

Title	Gas- and solid/liquid-phase reactions during pyrolysis of softwood and hardwood lignins
Author(s)	Asmadi, Mohd; Kawamoto, Haruo; Saka, Shiro
Citation	Journal of Analytical and Applied Pyrolysis (2011), 92(2): 417-425
Issue Date	2011-11
URL	http://hdl.handle.net/2433/150113
Right	© 2011 Elsevier B.V.; This is not the published version. Please cite only the published version. この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。
Type	Journal Article
Textversion	author

1

2 **Gas- and solid/liquid-phase reactions during pyrolysis of softwood and**
3 **hardwood lignins**

4

5 Mohd Asmadi¹, Haruo Kawamoto^{1*}, Shiro Saka¹

6

7 ¹Graduate School of Energy Science, Kyoto University

8 Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

9

10 * Corresponding author: Haruo Kawamoto

11 Graduate School of Energy Science, Kyoto University

12 Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

13 Tel/Fax: +81-75-753-4737

14 E-mail: kawamoto@energy.kyoto-u.ac.jp

15 **Abstract:**

16 Pyrolytic reactions of Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese
17 beech (*Fagus crenata*, a hardwood) milled wood lignins (MWLs) were studied with
18 thermogravimetry (TG) and by pyrolysis in a closed ampoule reactor (N₂/ 600 °C). The
19 data were compared with those of guaiacol/syringol as simple lignin model aromatic
20 nuclei. Several DTG peaks were observed around 300-350, 450, 590 and 650 °C. The
21 first DTG peak temperature (326 °C) of beech was lower than that (353 °C) of cedar.
22 This indicates that the volatile formation from cedar MWL is slightly delayed in heating
23 at 600 °C. The gas-phase reactions via GC/MS-detectable low MW products were
24 explainable with the temperature-dependent reactions observed for guaiacol/syringol in
25 our previous paper. The methoxyl groups became reactive at ~450 °C, giving O-CH₃
26 homolysis products (catechols/pyrogallols) and OCH₃ rearrangement products
27 (cresols/xilenols). The former homolysis products were effectively converted into
28 gaseous products (mainly CO) at >550–600 °C. **However, the GC/MS-detectable tar**
29 **yields, especially syringyl unit-characteristic products, were much lower than those from**
30 **guaiacol/syringol. Thus, contributions of higher MW intermediates and solid/liquid-**
31 **phase reactions are more important in lignin pyrolysis. From the results of stepwise**
32 **pyrolysis of char+coke fractions at 450 and 600 °C, the methoxyl group-related reactions**
33 **(450 °C) and intermediates gasification (600 °C) were suggested to occur also in the**
34 **solid/liquid phase. This was consistent with the DTG peaks observed around these**
35 **temperatures. These solid/liquid-phase reactions reduced the tar formation, especially**
36 **catechols/pyrogallols and PAHs. Different features observed between these two MWLs**
37 **are also focused.**

38
39
40
41
42

43 **Keywords:**

44 Lignin; Pyrolysis; Reactions; Gas phase; Solid/liquid phase; Softwood; Hardwood

45 1. Introduction

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

53 Initial pyrolytic reactions of lignin have been studied extensively by thermogravimetry
54 and NMR analysis and with model compounds. Major initial weight loss is observed in the
55 temperature range 300-400 °C in TG analysis [1–7]. Devolatilization tends to be more effective
56 in hardwood lignins [1,3,5,7], which was explained by the smaller contents of the condensed
57 (C-C) types of interphenylpropane-linkages, arising from the inclusion of the syringyl type.
58 How and Schultz [8] reported the cleavage of the β-ether linkage, the most abundant structure
59 in lignin, at a temperature as low as 220 °C based on the CP/MAS NMR data. Model
60 compound studies [9-15] suggest the pathways and molecular mechanisms for cleavage of the
61 ether linkages, including homolysis/heterolysis and role of quinone methide intermediate. The
62 model compound data were also used for the study of depolymerization behavior of isolated
63 lignins [14]. Chemical structures of the primary volatile products have been studied mainly
64 using gas chromatography (GC) coupled with mass spectrometry (MS) [16–21]. Various
65 monoaromatic compounds with guaiacyl or syringyl moiety have been identified, which have
66 various double bond side-chains such as >C=C<, -CHO and >C=O at positions para to the
67 phenolic hydroxyl groups.

68 These primary products are further pyrolyzed in gas and solid/liquid phases (secondary
69 reactions). Hosoya et al. [22] compared the primary pyrolysis and some secondary reactions
70 behaviors of softwood lignin and other carbohydrate constituents (cellulose and
71 hemicelluloses) with an open-top reactor at 800 °C. They found that gas-phase carbonization
72 (coking) was significant for lignin, although coking from cellulose- and hemicelluloses-derived
73 tars was observed only after condensing on the reactor wall with lower temperature. They also
74 found that methoxyl group was a key structure for these coking reactions of lignin and
75 proposed an *o*-quinonemethide as an intermediate [23].

76 The gas-phase conversions of lignin-derived tars were studied with a closed ampoule
77 reactor at 600 °C [24]. Major structural changes occur in side-chain and aromatic ring
78 substitution pattern: side-chain structures were changed from unsaturated to saturated types,
79 and this was explained with the condensation of the double bond structures followed by
80 cracking; aromatic ring substitution pattern was also changed simultaneously from guaiacol
81 (OCH₃) type to catechol (OH) and cresol (CH₃) types. Hosoya et al. [25] reported that these
82 pyrolysis reactions were very much influenced by the carbohydrate-derived vapors acting as a
83 H-donor. Gas formation behaviors were also compared between tar and char fractions from
84 cellulose and lignin [26]. However, these results are only for guaiacyl lignins, and further
85 conversion pathways from the catechol/cresol intermediates have not been studied.

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

94 The secondary reactions pathways of guaiacols and syringols have been studied with
95 simple model compounds such as guaiacol [23,28–34] and syringol [28,35,36]. Two types of
96 reactions relating to the methoxyl group occur at >450 °C, namely O-CH₃ homolysis and
97 radical-induced OCH₃ rearrangement (*ipso*-substitution) to convert methoxyl to methyl groups.
98 Catechols/pyrogallols and cresols/xilenols are the products formed through these respective
99 pathways, together with CH₄ formation. A large amount of coke (defined as a carbonaceous
100 substance via volatiles) is also formed at this stage [23,28]. Asmadi et al. [28] compared these
101 reactions between guaiacol and syringol in an ampoule reactor (N₂/ 600 °C). Syringol gave
102 more coke and CH₄ than guaiacol, and this was explained with the additional methoxyl group
103 in syringol.

104 Asmadi et al. [37] also compared the pyrolytic reactivities of the catechols/pyrogallols
105 and cresols/xilenols types intermediates in a closed ampoule reactor (N₂/ 600 °C). They found
106 that the reactivity increased with an increase in the number of substituent groups, and the
107 accelerating effect was greater for OH than for CH₃. Accordingly, catechols/pyrogallols were
108 effectively converted into gaseous products, mainly CO, at >550–600 °C, while
109 cresols/xilenols were converted much more slowly into demethylation products together
110 with H₂, CH₄ and coke. The syringol-derived intermediates with more substituents group
111 were generally more reactive than the corresponding guaiacol-derived intermediates.

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

119 2. Experimental

120 2.1 Materials

121 MWLs were isolated from Japanese cedar and Japanese beech wood samples
122 according to the reported procedure [38]. Guaiacol, syringol and other chemicals were
123 mainly purchased from Nacalai Tesque Inc. (Kyoto, Japan), as guaranteed grades. The
124 syringyl/guaiacyl (S/G) ratio of the beech MWL was evaluated as 2.3 from the
125 syringaldehyde/vanillin (S/V) ratio obtained by alkaline nitrobenzene oxidation.
126

127 2.2 Methods

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

135

136 2.2.1 Pyrolysis in a closed ampoule reactor

137 MWL (10 mg) was placed at the bottom of a Pyrex glass ampoule (internal
138 diameter 8.0 mm, length 120 mm, wall thickness 1.0 mm). The glass ampoule was closed
139 after exchanging the inside air with N₂ using an aspirator. The ampoule was heated for
140 40–600 s in an upright position, in a muffle furnace preheated to 600 °C, through a small
141 hole at the top of the furnace. **It took about 120s that the inside temperature was raised to**
142 **the set temperature (600 °C).** After pyrolysis, the ampoule was immediately cooled by
143 flowing air for 1 min, and **the non-condensable gases were recovered according to our**
144 **previously paper [26]. A glass tube with a septum rubber stopper was attached to the top**
145 **of the ampoule through a silicon tube. The air inside the resulting closed space was**
146 **exchanged with argon by using a vacuum pump and a gas tight syringe filled with argon,**
147 **the syringe was replaced by an empty syringe, and then the top of the ampoule was**
148 **broken to release the gaseous products into the closed space.** The non-condensable gases
149 were analyzed by gas chromatography (GC) as described later. **After the collection of the**
150 **gaseous products,** the ampoule was rinsed with MeOH (2×1.0 mL) to obtain MeOH-
151 soluble and insoluble (char+coke) fractions. The latter fraction, adhering to the ampoule,
152 was dried in an oven (105 °C) for 24 h, and the char+coke yield was determined from the
153 weight difference of the ampoule after incineration of char+coke in air at 600 °C for 2 h.
154 The MeOH-soluble tar yield was obtained by subtracting the amounts of char+coke and
155 non-condensable gases.

156

157 2.2.2 Pyrolysis in an open-top reactor

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

166

167 2.2.3 Stepwise pyrolysis of char+coke fractions

168 The MWLs and their char+coke fractions were pyrolyzed stepwise in the closed
169 ampoule reactor. MWL was first pyrolyzed at 350 °C for 300 s in a manner similar to that
170 described above. The resulting char+coke fraction after tar extraction with MeOH was
171 washed with distilled water, then oven dried at 105 °C for 24 h. The ampoule with
172 char+coke fraction was closed again after exchanging the inside air with N₂ using an
173 aspirator, and heated at 450 °C for 300 s. After tar extraction and drying, the resulting
174 char+coke fraction obtained at 450 °C was heated further at 600 °C for 300 s.

176 2.3 Product analysis

177 Non-condensable gases were determined with Micro GC using a Varian CP-4900
178 chromatograph under the following conditions: channel 1) column: MS5A 10 m; carrier
179 gas: argon; column temperature: 100 °C; column pressure: 170 kPa; thermal conductivity
180 detector (TCD); retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4), CH₄ (60.6) and CO
181 (86.9); channel 2) column: PoraPLOT Q 10 m; carrier gas: helium; column temperature:
182 80 °C; column pressure: 190 kPa; TCD detector; retention time (s): CO₂ (19.9).

183 Low molecular weight (MW) products in the MeOH-soluble fractions were
184 determined by GC-MS analysis. Identification of the products was achieved by
185 comparing retention times and mass fragmentation patterns with those of authentic
186 compounds or literature data according to our previous papers [22,24,27]. Quantification
187 was made from the relative peak area against *p*-dibromobenzene as an internal standard
188 **by using the response factors obtained for the authentic compounds**. GC/MS analysis was
189 carried out using a Hitachi G-7000 gas chromatograph and Hitachi M9000 mass
190 spectrometer under the following conditions: column: Shimadzu CBP-M25-O25 (length
191 25 m, diameter 0.25 mm); injector temperature: 250 °C; column temperature: 40 °C (1
192 min), 40 → 300 °C (1 → 53 min), 300 °C (53 → 60 min); carrier gas: helium; flow rate:
193 1.5 mL/min; emission current: 15 μA; ionization time: 100 ms.

194 Gel permeation chromatography (GPC) was carried out with a Shimadzu LC-10A
195 instrument under the following conditions; column: Shodex KF 801+KF 802+KF
196 802.5+KF 803; flow rate: 0.6 mL/min; eluent: THF; detector: UV_{254 nm}; temperature:
197 40 °C; retention times (min): guaiacol (64.6), syringol (65.2), pyrocatechol (63.9), 3-
198 methylcatechol (63.6), 4-methylcatechol (63.5), pyrogallol (62.2), 5-methylpyrogallol
199 (61.7), phenol (66.0), 2-ethylphenol (64.6), *o*-cresol (65.5), *p*-cresol (65.2), 2,3-xyleneol
200 (65.2), 2,4-xyleneol (64.9), 2,6-xyleneol (65.2), 2,3-benzofuran (70.3), biphenyl (68.7),
201 xanthene (69.7), naphthalene (71.2), 2-methylnaphthalene (70.2), 1-methylnaphthalene
202 (71.0), phenanthrene (70.5) and anthracene (70.3).

203 All experiments were repeated **at least three times, and the product yields** were
204 not very different in these sets of experiments, although the data presented in this paper
205 were not treated statistically. **We also confirmed that the relationships between the yields**
206 **and pyrolysis time or other pyrolysis parameters were not different in these experiments.**

207
208

209 **3. Results and discussion**

210 *3.1 Thermogravimetry and pyrolysis in an open-top reactor*

211 The TG and DTG curves of beech and cedar MWLs are depicted in Fig. 1.
212 Weight reduction started at temperatures slightly higher than 200 °C, and the major
213 initial weight loss was observed between 200 and 400 °C. The DTG peak temperature
214 (326 °C) of beech MWL was lower than that (353 °C) of cedar MWL, thus the pyrolytic
215 devolatilization of beech MWL occurred at a lower temperature than that of cedar. NMR
216 analysis [8] and model compound studies [9–15] suggest that the ether linkages between
217 phenylpropane units are cleaved in this temperature range. However, there are no papers
218 comparing the reactivities of pyrolytic cleavage of the ether linkages between guaiacyl
219 and syringyl lignins. Further study will be necessary to address the reason for such
220 difference in the DTG peak temperature.

221 After the initial weight loss around 300-400 °C, cedar MWL gave larger amount
222 of residues than beech MWL, and the weight differences were almost constant (7~8%)
223 for these two MWLs in the temperature range 400-800 °C. Thus, such difference would
224 arise from the difference in the initial devolatilization step. More efficient
225 devolatilization of hardwoods have been reported [1,3,5,7], and this is explained by the
226 lower contents of the condensed types of linkages in hardwood lignins, which are
227 resistant to pyrolytic depolymerization.

228 Several DTG peaks were also observed at higher temperatures, namely ~450,
229 ~590 and ~650 °C. Accordingly, some pyrolytic devolatilization occurs at these
230 temperatures. This is discussed later with the results of stepwise pyrolysis of char+coke
231 fractions from MWLs.

232 To confirm the TG results, the MWLs were pyrolyzed in an open-top reactor
233 under N₂ at 400 °C, which was slightly higher than the lowest DTG peak temperatures
234 and lower than the temperature range (~450 °C) reported for the O-CH₃ bond homolysis
235 and rearrangement reactions occurring [28]. Furthermore, the volatile products were
236 expected to be stabilized by condensing on the reactor wall at lower temperatures.
237 Accordingly, these pyrolysis conditions were thought to be suitable for investigating the
238 initial devolatilization process. As expected, the yields of volatile products (tar and gas)
239 were much higher for beech than for cedar (N₂/ 400 °C/ 180 s). Tar (45.3 wt%) and gas
240 (5.6 wt%) yields from beech MWL were almost double those (tar 23.5 wt%, gas 3.8
241 wt%) from cedar MWL.

242 243 *3.2 Pyrolysis in a closed ampoule reactor*

244 In the closed ampoule reactor, secondary reactions of the primary volatile
245 products are more prevalent, to form secondary products including coke and gas. Fig. 2
246 shows photographs of the reactors and MeOH-soluble fractions obtained by pyrolysis of
247 cedar and beech MWLs under N₂ at 600 °C for 40–600 s in the closed ampoule reactor,
248 and subsequent tar extraction with MeOH. Time-course changes of the MeOH-insoluble
249 (char+coke), MeOH-soluble (tar) and gas yields are also included.

250 Two kinds of carbonaceous substances were observed at the bottom and upper
251 side of the reactor wall. In this paper, “char” is defined as the insoluble substances
252 observed at the bottom of the ampoule where MWL was placed. On the other hand,
253 “coke” is defined as the insoluble substances stuck on the upper side of the reactor wall,
254 since the term “coke” is usually used for the carbonaceous substances formed via low
255 MW volatile intermediates. Char+coke yields tended to be lower in beech MWL than in
256 cedar. This may arise from the more efficient devolatilization of beech MWL in the
257 primary devolatilization step.

258 As reported previously [28,37], coke formation from guaiacol/syringol as model
259 aromatic nuclei occurred in two stages (1st stage: 80–120 s, 2nd stage: 120–600 s). Since
260 the 1st stage coking is related to the reactions of the methoxyl groups, syringol with
261 additional methoxyl group was much more effective than guaiacol. The 2nd stage coking
262 involved the coking reactions of volatile products, such as catechols, pyrogallols, cresols
263 and xylenols, and guaiacol was more effective in this 2nd stage coking. Although the
264 differences for the MWLs were smaller than those observed for guaiacol/syringol, the
265 beech MWL (syringol/guaiacyl ratio: 2.3/1) tended to produce more 1st stage coke, while
266 the 2nd stage coking was rather more noticeable for cedar MWL (mostly guaiacyl units)
267 (pictures in Fig. 2).

268 A noticeable difference was observed for the tar yields up to 120 s. The tar yield
269 from beech MWL gradually decreased with increasing pyrolysis time, whereas the tar
270 yield from cedar MWL had a maximum at 80 s. Such difference is consistent with the
271 lower devolatilization temperature of beech MWL (Fig. 1). Beech MWL may produce
272 volatile products earlier than cedar during heating up process, since it was required about
273 120 s for inside temperature of the ampoule to reach the set temperature 600 °C. This
274 may be related to the color change of the MeOH-soluble fractions. Color of the MeOH-
275 soluble fractions became brown in the early stage of pyrolysis (<80 s), and became
276 increasingly discolored with increasing pyrolysis time. This coloration and discoloration
277 behavior was slightly delayed in cedar MWL.

278 According to our previous paper [28], syringol gave more gas, especially CH₄ and
279 CO₂, than guaiacol under similar conditions. However, the gas yields were very similar
280 for cedar and beech MWLs. The yields of each gaseous component are shown in Fig. 3,
281 together with those from guaiacol and syringol. Although the yields were different
282 between MWLs and guaiacol/syringol, the formation behaviors of these gaseous products
283 were similar. Inside temperature of the ampoule was raised with increasing pyrolysis
284 time: 459 °C (40 s), 569 °C (80 s) and 590 °C (120 s). Formation of CO₂ started from 40
285 s where formation of other gaseous products was not effective. This indicates that CO₂ is
286 formed at lower pyrolysis temperature. Major CO₂, CH₄ and CO formation was observed
287 during heating up conditions (80~120 s). Based on the reactivities of the intermediates
288 from guaiacol/syringol in our previous paper [37], the O-CH₃ bond homolysis is a source
289 of CH₄ (400-450 °C), and decomposition of catechol/pyrogallol type intermediates gives
290 large amounts of CO (>550~600 °C). The H₂ formation was slightly delayed and

291 continued even after 120 s. This can be explained by the earlier proposal that the charring,
292 coking and PAH formation reactions generate hydrogen radicals [37]. Demethylation of
293 methylated phenols such as cresols and xylenols through substitution by hydrogen is
294 suggested as a source of CH₄ in the period 120-600 s [37].

295 The GC/MS-detectable low MW tar components in MeOH-soluble fractions
296 changed drastically with pyrolysis time. The total-ion chromatograms at 40 s (maximum
297 temperature: 459 °C) are shown in Fig. 4. These products were not compared
298 quantitatively, since some of the authentic compounds were not available for obtaining
299 their response factors in GC/MS analysis. Most of the products (40 s) from cedar and
300 beech MWLs were guaiacols and guaiacols/syringols, respectively, with various
301 substituents at the *p*-position of the phenolic hydroxyl groups. The side-chains included
302 saturated, unsaturated, aldehyde and ketone types, and these compositions were not
303 greatly different from the results obtained with the open-top reactor (N₂/ 400 °C/ 180 s).
304 Thus, the GC/MS-detectable tars at 40 s were the primary volatile products from the
305 MWLs.

306 By increasing the pyrolysis time to 80 s (maximum temperature: 569 °C), these
307 initial products disappeared almost completely, and catechols/pyrogallols and
308 cresols/xylenols became the major components, which are formed through O-CH₃ bond
309 homolysis and rearrangement reactions, respectively [28]. Fig. 5 shows the time-course
310 changes of the yields of these products, which were quantified with the authentic
311 compounds. Formation and decomposition behaviors of these products are explainable
312 with those of guaiacol/syringol reported previously [28,37], except for their yields
313 described later. Some 4-methyl derivatives (4-methylcatechol, *p*-cresol and 2,4-xyleneol)
314 tended to have higher relative concentrations in MWL than in guaiacol/syringol. These
315 products may arise from the side-chains of lignin phenylpropane-units. Short-lived
316 catechols/pyrogallols **1-6** (O-CH₃ bond homolysis products) are explained with their
317 higher decomposition reactivities to form CO and CO₂ (in the case of pyrogallols) [37],
318 and this is consistent with the CO and CO₂ formation in Fig. 3. As for cresols/xylenols **8-**
319 **11** (OCH₃ rearrangement products), demethylation of xylnols and cresols is reported to
320 occur more slowly at 120-600 s, giving cresols, phenols, CH₄, H₂ and coke [37].
321 Formation of PAHs was observed only at longer pyrolysis times >120 s.

322 Fig. 6 shows the yields of GC/MS-detectable tars, compared with those from
323 guaiacol/syringol [28]. The yields from the MWLs were much lower than those from
324 guaiacol/syringol. In particular, the syringyl unit-characteristic products were almost
325 negligible for beech MWL. Accordingly, most of the GC/MS-detectable tars from beech
326 MWL became guaiacyl unit-characteristic products (at 80-600 s), and their yields were
327 lower than those from cedar MWL. These results are consistent with our earlier
328 observation for Japanese cedar and Japanese beech wood samples under similar
329 conditions [27].

330 3.3 Stepwise pyrolysis of residues (char+coke)

331

332 According to the model compound studies [10,11,14], various guaiacol/syringol
333 derivatives with double bond side-chains are formed from lignin, including coniferyl
334 alcohol and stilbene from the β -ether and β -aryl types of model dimers, respectively.
335 These initial products may condense [39]. The three-dimensional structures of lignin also
336 prevent the formation of monoaromatic products. These processes may increase the
337 contribution of solid/liquid-phase pyrolysis for MWLs. As already described, the TG
338 analysis (Fig. 1) showed the DTG peaks at ~ 450 and ~ 590 $^{\circ}\text{C}$, which are in accordance
339 with the temperatures at which the O-CH₃ bond homolysis/rearrangement reactions and
340 gasification of catechol/pyrogallol type intermediates, respectively, are reported to start
341 in the gas phase [28,37]. These considerations suggest that similar reactions also occur
342 in the solid/liquid phase.

343 To confirm that hypothesis, cedar and beech MWLs or their char+coke fractions
344 were pyrolyzed stepwise (350 \rightarrow 450 \rightarrow 600 $^{\circ}\text{C}$). First, the MWLs were pyrolyzed in the
345 ampoule reactor at 350 $^{\circ}\text{C}$ for 300 s (Step 1), where the methoxyl groups are stable. After
346 tar extraction with MeOH and subsequent drying, the char+coke fractions (MeOH-
347 insoluble fractions) were pyrolyzed again at 450 $^{\circ}\text{C}$ for 300 s (Step 2), where the
348 methoxyl groups become reactive. The resulting char+coke fractions were further
349 pyrolyzed at 600 $^{\circ}\text{C}$ for 300 s (Step 3). The formation behaviors of gas, tar and
350 char+coke in each step are shown in Fig. 8, along with the photographs of the reactors
351 after tar extraction.

352 Although coke (insoluble substances observed around the upper side of the
353 reactor wall) was not observed in Step 1 (350 $^{\circ}\text{C}$), coke was clearly observed in Step 2
354 (450 $^{\circ}\text{C}$), where the methoxyl groups are reactive. This is consistent with the earlier
355 proposal that reactions of the methoxyl groups are important in coke formation [23]. The
356 amounts (not quantified) in Step 2 (450 $^{\circ}\text{C}$) were not so different from those of Step 3
357 (600 $^{\circ}\text{C}$). Thus, coke precursors were formed from the char fractions (350 $^{\circ}\text{C}$) at 450 $^{\circ}\text{C}$.
358 At this temperature, *o*-cresol, 2,4-xyleneol and 2,6-xyleneol, which are the products of the
359 OCH₃ rearrangement, were detected, although these yields were not large. **As for the
360 gaseous products, CH₄, which would form from the O-CH₃ bond homolysis followed by
361 H-abstraction, was produced more selectively in Step 2 (450 $^{\circ}\text{C}$).** Catechols/pyrogallols
362 were not observed in GC/MS analysis, which are also the products from the homolysis
363 pathway. These structures may be included in higher MW products.

364 At 600 $^{\circ}\text{C}$ (Step 3), the major products from the char+coke fractions (450 $^{\circ}\text{C}$)
365 were gaseous products. Although the yields can not be compared directly, total gas yields
366 (15.0 and 16.6 wt%, based on MWL) from these three steps of pyrolysis correspond to
367 50.0 and 56.1 % of those from the MWLs (600 $^{\circ}\text{C}$ / 600 s, Fig. 2), respectively. These
368 results suggest that contribution of solid/liquid-phase reactions in gas formation is not
369 small in MWL. **Formation of large amounts of CO in Step 3 (600 $^{\circ}\text{C}$) is explainable with
370 the decomposition of catechol/pyrogallol type structures [37]. Jakab et al. [2] reported the
371 two methane evolution profiles for MWLs with their maximum formation rates at ~ 400
372 and 600 $^{\circ}\text{C}$ in GC/MS analysis coupled with TG. These temperatures are close to those**

373 of methane formation through the O-CH₃ bond homolysis [28] and demethylation of
374 cresols/xylenols [37], respectively.

375 These lines of evidence confirm that reactions that were found to occur in the gas
376 phase also proceeded in the solid/liquid phase. The methoxyl group-related reactions (O-
377 CH₃ bond homolysis and OCH₃ rearrangement) occurred at 450 °C in the solid/liquid
378 phase to form gaseous products (especially CH₄), coke and smaller amounts of GC/MS-
379 detectable cresols/xylenols. No GC/MS-detectable catechols/pyrogallols were obtained.
380 At a higher temperature of 600 °C, gasification of the intermeditate structures in the
381 solid/liquid phase may become effective.

382 383 *3.4 GPC analysis of tar fractions*

384 Fig. 7 illustrates some GPC data of MeOH-soluble tar fractions in pyrolysis (a)
385 and stepwise pyrolysis (b) of the MWLs, compared with those (c) of guaiacol/syringol
386 pyrolysis. In early stage of pyrolysis (40 s), the signals from the MWLs (Fig. 7a) were
387 observed in higher MW regions than those from guaiacol/syringol (Fig. 7c). By
388 comparison with the chromatograms obtained with the open-top reactor, the products in
389 the closed ampoule reactor tended to have higher MWs. This tendency was more
390 noticeable for beech MWL. Condensation of the primary volatile products may be a
391 reason. Nakamura et al. [39] reported that guaiacol derivatives with double bond side-
392 chains, such as coniferyl alcohol and vinyl guaiacol, condensed rapidly even at a lower
393 temperature of 250 °C. Hosoya et al. [24] observed the structural changes of side-chain
394 from unsaturated to saturated types during pyrolysis of cedar MWL at 600 °C in an
395 ampoule reactor. They explained these structural changes with condensation and
396 subsequent cracking of the resulting condensates. Such condensation reactions, which
397 occurred before the methoxyl groups became reactive, may reduce the yields of GC/MS-
398 detectable low MW products, especially the syringyl unit-characteristic products (Figs. 5
399 and 6).

400 With increase in pyrolysis time to 600 s, high MW products disappeared and the
401 shapes of the chromatograms became similar for these MWLs (Fig. 7a) and
402 guaiacol/syringol (Fig. 7c). These chromatograms include two signals corresponding to
403 cresols/xylenols and PAHs. At this stage, the MeOH-soluble fractions became colorless
404 (pictures in Fig. 2).

405 In stepwise pyrolysis (Fig. 7b), the chromatograms (Step 1, 350 °C) are similar to
406 those with the open-top reactor (Fig. 7a). The char fractions obtained in Step 1 (350 °C)
407 gave tars which are observed in slightly lower MW regions (Step 2, 450 °C).
408 Interestingly, the char+coke fractions obtained in Step 2 (450 °C) gave almost no signals
409 at 600 °C (Step 3), unlike the formation of large signals around 64 and 69 min in
410 pyrolysis of MWLs and guaiacol/syringol. Accordingly, formation of tar including PAHs
411 is not important from the char+coke fractions obtained at 450 °C where the methoxyl
412 groups are reactive. This was also confirmed by GC/MS analysis. PAHs may form in the
413 gas phase probably via the intermediates formed through the O-CH₃ bond homolysis and

414 rearrangement pathways. In our previous paper [37], catechols/pyrogallols tended to
415 produce biphenyl, naphthalenes and phenanthrene more selectively, while cresols/xylenols
416 formed xanthenes and anthracene preferentially under similar conditions.

417 **Conclusions**

418 Fig. 9 illustrates a pyrolysis pathway of lignin in a closed ampoule reactor (N₂/
419 600°C), as proposed by the present and literature data. This includes gas- and
420 solid/liquid-phase reactions. Some important reactions are also included; ether cleavage
421 (depolymerization) (300-350 °C) [9-15], the methoxyl group-related reactions (400-
422 450 °C) [28], and gas and PAH formation from the pyrolysis intermediates (>550-
423 600 °C) [37]. The gas-phase reactions were explainable with the reactions of
424 guaiacol/syringol in our previous papers [28,37]. In lignin pyrolysis, contributions of the
425 gas-phase reactions are comparatively small due to side-chain network in lignin
426 macromolecule. Furthermore, low MW products formed from lignins in early stage,
427 which are guaiacols/syringols with double bond side-chains, are reactive for
428 condensation [24,39]. These reduce the yields of GC/MS-detectable low MW products.
429 Based on the results of stepwise pyrolysis of char+coke fractions at 450 and 600 °C, the
430 O-CH₃ bond homolysis/ rearrangement (450 °C) and intermediates gasification (600 °C) ,
431 both of which are reported in the gas-phase pyrolysis of guaiacol/syringol [28, 37], were
432 suggested to occur also in the solid/liquid phase. These solid/liquid-phase reactions gave
433 gaseous products, while reduced the yields of GC/MS-detectable low MW tars,
434 especially catechols/pyrogallols and PAHs. Coke precursors and smaller amounts of
435 cresols/xylenols were formed in the solid/liquid phase at 450 °C.

436 As for the differences for Japanese cedar (a softwood) and Japanese beech (a
437 hardwood) MWLs, the following results were obtained.

- 438 1. Japanese beech MWL produced volatile products at lower temperature than cedar.
439 Thus, volatile formation from beech MWL occurred slightly earlier than that from
440 cedar MWL in heating at 600 °C.
- 441 2. Japanese beech MWL tended to form more coke at a short pyrolysis time. This is
442 consistent with the higher coking reactivity of syringol than guaiacol in our previous
443 paper [28].
- 444 3. Yields of GC/MS-detectable low MW tars were lower in beech than in cedar when the
445 methoxyl groups became reactive (>450 °C). This was due to almost negligible yields
446 of the syringyl unit-characteristic products in beech MWL.

447 These results would be useful to improve the thermochemical conversion
448 processes such as fast pyrolysis and gasification.

449 **Acknowledgments**

453 This work was supported by a Grant-in-Aid for Scientific Research (B)(2) (No.
454 203801035007, 2008.4-2011.3) and the Kyoto University Global COE program of
455 “Energy Science in the Age of Global Warming”.

456 **References**

457

- 458 [1] O. Faix, E. Jakab, F. Till, T. Székely, *Wood Sci. Technol.* 22 (1988) 323.
459 [2] E. Jakab, O. Faix, F. Till, *J. Anal. Appl. Pyrol.* 40-41 (1997) 171.
460 [3] J. Li, L. Bin, X. Zhang, *Polym. Degrad. Stabil.* 78 (2002) 279.
461 [4] S. Kubo, J.F. Kadla, *J. Wood Chem. Technol.* 28 (2008) 106.
462 [5] Q. Liu, S. Wang, Y. Zheng, Z. Luo, K. Cen, *J. Anal. Appl. Pyrol.* 82 (2008) 170.
463 [6] S. Wang, K. Wang, Q. Liu, Y. Gu, Z. Luo, K. Cen, T. Fransson, *Biotechnol. Adv.* 27
464 (2009) 562.
465 [7] D.J. Gardner, T.P. Schultz, G.D. McGinnis, *J. Wood Chem. Technol.* 5 (1985) 85.
466 [8] J.F. Haw, T.P. Schultz, *Holzforschung* 39 (1985) 289.
467 [9] R. Brežný, V. Mihálov, V. Kváčik, *Holzforschung* 37 (1983) 199.
468 [10] H. Kawamoto, S. Horigoshi, S. Saka, *J. Wood Sci.* 53 (2007)168.
469 [11] H. Kawamoto, S. Horigoshi, S. Saka, *J. Wood Sci.* 53 (2007)268.
470 [12] H. Kawamoto, T. Nakamura, S. Saka, *Holzforschung* 62 (2008) 50.
471 [13] H. Kawamoto, M. Ryoritani, S. Saka, *J. Anal. Appl. Pyrol.* 81 (2008) 88.
472 [14] T. Nakamura, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 81 (2008) 173.
473 [15] T. Watanabe, H. Kawamoto, S. Saka, *Holzforschung*, 63 (2009) 424.
474 [16] C. Saiz-Jimenez, J.W. De Leeuw, *Org. Geochem.* 10 (1986) 869.
475 [17] R.J. Evans, T.A. Milne, M.N. Soltys, *J. Anal. Appl. Pyrol.* 9 (1986) 207.
476 [18] O. Faix, D. Meier, I. Grobe, *J. Anal. Appl. Pyrol.* 11 (1987) 403.
477 [19] W. Genuit, J.J. Boon, O. Faix, *Anal. Chem.* 59 (1987) 508.
478 [20] P.F. Greenwood, J.D.H. van Heemst, E.A. Guthrie, P.G. Hatcher, *J. Anal. Appl.*
479 *Pyrol.* 62 (2002) 365.
480 [21] J.R. Obst, *J. Wood Chem. Technol.* 3 (1983) 377.
481 [22] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 78 (2007) 328.
482 [23] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 84 (2009) 79.
483 [24] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 83 (2008) 78.
484 [25] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 85 (2009) 237.
485 [26] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.* 83 (2008)71.
486 [27] M. Asmadi, H. Kawamoto, S. Saka, *J. Wood Sci.* 56 (2010) 319.
487 [28] M. Asmadi, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrol.*, in press
488 (doi:10.1016/j.jaap.2011.04.011).
489 [29] J.R. Lawson, M.T. Klein, *Ind. Eng. Chem. Fundam.* 24 (1985) 203.
490 [30] A.I. Vuori, J.B. Bredenberg, *ACS Division of Fuel Chemistry* 30 (1985) 366.
491 [31] A.I. Vuori, *Fuel* 65 (1986) 1575.
492 [32] A.I. Vuori, J.B. Bredenberg, *Ind. Eng. Chem. Res.* 26 (1987) 359.
493 [33] M.M. Suryan, S.A. Kafafi, S.E. Stein, *J. Am. Chem. Soc.* 111 (1989) 1423.
494 [34] E. Dorrestijn, P. Mulder, *J. Chem. Soc.* 2 (1999) 777.
495 [35] C.P. Masuku, *Holzforschung* 45 (1991) 181.
496 [36] C.H. Vane, G.D. Abbott, *Org. Geochem.* 30 (1999) 1535.

- 497 [37] M. Asmadi, H. Kawamoto, S. Saka, J. Anal. Appl. Pyrol., in press
498 (doi:10.1016/j.jaap.2011.04.012).
499 [38] A. Bjorkman, Svensk Paperstidn. 59 (1956) 477.
500 [39] T. Nakamura, H. Kawamoto, S. Saka, J. Wood Chem. Technol. 27 (2007) 121.

Figure Legends

Fig. 1. TG and DTG curves of Japanese beech and Japanese cedar MWLs (heating rate: 10 °C/min; N₂ flow rate: 10 mL/min).

Fig. 2. Photographs of ampoule reactors (after tar extraction) and MeOH-soluble tar fractions, and yields of MeOH-insoluble (char+coke), MeOH-soluble (tar) and gas fractions during pyrolysis of Japanese beech and Japanese cedar MWLs in an ampoule reactor (N₂/600 °C/40–600 s).

Fig. 3. Yields of gaseous products from Japanese beech and Japanese cedar MWLs, compared with those from guaiacol and syringol (ampoule reactor/N₂/600 °C/40–600 s). ^a Ref. [28].

Fig. 4. Total-ion chromatograms in GC/MS-analysis of the MeOH-soluble fractions obtained from pyrolysis of Japanese beech and Japanese cedar MWLs in a closed ampoule reactor (600 °C/ 40 s). G: 4-hydroxy-3-methoxyphenyl, S: 3,5-dimethoxy-4-hydroxyphenyl.

Fig. 5. Yields of GC/MS-detectable tar components during pyrolysis of Japanese beech and Japanese cedar MWLs in a closed ampoule reactor (N₂/600 °C/40–600 s).

Fig. 6. Changes in the GC/MS-detectable tar yields during pyrolysis of Japanese beech and Japanese cedar MWLs, compared with those of guaiacol and syringol (closed ampoule reactor/N₂/600 °C). ^a Guaiacyl unit-characteristic products: **1-3** and **7-10**, ^b syringyl unit-characteristic products: **4-6** and **11**, ^c PAHs: **12-18**, ^d Ref. [28].

Fig. 7. Formation behaviors of gas, tar and coke in stepwise pyrolysis of Japanese cedar and Japanese beech MWLs and their char+coke fractions (MeOH-insoluble residues) in an

ampoule reactor. Pictures: reactors after pyrolysis and subsequent tar extraction with MeOH, ^a MWL/N₂/350 °C/300 s, ^b Residue from Step 1 (350 °C)/N₂/450 °C/300 s, ^c Residue from Step 2 (450 °C)/N₂/600 °C/300 s.

Fig. 8. GPC chromatograms of MeOH-soluble tar fractions (detector UV_{254nm}) obtained from pyrolysis (a) and stepwise pyrolysis (b) of Japanese beech and Japanese cedar MWLs, as compared with those (c) of guaiacol and syringol of our previous data (Ref. [28]). Pyrolysis conditions of MWLs and guaiacol/syringol: closed ampoule/N₂/600 °C, stepwise pyrolysis conditions: see footnote of Fig. 7, **(I)** catechols and pyrogallols (compounds: **1–6**); **(II)** cresols and xylenols (compounds: **7–11**); **(III)** benzofuran, xanthene and PAHs (compounds: **12–18**).

Fig. 9. A proposed gas- and solid/liquid-phase pyrolysis pathway of lignin in a closed ampoule reactor under N₂ at 600 °C.

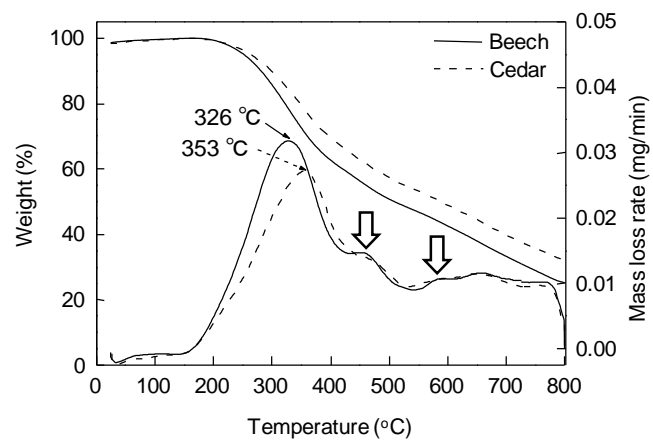


Fig. 1. TG and DTG curves of Japanese beech and Japanese cedar MWLs (heating rate: 10 °C/min; N₂ flow rate: 10 mL/min).

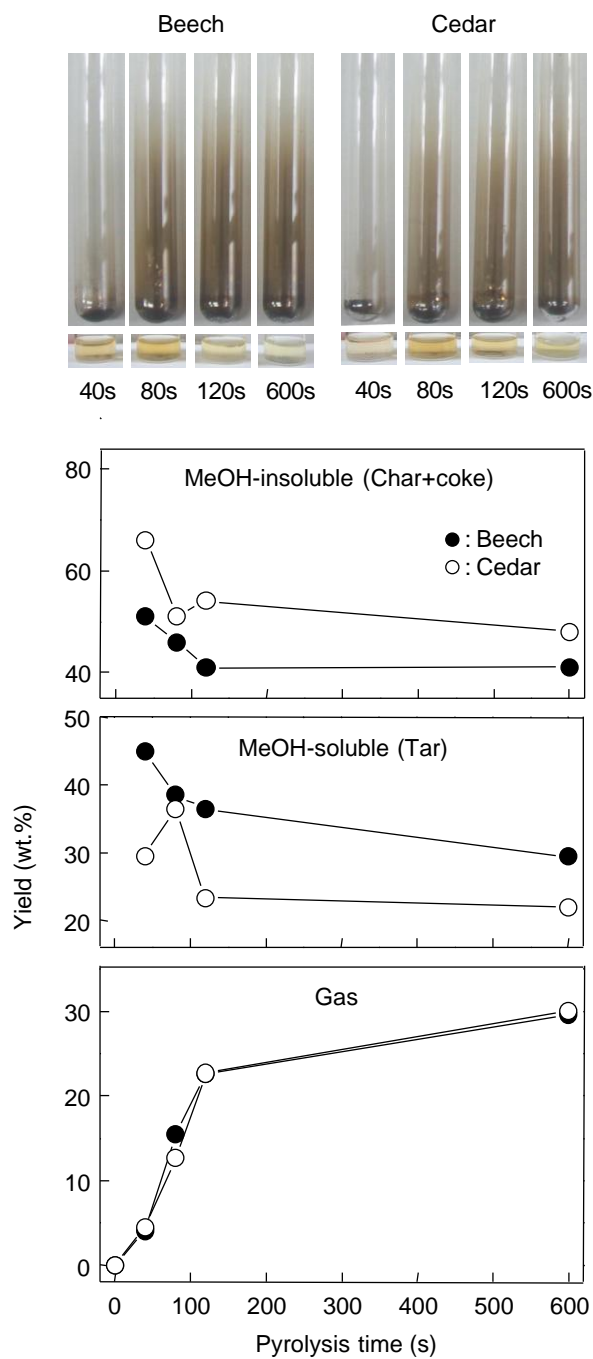


Fig. 2. Photographs of ampoule reactors (after tar extraction) and MeOH-soluble tar fractions, and yields of MeOH-insoluble (char+coke), MeOH-soluble (tar) and gas fractions during pyrolysis of Japanese beech and Japanese cedar MWLs in an ampoule reactor ($N_2/600\text{ }^\circ\text{C}/40\text{--}600\text{ s}$).

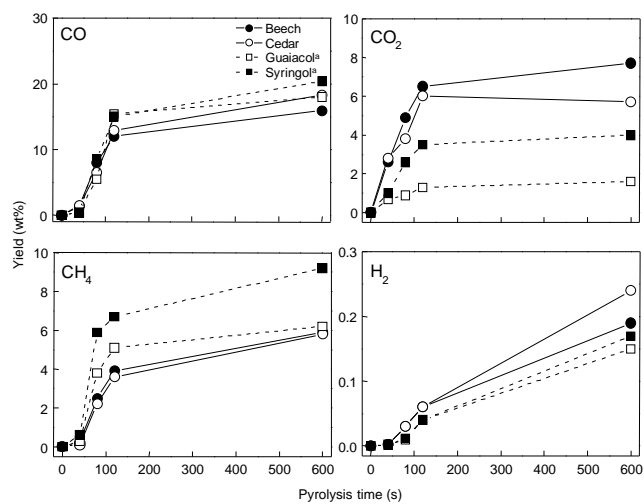


Fig. 3. Yields of gaseous products from Japanese beech and Japanese cedar MWLs, compared with those from guaiacol and syringol (ampoule reactor/N₂/600 °C/40–600 s). ^a Ref. [28].

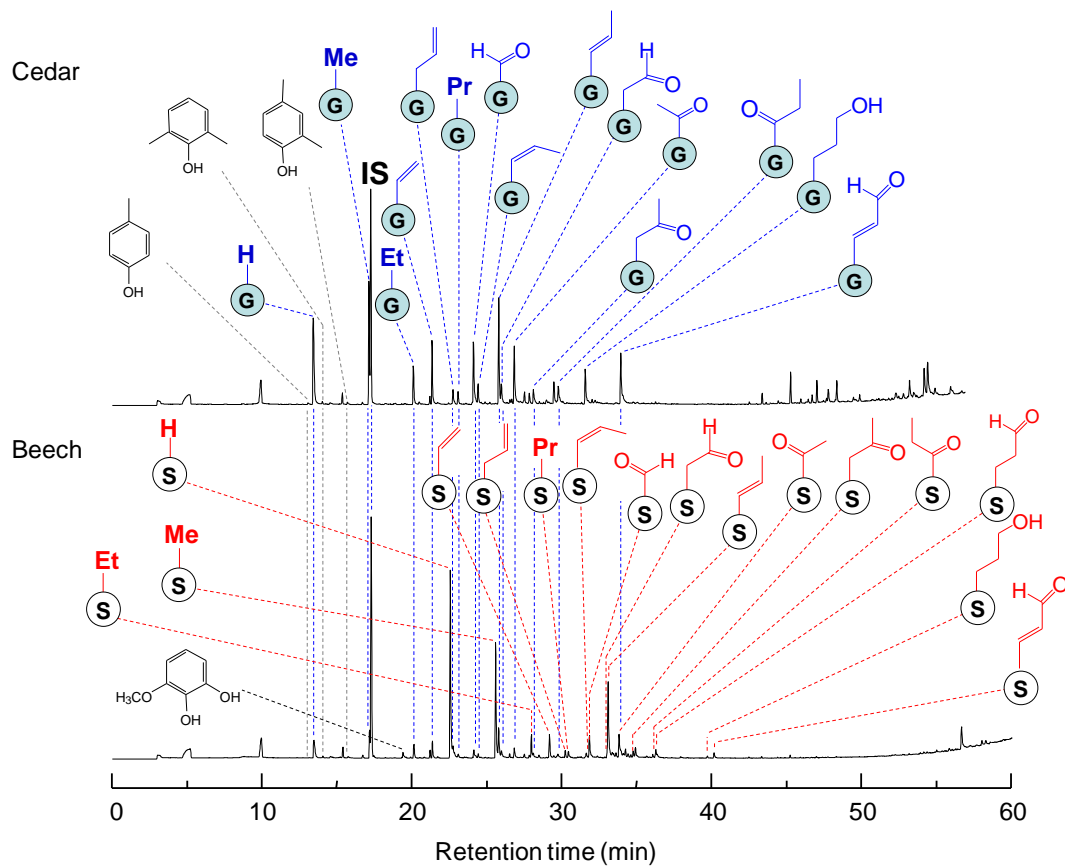


Fig. 4. Total-ion chromatograms in GC/MS-analysis of the MeOH-soluble fractions obtained from pyrolysis of Japanese beech and Japanese cedar MWLs in a closed ampoule reactor (600 °C/ 40 s). G: 4-hydroxy-3-methoxyphenyl, S: 3,5-dimethoxy-4-hydroxyphenyl.

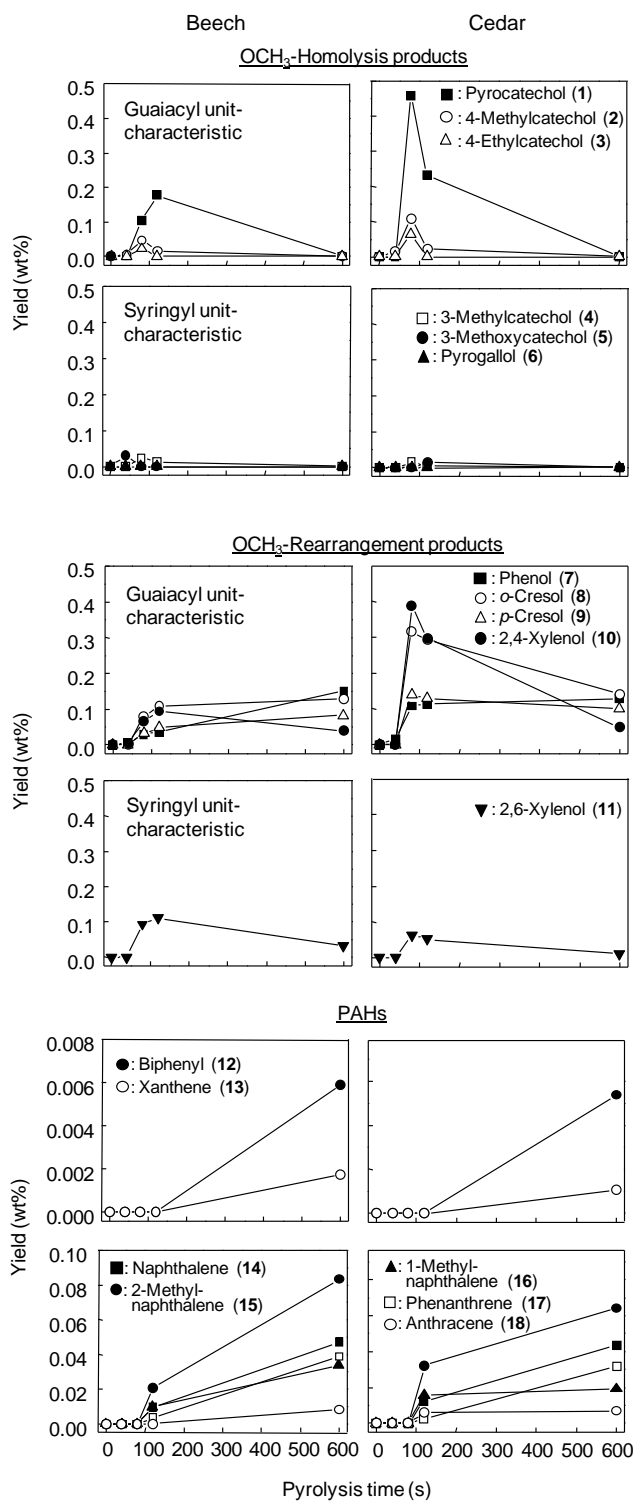


Fig. 5. Yields of GC/MS-detectable tar components during pyrolysis of Japanese beech and Japanese cedar MWLs in a closed ampoule reactor (N₂/600 °C/40–600 s).

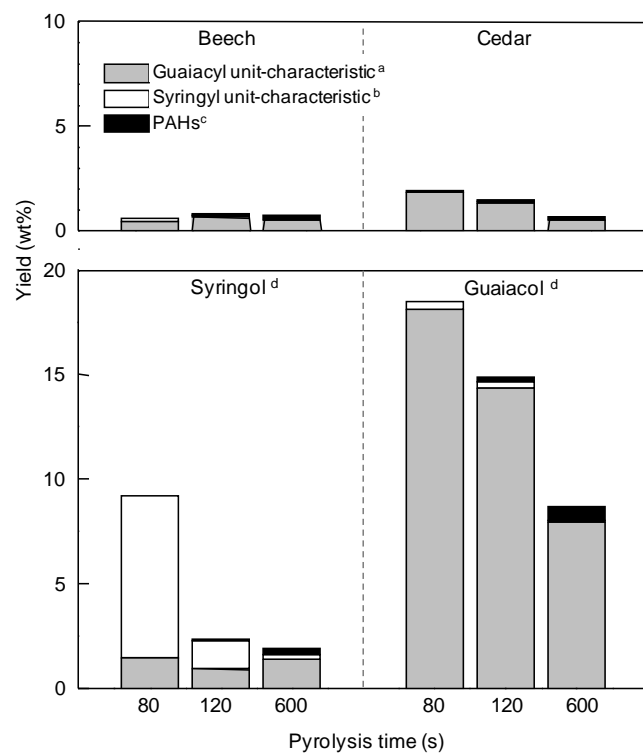


Fig. 6. Changes in the GC/MS-detectable tar yields during pyrolysis of Japanese beech and Japanese cedar MWLs, compared with those of guaiacol and syringol (closed ampoule reactor/ $N_2/600$ °C). ^a Guaiacyl unit-characteristic products: **1-3** and **7-10**, ^b syringyl unit-characteristic products: **4-6** and **11**, ^c PAHs: **12-18**, ^d Ref. [28].

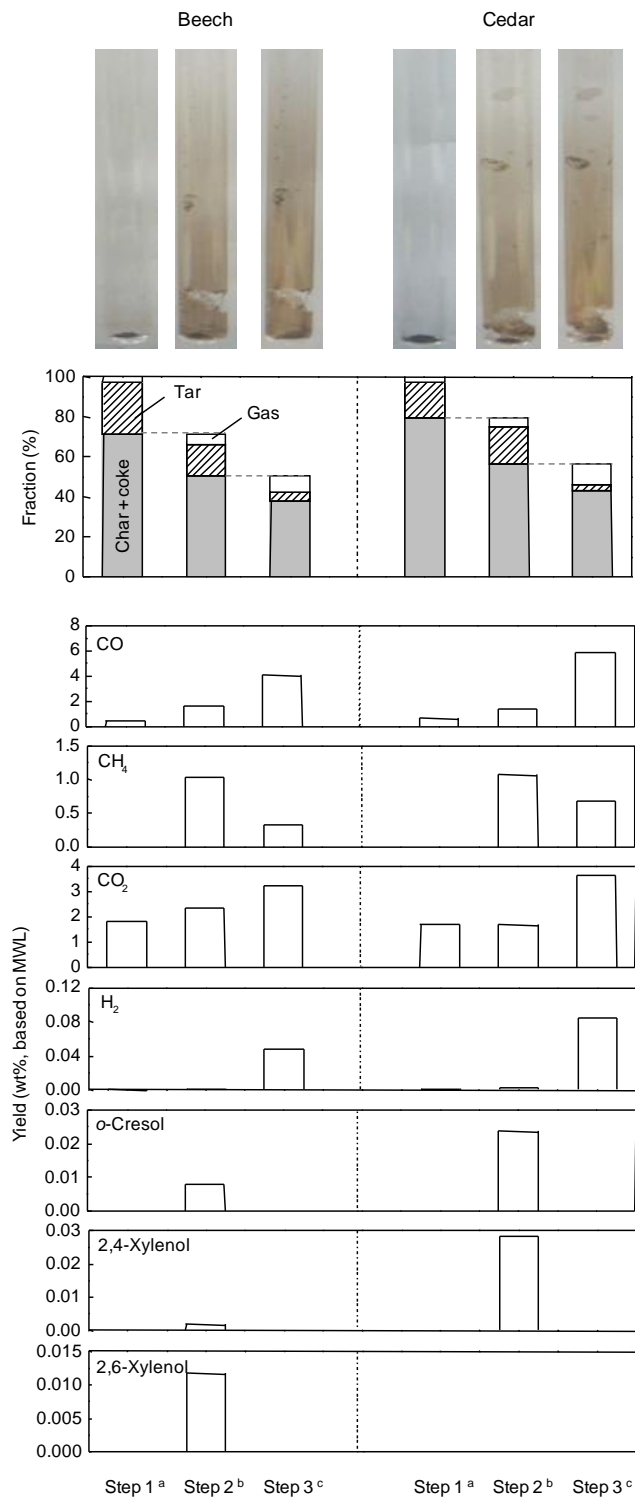


Fig. 7. Formation behaviors of gas, tar and coke in stepwise pyrolysis of Japanese cedar and Japanese beech MWLs and their char+coke fractions (MeOH-insoluble residues) in an ampoule reactor. Pictures: reactors after pyrolysis and subsequent tar extraction with MeOH,
^a MWL/N₂/350 °C/300 s, ^b Residue from Step 1 (350 °C)/N₂/450 °C/300 s, ^c Residue from Step 2 (450 °C)/N₂/600 °C/300 s.

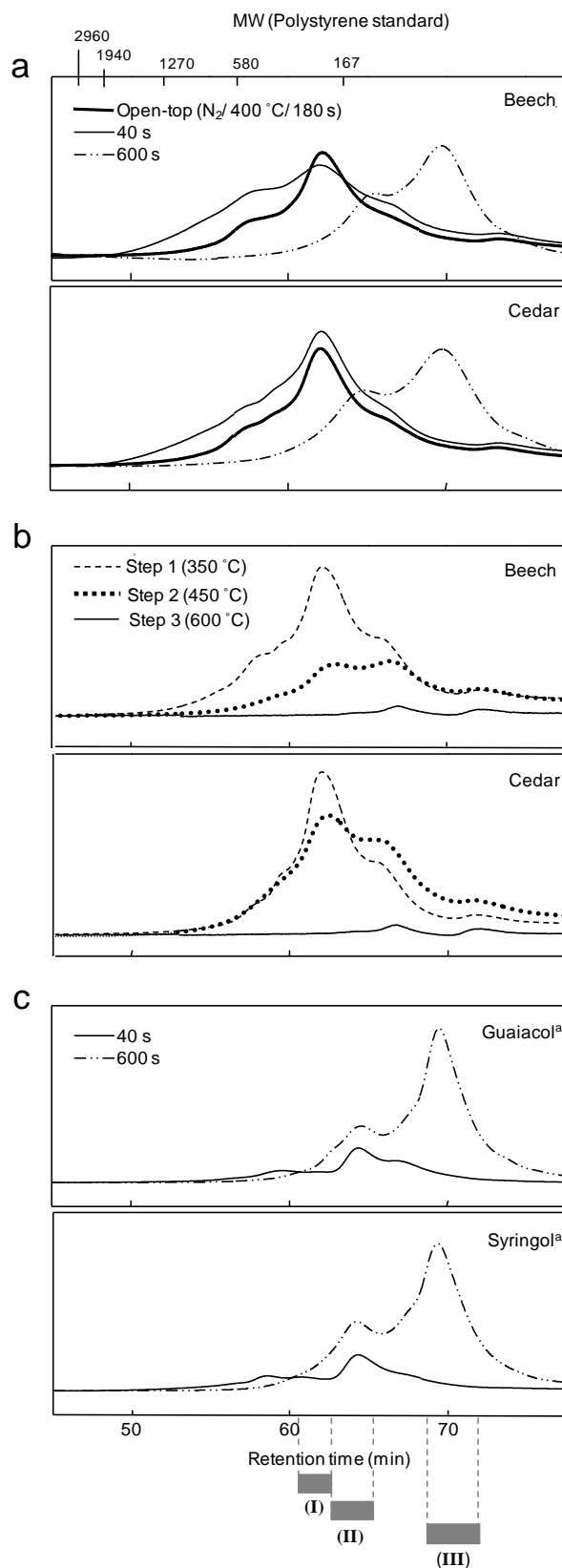


Fig. 8. GPC chromatograms of MeOH-soluble tar fractions (detector UV_{254nm}) obtained from pyrolysis (a) and stepwise pyrolysis (b) of Japanese beech and Japanese cedar MWLs, as compared with those (c) of guaiacol and syringol of our previous data (Ref. [28]). Pyrolysis conditions of MWLs and guaiacol/syringol: closed ampoule/N₂/600 °C, stepwise pyrolysis conditions: see footnote of Fig. 7, (I) catechols and pyrogallols (compounds: 1–6); (II) cresols and xylenols (compounds: 7–11); (III) benzofuran, xanthene and PAHs (compounds: 12–18).

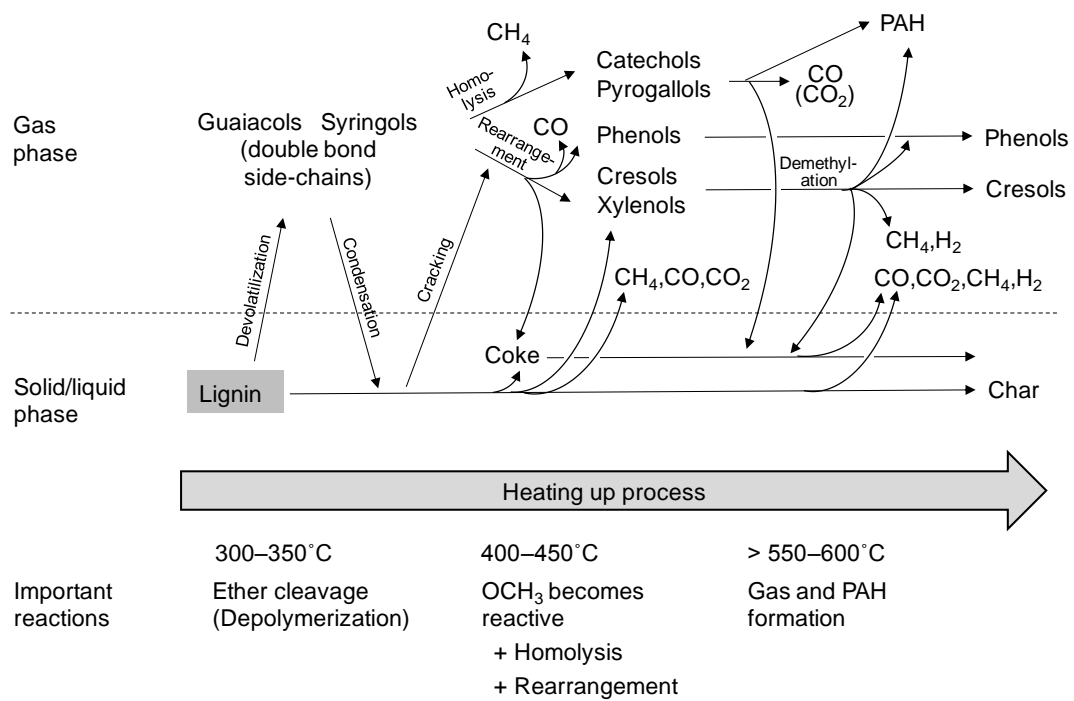


Fig. 9. A proposed gas- and solid/liquid-phase pyrolysis pathway of lignin in a closed ampoule reactor under N₂ at 600 °C.

