Title:

Role of methoxyl group in char formation from lignin-related compounds

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Abstract:

Although lignin carbonization is an important process in wood pyrolysis, the molecular mechanism has not been clarified yet. In this study, the vapor-phase carbonization of various lignin-related compounds was studied under the pyrolysis conditions of N_2/ 600 ºC/ 80 s. The methoxyl groups were found necessary for char formation. Interestingly, ethoxyl group was not effective in such char formation. Guaiacol and 2-ethoxyphenol gave pyrocatechol (formed through thermal homolysis of the O-R bonds) and the ether-rearranged products (*o*-cresol, 2-ethylphenol, xanthenes and 2,3-benzofuran). The latter products are likely formed via an *o*-quinone methide intermediate, initiated from the H-abstraction of the phenolic hydroxyl groups. 2-Ethoxyphenol gave larger amounts of 2,3-benzofuran and less xanthenes and char than guaiacol, with yields of other products similar. Such reactivity difference is explainable with the different reactivities of the *o*-quinone methide intermediates. Based on the results, *o*-quinone methide is proposed as an important intermediate for lignin char formation during pyrolysis.

Keywords:

1. Introduction

Pyrolysis is the fundamental process of carbonization, fast pyrolysis and gasification of woody biomass [1]. The molecular mechanisms of wood pyrolysis are therefore important for understanding and improving these thermochemical conversion processes.

Lignin, which is normally contained in wood in 20-30%, is a polymer of phenylpropanes linked through ether and C-C linkages [2]. Three types of aromatic rings exit, guaiacyl (4-hydroxy-3-methoxyphenyl), syringyl (3,5-dimethoxy-4-hydroxyphenyl) and *p*-hydroxyphenyl types, exist [2]. The aromatic type is different dependent on the species, such as softwoods, hardwoods and herbaceous plants. This study focuses on the softwood lignin which is mainly guaiacyl type.

The pyrolytic weight-loss behavior of lignin has been studied with thermogravimetry [3]. Lignin has a tendency to form the volatile products in a wide range of temperature between 200-500ºC [3]. The chemical structures of various volatile products have been elucidated with the isolated compounds [4,5] or by gas chromatography-mass spectrometry (GC-MS) [6-9]. From the softwood samples, various low molecular weight (MW) products with guaiacyl units have been reported as the primary pyrolysis products, which include coniferyl alcohol, coniferyl aldehyde, isoeugenol, vanillin and so on [6-9]. Many papers have also focused on the pyrolytic

reactions of the ether and C-C linkage-types of structures in lignin by using various model dimers [10-16] and the isolated lignins [16]. Nakamura et al. [16] reported that the milled wood lignin (MWL) isolated from the Japanese cedar (*Cryptomeria japonica*) wood was pyrolyzed to form the condensation (< 200 °C), low MW (300-350 °C) and carbonized products (350-400 °C) during the increased temperature. Some low temperature condensation mechanisms [10-13] and depolymerization (ether cleavage) mechanisms have been discussed in the literatures. However, the carbonization mechanism has not yet been discussed.

Hosoya et al. [17-19] have reported the formation and secondary decomposition behaviors of the primary tar (volatile) fractions from lignin under pyrolysis gasification conditions (without addition of any gasifying agents), as compared with cellulose, hemicelluloses and wood samples. Although the cellulose-derived tar fraction was gasified quickly, gas formation from the lignin-derived fractions was very slow [18]. Instead, some structural changes of the tar components and vapor-phase carbonization were observed for lignin [19]. They also reported that this carbonization was closely related to the disappearance of the O-CH$_3$ groups in lignin aromatic rings [18].

In this paper, carbonization reactivities of various lignin-derived tar components are described, focusing on the O-CH$_3$ groups. The reaction pathways which are related to the carbonization are proposed.

2. Experimental

2.1. Materials

Model compounds (4-methylguaiacol, 4-ethylguaiacol, isoeugenol, eugenol, vanillin, acetovanillone, phenol, *o*-cresol, *p*-cresol, 2,4-xylenol, 4-methylcatechol, 4-ethylcatechol, 2-ethoxyphenol and 2-hydroxymethylphenol) were purchased from Nacalai Tesque Co. 4-Vinylguaiacol was prepared according to the literature [20]. 4-Propylguaiacol was prepared by hydrogenation of isoeugenol on 10% Pd/C.

2.2. Pyrolysis and product analysis

The sample (10 mg) was placed at the bottom of a Pyrex glass ampoule. The ampoule was closed in N_2 (internal diameter: 8.0 mm, length: 120 mm, glass thickness: 1.0 mm), and the whole ampoule was heated in a muffle furnace (600 °C) for 80 s. During pyrolysis, the ampoule was maintained in the upright setting. After pyrolysis, the ampoule was immediately cooled with flowing air (1 min) and subsequently in cold water (1 min). After the ampoule was opened, the inside was extracted with methanol (1.0 ml) to give the soluble and insoluble portions. The insoluble portions, which were obtained as black solids, were defined as the char fractions in this paper. The yield of char was determined from the weight of the oven-dried (105 °C for 24h) ampoule after extraction.

The tar fraction was analyzed by GC-MS with a Hitachi G-7000 gas chromatograph and a Hitachi M9000 mass spectrometer under the following conditions:

column: Shimadzu CBP-M25-O25 (length: 25 m, diameter: 0.25 mm), injector temperature: 250 °C, column temperature: 40 °C (1 min), 40 → 300 °C (1 → 53 min), 300 °C (53 → 60 min), carrier gas: helium, flow rate: 1.5 ml/min, emission current: 20 μA, ionization time: 2.0 ms. Identification of the products was conducted from the comparison of the retention times and the mass fragmentation patterns with those of the authentic compounds. The xanthene derivatives other than *9H*-xanthene were identified only from their fragmentation patterns. The yields of the products were determined from the peak areas in the total ion chromatograms as compared with that of *p*-dibromobenzene as an internal standard.

3. Results and discussion

Figure 1 shows the pictures of the ampoules after pyrolysis (N_2/ 600 °C/ 80 s) and subsequent tar extraction. The compounds except 2-ethoxyphenol are volatile products previously reported in lignin pyrolysis [6-9, 17].

Substantial amount of char was formed only from the compounds with the guaiacyl-units, especially guaiacol and derivatives with the C=C or C=O side-chains. This carbonization proceeds probably in vapor-phase after volatilization of the compounds, since these were placed at the bottom of the ampoule before pyrolysis. Interestingly, char formation from 2-ethoxyphenol was negligible. Thus, the methoxyl group was suggested as a key structure for lignin char formation. These results are in

good agreement with our previous observation that the vapor-phase carbonization of the lignin-derived volatile products was closely related to the disappearance of the methoxyl groups [18].

Higher char formation reactivities of the unsaturated derivatives with $>C=C<$ side-chains than the saturated ones would be related to their higher polymerization reactivities. Nakamura et al. [14] have reported that lignin-related $>C_\alpha=C_\beta<$ structures were very reactive for thermal polymerization via styrene-type radical polymerization mechanism. Hosoya et al. [19] have also suggested similar polymerization prevailing during secondary reactions of lignin-derived pyrolysis vapors at 600°C.

Comparison of the pyrolysis products between guaiacol and 2-ethoxyphenol will give information about the role of the methoxyl group in carbonization. Replacement of the methoxyl group in guaiacol with ethoxyl group should change the reaction pathways to those which do not form the carbonized products. Figure 2 shows the total ion chromatograms of the MeOH-soluble portions. 2,3-Benzofuran (**2**) was identified along with pyrocatechol (**5**), *o*-cresol (**3**), 2-ethylphenol (**4**) and phenol (**1**). 2,3-Benzofuran was newly identified in this paper from lignin-related compounds.

Several peaks (named as compounds **6-9**) were observed around the retention times of 25-35 min. These signals were larger in guaiacol. Figure 3 shows the mass spectra of these peaks **6-9**. Compound **6** was identified as *9H*-xanthene by comparing the retention time and the mass fragmentation pattern with those of the

authentic compound.   Compounds **7-9** also had the fragment ion (m/z=181) which corresponds to the molecular ion of *9H*-xanthene.   Furthermore, the molecular ions (m/z=196, 198, 212) observed for compounds **7-9**, respectively, indicate xanthene derivatives with CH_3 and/or OH substituents as shown in Fig. 3, although the positions of the substituent groups are unknown at the moment.

Table 1 summarizes the product yields from guaiacol and 2-ethoxyphenol.   The xanthene derivatives were not quantified due to lack of the proper authentic compounds other than compound **6**.   The total yields of the products including char was 58.1 (guaiacol) and 64.7 % (2-ethoxyphenol).   Main differences are observed in the yields of 2,3-benzofuran, char and xanthenes.   As already described, the char yield from 2-ethoxyphenol was undetectable as compared with that (17 %) from guaiacol.   Instead, 2-ethoxyphenol gave 2,3-benzofuran (17 %) (cf. 0.95 % from guaiacol).   The yields of other types of the products were not so different between the two compounds.

The different product compositions between guaiacol and 2-ethoxyphenol are discussed with the reaction pathways in Fig. 4.   As for pyrolysis of guaiacol and other methyl phenyl ether-type compounds, two types of the reactions have been proposed, the O-CH_2R homolysis (reaction a) and the radical-induced reaction (b) [21].   The former reaction a gives a catechol radical and an alkyl radical ($\cdot CH_2$R).   The catechol radical is further stabilized to catechol via H-abstraction.

Reaction b gives the ether rearranged products.   This reaction is reported to be

initiated from the phenoxy radical formation [21].   The intramolecular H-abstraction at the methyl (or methylene) group by the phenoxy radical and subsequent 1,2-aryl migration have been proposed for the ether-rearrangement mechanism [21, 22].   This type of 1,2-aryl migration has been supported from the high yield formation of *o*-hydroxybenzaldehyde from guaiacol in the presence of cumene (a H-donor) [21]. Benzaldehyde has also been obtained in pyrolysis of anisol (methyl phenyl ether) [23]. These 1,2-aryl migration products are further converted to the *o*-quinone methides. *o*-Quinone methide **10** has been proposed as a key intermediate for the formation of *o*-cresol (**3**) [24, 25].   Consequently, *o*-cresol (**3**) and 2-ethylphenol (**4**) are formed from the corresponding *o*-quinone methides **10** and **11**, respectively.   *o*-Cresol from 2-ethoxyphenol and 2-ethylphenol from guaiacol would be formed through some alternation of the side-chains (i.e. cracking or addition type reaction).

Diels-Alder type reactions proceed in *o*-quinone methide **10** [25-33].   The spiro-type dimer **12** and trimer **13** have been isolated from compound **10** (Fig. 5) [30-33].   Trimer **13** includes a similar ring-system to xanthene.   In our experiments, these dimer and trimer were not detected probably due to the higher pyrolysis temperature.   From these lines of consideration, the formation mechanisms of xanthenes **6-9** is suggested to include the Diels-Alder type reactions as illustrated in Fig. 5, although it is not clear whether these reactions include the spiro-type intermediates or not.

A proposed formation mechanism of 2,3-benzofuran (**2**) is illustrated in Fig. 6. *o*-Quinone methide **11** has an allyl methyl group which has comparatively weak C-H bonds. In pyrolysis, this weak C-H bond is dissociated through H-abstraction by other radical species to form the allyl radical intermediate, and the following cyclization gives 2,3-benzofuran (**2**). Thus, *o*-quinone methide **10** from guaiacol does not form 2,3,-benzofuran (**2**) directly. Formation of small amount (0.95 %) of compound **2** from guaiacol may be derived from the addition of the methyl group to *o*-quinone methide **10** or *o*-cresol. This is also consistent with the formation of small amount of 2-ethylphenol (**4**) from guaiacol.

Consequently, pyrocatechol (**5**) (20 % from guaiacol, 24 % from 2-ethoxyphenol) is produced from the direct homolysis pathway (a, Fig. 4), while *o*-cresol (**3**), 2-ethylphenol (**4**), 2,3-benzofuran (**2**) and xanthenes (**6-9**) are the products from the radical-induced rearrangement (b).

The yields of the hydrogenation products of *o*-quinone methides [*o*-cresol (**3**), 2-ethylphenol (**4**)] are not so different (16.2 % from guaiacol, 16.9 % from 2-ethoxyphenol). However, the yields of 2,3-benzofuran (**2**) (0.95 and 17%) and char (17% and undetectable) are quite different in pyrolysis of guaiacol and 2-ethoxyphenol, respectively. Such differences in product compositions may arise from the different reactivities of *o*-quinone methides **10** and **11**. *o*-Quinone methide **11** with reactive allyl group tends to be converted to 2,3-benzofuran instead of the carbonized products.

Formation of dimers through Diels-Alder type reaction (Fig. 5) indicates that *o*-quinone methide **10** can polymerize.　This polymerization would be related to the carbonization, i.e. the formation of the polycyclic aromatic hydrocarbon type structures, because the Diels-Alder reaction forms the multi-ring systems and reactive diphenyl methane structures.　Additional methyl group in compound **11** reduces the Diels-Alder reactivity due to the increasing steric hindrance.　This hypothesis is also supported by the lower yields of the dimers (xanthenes) from 2-ethoxyphenol than guaiacol (Fig. 2).

　　2-Hydroxymethylphenol, which is used for *in situ* formation of *o*-quinone methide **10** [24, 32], gave substantial amount (55 %) of the carbonized products mainly at the bottom of the reactor, along with several large xanthenes peaks in the GC-MS total-ion chromatogram (Fig. 7).　Thus, 2-hydroxymethylphenol is very reactive enough to form the carbonized products before volatilization.　These results also support the hypothesis that *o*-quinone methide **10** is an important intermediate for lignin carbonization.

　　The results of this paper were obtained under the specific pyrolysis conditions of vapor-phase in a closed reactor.　Thus, careful consideration is required for generalization of this proposed mechanism for various thermochemical processes such as gasification and carbonization.　In gasification, this type of carbonization mechanism would be included in the vapor-phase secondary reactions of the pyrolysis vapor.　Althernatively, solid lignin is also converted to the primary char in solid-phase.

In this process, *o*-quinone methide is also expected as a key intermediate, since the *o*-quinone methide formation requires only phenyl methyl ether structures in the presence of other radical species.

Wood carbonization is conducted in open and closed reactor.   Even in the open reactor, mass transfer of the lignin-derived pyrolysis vapor is expected to be inhibited in wood tissues.   Cell structures and composite structures of crystalline cellulose and a lignin-hemicellulose matrix would make the volatilization difficult.   In such case, secondary carbonization would be competitive with the volatilization.   Since wood is a composite material of carbohydrates and lignin, interactions between these components and their pyrolysis products would also be considered.   These interactions will be reported in the following paper [34].

4. Conclusions

Effective carbonization required phenyl methyl ether structure in lignin-related compounds in N_2 at 600ºC for short pyrolysis time.   Contrary to this, 2-ethoxyphenol (a phenyl ethyl ether) gave 2,3-benzofuran instead of char and dimers of *o*-quinone methide which are formed through Diels-Alder type reaction.   Based on the results, *o*-quinone methide is proposed as a key intermediate for lignin char formation during pyrolysis.

Acknowledgement

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Legend of tables and figures

Table 1   The product yields (wt%) from guaiacol and 2-ethoxyphenol (N_2/ 600 $^{\circ}$C/ 80 s).

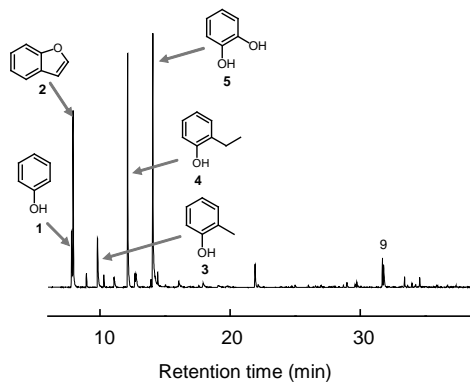Fig. 1   The pictures of the ampoules after pyrolysis and tar-extraction (N_2/ 600 $^{\circ}$C/ 80 s).

Fig. 2   Total-ion chromatograms in GC-MS analysis of the tar fraction obtained from guaiacol and 2-ethoxyphenol (N_2/ 600 $^{\circ}$C/ 80 s).
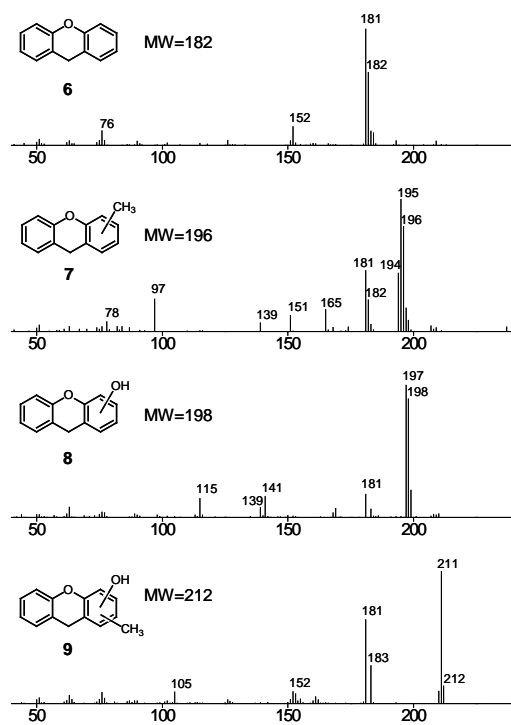
Fig. 3   Mass spectra of the peaks of compounds **6-9** in the GC-MS analysis of the tar
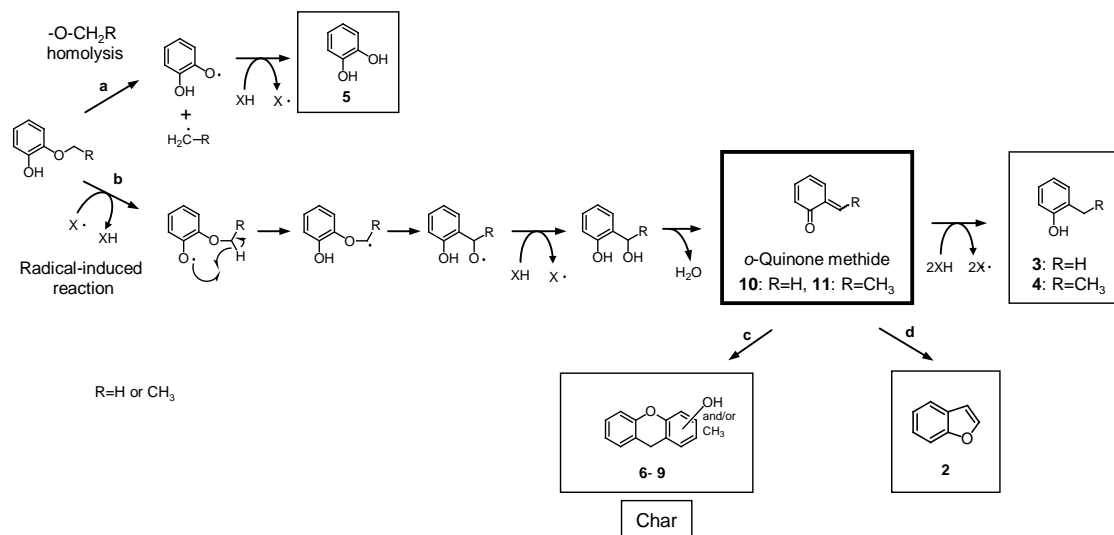
fractions.

Fig. 4   Proposed pyrolysis pathways of guaiacol and 2-ethoxyphenol.
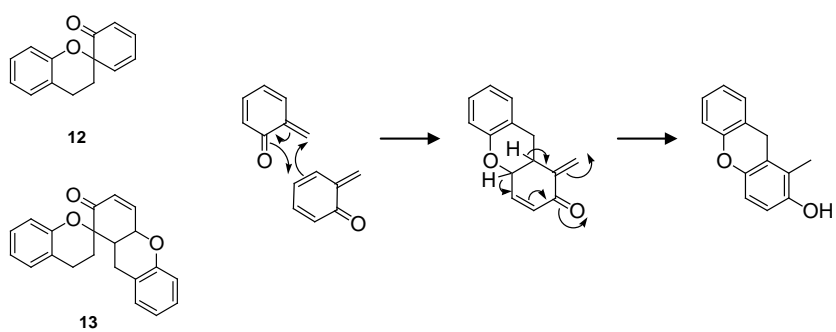

Fig. 5   Diels-Alder type reactions to form the dibenzopyran-type structure.
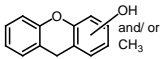
Fig. 6   Formation mechanism of 2,3-benzofuran from **11**.

Fig. 7   The picture of the ampoule and the total-ion chromatogram in GC-MS analysis

of the tar fraction obtained from 2-hydroxymethylphenol (N_2/ 600 ^{o}C/ 80 s).

Table 1
The product yields (wt%) from guaiacol and 2-ethoxyphenol (N_2/ 600°C/ 80 s).

	5	3	4	2	1		Char
Guaiacol (**1**) (R=CH$_3$)	20	15	1.2	0.95	3.9	+++[a]	17
2-Ethoxyphenol (**2**) (R=Et)	24	4.9	12	17	6.8	+	ND[b]

[a] not determined quantitatively. [b] not detected.

Fig. 1 The pictures of the ampoules after pyrolysis and tar-extraction (N$_2$/ 600 ^{o}C/ 80 s).

Fig. 2 Total-ion chromatograms in GC-MS analysis of the tar fraction obtained from guaiacol and 2-ethoxyphenol (N_2/ 600 ºC/ 80 s).

Fig. 3 Mass spectra of the peaks of compounds **6-9** in the GC-MS analysis of the tar fractions.

Fig. 4 Proposed pyrolysis pathways of guaiacol and 2-ethoxyphenol.

Fig. 5 Diels-Alder type reactions to form the dibenzopyran-type structure.
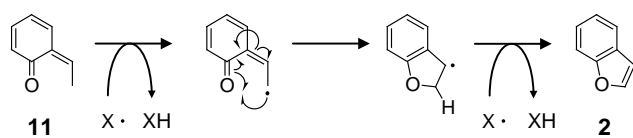
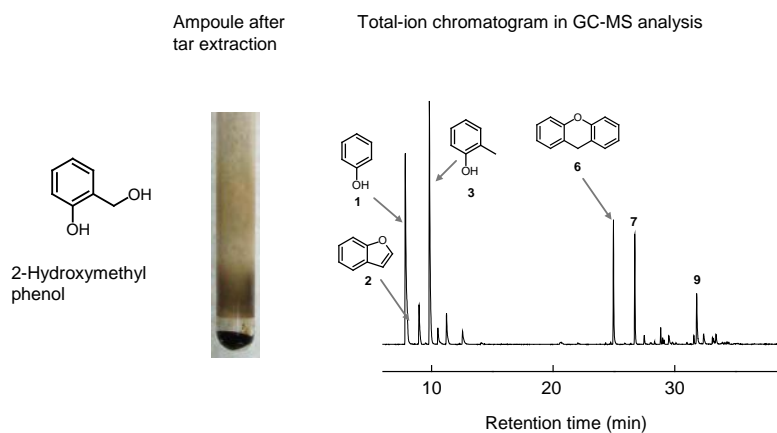Fig. 6 Formation mechanism of 2,3-benzofuran from **11**.

Fig. 7 The picture of the ampoule and the total-ion chromatogram in GC-MS analysis of the tar fraction obtained from 2-hydroxymethylphenol (N_2/ 600 ºC/ 80 s).