compound, **Ap** or **Vg**, at the end of the reaction (120 min) in system Cr0', Cr10', Cr25', Cr50', Cr75', or Vg, respectively (see Additional file 1: Table S1). The formation of a molecule of **ApVg** consumes two molecules of **Vg** or each molecule of **Ap** and **Vg**, either of which was originally the starting compound but inter-converted to each other during the reaction owing to the establishment of pre-equilibrium, resulting in usage of twice amount of **ApVg** in the calculation. Thus, it was confirmed that side reactions, including further condensation, progressed only slightly in all systems.

The characteristic findings in this report are as follows: (i) No self-condensation products of **Ap** were formed even in system Cr0', as well as in the others, as described above; (ii) **ApVg** was formed exclusively in systems Cr0' and Vg, and its formation was greater than that of **ApCr** in systems Cr10' and Cr25', but slightly less significant than that of **ApCr** even in system Cr50'; (iii) The formation of **ApVg** gradually decreased with increasing initial concentration of **Cr** despite the small decreases, whereas that of **ApCr** gradually increased; (iv) The formation of **ApVg** in system Vg exhibited almost the same behavior as that in system Cr0'.

The α -5-type and α -1-type self-condensation products of **Ap**, 1-[2-hydroxy-5-(1-hydroxyethyl)-3-methoxyphenyl]-1-(4-hydroxy-3-methoxyphenyl)ethane and 1,1-bis(4-hydroxy-3-methoxyphenyl)ethane, respectively (Fig. 4), were expected to form. However, as per finding i), these compounds were not isolated. Because further condensation of dimers was confirmed to be a minor reaction, as described above, the absence of these self-condensation products of **Ap** does not result from their further condensation, but from their small formation.

Moreover, finding (i) is quite different from the result obtained in our previous studies, in which soda cooking treatments of **Va** were conducted under similar conditions as those in this report [24, 25]. The **Va** self-condenses more frequently than condensation with coexisting **Cr**. The absence of self-condensation of **Ap** observed in this report results from either of the low reactivity of **Ap** as a nucleophile or that of **QM_{Ap}** as an electrophile, or both. The low reactivity of **QM_{Ap}** as an electrophile seems most decisive than the others, because of the following observations: a) The condensation reactions in system Cr75' (Fig. 6e), in which the nucleophile

was mostly **Cr** (75 mmol/L), progressed slower than those in system Cr75 employed in our previous reports (Table 1), also in which the nucleophile was mostly **Cr** (75 mmol/L) [24, 25]. This shows that nucleophilic addition of **Cr** to **QM_{Ap}** is slower when compared with that to **QM_{Va}**. b) The concentration of **QM_{Ap}** present in system Cr75' is presumed to be higher than that of **QM_{Va}** in system Cr75. This presumption is based on both the Hammond postulate and our previous result which states that the formation of **QM_{Ap}** is much faster than that of **QM_{Va}** in alkaline treatment using the same concentration of NaOH as this report at a lower temperature of 95 °C [28]. The Hammond postulate says that the stability of a compound is higher than that of another compound under certain conditions when the formation of the former compound is faster than that of the latter compound from an original specific compound under these conditions. It is thus confirmed that the low reactivity of **QM_{Ap}**, as an electrophile, in the condensation reactions in observation a) is not apparent, but absolute. The low reactivity is attributed to the presence of methyl group at the β -position of **QM_{Ap}**. The presence lowers the reactivity via the steric and electronic factors and results in the above-described absence of the self-condensation products of **Ap**.

The finding (ii) shows that **Vg** reacts at its β -carbon with **QM_{Ap}** much more rapidly than **Ap** reacts at its aromatic C5-carbon with it. In system Cr50', the formation rate of **ApVg** was similar to that of **ApCr** (Fig. 6d). Because the concentration of **Vg** was always lower than 5 mmol/L in system Cr50' (Fig. 6d), in which the concentration of **Cr** was equal to or just slightly lower than 50 mmol/L (Fig. 6i), the rate of the reaction of **Vg** with **QM_{Ap}** can be at least more than 10 times of that of **Cr** with **QM_{Ap}**. Notably, 1-(4-hydroxy-3-methoxyphenyl)-1-(2-hydroxy-3-methoxy-5-vinyl)ethane, which is the α -5-type condensation product between **QM_{Ap}** and **Vg**, did not form at all. Thus, **Vg** reacts exclusively at its β -carbon in the side chain with **QM_{Ap}**. Although **ApVg'**, which is the HO⁻ adduct of **QM_{ApVg}**, was expected to form (Fig. 4) similarly to the formation of **Ap** from **QM_{Ap}**, it was not detected at all. Although this absence cannot be rationally explained only on the basis of the results obtained in this report, the thermodynamic stability of **ApVg'** may be much lower than that of **ApVg**. The *cis* counterpart of **ApVg** was not formed. Although the *cis* counterpart must be thermodynamically less stable than **ApVg**, it is unclear whether the difference in their thermodynamic stabilities is sufficiently large to result in an absence.

The finding (iii) naturally shows that the reactions of **Vg** and **Cr** with **QM_{Ap}** are competitive with each other. However, the large increase in the concentration of **Cr** with the variation from system Cr0' to Cr75' did not

remarkably affect the competitive reaction of **Vg** with **QM_{Ap}**. Thus, the reaction of **Vg** with **QM_{Ap}** is much faster than that of **Cr** with **QM_{Ap}**, as described above.

The finding (iv) supports the establishment of an equilibrium between **Ap** and **Vg** before the clear progress of the condensation reactions.

It was thus clarified that **Ap** undergoes the condensation reactions much slower than **Va**. This low reactivity of **Ap** is mainly attributed to the steric factor of the side chain larger than that of **Va**. However, because even the steric factor of the side chain of **Ap** is much smaller than that of native lignin and residual lignin in being cooked pulp, it is suggested that condensation reactions of lignin in soda cooking processes progress less frequently than those we have believed for far.

Because the major condensation product, **ApVg**, was the α - β -type, the formation of which has not been well known as a condensation mode, its formation is a new finding of this report. In this study, the α - β -type condensation progressed much faster than the most common condensation mode, the α -5-type. The α - β -type condensation can progress between two phenolic substructures, either of which has a conjugated carbon-carbon double bond at the side chain. Such phenolic substructures with unsaturated side chains may not exist with large amounts in residual or dissolved lignin in alkaline cooking processes when compared with the amount of aromatic nuclei, most of all which are reaction sites in the α -5-type condensation. Candidates for such phenolic substructures with unsaturated side chains are C_6 - C_2 -type enol ethers and stilbenes, which are produced from the **QMs** derived from β -*O*-4 and β -5 substructures, respectively, by releasing the γ -position as the formaldehyde (HCHO) molecule in alkaline cooking processes, as well as coniferyl alcohol, which can be produced as the counterpart of releasing phenoxides in the common β -*O*-4 bond cleavage in kraft cooking processes, and others. When it is also taken into consideration that the steric factor is larger in actual alkaline cooking processes than in this model experiment, the predominant progress of the α - β -type condensation found in this report supports our previous suggestion that the progress of the condensation reactions of lignin, at least whose modes are the common α -5- and α -1-types, is not necessarily an important factor in suppressing delignification in the later stages of alkaline cooking processes [25]. However, the condensation reaction of lignin certainly progresses when steric factor is not large. Thus, it may not result in polymerization of lignin, but in structural alteration of residual and dissolved lignin, which will affect their usability in subsequent biomass utilization.

Formation of minor monomeric products

It was presumed in our previous report that **QM_{Va}** oxidizes **Va** to **V**, whereas **QM_{Va}** itself is reduced to **Cr** in systems Cr0–Cr75 [24]. Hence, the formation of **AG** in this study may be explained by the progress of this type of reaction, namely, the oxidation of **Ap** by **QM_{Ap}** (Fig. 8), despite the lack of detection of the reduction product of **QM_{Ap}** (4-ethyl-2-methoxyphenol, ethylguaicol). The yields of **AG** were 1.0% (± 0.0), 0.9% (± 0.0), 0.9% (± 0.1), 0.8% (± 0.0), 0.8% (± 0.1), and 0.9% (± 0.1) in systems Cr0', Cr10', Cr25', Cr50', Cr75', and Vg, respectively, at the end of the reactions based on the initial molar amount of **Ap** or **Vg** (the values in parentheses are standard deviations obtained by the three duplications). These yields were clearly lower than those of **V** in our previous report [24], which suggests that **QM_{Ap}** has a reactivity lower than **QM_{Va}** in this type of reaction. Anyway, the formation of **AG** is a minor reaction.

It was also presumed in our previous report that the precursor produced primarily in the formation of the

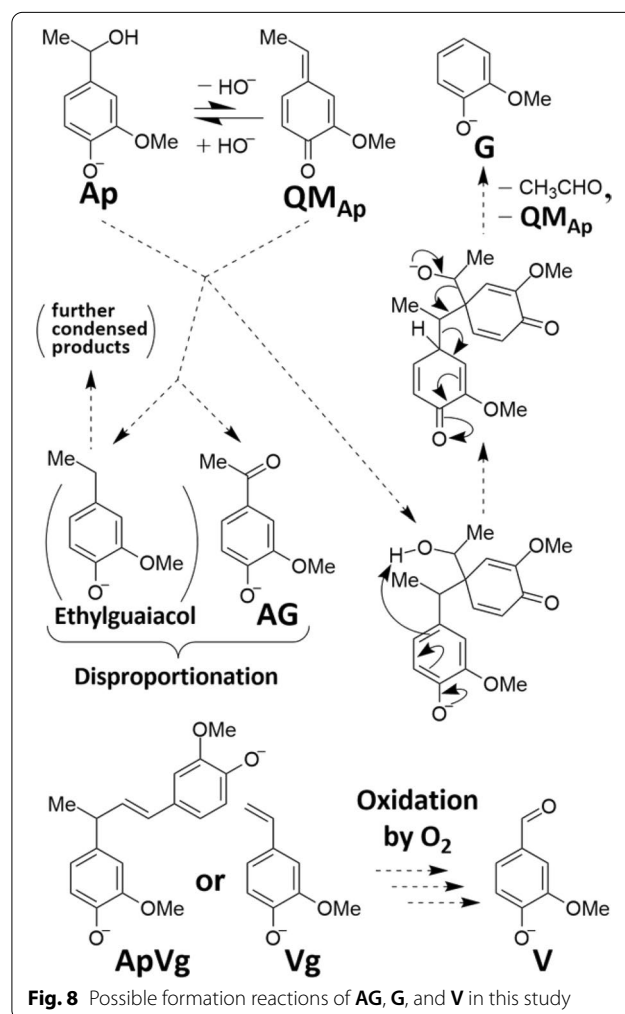


Fig. 8 Possible formation reactions of **AG**, **G**, and **V** in this study

α -1-type self-condensation product of **Va** can be rearranged to afford **G** and **QM_{Va}** by releasing the HCHO molecule in systems Cr0–Cr75 [24]. Thus, as shown in Fig. 8, the formation of **G** in this study can be explained by the progress of this type of reaction, namely, the rearrangement of the precursor of the α -1-type self-condensation product of **Ap** to afford **G** and **QM_{Ap}** by releasing the acetaldehyde (CH₃CHO) molecule, despite the lack of detection of the α -1-type self-condensation product of **Ap**. The precursor may exclusively undergo rearrangement to afford **G**, **QM_{Ap}**, and CH₃CHO without progressing to the α -1-type self-condensation product. The yields of **G** were 5.4% (\pm 0.1), 4.7% (\pm 0.1), 5.0% (\pm 0.1), 5.2% (\pm 0.3), 4.5% (\pm 0.7) and 5.2% (\pm 0.2) in systems Cr0', Cr10', Cr25', Cr50', Cr75', and Vg, respectively, at the end of the reactions based on the initial molar amount of **Ap** or **Vg**, which were comparable to those detected in our previous report [24].

A possible reaction for the formation of **V** involves the oxidation of **Vg** or **ApVg** by oxygen, possibly contaminating the system. It was shown that the guaiacoxystyrene (4-hydroxy-3-methoxystyrene) substructure, which is **Vg** itself or a constituent of **ApVg**, is quite labile to oxygen oxidation under alkaline conditions, affording **V** in high yield [29, 30]. The yields of **V** were only 0.4% (\pm 0.0), 0.5% (\pm 0.0), 0.5% (\pm 0.1), 0.5% (\pm 0.1), 0.4% (\pm 0.0) and 0.7% (\pm 0.2) in systems Cr0', Cr10', Cr25', Cr50', Cr75', and Vg, respectively, at the end of the reactions based on the initial molar amount of **Ap** or **Vg**, indicating that the formation of **V** is a minor reaction.

Conclusions

The condensation reaction of lignin was quantitatively examined in a model system in which a phenolic lignin model compound, **Ap**, was reacted with or without another phenolic lignin model compound, **Cr**, under soda cooking conditions with various initial concentrations of **Cr**.

Ap was primarily converted to **Vg** via **QM_{Ap}** to establish an equilibrium between these compounds before the progress of condensation reactions. The ratio, **[Vg]/[Ap]**, showed a value of 1.3–1.4 in this equilibrium.

Only **ApCr**, the α -5-type condensation product between **Ap** and **Cr**, and **ApVg**, the α - β -type condensation product between **Ap** and **Vg** or between two molecules of **Vg**, were isolated and identified without any self-condensation products of **Ap**. This is in contrast to the same soda cooking treatment of **Va** with or without **Cr** conducted in our previous reports, where the self-condensation reactions of **Va** preferentially progressed [24, 25]. The formation of **ApVg** was over 10 times faster than that of **ApCr**. Thus, the α - β -type condensation was suggested to be the major mode in condensation reaction

of lignin. This type of condensation has not yet been well known, and hence is a new finding in this report.

This new finding, as well as others, suggests that the progress of the condensation reaction of lignin is not necessarily an important factor in suppressing delignification in the later stages of alkaline cooking processes.

Abbreviations

AG: Acetoguaiacone (4-acetyl-2-methoxyphenol); **Ap**: Apcynol (4-(1-hydroxyethyl)-2-methoxyphenol); **ApCr**: The α -5-type condensation product between **Ap** and **Cr** (1-(4-hydroxy-3-methoxyphenyl)-1-(2-hydroxy-3-methoxy-5-methylphenyl)ethane); **ApVg**: The α - β -type condensation product between **Ap** and **Vg** or between two molecules of **Vg** (*trans*-1,3-bis(4-hydroxy-3-methoxyphenyl)but-1-ene); **ApVg'**: The H₂O adduct of **ApVg** (1,3-bis(4-hydroxy-3-methoxyphenyl)butan-1-ol); **Cr**: Creosol (2-methoxy-4-methylphenol); **G**: Guaiacol (2-methoxyphenol); **IS**: Internal standard compound (3-ethoxy-4-hydroxybenzaldehyde); **QM**: Quinone methide intermediate; **QM_{Ap}**: The **QM** derived from **Ap** or **Vg**; **QM_{ApVg}**: The **QM** derived from **ApVg**; **QM_{Va}**: The **QM** derived from **Va**; **QM_{VaVa}**: The **QM** derived from **VaVa**; **V**: Vanillin; **Va**: Vanillyl alcohol; **VaCr**: The α -5-type condensation product between **Va** and **Cr** (2-(4-hydroxy-3-methoxybenzyl)-6-methoxy-4-methylphenol); **VaVa**: The α -5-type self-condensation product of **Va** (2-(4-hydroxy-3-methoxybenzyl)-4-hydroxymethyl-6-methoxyphenol); **VaVa'**: The α -1-type self-condensation product of **Va** (bis(4-hydroxy-3-methoxyphenyl)methane); **VaVaVa'**: The α -5/ α -1-type self-condensation product of **Va** (2,4-bis(4-hydroxy-3-methoxybenzyl)-6-methoxyphenol); **Vg**: Vinylguaiacol (2-methoxy-4-vinylphenol).

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s10086-022-02069-8>.

Additional file 1: Figure S1. 1H-NMR, 13C-NMR, 13C-NMR DEPT135, ESI-MS, 2D-NMR 1H-1H COSY, 2D-NMR 1H-13C HSQC, and 2D-NMR 1H-13C HMBC spectra of **Vg**. **Figure S2.** Those of **ApCr**. **Figure S3.** Those of **ApVg**. **Table S1.** Yields or recovery yield of **Ap**, **Vg**, **ApCr**, and **ApVg**, and total yields of these compounds at all data points. Assignments of the 1H- and 13C-NMR spectral peaks of **V**, **AG**, and **G**.

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Author contributions

TK conducted the experiments, analyzed the obtained data, and wrote the draft of this manuscript under the supervision of TY. TY completed the final manuscript. Both authors have read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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