



## Gas- and solid/liquid-phase reactions during pyrolysis of softwood and hardwood lignins

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### ABSTRACT

Pyrolytic reactions of Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) milled wood lignins (MWLs) were studied with thermogravimetry (TG) and by pyrolysis in a closed ampoule reactor ( $N_2/600^\circ C$ ). The data were compared with those of guaiacol/syringol as simple lignin model aromatic nuclei. Several DTG peaks were observed around 300–350, 450, 590 and 650 °C. The first DTG peak temperature (326 °C) of beech was lower than that (353 °C) of cedar. This indicates that the volatile formation from cedar MWL is slightly delayed in heating at 600 °C. The gas-phase reactions via GC/MS-detectable low MW products were explainable with the temperature-dependent reactions observed for guaiacol/syringol in our previous paper. The methoxyl groups became reactive at  $\sim 450^\circ C$ , giving O-CH<sub>3</sub> homolysis products (catechols/pyrogallols) and OCH<sub>3</sub> rearrangement products (cresols/xlenols). The former homolysis products were effectively converted into gaseous products (mainly CO) at  $>550\text{--}600^\circ C$ . However, the GC/MS-detectable tar yields, especially syringyl unit-characteristic products, were much lower than those from guaiacol/syringol. Thus, contributions of higher MW intermediates and solid/liquid-phase reactions are more important in lignin pyrolysis. From the results of stepwise pyrolysis of char + coke fractions at 450 and 600 °C, the methoxyl group-related reactions (450 °C) and intermediates gasification (600 °C) were suggested to occur also in the solid/liquid phase. This was consistent with the DTG peaks observed around these temperatures. These solid/liquid-phase reactions reduced the tar formation, especially catechols/pyrogallols and PAHs. Different features observed between these two MWLs are also focused.

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### 1. Introduction

Lignin is an aromatic polymer consisting of phenylpropane-units linked through ether- and condensed-types of linkages. The aromatic ring structures are different depending on the wood species; softwood lignins have 4-hydroxy-3-methoxyphenyl (guaiacyl) type with small amount of *p*-hydroxyphenyl type, while hardwood lignins contain 3,5-dimethoxy-4-hydroxyphenyl (syringyl) type as well as the guaiacyl type. Accordingly, such difference in the aromatic ring structure is expected to affect the pyrolysis behaviors of softwood and hardwood lignins.

Initial pyrolytic reactions of lignin have been studied extensively by thermogravimetry and NMR analysis and with model compounds. Major initial weight loss is observed in the temperature range 300–400 °C in TG analysis [1–7]. Devolatilization tends to be more effective in hardwood lignins [1,3,5,7], which was explained by the smaller contents of the condensed (C–C) types of interphenylpropane-linkages, arising from the inclusion of the

syringyl type. Haw and Schultz [8] reported the cleavage of the  $\beta$ -ether linkage, the most abundant structure in lignin, at a temperature as low as 220 °C based on the CP/MAS NMR data. Model compound studies [9–15] suggest the pathways and molecular mechanisms for cleavage of the ether linkages, including homolysis/heterolysis [12] and role of quinone methide intermediate [12,13]. The model compound data were also used for the study of depolymerization behavior of isolated lignins [14]. Chemical structures of the primary volatile products have been studied mainly using gas chromatography (GC) coupled with mass spectrometry (MS) [16–21]. Various monoaromatic compounds with guaiacyl or syringyl moiety have been identified, which have various double bond side-chains such as  $>C=C<$ ,  $-CHO$  and  $>C=O$  at positions para to the phenolic hydroxyl groups.

These primary products are further pyrolyzed in gas and solid/liquid phases (secondary reactions). Hosoya et al. [22] compared the primary pyrolysis and some secondary reactions behaviors of softwood lignin and other carbohydrate constituents (cellulose and hemicelluloses) with an open-top reactor at 800 °C. They found that gas-phase carbonization (coking) was significant for lignin, although coking from cellulose- and hemicelluloses-derived tars was observed only after condensing on the reactor wall

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with lower temperature. They also found that methoxyl group was a key structure for these coking reactions of lignin [23].

The gas-phase conversions of lignin-derived tars were studied with a closed ampoule reactor at 600 °C [24]. Major structural changes occur in side-chain and aromatic ring substitution pattern: side-chain structures were changed from unsaturated to saturated types, and this was explained with the condensation of the double bond structures followed by cracking; aromatic ring substitution pattern was also changed simultaneously from guaiacol (OCH<sub>3</sub>) type to catechol (OH) and cresol (CH<sub>3</sub>) types. Hosoya et al. [25] reported that these pyrolysis reactions were very much influenced by the carbohydrate-derived vapors acting as a H-donor. Gas formation behaviors were also compared between tar and char fractions from cellulose and lignin [26]. However, these results are only for guaiacyl lignins, and further conversions from the catechol/cresol intermediates have not been studied.

Unlike the guaiacyl lignins, there are few papers relating to the pyrolytic reactions of syringyl and hardwood lignins. Asmadi et al. [27] compared the pyrolysis behaviors of Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) wood samples. As for lignin-related products, coke formation was observed more extensively for beech wood; although syringol (2,6-dimethoxyphenol) derivatives with various double bond side-chains were obtained as well as the corresponding guaiacol (2-methoxyphenol) types in GC/MS-analysis, the compositions became similar for the two species after a long heating time.

The secondary reactions pathways of guaiacols and syringols have been studied with simple model compounds such as guaiacol [23,28–34] and syringol [28,35,36]. Two types of reactions relating to the methoxyl group occur at >450 °C, namely O–CH<sub>3</sub> homolysis and radical-induced OCH<sub>3</sub> rearrangement (*ipso*-substitution) to convert methoxyl to methyl groups. Catechols/pyrogallols and cresols/xilenols are the products formed through these respective pathways, together with CH<sub>4</sub> formation. A large amount of coke is also formed at this stage [23,28]. Asmadi et al. [28] compared these reactions between guaiacol and syringol in an ampoule reactor (N<sub>2</sub>/600 °C). Syringol gave more coke and CH<sub>4</sub> than guaiacol, and this was explained with the additional methoxyl group in syringol.

Asmadi et al. [37] also compared the pyrolytic reactivities of the catechols/pyrogallols and cresols/xilenols in a closed ampoule reactor (N<sub>2</sub>/600 °C). They found that the reactivity increased with an increase in the number of substituent group, and the accelerating effect was greater for OH than for CH<sub>3</sub>. Accordingly, catechols/pyrogallols were effectively converted into gaseous products, mainly CO, at >550–600 °C, while cresols/xilenols were converted much more slowly into demethylation products together with H<sub>2</sub>, CH<sub>4</sub> and coke. The syringol-derived intermediates with more substituents were generally more reactive than the corresponding guaiacol-derived intermediates.

Thus, information on the pyrolytic reactions of guaiacol and syringol is available. With these knowledges, it is possible to compare the pyrolysis behaviors of softwood and hardwood lignins. In the present work, pyrolytic reactions of milled wood lignins (MWLs) isolated from Japanese cedar (*C. japonica*, a softwood) and Japanese beech (*F. crenata*, a hardwood) were studied at the molecular level, focusing on the gas- and solid/liquid-phase reactions.

## 2. Experimental

### 2.1. Materials

MWLs were isolated from Japanese cedar and Japanese beech wood samples according to the reported procedure [38]. Guaia-

col, syringol and other chemicals were mainly purchased from Nacalai Tesque Inc. (Kyoto, Japan), as guaranteed grades. The syringyl/guaiacyl (S/G) ratio of the beech MWL was evaluated as 2.3 from the syringaldehyde/vanillin (S/V) ratio obtained by alkaline nitrobenzene oxidation.

### 2.2. Methods

The TG analysis was conducted with a Shimadzu TGA 50 instrument (Shimadzu, Kyoto, Japan). Sample (1 mg) was heated in a platinum cell at 10 °C/min under nitrogen flow (10 mL/min). Two types of reactors were used in this study, namely an open-top and a closed ampoule reactor. The open-top reactor was used to study the initial devolatilization step, since the volatile (tar) products are cooled by condensing on the upper side of the reactor wall. Secondary reactions of the volatile products were expected to occur in the closed ampoule reactor.

#### 2.2.1. Pyrolysis in a closed ampoule reactor

MWL (10 mg) was placed at the bottom of a Pyrex glass ampoule (internal diameter 8.0 mm, length 120 mm, wall thickness 1.0 mm). The glass ampoule was closed after exchanging the inside air with N<sub>2</sub> using an aspirator. The ampoule was heated for 40–600 s in an upright position, in a muffle furnace preheated to 600 °C, through a small hole at the top of the furnace. It took about 120 s that the inside temperature was raised to the set temperature (600 °C). After pyrolysis, the ampoule was immediately cooled by flowing air for 1 min, and the non-condensable gases were recovered according to our previously paper [26]. A glass tube with a septum rubber stopper was attached to the top of the ampoule through a silicon tube. The air inside the resulting closed space was exchanged with argon by using a vacuum pump and a gas tight syringe filled with argon, the syringe was replaced by an empty syringe, and then the top of the ampoule was broken to release the gaseous products into the closed space. The non-condensable gases were analyzed by gas chromatography (GC) as described later. After the collection of the gaseous products, the ampoule was rinsed with MeOH (2 × 1.0 mL) to obtain MeOH-soluble and insoluble (char + coke) fractions. The latter fraction, adhering to the ampoule, was dried in an oven (105 °C) for 24 h, and the char + coke yield was determined from the weight difference of the ampoule after incineration of char + coke in air at 600 °C for 2 h. The MeOH-soluble tar yield was obtained by subtracting the amounts of char + coke and non-condensable gases.

#### 2.2.2. Pyrolysis in an open-top reactor

Similar pyrolysis experiments were conducted with an open-top reactor, which consisted of a glass tube reactor (10 mm in diameter and 300 mm long) attached to a nitrogen bag. MWL (10 mg) was placed at the bottom of the tube reactor, and about two thirds of the reactor from the bottom was heated for 180 s by inserting it into a muffle furnace preheated at 400 °C, through a small hole at the top of the furnace. After pyrolysis, the reactor was removed from the furnace and cooled by flowing air for 1 min. The non-condensable gases were analyzed by GC, and the tar and char + coke fractions were obtained by a procedure similar to that described above.

#### 2.2.3. Stepwise pyrolysis of char + coke fractions

The MWLs and their char + coke fractions were pyrolyzed stepwise in the closed ampoule reactor. MWL was first pyrolyzed at 350 °C for 300 s in a manner similar to that described above. The resulting char + coke fraction after tar extraction with MeOH was washed with distilled water, then oven dried at 105 °C for 24 h. The ampoule with char + coke fraction was closed again after exchanging the inside air with N<sub>2</sub> using an aspirator, and heated at 450 °C

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