

In situ assessment of lignin pyrolysis reactions and their interactions with polysaccharides in Japanese cedar wood cell walls by TG-MS and Py-GC/MS

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ABSTRACT

Understanding the thermal degradation of lignin and polysaccharides in wood cell walls is essential for optimizing biomass pyrolysis. In this study, Japanese cedar (*Cryptomeria japonica*) was analyzed using thermogravimetric-mass spectrometry (TG-MS). Coupled with pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), TG-MS enabled semi-quantitative analysis of key volatile products evolved during thermal degradation, each corresponding to distinct m/z values. Comparison between intact wood and isolated milled wood lignin (MWL) revealed the influence of cell wall supramolecular structures on lignin pyrolysis. The water (m/z 18) evolution profiles from both materials exhibited six distinct peaks, indicating stepwise lignin decomposition across six temperature ranges up to 1000 °C. β -Ether cleavage predominantly yielded coniferyl aldehyde rather than coniferyl alcohol at early stages, suggesting a polymer effect that promotes *in situ* C_γ oxidation—an observation rarely observed in model compound studies. The formation temperatures of pyrolysis products followed the order: β -ether bond cleavage < side-chain saturation < methoxy group demethylation. In intact wood, secondary reactions such as side-chain saturation and demethylation occurred at significantly lower temperatures than in MWL. Since the pyrolysis product profiles of MWL remained largely unaffected by the addition of sugars, the enhanced reactivity in wood is attributed to the influence of the cell wall ultrastructure. This study is the first to provide detailed *in situ* insights into the thermal degradation behavior of lignin and polysaccharides within wood cell walls, offering valuable contributions to the field of wood pyrolysis.

1. Introduction

Biomass pyrolysis serves a fundamental basis of various thermochemical conversion processes, including carbonization, gasification, and fast pyrolysis for bio-oil production [1]. A comprehensive understanding of the underlying pyrolysis mechanisms is essential for optimizing these technologies and maximizing the value of biomass-derived products [2,3].

Lignocellulosic biomass, such as wood and agricultural residues, is a promising feedstock for the production of biofuels and value-added chemicals due to its abundant production and sustainability [4]. Among its major constituents, lignin is particularly attractive for the production of aromatic chemicals [5]. The molecular mechanisms of lignin pyrolysis have been extensively studied using model compounds such as dimers and trimers [6–14], which have provided insights into the degradation pathways of specific linkages, including β -ether

bond—the most abundant linkage type—and their cleavage mechanisms (i.e., homolysis vs. heterolysis) [15]. However, corresponding information for lignin polymers remains limited, largely due to the analytical challenges associated with complex pyrolysis product [16]. Consequently, it remains unclear whether the same mechanisms proposed in model compound studies also apply to polymeric lignins and to lignin in wood cell walls [17], where cellulose microfibrils are embedded in the lignin-hemicellulose matrix to form nano-sized supramolecular architecture [18]. Although recent solid-state NMR analyses have revealed interactions among cell wall components [19,20], the ultrastructure remains largely unclear [21].

To investigate pyrolysis in such complex systems, thermogravimetric (TG) analysis has been widely employed due to its ability to monitor weight loss as a function of temperature. However, TG alone provides no chemical insight into the volatile products evolved during pyrolysis. To address this limitation, various analytical techniques have been

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developed including pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), thermogravimetric Fourier transform infrared spectroscopy (TG- FTIR) [22,23], and thermogravimetric-mass spectrometry (TG-MS) [24,25]. These methods enable detailed analysis of evolved gases, offering deeper insights into pyrolysis reaction pathways. Among them, TG-MS is particularly promising, as it provides real-time mass spectral data throughout the entire heating process. This enables the construction of temperature-resolved evolution profiles for individual m/z values, directly linking product formation to specific thermal events.

While TG-MS offers real-time monitoring of evolved volatiles, its primary limitation is the lack of chromatographic separation. Furthermore, the use of electron ionization (EI) causes extensive fragmentation of volatile products, resulting in complex mass spectra where fragment ions from co-evolving compounds overlap. This complexity makes it difficult to trace the formation of individual compounds. Consequently, most previous applications of TG-MS have focused on low-mass species such as CO, CO₂, H₂O [24,26,27]. Only a limited number of studies have addressed lignin-derived aromatic compounds with higher m/z values, and even fewer have carefully assigned these m/z signals to specific chemical structures [28–32]. To reduce fragmentation, soft ionization techniques such as photoionization (PI) mass spectrometry have been applied to biomass pyrolysis [33,34], yielding significant simpler mass spectra. However, EI-induced fragmentation can be advantageous in distinguishing compounds with identical molecular weights and similar functionalities, such as benzyl and conjugated carbonyl groups. Therefore, in this study, we employed standard 70 eV EI, which is integrated into our TG-MS system. A similar approach using PI techniques will be considered in future work.

To identify the volatile products from the TG-MS data, each mass signal at a specific m/z value in the spectrum—obtained as a mixture of all volatile products and their fragmentation ions—must be accurately correlated with the corresponding volatile compounds. Since the chemical structure of lignin varies by wood type, we selected Japanese cedar (*Cryptomeria japonica*), a softwood species composed exclusively of guaiacyl (4-hydroxy-3-methoxyphenyl) units. Hardwood species, which contain syringyl (3,5-dimethoxy-4-hydroxyphenyl) units in addition to guaiacyl units, are expected to exhibit more complex mass spectra and are thus more challenging to analyze.

In this study, we aimed to construct temperature-resolved formation profiles for specific lignin-derived volatile products by identifying diagnostic m/z signals—unique, non-overlapping fragment ions assignable to individual compounds. Based on these profiles, we subsequently investigated how the supramolecular architecture of the cell wall influences the progression of both primary and secondary lignin pyrolysis reactions.

2. Materials and methods

2.1. Material preparation

To remove extractives, Japanese cedar wood flour (particle size < 1 mm) was immersed in acetone at room temperature for 8 h, and this procedure was repeated with fresh acetone until it became colorless, followed by oven-drying at 105 °C overnight. The resulting extractive-free wood flour was used for subsequent analyses and MWL preparation.

MWL was prepared following the method by Lundquist et al [35], a modified Björkman procedure known to yield MWL with substantially lower residual polysaccharide content (<0.3 %) compared with the original method [36]. Extractive-free wood flour (150 g) was ball-milled for 48 h with external water cooling. The resulting powder was extracted five times with 1,4-dioxane/water (96:4, v/v) at room temperature. The combined supernatants were concentrated to yield crude MWL, which was purified by stepwise precipitation: first dissolved in acetic acid/water (9:1, v/v) and precipitated into excess water, then redissolved in chloroform/ethanol (2:1, v/v) and precipitated into diethyl ether,

affording 858 mg of purified brown MWL powder.

MWL is widely used as an isolated lignin preparation, it is well established that the ball-milling-based extraction process can induce partial structural modifications compared with native lignin in the cell wall. In particular, partial cleavage of β -O-4 ether linkages has been reported in previous studies [37,38]. Nonetheless, MWL is still regarded as the closest available form to native lignin, because the extent of such structural alternation is limited and the polysaccharide content is extremely low. Therefore, interference from co-extracted carbohydrates is expected to be negligible, making MWL an appropriate reference for examining lignin pyrolysis reactions without the influences of polysaccharide components and cell wall ultrastructure.

MWL-monosaccharide mixtures were prepared by thoroughly grinding MWL with D-glucose or D-mannose (Nacalai Tesque, Kyoto, Japan) at a weight ratio of 5:1 (w/w) using a mortar and pestle.

2.2. Thermogravimetric-mass spectrometry (TG-MS)

TG-MS analysis was performed to investigate the volatile compounds evolved during pyrolysis. A thermal analyzer (STA 449 F3 Jupiter, Netzsch-Gerätebau GmbH, Selb, Germany) was coupled to a GC-MS system (JMS-Q1600GC, JEOL Ltd., Tokyo, Japan). Approximately 3 mg of each sample was loaded into an alumina crucible, which is chemically inert and may not exhibit catalytic activity under pyrolysis conditions [39], and heated from 40 °C to 1050 °C at 10 °C/min under a nitrogen flow (50 mL/min, 99.9998 % purity). The evolved volatiles were transferred through a 300 °C isothermal transfer line and introduced directly into the mass spectrometer through a blank capillary tube (2.5 m length $\times$ 0.25 mm i.d., oven temperature 300 °C), bypassing GC separation. MS spectra were recorded over an m/z range of 15–300 using electron impact ionization (70 eV) at an ion source temperature of 300 °C.

2.3. Pyrolysis-GC/MS analysis (Py-GC/MS)

Fast pyrolysis was carried out using a Curie-point pyrolyzer (JCI-22, Japan Analytical Industry Co., Ltd., Osaka, Japan). Approximately 0.4 mg of Japanese cedar wood flour was wrapped in a 590 °C Curie-point foil and inductively heated for 5 s. The volatiles evolved during pyrolysis were introduced into the same GC-MS system used for the TG-MS analysis and separated on an HP-5 column (30 m $\times$ 0.32 mm i.d., 0.25 μ m film thickness) under the following conditions: split ratio, 10:1; injector temperature, 250 °C; oven temperature, 50 °C (held for 2 min) to 300 °C at 10 °C/min (held for 4 min); carrier gas, nitrogen (1.4 mL/min); MS conditions, identical to those used in the TG-MS analysis.

3. Results and discussion

3.1. TG-MS analysis

The TG and DTG curves for Japanese cedar wood and its MWL fraction are shown in Fig. 1, with the DTG peaks at 353 °C and 348 °C,

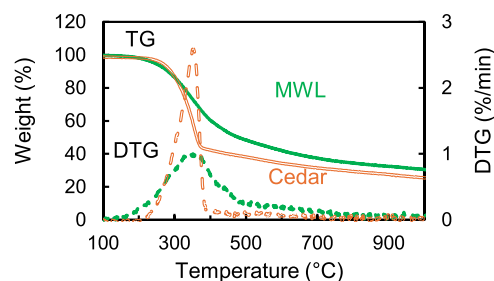


Fig. 1. TG and DTG curves of Japanese cedar wood and MWL (heating rate: 10 °C/min, N₂ flow rate: 50 mL/min).

respectively. Since cellulose degrades mainly around the DTG peak temperature, similar DTG peak temperatures indicate that efficient thermal degradation of cellulose and lignin occur at similar temperatures. Notably, the temperature range where the weight loss was observed was wider for MWL than for wood, which is discussed later in detail.

During TG-MS analysis, the mass spectra of volatile products generated from wood and MWL are continuously recorded as mixtures of all volatile compounds and their fragments. To clarify the temperature range in which lignin-derived products are generated, Fig. 2 shows the cumulative mass spectra within designated temperature ranges during TG-MS analysis of Japanese cedar wood. The highest m/z value observed from wood polysaccharides was 127 ($M^+ + 1$ of 5-hydroxymethylfurfural); therefore, signals at m/z 128 and above are attributed to lignin-derived products. This attribution is further supported by the cumulative Py-GC/MS mass spectrum of highly purified, demineralized softwood pulp (Figure S1), which contains only cellulose- and hemicellulose-derived products. In this carbohydrate-only spectrum, signals above m/z 128 were barely detectable and remained as based lines, indicating that contributions from polysaccharides in this m/z region are negligible. These lignin-derived signals began to appear at around 260 °C under the present experimental conditions, and became prominent in the temperature range of 300–380 °C. The signals decreased sharply around 380 °C and almost disappeared above 400 °C, where the weight-loss rate also significantly decreased in the TG curve.

In the dimer region (m/z 200–300, Figure S2), a stilbene was observed at m/z 272, along with several other unidentified signals. These dimers were also generated in significant amounts at 280–360 °C, similar to the monomeric products.

These observations highlight the importance of the 280–380 °C temperature range for the analysis of lignin-derived monomers and

dimers. The signal intensities of these compounds reach a maximum at approximately 350 °C, which coincides with the DTG peak temperature of MWL. Therefore, the mass spectra accumulated over the 300–350 °C range were used for the assignment of signals to the corresponding products.

3.2. Assignment of TG-MS m/z values to individual volatile products using Py-GC/MS

To enable a detailed discussion of the individual volatile products derived from lignin, it is essential to assign the mass spectral signals observed in the complex mixture to specific compounds. For this purpose, pyrolysis-GC/MS analysis of Japanese cedar wood was conducted using a Curie point injector with the GC installed in the TG-MS analyzer, under mass spectrometric conditions identical to those used for the TG-MS analysis. A pyrofoil with a Curie point of 590 °C was selected, as most primary and secondary pyrolysis products are generated at this temperature. The sample rapidly reached 590 °C; however, during the heating process, primary pyrolysis reactions occurred, and some of the primary products were further degraded into secondary pyrolysis products. The evolved volatiles were carried by a flow of helium into the GC inlet for subsequent GC/MS analysis. The total-ion chromatogram (TIC) obtained from this analysis is presented in Fig. 3, where the numbered peaks correspond to the compounds identified. From the mass spectra of the individual chromatographic peaks, a total of 30 volatile products were identified.

Levoglucosan (1,6-anhydro- β -D-glucopyranose, **1**), furfural (**2**), 5-hydroxymethylfurfural (5-HMF, **3**), and compounds **4** and **5** are polysaccharide-derived products, formed through pyrolytic reactions including transglycosylation and dehydration. Glycolaldehyde (**6**) and ethylene glycol (**7**), are primarily produced via fragmentation of carbohydrates, but may also originate from the propyl side chains of lignin. Compounds **8–30** are assigned to lignin-derived aromatic compounds, most of which contain a guaiacyl unit, which is the main aromatic nuclei in Japanese cedar (a softwood) lignin.

Lignin is a polymer composed of phenylpropane units, primarily linked through two types of bonds: ether linkages (C-O) and condensed linkages (C-C) [40]. The primary pyrolysis products from lignin are generally formed through the cleavage of the propyl side chain and its ether linkages [8]. Based on previous studies using lignin model dimers and trimers, the α - and β -ether bonds are readily cleaved at relatively mild temperatures (250–400 °C) [10], mostly via homolytic mechanisms, except for the heterolysis of the α -ether bonds at phenolic ends. In contrast, condensed linkages are relatively stable, and the β -aryl type structures lead to the formation of stilbene (**17**) as a major dimer, as shown in Fig. 3.

The pyrolysis reaction pathways of lignin, as revealed by previous studies using model compounds, are summarized in Fig. 4. Cleavage of the β -ether bonds, the most abundant type of linkage, yields coniferyl alcohol (CA, **15**). CA is highly unstable and undergoes further reactions to produce oxidation products such as coniferyl aldehyde (Cald, **14**), as well as reduction products including isoeugenol (IE, **12**), eugenol (**13**), vinyl guaiacol (VG, **11**), and dihydro-coniferyl alcohol (DCA, **16**), along with various condensation products. This transformation pathway is referred to in this study as the "CA pathway." It is noteworthy that compounds containing carbonyl groups in the side chain are not generated via the CA pathway but rather through alternative mechanisms. For example, vanillin (**20**) is produced via cleavage of the $C_{\alpha}-C_{\beta}$ bond in the lignin side chain, likely through a cyclic Grob-type reaction [9].

As shown in Fig. 4, most of the primary pyrolysis products from lignin contain side-chain double bonds, such as C=C or C=O bonds, along with the phenolic OH groups at the para position of the guaiacyl units. As the temperature increases, these unsaturated side chains are converted to hydrogen or saturated alkyl groups (methyl, ethyl, propyl), which are characteristic of secondary pyrolysis products. In addition to

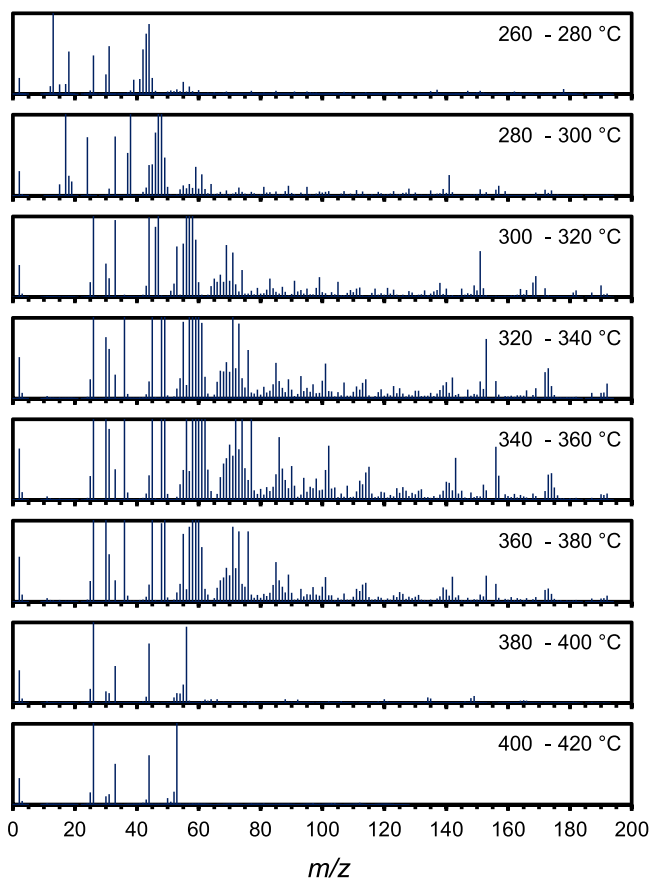


Fig. 2. Temperature dependence of mass spectra from TG-MS analysis of Japanese cedar wood (heating rate: 10 °C/min, N₂ flow rate: 50 mL/min).

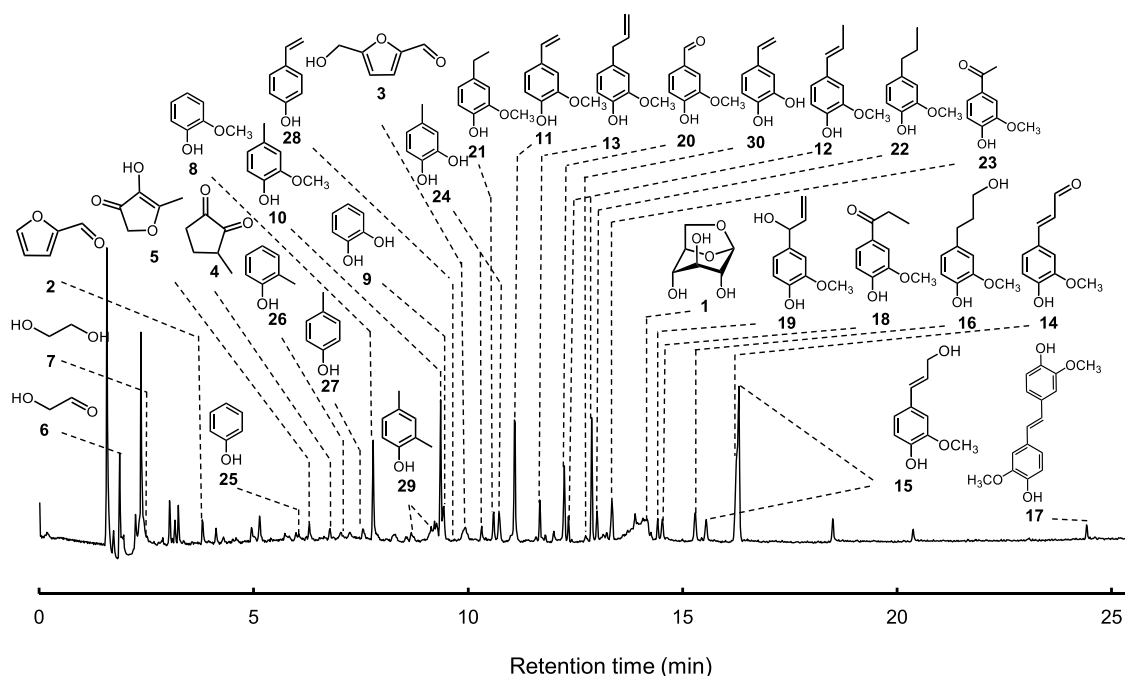


Fig. 3. Total-ion chromatogram and peak assignment in Py-GC/MS analysis of Japanese cedar wood (590 °C, 5 s retention time).

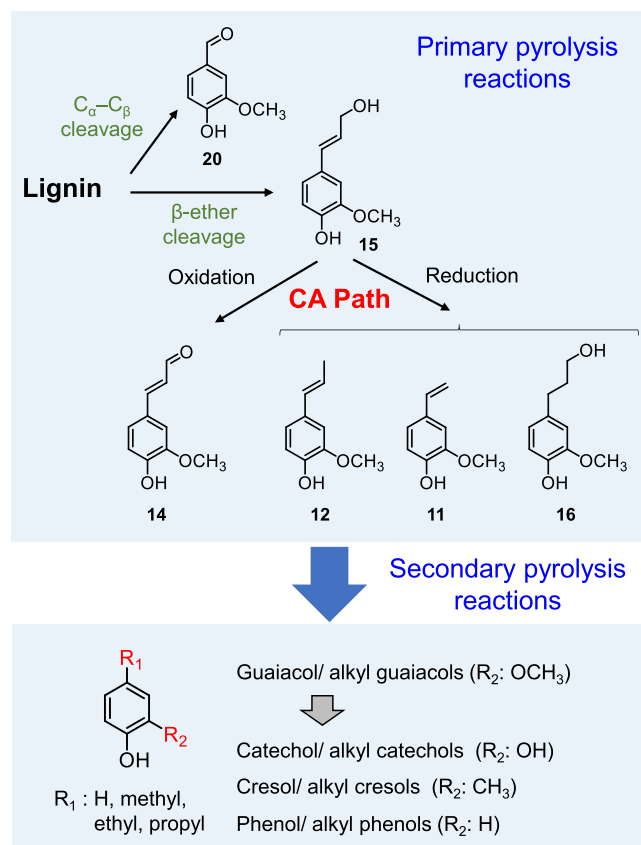


Fig. 4. Primary and secondary pyrolysis pathways of Japanese cedar (a soft-wood) lignin, as proposed based on model compound studies (adapted from Kawamoto) [15].

the side-chain structure, aromatic structures are also transformed from guaiacyl-type to catechol-type [catechol (9), methyl catechol (24), and vinyl catechol (30)], cresol-type [o-cresol (26) and 2,4-dimethyl phenol

(29)], and phenol-type [phenol (25), 4-methyl phenol (27), and vinyl phenol (28)]. These compounds are the well-known secondary pyrolysis products, observed during the gas-phase pyrolysis of guaiacols at temperatures higher than 450 °C [41]. They are formed through homolysis of O-CH₃ bonds, rearrangement from methoxyl to methyl groups via spiro-ether intermediates, and deformylation via o-hydroxy aldehyde intermediates, respectively [6,42].

As described earlier, 5-HMF is the polysaccharide-derived product that exhibits the highest *m/z* value (*M*⁺ 126 and its isotope signal at 127). Although the molecular mass of levoglucosan is 168, it did not produce an *M*⁺ ion, but instead yielded only fragment ions with *m/z* values of 73 and lower [43]. Therefore, the sum of all signals at *m/z* 128 or greater serves as a useful indicator of lignin-derived volatiles.

Although the fast pyrolysis performed using the Curie point injector and the slow heating profile of TG analysis are not strictly identical in terms of thermal conditions, the volatile products generated by both methods are considered to be qualitatively comparable. Therefore, the mass spectra obtained by Py-GC/MS analysis were used to interpret those obtained by TG-MS analysis. To facilitate this comparison, we systematically examined the relationship between the total-ion chromatogram (TIC) and individual mass chromatograms (i.e., extracted ion chromatograms for specific *m/z* values) up to *m/z* 300. This approach enabled us to identify *m/z* values that could be classified into three categories: those assignable to a single compound, those likely representing a small number of compounds, and those indicative of specific functional groups rather than exact molecular structures. To ensure the reliability of these signal assignments, the mass spectra were cross-referenced with established EI-MS databases for biomass pyrolysis [33, 44].

Representative examples of these classifications of mass chromatograms are shown in Fig. 5, S3, S4, and the corresponding *m/z* values and their assigned chemical structures are summarized in Table 1. The assigned key *m/z* signals are indicated in the TG-MS spectra of Japanese cedar wood (300–350 °C) in Fig. 6, along with the associated chemical structures.

The mass chromatograms shown in Figure S3 correspond to *m/z* values that are representative of carbohydrate-derived volatiles and fragmentation products. Among the carbohydrate-derived volatiles, the *m/z* values 47, 96, 97, 112, and 114 were assigned to levoglucosan (1),

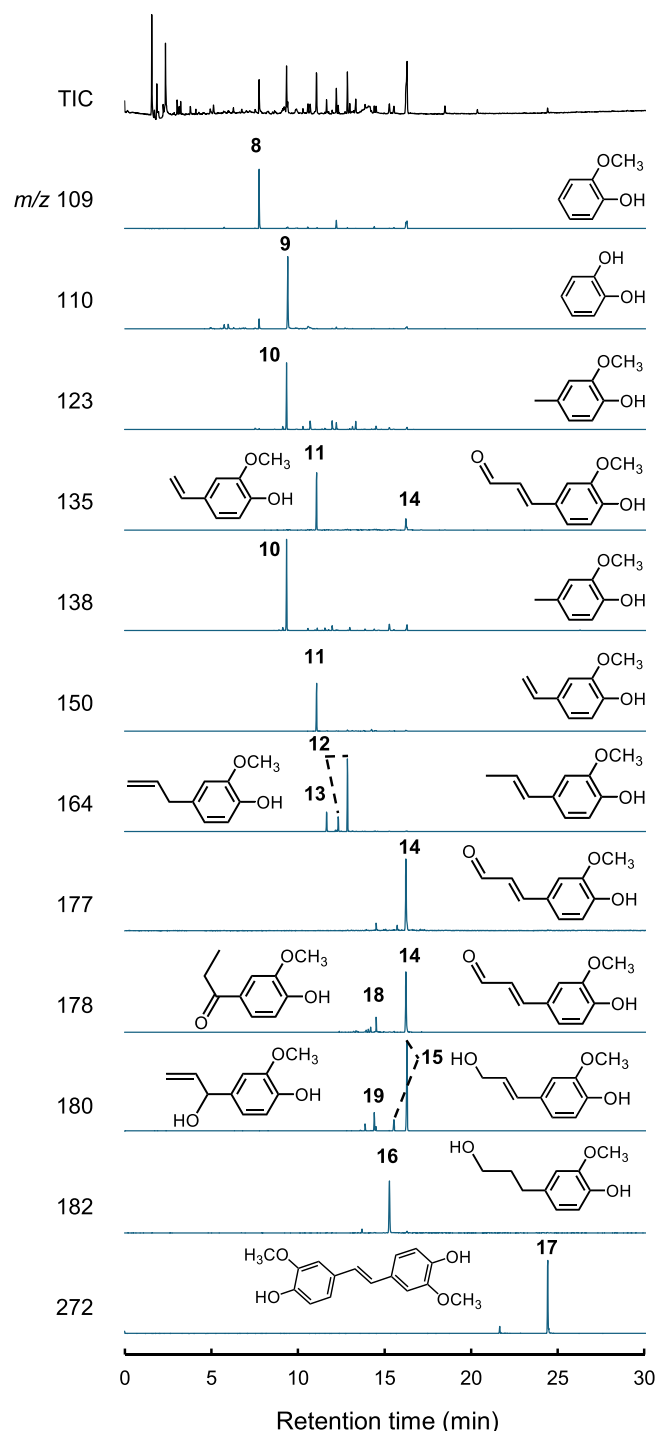


Fig. 5. Comparison of the total-ion chromatogram (TIC) obtained from Py-GC/MS analysis of Japanese cedar wood with the mass chromatograms of m/z values characteristic of lignin-derived aromatic products (specifically identified almost pure compound).

furfural (2), 5-HMF (3), and compounds 4 and 5, respectively, each attributable to a nearly pure compound. The m/z 73 is a relatively strong fragment ion of levoglucosan (1); however, caution is required when using this value to identify levoglucosan, as methyl acetate—a possible pyrolysis product—and various aliphatic compounds—likely introduced as contaminants—also generate fragment ions at m/z 73. The m/z values of 31 and 33 were used to represent the fragmentation products, glycolaldehyde (6) and ethylene glycol (7), respectively.

Fig. 5 presents mass chromatograms of lignin-derived compounds,

Table 1

Linking m/z values to chemical structures of products (Japanese cedar).

m/z	Compound	Reliability	Major contaminant
Carbohydrate derived products			
47	Levoglucosan (1)	S	
96	Furfural (2)	aS	
97	5-HMF (3)	aS	
112	Dehydration prod. (4)	aS	
114	Dehydration prod. (5)	aS	
Fragmentation products			
31	Glycolaldehyde (6)	aS	
33	Ethylene glycol (7)	aS	
Lignin derived products			
109	Guaiacol (8)	aS	
110	Catechol (9)	aS	
123	Methyl guaiacol (10)	aS	
135	Vinyl guaiacol (11)	aS	14
138	Methyl guaiacol (10)	aS	
150	Vinyl guaiacol (11)	S	
164	Isoeugenol (12)	aS	13
177	Coniferyl aldehyde (14)	aS	18
178	Coniferyl aldehyde (14)	aS	18
180	Coniferyl alcohol (15)	aS	19
182	Dihydro-coniferyl alcohol (16)	aS	
272	Stilbene (17)	S	
81	8 + Vanillin (20)	T	
152	Ethyl guaiacol (21) + 20	T	
166	Propyl guaiacol (22)	T	
	+ Acetovanillone (23)		
151	α -C=O (20, 23, 18)	M	11
77	10, 11, 12, 13, 14, 15	M	
78	10, 11, 12, 13, 14, 15, 24	M	
94	10, 12, 13, 14, 15, 16, 18, 19, 22, 25	M	
108	11, 14, 15, 18, 20, 23, 26, 27	M	
120	12, 13, 14, 15, 28	M	
122	10, 12, 13, 15, 16, 18, 19, 21, 22, 29	M	
136	11, 14, 15, 20, 23, 30	M	
137	15, 16, 18, 19, 21, 22	M	

S: single compound, aS: almost single compound, T: two compounds, M: many compounds

most of which can be largely attributed to individual molecular species. These include guaiacol (8, m/z 109), catechol (9, m/z 110), methyl guaiacol (10, m/z 123 and 138), VG (11, m/z 135 and 150), IE (12) and eugenol (13) (both at m/z 164), Cald (14, m/z 177 and 178), CA (15, m/z 180), DCA (16, m/z 182), and stilbene (17, m/z 272).

It should also be noted that small contributions from Cald (14), DCA (16), and compounds 18 and 19 were detected at m/z 135 (VG), 177 (Cald), 178 (Cald), and 180 (CA), respectively. Therefore, when analyzing these target compounds, these minor contaminants may be included, although their amounts are relatively small. Under slow pyrolysis conditions, such as in TG analysis, the formation of compounds 18 and 19 was not significant compared to the products of the CA pathway. Thus, m/z 178 and 180 can be reliably used to assess the formation of Cald and CA, respectively. IE (12) and eugenol (13), which are isomers differing in the position of the side-chain C=C bond, cannot be assessed separately at m/z 164. Both are secondary pyrolysis products of CA, and the more stable IE is generally preferentially formed over eugenol. Thus, m/z 164 can be used here as a marker for IE. In contrast, Cald (14), which can also contribute to m/z 135 (VG), is a key product of the CA pathway; therefore, m/z 150 is a more preferable marker for VG.

Although such limitations exist, all of the CA pathway products can be assessed during TG-MS analysis of softwood lignin, which consists solely of guaiacyl units.

Figure S4 shows mass chromatograms corresponding to m/z values shared by two compounds or associated with specific functional groups. For example, m/z 81 includes contributions from both vanillin (20) and guaiacol (8). Vanillin is a primary lignin pyrolysis product formed via C α -C β bond cleavage, whereas guaiacol is a secondary product produced via decarbonylation of vanillin moieties and elimination of side chain at the para position relative to phenolic OH [45]. Accordingly, as discussed

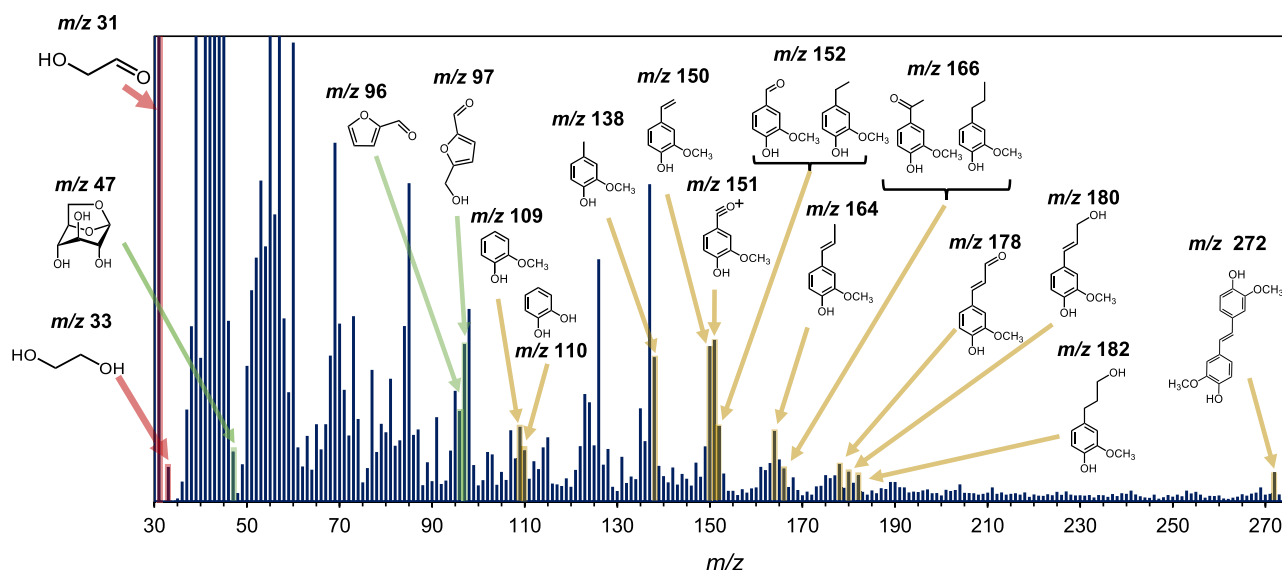


Fig. 6. The m/z values and corresponding chemical structures of individual volatile products identified in the mass spectra obtained during the heating process at 300–350 °C in TG-MS analysis of Japanese cedar wood.

earlier, m/z 109 is the more appropriate marker to represent guaiacol.

The signal at m/z 152 includes both vanillin (20) and ethyl guaiacol (21), making it less suitable as a specific marker for vanillin. In contrast, m/z 151, although containing minor contributions from VG (11), is primarily composed of compounds with α -carbonyl side chains. Therefore, combined use of m/z 151 and 152 is recommended for accurately discussing vanillin formation, as discussed later. Similarly, m/z 166 contains signals from both propyl guaiacol (22) and acetovanillone (23), and can be interpreted more accurately when m/z 151 is also considered. Other m/z values containing multiple lignin-derived compounds were identified at 77, 78, 94, 108, 120, 122, 136, and 137. The corresponding mass chromatograms are shown in Figure S5.

3.3. Pyrolytic reactions of lignin polymer and lignin in wood

Fig. 7 shows the evolution profiles of water (m/z 18) and CO_2 (m/z 44) during the thermal degradation of Japanese cedar wood and MWL. As shown in Fig. S6, the major pyrolysis products from lignin and carbohydrate contribute negligibly to the signals at m/z 18 and 44 under 70 eV EI conditions. In particular, the fragment ions from these compounds exhibit almost no intensity at m/z 18, confirming that the evolution profile of this ion predominantly reflects H_2O , with minimal interference from other volatiles. By plotting the MS signal intensity for a specific m/z value against TG analysis temperature, the evolution behavior of a given volatile product can be semi-quantitatively assessed. For MWL, distinct m/z 18 peaks were observed at 234, 327, 433, 547, 762, and 898 °C, indicating that water was generated through multiple, stepwise thermal decomposition reactions occurring stepwise. In contrast, formation of CO_2 at temperature below 350 °C was relatively minor, whereas in the higher temperature range, CO_2 evolution exhibited peaks at temperatures similar to those of water.

These results indicate that lignin undergoes thermal decomposition over a broad temperature range. Notably, aromatic ring-containing volatiles become negligible above approximately 450 °C. In Japanese cedar wood, water evolution is partly attributable to the decomposition of polysaccharides [46]. The most prominent peak is likely associated with the pyrolysis of carbohydrates, particularly cellulose. However, at higher temperatures above 400 °C—where the weight loss of wood polysaccharide-derived char is minimal—the water formation profile closely resembles that of MWL, although there are slight differences in the temperature ranges. This suggests that the reactivity of secondary

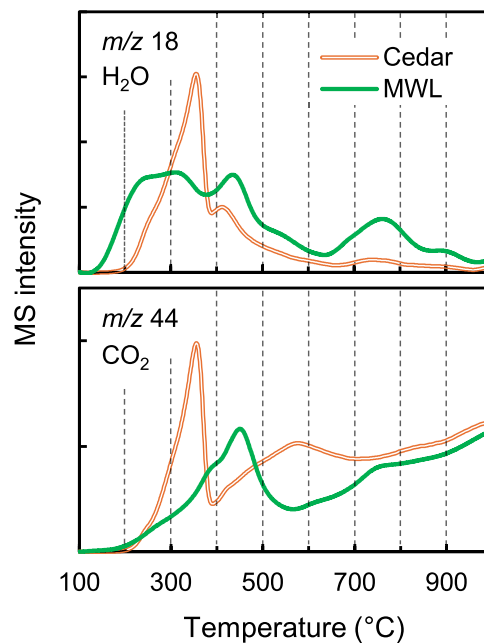


Fig. 7. Water (m/z 18) and CO_2 (m/z 44) evolution profiles during TG-MS analysis of Japanese cedar wood and MWL (heating rate: 10 °C/min, N_2 flow rate: 50 mL/min).

degradation of MWL and lignin within the cell wall differ slightly. Nevertheless, these findings indicate that lignin in the wood cell wall degrades over a broad temperature range, in a manner similar to that of isolated MWL.

Fig. 8 presents the evolution profiles of characteristic m/z values for lignin- and carbohydrate-derived products, in comparison with the DTG curves. Carbohydrate-derived products are represented as the sum of the signals at m/z 47, 96, 97, 112, and 114, as listed in Table 1. For lignin-derived aromatic products, three approaches were considered: (A) the sum of lignin-derived signals at the m/z values specified in Table 1, (B) the sum of signals at m/z values of 128 and above, and (C) the combination of approaches (A) and (B). As discussed later, the temperature ranges of the evolution curve peaks vary depending on the type of lignin-

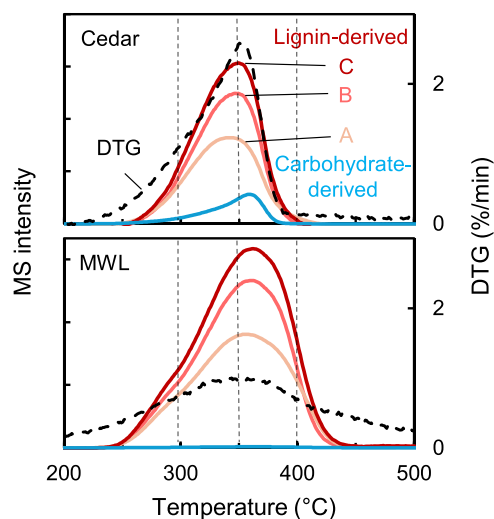


Fig. 8. Evolution curves of volatile products during TG-MS analysis of Japanese cedar wood and MWL (heating rate: 10 °C/min, N₂ flow rate: 50 mL/min). * carbohydrate-derived products: sum of signals for m/z 47, 96, 97, 112, and 114. * lignin-derived products: (A) sum of lignin-derived signals at the m/z values specified in Table 1 (m/z 77, 78, 81, 94, 108, 109, 110, 120, 122, 123, 135, 136, 137, 138, 150, 151, 152, 164, 166, 177, 178, 180, 182, 272). (B) sum of signals at m/z values of 128 and above. (C) combination of (A) and (B).

derived product—namely, primary or secondary pyrolysis products.

However, the three evolution profiles for lignin-derived products (A)–(C) did not differ significantly, suggesting that these m/z selections include both types of products in a balanced manner. These results provide important insights into the application of the TG-MS method to lignocellulosic biomass types beyond softwoods. In the case of hardwoods and herbaceous plants, the presence of syringyl and *p*-hydroxyphenyl units, in addition to guaiacyl units, complicates the assignment of m/z values to specific compounds due to signal overlap. Nevertheless, the use of the summed signals at m/z values of 128 and above is applicable to all types of lignocellulosic biomass. In MWL, the formation profiles of lignin-derived aromatic products are well aligned with the DTG curve.

Below 250 °C and above 450 °C, the formation of lignin-derived aromatic compounds was limited; the major products in these regions

were water and non-condensable gases, including CO₂. As shown in Fig. 7, water is selectively produced from MWL at such low pyrolysis temperatures. In wood, the DTG peak temperature closely coincides with the peak in the formation profile of carbohydrate-derived products. This can be attributed to the production of levoglucosan and other compounds during the pyrolysis of cellulose, which is the most thermally stable component of wood due to its crystalline structure, and contributes most significantly to the weight loss observed during pyrolysis [45]. In contrast, the peaks in the formation profiles of lignin-derived aromatic products appear at slightly lower temperatures than the DTG peak.

The formation behavior of individual products can be more clearly discussed in Fig. 9, which shows the evolution profiles for four groups of volatiles: lignin-derived CA pathway products, lignin-derived secondary pyrolysis products, fragmentation products, and carbohydrate-derived products, for both wood and MWL. The DTG curves are also included for comparison. As discussed earlier, vanillin and acetovanillone—both primary pyrolysis products—were detected at m/z values of 152 and 166, along with ethyl guaiacol and propyl guaiacol—both secondary pyrolysis products—, respectively. As a result, these primary products are included in the formation profiles categorized as secondary products. The corresponding peak temperatures for these signals are summarized in Fig. 10.

All the carbohydrate-derived products from wood shown in Fig. 9 exhibited the formation profiles similar to the summation profile in Fig. 8, indicating that these products are extensively generated at relatively higher temperatures where crystalline cellulose degrades. In contrast, shape of the profile of fragmentation products is well in line with the DTG curve of wood, suggesting that the fragmentation reactions occur along with the weight loss of wood. Very low intensity of carbohydrate-derived products from MWL is attributable to the low carbohydrate content of MWL. The MWL also generated fragmentation products throughout the weight-loss process, probably from the propyl side chains.

Regarding the lignin-derived aromatic compounds in wood, peak temperatures of their formation profiles significantly varied; the peak of CA path products are generally observed in the temperature range lower than the DTG peak temperature; however, the peaks of secondary pyrolysis products tend to align with the DTG peak temperature. This is understandable with the sequential occurrence of the pyrolysis reactions, primary CA path → secondary reactions, during TGA. The profiles of m/z 152 and 166, corresponding to ethyl guaiacol and propyl

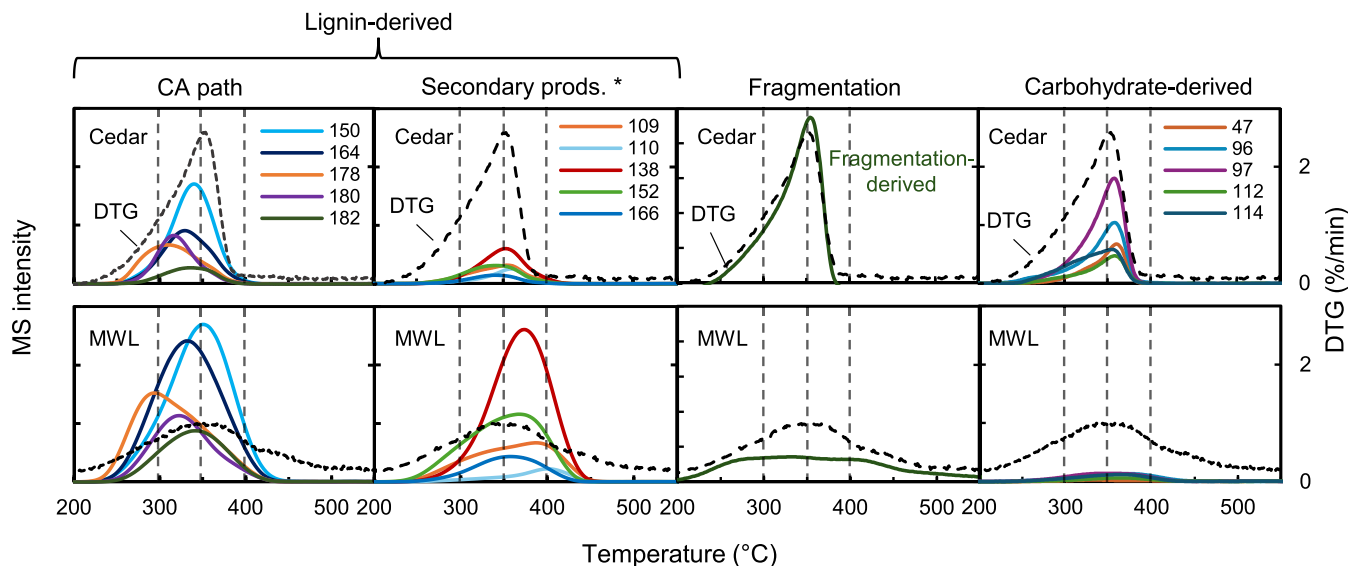


Fig. 9. Evolution curves of volatile products during TG-MS analysis of Japanese cedar wood and MWL (heating rate: 10 °C/min, N₂ flow rate: 50 mL/min). * Including vanillin (m/z 152) and acetovanillone (m/z 166) as primary products.

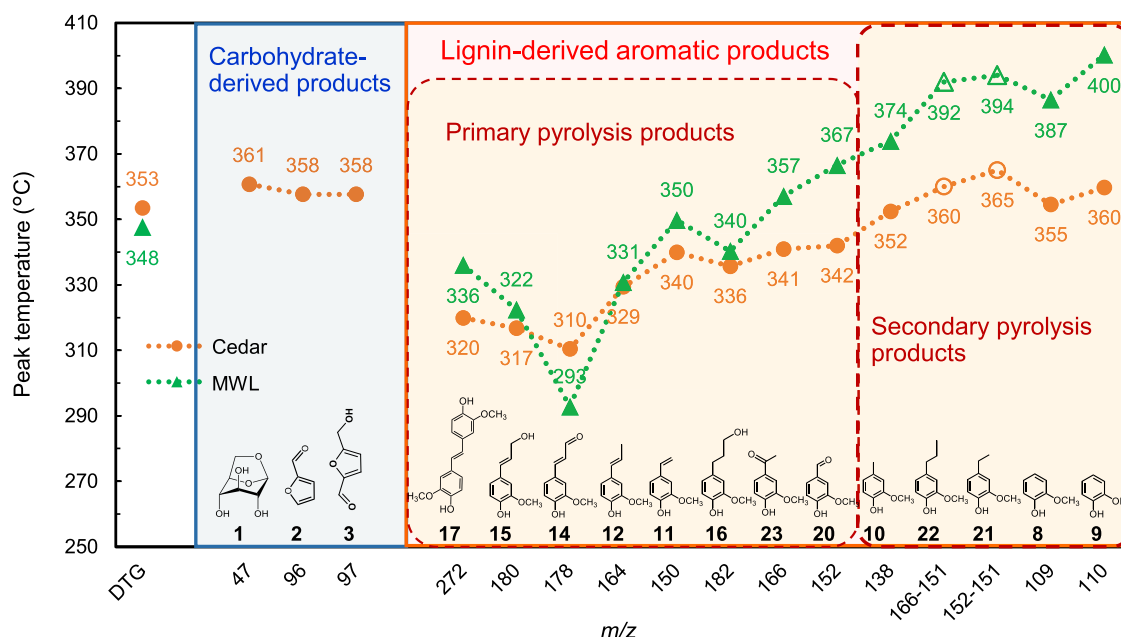


Fig. 10. Peak temperatures of evolution curves for various volatile compounds and DTG curves obtained from TG-MS analysis of Japanese cedar wood and MWL (heating rate: 10 °C/min, N₂ flow rate: 50 mL/min). Open circle and open triangle: estimated peak temperatures obtained by the comparison of the profiles of m/z 152 (vanillin + ethyl guaiacol) and 166 (acetovanillone + propyl guaiacol) with that of m/z 151 (α -C=O) (Fig. 11).

guaiacol, respectively, exhibited the exception due to the presence of the primary products, vanillin and acetovanillone, as described earlier.

In Fig. 11, the profiles of m/z 152 and 166 are compared with the α -C=O indicator at m/z 151, by normalizing the intensities to the same height, allowing a rough estimation of the peak temperatures of ethyl guaiacol and propyl guaiacol formation at approximately 394 °C and 392 °C for MWL and 365 °C and 360 °C for wood, respectively, based on their difference profiles.

Interestingly, shoulders were observed around the formation peak temperatures of MWL in the wood profiles, suggesting that a portion of lignin in wood exhibited thermal reactivity for the production of ethyl guaiacol and propyl guaiacol similar to that of MWL.

The peak temperatures of secondary pyrolysis products significantly varied between wood and MWL as shown in Fig. 10, exhibiting the trend of 16–40 °C lower in wood than in MWL. This suggests that the secondary degradation of lignin in wood takes place at lower temperatures than in MWL.

Removal of aromatic substituents is a well-known reaction during

pyrolysis of coal and lignin [47,48], likely occurring via substitution with hydrogen radicals, as illustrated in Fig. 12. A hydrogen radical adds to the benzene ring, forming an unstable intermediate in which aromaticity is lost. Aromaticity is then restored through the elimination of aromatic substituents or methyl of methoxymethyl groups via β -scission reactions. Therefore, if hydrogen radicals are generated in the vicinity of lignin in wood, such secondary reactions may occur at lower temperatures. To confirm this hypothesis, further studies are necessary. The presence of hydrogen radicals in wood during pyrolysis can be suggested by the formation of DCA from CA in CA pathway.

An unexpected result was the preferential formation of Cald in the early stage of pyrolysis in MWL, as Cald is generally considered to be produced via oxidation of CA [13], a primary product formed by the cleavage of β -ether bonds. A similar trend was also observed during wood pyrolysis. This phenomenon has not been reported in previous studies using model compounds, suggesting a polymer effect.

A plausible mechanism for the preferential formation of Cald is illustrated in Fig. 13. The phenolic end can form a quinone methide intermediate through the elimination of an OH or OR group from the C $_{\alpha}$ position, which is supported by water evolution beginning just above 100 °C (Fig. 7) and Cald formation starting around 220 °C (Fig. 9). The quinone methides formed at 100–220 °C may undergo condensation

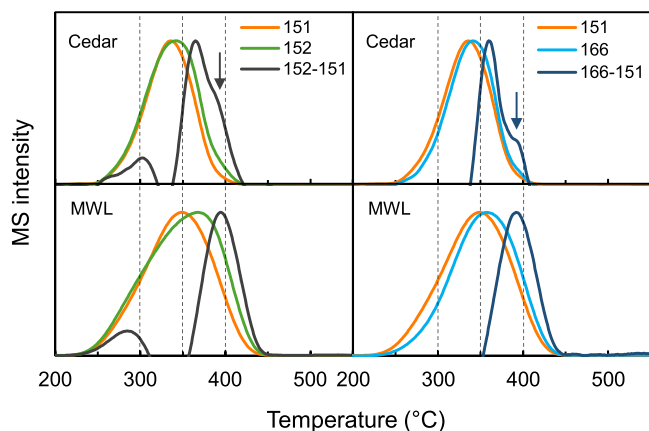


Fig. 11. Profiles of m/z 152 (vanillin + ethyl guaiacol) and 166 (acetovanillone + propyl guaiacol) compared with that of m/z 151 (C_{α} =O), along with their difference curves. All profiles were normalized to the same peak intensity.

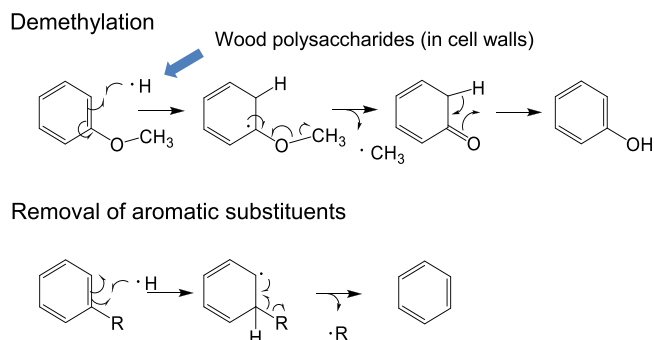


Fig. 12. Plausible mechanism of the removable of aromatic substituents and methoxy demethylation by the action of hydrogen radicals, explaining the enhanced lignin secondary pyrolysis in Japanese cedar wood.

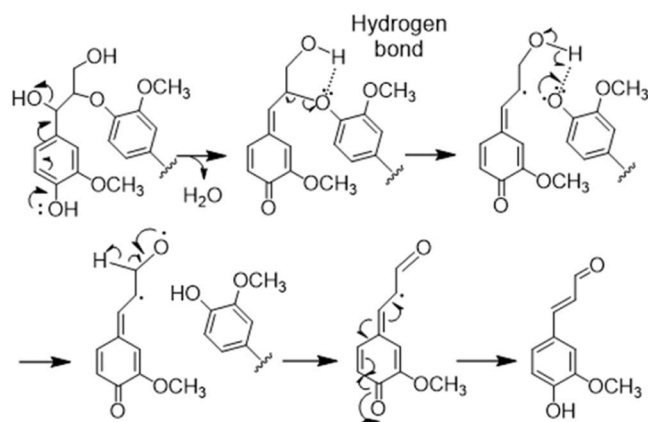


Fig. 13. A proposed mechanism of *in situ* γ -carbon oxidation occurring simultaneously with β -ether cleavage at relatively low temperatures.

[49]. The observed low-temperature cleavage of β -ether bonds is likely due to the reduced bond dissociation energy of the C_β -O bond in the quinone methide, attributed to its strong electron-withdrawing nature [50]. This homolytic cleavage ultimately leads to the formation of CA. The higher onset temperature of water evolution in wood compared to MWL suggests that quinone methide formation from phenolic ends is suppressed in wood.

Simultaneous oxidation at the C_γ position can be explained by assuming the presence of intramolecular hydrogen bonding in lignin macromolecules. In a structure where hydrogen bonding occurs between the C_γ -OH and the C_β oxygen, the resulting phenoxy radical can abstract a hydrogen atom from the γ -OH, forming a C_γ -O $\bullet$ radical. This radical is subsequently converted to C_γ =O through the release of a hydrogen radical via a β -scission reaction. This reaction pathway reasonably accounts for the formation of Cald instead of CA. The presence of intramolecular hydrogen bonding within lignin macromolecules is also plausible for stabilizing the structure.

3.4. Effects of monosaccharide addition on lignin pyrolysis

To investigate the influence of cell wall supramolecular structure on lignin secondary pyrolysis, the effects of monosaccharide addition on MWL pyrolysis were examined. Glucose and mannose were used in place of cellulose and holocellulose to eliminate the influence of cellulose crystallinity and physical microfibril architecture, thereby allowing the intrinsic chemical effects of carbohydrate units on lignin reactivity to be evaluated. TG-MS analysis was conducted on MWL mixed with glucose or mannose (5:1, w/w) to assess their impact on the formation of major secondary products: methylguaiacol (m/z 138), guaiacol (m/z 109), and catechol (m/z 110).

Figure S7 shows the TG/DTG curves alongside water (m/z 18) evolution profiles. Monosaccharide addition lowered the onset temperature of weight loss in the TG curves, with distinct DTG peaks observed at 234 °C for glucose and 219 °C for mannose. These peaks were absent in pure MWL, indicating that the low-temperature weight loss originates from sugar decomposition. Water evolution profiles exhibited peaks at similar temperatures, supporting thermal polymerization accompanied by water release. This corresponds to the well-known initial pyrolysis behavior of reducing sugars, including the reducing ends of polysaccharides [51]. The onset temperatures suggest polymerization reactivity follows the order: mannose > glucose. The observed weight loss (~10–12 %) near 225 °C matches theoretical values for water elimination, supporting this interpretation.

Figure S8 shows the formation profiles of levoglucosan, levomannosan, 5-HMF, and furfural. Both 5-HMF and furfural exhibited two peaks—around 230–240 °C and 300 °C—with greater intensity at the lower temperature. In contrast, levoglucosan and levomannosan

appeared only at higher temperatures. Levomannosan, detected at m/z 47, is an anhydrosugar derived from mannose or its polymers. These temperature ranges align with DTG peaks, indicating that polymerization products formed at lower temperatures undergo further pyrolysis near 300 °C. Thus, 5-HMF and furfural are primarily generated from reducing monosaccharides, whereas levoglucosan and levomannosan are formed preferentially from polysaccharides at elevated temperatures.

Despite influencing the initial stage of thermal behavior, the addition of monosaccharides had little impact on lignin pyrolysis. As shown in Figure S9, the evolution profiles of secondary lignin products—methyl guaiacol, guaiacol, and catechol—remained largely unchanged, except for the profile at m/z 110 (catechol), where the intensity in the lower temperature range increased in the presence of glucose and mannose. Nevertheless, the peak temperatures were consistent with those observed for pure MWL, suggesting that the modification of secondary lignin pyrolysis reactivity by monosaccharide addition is insufficient to account for the substantial differences observed in wood (Fig. 10). Consequently, while monosaccharides influence thermal behavior through polymerization and secondary decomposition, their direct impact on lignin-derived volatiles is limited. This supports the notion that enhanced lignin secondary pyrolysis in native cedar wood is driven more by the supramolecular structure of the cell wall than by direct sugar-lignin interactions.

4. Conclusions

In this study, a thermogravimetric-mass spectrometry (TG-MS) method was established to investigate the pyrolysis behavior of lignin macromolecules and lignin embedded within the cell walls of Japanese cedar (*Cryptomeria japonica*). Coupled with pyrolysis-GC/MS, this approach enabled the identification of some volatile compounds through their m/z signals, allowing for semi-quantitative analysis during TGA.

Water evolution profiles (m/z 18) from MWL and wood revealed six distinct peaks or shoulders below 1000 °C, indicating that lignin decomposes over multiple temperature ranges. Notably, the formation of lignin-derived volatile aromatic compounds below 450 °C was of particular focus in this study. Within this temperature range, the thermal reactions occurred sequentially in the order: β -ether bond cleavage < side-chain saturation < methoxy group demethylation, removal of aromatic substituents.

Among the identified products, coniferyl alcohol and its degradation compounds were confirmed as key products derived from β -ether bond cleavage, the most abundant linkage in lignin. Notably, coniferyl aldehyde was predominantly formed in the early stages, suggesting a polymer effect that promotes *in situ* C_γ oxidation. A plausible reaction mechanism has been proposed to explain this behavior.

Importantly, in intact wood, secondary pyrolysis reactions such as side-chain saturation, methoxy demethylation, and removal of aromatic substituents occurred at significantly lower temperatures than in MWL. The addition of glucose or mannose did not influence the thermal degradation profile of MWL, suggesting that the enhanced reactivity observed in native wood arises from the supramolecular architecture of the cell wall.

This study is the first to detail the thermal degradation behavior of both lignin and polysaccharides in wood cell walls using TG-MS. The findings provide new insights into the molecular mechanisms governing wood pyrolysis and underscore the critical role of cell wall structure in determining pyrolytic reactivity.

Abbreviations

TG-MS, Thermogravimetric-mass spectrometric analysis; Py-GCMS, Pyrolysis-gas chromatography-mass spectrometry; MWL, Milled wood lignin; TIC, Total-ion chromatogram; 5-HMF, 5-hydroxymethylfurfural;

CA, Coniferyl alcohol; Cald, Coniferyl aldehyde; IE, Isoeugenol; VG, Vinyl guaiacol; DCA, Dihydro-coniferyl alcohol

CRedit authorship contribution statement

Daijiro Taira: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Takashi Nomura:** Validation, Data curation. **Eiji Minami:** Writing – review & editing, Validation. **Haruo Kawamoto:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2026.107638](https://doi.org/10.1016/j.jaap.2026.107638).

Data availability

The data that has been used is confidential.

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