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## Influence of inorganic matter on wood pyrolysis at gasification temperature

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**Abstract** The influence of inorganic matter on the pyrolysis of Japanese cedar (*Cryptomeria japonica*) wood was studied at a gasification temperature of 800°C with demineralization through acid washing. Some influences on the formation of char, tar, and low molecular weight products coincided with results reported at temperatures lower than the gasification temperature. However, the carbonization behavior of the volatile products and the yield of polysaccharide fraction were not able to be explained as a sum of the pyrolysis of cellulose, hemicellulose, and lignin even after demineralization. These results suggest some interactions between wood constituent polymers other than the influence of inorganic matter.

**Key words** Pyrolysis · Gasification · Inorganic · Wood · Interaction between wood constituents

### Introduction

Wood gasification is considered as a two-stage process, which includes primary pyrolysis to form primary tar and char, followed by their reactions with gasifying agents such as oxygen and/or steam.<sup>1</sup> Therefore, the primary pyrolysis, which acts as a source of the reactants to the second step, is important to understand the overall gasification process on a molecular basis, thereby providing the opportunity to develop a more effective process.

Wood is a composite material consisting of cellulose, hemicellulose, and lignin as major cell wall constituent polymers with relatively small amounts of inorganic matter and low molecular weight (MW) organic compounds (extractives). Thus, the primary pyrolysis should be understood in

terms related to the behaviors of these cell wall constituents. We previously reported the pyrolysis behaviors of cellulose, hemicellulose (glucomannan and xylan), and milled wood lignin (MWL) at a gasification temperature of 800°C and also reported that wood pyrolysis cannot be explained as the sum of these behaviors, probably due to some interactions between wood constituents.<sup>2</sup>

Although cellulose, hemicellulose, and lignin are believed to be pyrolyzed independently in wood,<sup>3–5</sup> inorganic matter is reported to modify wood pyrolysis substantially according to studies with metal-impregnated<sup>6–16</sup> or demineralized samples<sup>4,7,10,14–21</sup> at temperatures lower than those used for gasification. Generally, enhanced formation of char<sup>10,11,14,15,18,20</sup> and gaseous products<sup>10,16,20</sup> and inhibited formation of the volatile products<sup>11,14,20</sup> are reported as the influence of inorganic matter. As for the volatile products, inorganic matter tends to increase the yields of glycolaldehyde and hydroxyacetone<sup>11,12,14,20</sup> and decrease the yields of anhydrosugars<sup>6–8,11,13,14,17–21</sup> and some low MW products derived from lignin.<sup>9,17</sup> However, the influence of inorganic matter at gasification temperature has not been well studied to date.

This article discusses the influence of inorganic matter on wood pyrolysis investigated at gasification temperature using demineralized wood with some results suggesting interaction between wood constituent polymers.

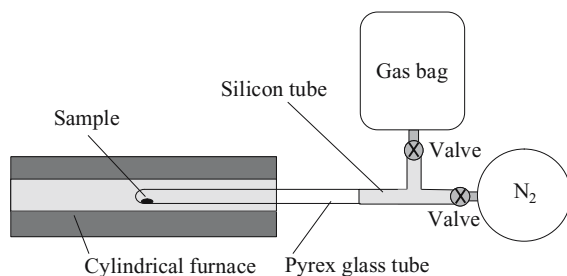
### Experimental

#### Materials

Japanese cedar (*Cryptomeria japonica*) wood flour (<80 mesh) extracted with ethanol/benzene (2:1, v/v) and a demineralized wood sample were used. The demineralized sample was prepared by washing with 0.05 M HCl/methanol at room temperature for 24 h twice and subsequently with methanol (MeOH) repeatedly until the electronic conductivity of the washing became constant. Table 1 summarizes the ash contents evaluated by incineration in air at 600°C for 2 h and the contents of major inorganic elements deter-

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mined by inductively coupled plasma (ICP) emission spectrophotometry (Ca, Mg, and Fe) and atomic absorption spectrometry (K and Na). By acid washing, the ash content [0.41% (w/w)] was reduced to an undetectable level, and the total amount of the five major elements in Table 1 was reduced from 2304 to 150 ppm.

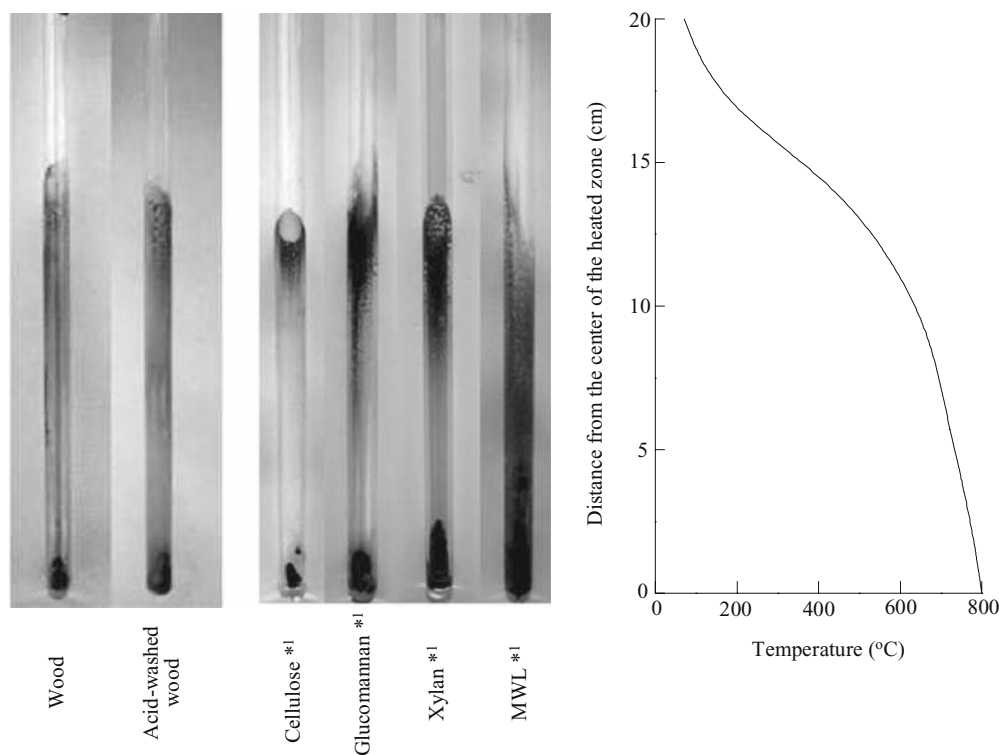


**Fig. 1.** Experimental setup

## Pyrolysis

Pyrolysis was conducted with the experimental setup shown in Fig. 1.<sup>2</sup> Sample (50 mg) was placed at the bottom of a tube reactor made of Pyrex glass (internal diameter: 10 mm, length: 300 mm) attached to a nitrogen bag through a silicon tube. After replacing the air in the reactor with nitrogen, pyrolysis was conducted by inserting the reactor into a cylindrical furnace preheated at 800°C (center of the furnace) for 30 s. The bottom of the tube reactor was placed at the center of the heated zone of the cylindrical furnace. The temperature profile in the reactor under equilibrium conditions is shown in Fig. 2 with the photographs of the reactor after pyrolysis and tar extraction. After pyrolysis, the reactor was immediately cooled with air flow for 1 min, and the reaction mixture was extracted with 1.0 ml of isopropanol (*i*-PrOH) twice and successively with 1.0 ml of water twice to give *i*-PrOH-soluble and water-soluble tar fractions. The residue that remained is defined as a char fraction in this

**Fig. 2.** Pyrolysis reactors after pyrolysis ( $N_2/800^\circ C/30s$ ) and tar extraction and temperature profile of the reactor. Pyrolysis reactors for cellulose, glucomannan, xylan, and milled wood lignin (MWL) are from Hosoya et al.<sup>2</sup>



**Table 1.** Ash content and composition of major inorganic elements in raw and acid-washed wood samples

Sample	Ash content <sup>a</sup> (% w/w)	Content of inorganic element <sup>b</sup> (ppm)				
		K	Na	Ca	Mg	Fe
Wood	0.41	1100	100	780	280	44
Acid-washed wood	ND	15	42	64	3.8	25

ND, not detected

<sup>a</sup>Determined by incineration in air at 600°C for 2 h

<sup>b</sup>Ca, Mg, and Fe determined by inductively coupled plasma emission spectrophotometry; K and Na determined by atomic absorption spectrometry

article. The amounts of the gaseous, tar, and char fractions were determined from the weight difference of the reactor after pyrolysis or extraction. A second set of samples was pyrolyzed under the same conditions to obtain *N,N*-dimethylformamide (DMF) extracts for oxime-trimethylsilyl (TMS) analysis of the major low MW products from wood polysaccharides by extracting the products with 1.0 ml of DMF twice.

## Product analysis

### *i*-PrOH-soluble fraction

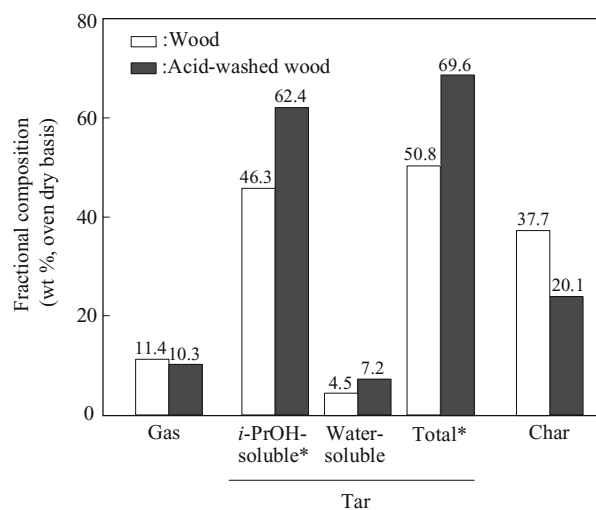
Gas chromatography-mass spectrometric (GC-MS) analysis was carried out using a Hitachi G-7000 gas chromatograph and Hitachi M9000 three-dimensional quadrupole mass spectrometer. A Shimadzu CBP-5 (length: 25 m, diameter: 0.25 mm) was used as a capillary column. The temperature program was 1.0 min at 30°C, 2.0°C/min to 250°C and 10 min at 250°C. Helium was used as a carrier gas at a flow rate of 1.5 ml/min. Injector and detector temperatures were both 250°C. *myo*-Inositol hexaacetate was used as an internal standard. The mass fragmentation patterns of the products characterized by GC-MS analysis are shown in our previous report.<sup>2</sup>

GC analysis with flame ionization detection (FID) of the DMF extracts after oximation-TMS derivatization was conducted to quantify the major low MW products from wood polysaccharides (oxime-TMS analysis). The oximation and trimethylsilylation conditions are described elsewhere.<sup>22</sup> GC-FID analysis was carried out using a Shimadzu GC-18B. A Shimadzu CBP-5 (length: 25 m, diameter: 0.25 mm) was used as a capillary column. The temperature program was 1.0 min at 80°C, 4.0°C/min to 250°C and 10 min at 250°C. Helium was used as a carrier gas at a flow rate of 1.5 ml/min. Injector and detector temperatures were both 250°C. Biphenyl was used as an internal standard.

High performance liquid chromatography (HPLC) was conducted with a Shimadzu LC-10A equipped with a SPD-10Avp detector (280 nm) and STR-ODS II (Shinwa) column. The following linear gradient solvent system was used at a flow rate of 0.7 ml/min: MeOH/H<sub>2</sub>O [30/70 (v/v)] to 100/0 (v/v) for 40 min and 100/0 for 10 min. 1,4-Dibromobenzene was used as an internal standard.

### Water-soluble fraction

Water-soluble fraction was characterized with gel permeation chromatography (GPC) using a Shimadzu LC-10A equipped with a SPD-10Avp detector (220 nm) and Shodex KF 801 + KF 802 + KF 802.5 + KF 803L columns after acetylation with acetic anhydride and pyridine at room temperature for 12 h. Tetrahydrofuran was used as an eluent at a flow rate of 0.6 ml/min. Hydrolysable sugar content was determined with the alditol-acetate method after hydrolysis with aqueous 2 N trifluoroacetic acid solution at 100°C for 1 h.



**Fig. 3.** Influence of acid washing on product composition of wood pyrolysis. Asterisks indicate fractions with product water

## Results and discussion

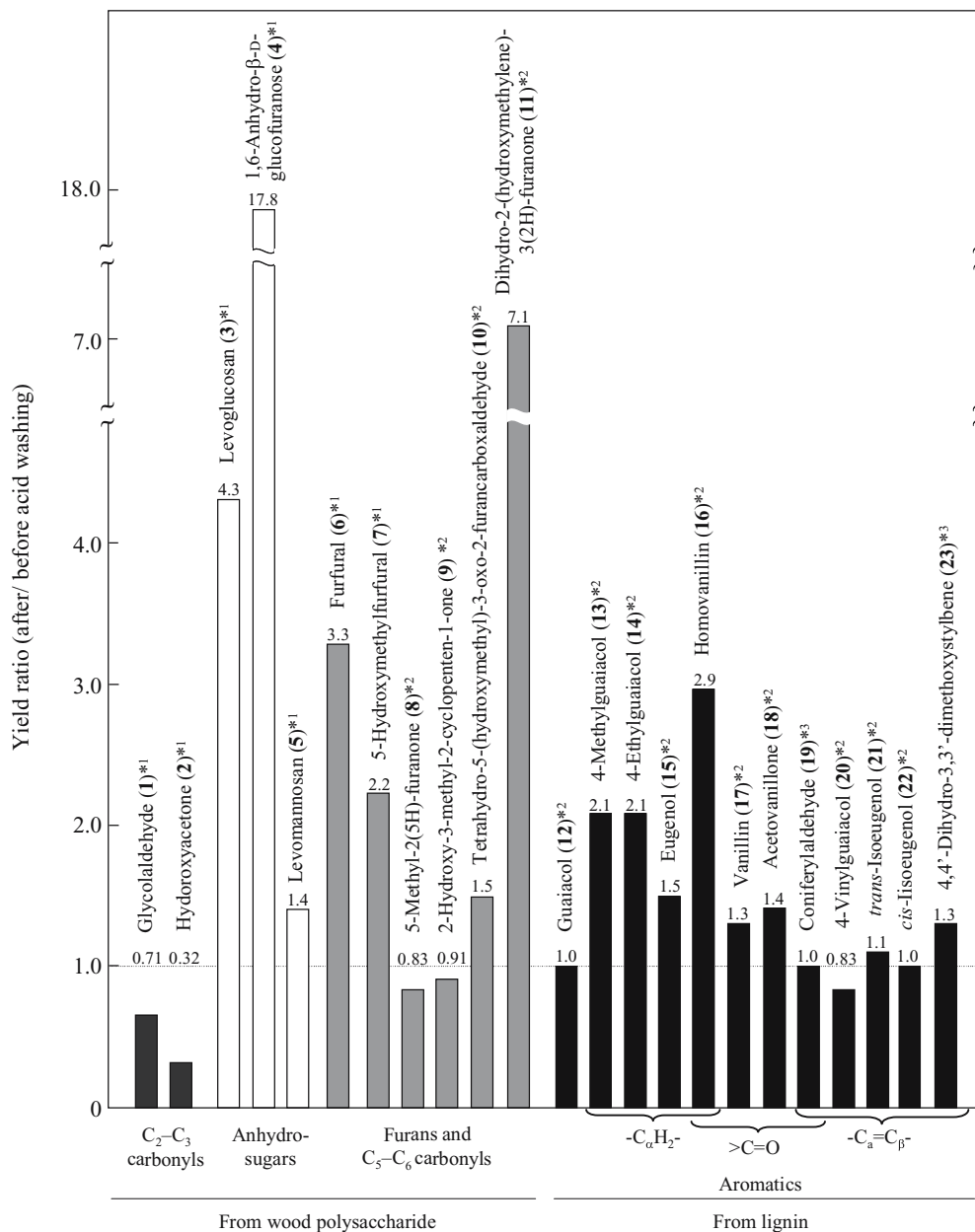
### Forming behaviors of gas, tar, and char

Figure 3 shows the fractional compositions of the products after pyrolysis of wood and acid-washed wood samples in N<sub>2</sub> at 800°C for 30 s. Acid washing substantially decreased the char yield [from 37.7% to 20.1% (w/w)] and increased the tar yield [from 50.8% to 69.6% (w/w)]. These results are in good agreement with the literature,<sup>14,15,18,20</sup> which describes the influence of acid washing of wood at lower pyrolysis temperature of 300–500°C. It is also reported that some inorganic matter impregnated in wood,<sup>15,16</sup> cellulose,<sup>11,14</sup> and other samples<sup>10,21</sup> increases the char yield and decreases the tar yield. Thus, the present results would be derived from the removal of the inorganic matter in wood through acid washing.

In the photographs of the reactors after tar extraction (Fig. 2), two types of carbonized products are observed; one is at the bottom of the reactor where the sample was placed, and the other is at the upper side of the reactor after volatilization and subsequent condensation of the volatile products. These carbonized products are defined in this article as “primary char” and “secondary char,” respectively. Acid washing showed little influence on the secondary char-forming behavior of wood, and, hence, the decreased char yield in Fig. 3 may be attributed to the inhibited formation of the primary char.

We previously reported that the secondary char-forming behaviors, which are different between wood polysaccharides and lignin, become ambiguous in wood pyrolysis.<sup>2</sup> As shown in Fig. 2, secondary char formation in wood polysaccharide pyrolysis was observed at the upper side of the reactor with lower temperature after volatilization and condensation of the primary products. On the other hand, volatiles from lignin were carbonized in the vapor phase to form secondary char from the bottom to the upper side of the reactor continuously. Even in the acid-washed wood,

**Fig. 4.** Influence of acid washing on yields of major pyrolysis products. *Asterisk 1*, analysis by gas chromatography with flame ionization detection (oxime-trimethylsilylation method); *asterisk 2*, analysis by gas chromatography-mass spectrometry; *asterisk 3*, analysis by high performance liquid chromatography



these characteristic secondary char-forming behaviors remained ambiguous. These results suggest that some factors other than the influence of inorganic matter modify the secondary char formation from wood polysaccharide and lignin in demineralized wood.

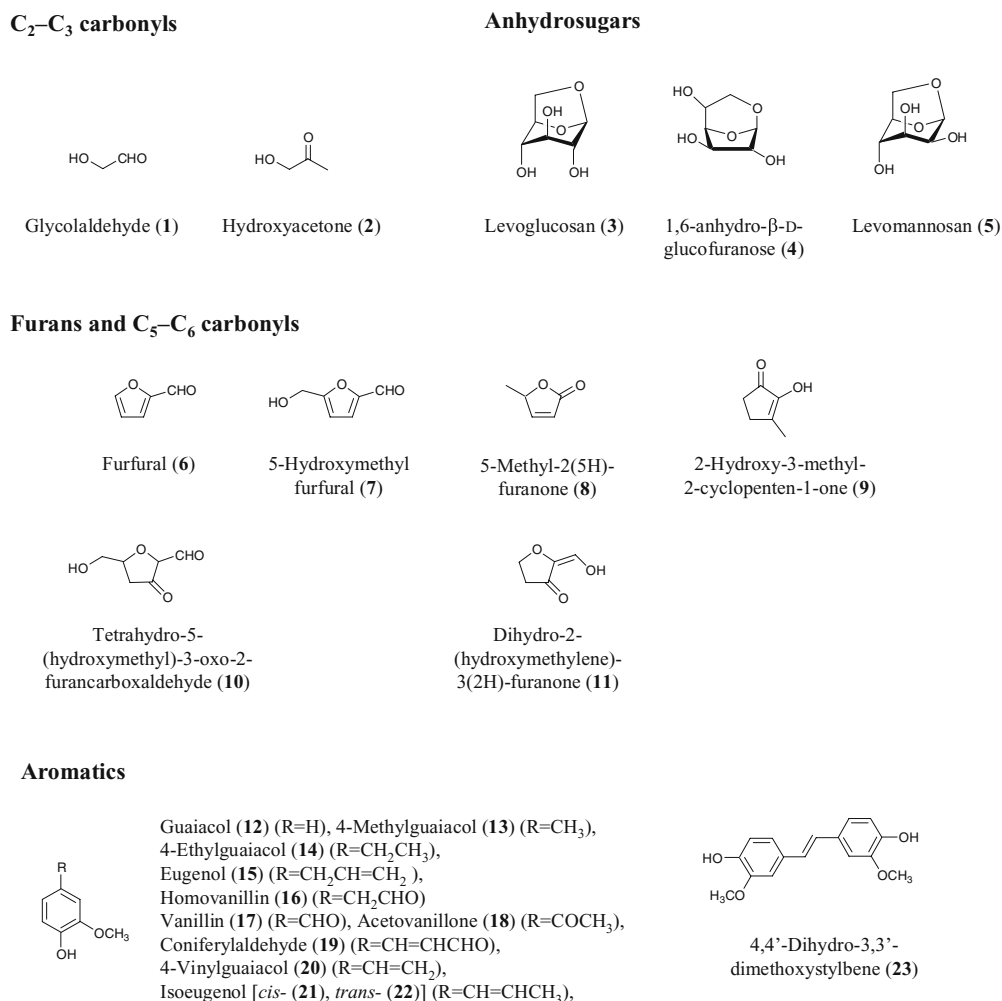
#### Low molecular weight products in *i*-PrOH-soluble fraction

Figure 4 summarizes the influence of acid washing (demineralization) on the yields of some major low MW products (for structures, see Fig. 5) by introducing “yield ratio” (after/before acid washing). Yield ratio (after/before acid washing) was obtained by dividing the yield from the acid-washed wood by that from the original raw wood. A value larger than 1.0 means the enhanced formation through acid

washing and indicates inhibited formation by inorganic matter.

#### Products from wood polysaccharides

Acid washing tended to increase the anhydrosugar yields by 1.4–17.8 times with decreasing yields of  $C_2$ – $C_3$  carbonyls. These results coincide well with the reported influence studied with acid-washed wood at temperatures lower than that used for gasification.<sup>14,18,20</sup> The opposite tendency is also reported for the impregnation of inorganic matter with wood and cellulose.<sup>6,11,13,14</sup> Consequently, inorganic matter in a wood sample, which is effectively removed through acid washing, is considered as a factor affecting the yields of anhydrosugars and  $C_2$ – $C_3$  carbonyls in this study. From the

**Fig. 5.** Chemical structures of major pyrolysis products

study with metal-impregnated samples,<sup>7,14,17</sup> some alkali and alkaline earth metals are reported as especially important in affecting these yields, although the mechanism is still unknown. Furthermore, some researchers<sup>12,20</sup> explain the trade-off relationship of these yields by introducing two competitive pathways to anhydrosugar and C<sub>2</sub>–C<sub>3</sub> carbonyls, respectively, which are differently affected by inorganic matter.

The influence on the anhydrosugar yield was found to be quite different depending on the structure [yield ratios (after/before acid washing): 1,6-anhydro- $\beta$ -D-glucofuranose (4) (17.8) > levoglucosan (3) (4.3) > levomannosan (5) (1.4)]. Although both levoglucosan (3) and its furanose isomer (4) are formed from the glucose moiety in wood polysaccharide, the present results indicate much stronger influence on the anhydrofuranose (4) formation than levoglucosan (3). Although details of the mechanism are presently unknown, these results are interesting in terms of their formation mechanisms.

Acid washing increased the yields of furans and other C<sub>5</sub>–C<sub>6</sub> carbonyls with some exceptions including 5-methyl-2(5H)-furanone (8) and 2-hydroxy-3-methyl-2-cyclopenten-1-one (9). Although tetrahydro-5-(hydroxymethyl)-3-oxo-2-furancarboxaldehyde (10) and dihydro-2-

(hydroxymethylene)-3(2H)-furanone (11) are expected to be formed in similar pathways from cellulose and xylan, respectively, they showed quite different yield ratios (after/before acid washing) of 1.5 (compound 10) and 7.1 (compound 11). Inorganic matter in wood is reported to exist in close association with the 4-*O*-methylglucuronic acid moiety of xylan<sup>23</sup> in hemicellulose in the heterogeneous cell wall construction, which consists of cellulose fibrils surrounded by the hemicellulose–lignin matrix.<sup>24</sup> Therefore, these different influences may be attributed to this heterogeneous distribution of inorganic matter in wood.

#### Products from lignin

As for lignin-derived products, most of the low MW products increased in their yields by acid washing (Fig. 4). In particular, yields of C <sub>$\alpha$</sub> -methylene (benzyl methylene) or C <sub>$\alpha$</sub> -carbonyl types increased substantially [yield ratio (after/before acid washing): 1.3–2.9]. Some of these results coincide with the report on pyrolysis at lower temperature (620°C) by Kleen and Gellerstedt,<sup>17</sup> who described the enhanced formation of 4-methylguaiacol (13), eugenol (15), homovanillin (16), vanillin (17), and acetovanillone (18)

**Table 2.** Hydrolysable sugar contents of water-soluble fractions and anhydrosugar yields from various samples

Sample	Water-soluble fraction		Yield of anhydrosugars <sup>a</sup> (% w/w)			
	Yield (% w/w)	Hydrolysable sugar content (% w/w)	Levoglucosan	AF	Levomannosan	Total
Acid-washed wood	7.2 (11.9) <sup>b</sup>	6.7	5.0 (3.7)	0.17 (0.23)	1.2 (0.22)	6.4 (4.2)
Wood	4.5	4.1	1.2	Trace	0.61	1.8
Cellulose <sup>c</sup>	21.6	25.8	7.6	0.47	–	8.1
Glucomannan <sup>c</sup>	9.0	25.0	0.43	0.03	1.9	2.4
Xylan <sup>c</sup>	5.2	20.6	ND	ND	ND	–

AF, 1,6-Anhydro- $\beta$ -D-glucofuranose

<sup>a</sup>Determined in the isopropanol-soluble fraction

<sup>b</sup>Numbers in parentheses estimated from the composition of Japanese cedar (cellulose 48.6%, glucomannan 11.5%, xylan 7.6%, lignin 32.3%)<sup>25</sup>

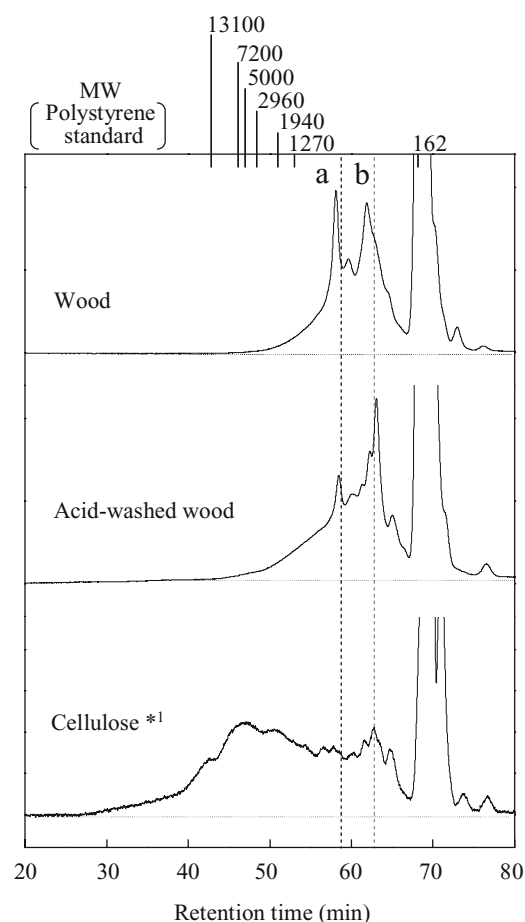
<sup>c</sup>Results from Hosoya et al.<sup>2</sup> for the same pyrolysis conditions

from thermochemical pulp through acid washing. Ripley and Fung<sup>9</sup> reported that the addition of alkali metal salt inhibited the formation of 4-methylguaiacol (**13**) and eugenol (**15**) in spruce MWL pyrolysis at 425°C. Although further study is necessary to identify the mechanism, inorganic matter may activate the benzyl methylene and conjugated C=O structures for further degradation.

#### Water-soluble fraction

Water-soluble fractions from wood polysaccharides were polysaccharide-based products as indicated by the results of GPC analysis and their hydrolysable sugar contents [20.6%–25.8% (w/w)].<sup>2</sup> Polysaccharide would be formed through ring-opening polymerization of anhydrosugars, the primary products from wood polysaccharides, after condensation at the reactor wall with temperature lower than their boiling points.<sup>2</sup> Table 2 summarizes the yields and hydrolysable sugar contents of the water-soluble fractions compared with the anhydrosugar yields. The yields expected for the individual pyrolysis of cellulose, hemicellulose, and lignin and their mixture (cellulose 48.6%, glucomannan 11.5%, xylan 7.6%, lignin 32.3%) reported for Japanese cedar wood<sup>25</sup> are also included in parentheses.

The yield of water-soluble fraction increased from 4.5% to 7.2% (w/w) through acid washing. However, this yield is still lower than the expected yield (11.9%). Furthermore, the hydrolysable sugar content (6.7%) is substantially lower than those (20.6%–25.8%) of the water-soluble fractions obtained from the wood polysaccharide samples. From the GPC chromatograms of the water-soluble fractions after acetylation (Fig. 6), the MW of the water-soluble fraction from acid-washed wood is considerably lower than those from the wood polysaccharide samples such as cellulose. These results indicate that the nature of the water-soluble fraction from acid-washed wood is also substantially different from those expected from the pyrolysis of wood polysaccharide samples. Contrary to this, anhydrosugar yield dramatically increased through acid washing from 1.8% to 6.4%, which is rather larger than the expected yield of 4.2%. This series of evidence suggests that the reactivity of anhydrosugar for ring-opening polymerization is substantially reduced in pyrolysis of raw and acid-washed wood samples.



**Fig. 6.** Gel permeation chromatograms of water-soluble fractions obtained from raw and acid-washed wood samples and cellulose after acetylation. *a*, Retention time of glucose pentaacetate; *b*, retention time of levoglucosan triacetate. Detection at 220 nm. Results for cellulose from Hosoya et al.<sup>2</sup>

#### Conclusions

Influences of inorganic matter on the formation of gas, tar, char, and some major low MW products from wood pyrolysis were identified at the gasification temperature of 800°C. Inorganic matter reduces the tar yield with enhanced char formation, while most of the low MW products are reduced



in yield in the presence of inorganic matter except for C<sub>2</sub>–C<sub>3</sub> carbonyls.

Some results including the formation of secondary char and the water-soluble fraction (yield, hydrolysable sugar content, and MW) were not able to be explained in terms of the combined pyrolysis of cellulose, hemicellulose, and lignin even after demineralization. These results suggest some interactions between wood constituent polymers, although physical and chemical alterations of the wood sample may be significant.

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