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ORIGINAL ARTICLE

# Reaction behavior of milled wood lignin in an ionic liquid, 1-ethyl-3-methylimidazolium chloride

**Shintaro Ogawa · Hisashi Miyafuji**

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**Abstract** We investigated the reaction behavior of milled wood lignin (MWL) obtained from Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]). This solvent can liquefy wood. The sample was treated with [C2mim][Cl] at 120 °C using an oil bath or microwave irradiation. MWL easily dissolved in [C2mim][Cl]. Although solubilized, MWL was slightly depolymerized and it retained its high molecular weight after 96 h of treatment. Only small amounts of low molecular weight compounds such as vanillin, coniferylaldehyde, syringaldehyde and sinapylaldehyde were produced. As the treatment time was extended the chlorine from [C2mim][Cl] reacted with the MWL. These results indicate that MWL is stable in [C2mim][Cl] although limited depolymerization and modification by [C2mim][Cl] occurred.

**Keywords** Milled wood lignin · Ionic liquid · 1-ethyl-3-methylimidazolium chloride · Reaction behavior · Heating method

## Introduction

To reduce greenhouse gas emissions and the dependence on fossil fuel resources, the use of biomass as an alternative feedstock to fossil fuel resources is of interest because it is carbon neutral. Currently, food resources such as sugar cane and corn are used for the production of bioethanol. However, the use of food resources may cause an increase in food prices.

Lignocellulosics such as wood do not compete with food resources and they are abundant. They are a promising source of biomass. Wood is mainly composed of cellulose, hemicellulose and lignin and it has a strong and complicated molecular structure because cellulose is covered with hemicellulose and lignin [1]. To use the components of wood effectively as an energy resource and as chemicals, chemical processing such as acid hydrolysis [2], pyrolysis [3], enzymatic saccharification [4], and treatment with supercritical fluids [5] has been investigated.

Recently, ionic liquids have been shown to be an attractive new medium for the chemical processing of wood. Ionic liquids are organic salts with melting points around ambient temperature. They are regarded as green solvents because they have many notable characteristics such as non-volatility, flame retardance and low viscosity. It was found that the treatment of wood flour from Japanese beech (*Fagus crenata*) with an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), resulted in the liquefaction of the wood components with the production of low molecular weight compounds [6]. Differences exist in the reaction behavior of Western red cedar compared with Japanese beech [7], and the reaction is promoted by oxygen and water in the reaction system [8]. Ionic liquids have also been used to extract the components of wood. After wood samples were dissolved in 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) [9] and 1-H-3-methylimidazolium chloride ([Hmim][Cl]) [10], cellulose rich materials and carbohydrate-free lignin were obtained when using proper reconstitution solvents.

Several studies on the separation of various macromolecular lignins from lignocellulosics by chemical treatment

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S. Ogawa · H. Miyafuji (✉)
Division of Environmental Sciences, Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Hangi-cho, Shimogamo, Sakyo-ku, Kyoto 606-8522, Japan
e-mail: miyafuji@kpu.ac.jp

have been carried out. Stärk et al. [11] revealed that organosolv lignin degraded oxidatively with the production of some low molecular weight compounds in an ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, when using $Mn(NO_3)_2$ as the catalyst. Cox et al. [12] reported that the lignin extracted from oak wood with [C2mim][OAc] depolymerized in [Hmim][Cl] although the molecular weight of the lignin fragments after depolymerization was roughly the same regardless of the reaction temperature. Wen et al. [13] revealed that the number of aliphatic hydroxyl groups decreased and the number of phenolic hydroxyl groups increased in an alkaline lignin that was isolated from poplar after treatment with [C2mim][OAc]. According to Pu et al. [14] the solubility of the lignin isolated from pine kraft pulp increases as follows: $MeSO_4^- > Cl^-, Br^- \gg PF_6^-$ for 1-*n*-butyl-3-methylimidazolium-based ionic liquids.

Studies into the reaction of lignin model compounds in ionic liquids have also been carried out. By treating eugenol or 4-ethylguaiacol with various imidazolium-based ionic liquids, the side chain reactions of lignin have been studied [15]. According to Kubo et al. [16], Guaiacylglycerol-β-guaiacyl ether (GG), which is commonly used as a model compound for the β-O-4 ether linkage of lignin produced an enol ether, 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-2-propenol, upon treatment in dialkylimidazolium chloride and acetate ionic liquids . Jia et al. [17] studied the decomposition products of GG and veratrylglycerol-β-guaiacyl ether treated in the acidic ionic liquid, [Hmim][Cl].

However, these studies into lignin model compounds or chemically modified lignins such as organosolv lignin and alkaline lignin did not reveal information about the reactions of native lignin in wood. In this study, we used milled wood lignin (MWL), which is deemed to be the least modifiable chemical structure of lignin, and studied the reaction behavior of MWL and the reaction products obtained from MWL in [C2mim][Cl]. Moreover, we investigated differences in the reaction behavior of MWL reaction systems heated by an oil bath and by microwave irradiation.

## Materials and methods

### Samples and chemicals

Wood flour was ground using a Wiley mill (WM-3, Irie Shokai Co., Ltd, Tokyo, Japan) to between 180 and 90 μm from the sapwood of Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*). These were used as wood raw materials. Wood flour was extracted by Soxhlet extraction using ethanol/benzene (1:2, v/v) for 24 h, and it was then dried at 105 °C for 24 h. MWL was prepared from these extractive-free woods according to the method of Björkman [18]. However, the wood flour was ground in a planetary ball mill for 48 h without any additives.

The ionic liquid, [C2mim][Cl], was purchased from Tokyo Chemical Industry. Co., Ltd, Tokyo, Japan. Its chemical structure is shown in Fig. 1. Dehydrated dimethyl sulfoxide (DMSO), methanol and potassium bromide were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Lithium chloride was purchased from Nacalai Tesque, Inc., Kyoto, Japan.

### Treatment with [C2mim][Cl]

3 g of [C2mim][Cl] was heated at 120 °C in a 100-mL glass flask in an oil bath or by microwave irradiation in a microwave generator (green-motif-ic, J-SCIENCE LAB Co., Ltd, Kyoto, Japan). After the [C2mim][Cl] melted, 0.09 g MWL was added to the flask. 0 h of treatment was defined as the point where all the MWL particles were dissolved in the flask. It took 15 min for the reaction media to become transparent.

### Evaluation methods

At a specific treatment time, 100 μL of the reaction media was sampled and diluted with 100 μL DMSO containing 0.1 M lithium chloride. The mixture was filtered through a 0.45-μm filter. On the filtrate, gel permeation chromatography (GPC) analysis was carried out by a GPC system (Shimadzu, Ltd., Kyoto, Japan) equipped with pump (LC-10AT), column oven (CTO-10A), and ultraviolet–visible detector (SPD-10A) set at 280 nm to determine the molecular weight distribution of the solubilized MWL in [C2mim][Cl]. Analysis conditions were a Shodex SB-803 HQ column, a flow rate of 0.3 mL/min, DMSO containing 0.1 M lithium chloride as eluent after passing through the degasser (DGU-14A, Shimadzu, Ltd., Kyoto, Japan), and a column temperature of 60 °C. Pullulan (Shodex standard P-82) was used as the standard for the molecular weight distribution.

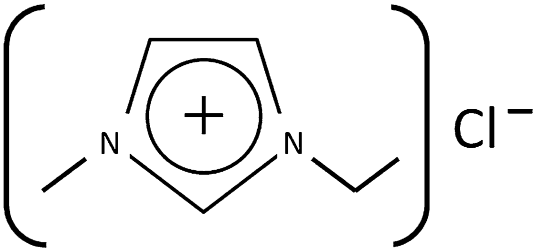

**Fig. 1** 1-Ethyl-3-methylimidazolium chloride ([C2mim][Cl])

To determine the viscosity of the reaction media, the MWL was dissolved in [C2mim][Cl] at various concentrations. $\eta_0$ and $\eta$ represent the viscosity of [C2mim][Cl] and that of the reaction media and was measured at 120 °C using a viscometer (SV-1A, A & D Company, Ltd., Kyoto, Japan). $\eta_{sp}$, the specific viscosity, was calculated using Eq. (1) for the reaction media at various MWL concentrations. From the relationship between concentration and $\eta_{sp}/c$ (c: concentration of MWL), it is possible to speculate about the state of the MWL molecules in the reaction media.

$$\eta_{sp} = \left(\frac{\eta}{\eta_0}\right) - 1. \tag{1}$$

To identify the low molecular weight compounds obtained from the MWL in [C2mim][Cl], high performance liquid chromatography (HPLC) analysis was carried out by a HPLC system (Shimadzu, Ltd., Kyoto, Japan) equipped with pump (LC-10AD), column oven (CTO-10A), and ultraviolet–visible detector (SPD-10A) set at 280 nm. The samples for this analysis were prepared as follows: at a specified treatment time, 20 µL of the reaction solution was obtained and diluted to 180 µL with ultrapure water. This mixture was filtered through a 0.45-µm filter and the filtrate was used for analysis. Analysis conditions were a Cadenza CD-C18 column, a flow rate of 1.0 mL/min, a methanol/ultrapure water eluent (20/80–100/0, 0–60 min followed by 100/0, 60–70 min) after passing through the degasser (DGU-14A, Shimadzu, Ltd., Kyoto, Japan), and a column temperature of 40 °C.

To study the solubilized polymeric compounds in [C2mim][Cl], 100 mL distilled water was poured into the flask at a specific reaction time to quench the reaction, and to precipitate the solubilized polymeric compounds. After stirring for 24 h at room temperature, the water-insoluble portions were filtered, washed several times with distilled water, dried in an oven at 105 °C for 24 h and weighed. The yield was calculated using Eq. (2).

$$\text{Yield (\%)} = \text{weight of water-insoluble portion} / \text{weight of initial MWL} \times 100. \tag{2}$$

Fourier transform infrared spectra of the water-insoluble portions were obtained using a Shimadzu 8200PC spectrophotometer by the potassium bromide pellet method. The spectral range was from 4,000 to 400 cm$^{-1}$ with 20 accumulations.

The elemental compositions of the water-insoluble portions were studied using a field emission type scanning electron microscope (S-4800, Hitachi, Tokyo, Japan) coupled with an energy dispersive X-ray (EDX) analyzer (Genesis XM2, EDAX Japan, Tokyo, Japan).

The chlorine content of the water-insoluble portions were determined according to the oxygen flask combustion method as described in the Japan Industrial Standard (JIS) K 7229 [19].

## Results and discussion

### GPC analysis of the solubilized compounds in [C2mim][Cl]

The molecular weight distribution of the solubilized compounds in [C2mim][Cl] was studied by GPC, as shown in Fig. 2. Peaks from [C2mim][Cl] are not visible in this figure because of their long elution time of around 80 min. Therefore, Fig. 2 shows the molecular weight distribution of the MWL solubilized in [C2mim][Cl]. For the Japanese cedar heated by an oil bath (Fig. 2a), two peaks are present around 212,000, and peaks are present between 11,800 and 180 for the MW experiment. The former peak disappeared and the latter peak shifted slightly toward lower molecular weight as the treatment time was increased. In addition, a peak at less than 180 from the MW experiment, which is close to the molecular weight of coniferylaldehyde (MW: 178), appears with an increase in treatment time. However, the most prominent peak is between 180 and 5,900 in the MW experiment even after 96 h of treatment. These results indicate that although the MWL from Japanese cedar is depolymerized, this depolymerization does not result in the

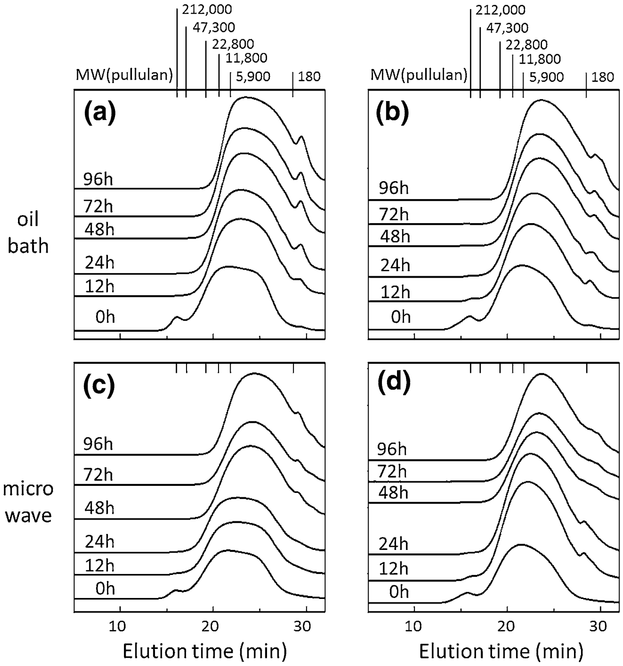

**Fig. 2** Gel permeation chromatograms for the MWL obtained from Japanese cedar (**a**, **c**) and Japanese beech (**b**, **d**) in [C2mim][Cl] at 120 °C over various treatment times. *Top* treated with an oil bath, *Bottom* treated with microwave irradiation

whole MWL being converted to monomer level. A similar trend is apparent for the MWL from Japanese beech that was treated using an oil bath (Fig. 2b). This means that no significant difference exists in the depolymerization behavior of the MWL from Japanese cedar and that from Japanese beech.

Figure 2c, d shows GPC chromatograms for the MWL from Japanese cedar and Japanese beech in [C2mim][Cl] upon microwave irradiation heating. The peak changes shown in Fig. 2c, d are very similar to those in Fig. 2a, b, respectively. These indicate that the heating method has little influence on the depolymerization behavior.

To understand the stabilization of the MWL in [C2mim][Cl], the viscosity of [C2mim][Cl] after MWL dissolution at 120 °C was determined. Figure 3 shows the relationship between the MWL concentration and $\eta_{sp}/c$ for each concentration. $\eta_{sp}/c$ was found to decrease as the concentration increased. Huggins plots of the MWL could not be approximated by linear approximation. This relationship as shown in Fig. 3 is due to a typical polyelectrolyte. It is reported that dispersibility of a polyelectrolyte decreases with increasing the concentration of a polyelectrolyte in a solvent [20]. Therefore, it is considered that MWL exists as a polyelectrolyte in [C2mim][Cl], and MWL molecules have low dispersibility at high concentration region in Fig. 3. That is, the MWL molecules are thought to aggregate in [C2mim][Cl]. Therefore, the reactivity in [C2mim][Cl] was quite low with regard to MWL molecule interaction.

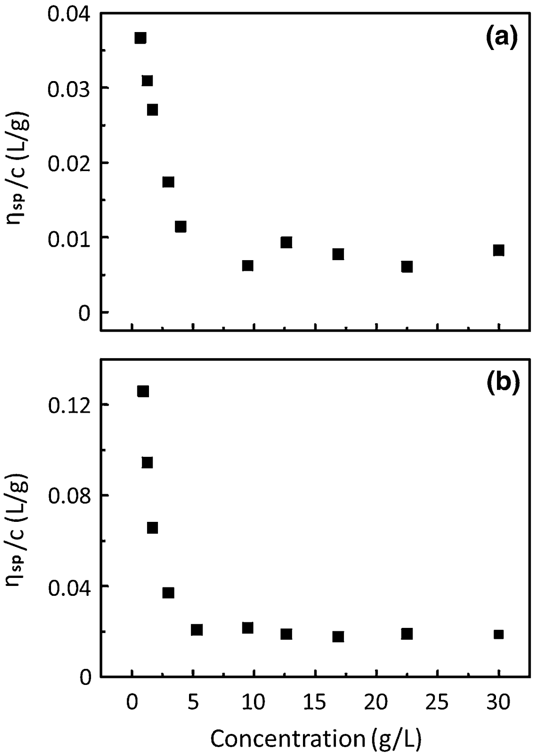

**Fig. 3** Huggins plots for a mixture of [C2mim][Cl] and the MWL obtained from Japanese cedar (**a**) and Japanese beech (**b**) treated at 120 °C. $\eta_{sp}$ and c represent the specific viscosity and the concentration measured at 120 °C, respectively

## HPLC analysis of the solubilized compounds in [C2mim][Cl]

HPLC analyses were performed to study the low molecular weight compounds detected by GPC. Vanillin and coniferylaldehyde were identified in [C2mim][Cl] as decomposition products of the MWL from Japanese cedar. In addition, syringaldehyde and sinapylaldehyde were also present in the MWL of Japanese beech.

For the MWL from Japanese cedar heating in an oil bath (Fig. 4a), the yields of vanillin and coniferylaldehyde were 1.4 and 0.36 % at 72 h of treatment time, respectively. The yields of these compounds decreased to 0.94 and 0.20 %, respectively, at 96 h. For the MWL from Japanese beech heating in an oil bath (Fig. 4b), the maximum yields of coniferylaldehyde and sinapylaldehyde were 0.12 and 0.28 % at treatment times of 48 h and 24 h, respectively. However, the yields of vanillin and syringaldehyde tended to increase as the treatment time increased.

Figure 4c, d shows the yields of these low molecular weight compounds obtained from the MWL of Japanese cedar and Japanese beech, respectively, for the [C2mim][Cl] that was heated by microwave irradiation. In Fig. 4c, the maximum yields of vanillin and coniferylaldehyde were 0.15 % at 72 h and 0.08 % at 12 h,

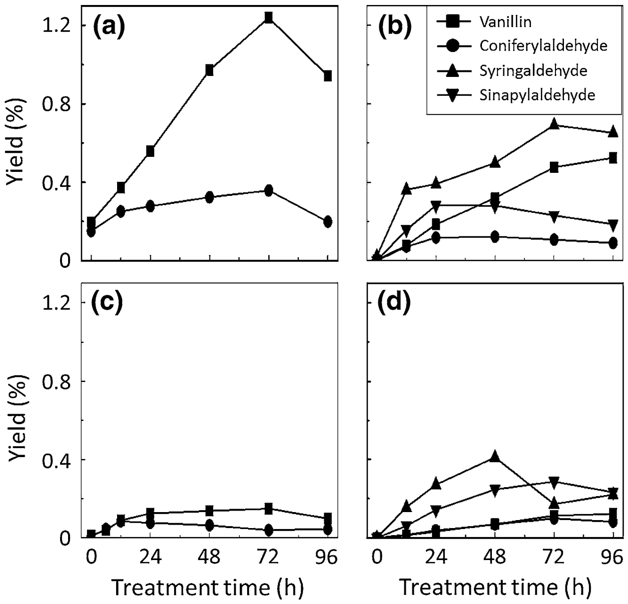

**Fig. 4** Changes in yield for various compounds obtained from the MWL from Japanese cedar (**a**, **c**) and Japanese beech (**b**, **d**) treated in [C2mim][Cl] at 120 °C. *Top* oil bath, *Bottom* microwave

respectively. After reaching the maximum, their yields decreased to 0.10 and 0.05 % at 96 h. In Fig. 4d, however, syringaldehyde was at a maximum (0.41 %) at 48 h. Vanillin and coniferylaldehyde tended to increase as the treatment time increased although the yield of coniferylaldehyde and sinapylaldehyde decreased slightly at 96 h. The yields of vanillin, coniferylaldehyde and sinapylaldehyde were 0.12, 0.08 and 0.23 %, respectively, even after 96 h of treatment.

Compared with the results of oil bath heating, the yields of these low molecular compounds were low upon microwave irradiation heating. The reasons for this difference in yields are not currently clear. In both heating methods, however, the yields of the low molecular compounds are less than a few percent during the treatment. These results indicate that the depolymerization of MWL is limited and MWL is relatively stable in [C2mim][Cl]. These results are similar to the GPC analyses results shown in Fig. 2.

### Water-insoluble portions from [C2mim][Cl]

Figure 5 shows changes in the yields of the water-insoluble portions obtained during treatment in [C2mim][Cl] upon oil bath heating and microwave irradiation heating. For the MWL from Japanese cedar, as shown in Fig. 5a, the yield of the water-insoluble portion obtained by oil bath heating was 83.1 wt % at 0 h, and this decreased gradually to 67.5 % at 96 h with an increase in the treatment time. The yields obtained with microwave irradiation were 67.2 % at 0 h and 61.4 % at 96 h. For the MWL from Japanese beech, as shown in Fig. 5b, the yield of the water-insoluble portion obtained by heating in an oil bath decreased from 75.8 to 58.9 wt %, and that obtained with microwave irradiation decreased from 65.9 to 50.6 wt %, respectively, upon 96 h of treatment.

The reason for the yields not being 100 % at 0 h may be that a part of the MWL dissolved in a mixture of [C2mim][Cl] and water without precipitating after the addition of water to the [C2mim][Cl] solution containing the MWL. When the MWL from Japanese cedar was treated in [C2mim][Cl]–water (1:9,v/v) at room temperature for 24 h, the yield of the recovered MWL was about 80 % (data not shown). However, no other prominent peaks except for the compounds shown in Fig. 4 are present in the HPLC chromatograms. Therefore, the unrecovered compounds that did not precipitate may be lignin oligomers. To reveal this inference, we are planning to conduct additional studies.

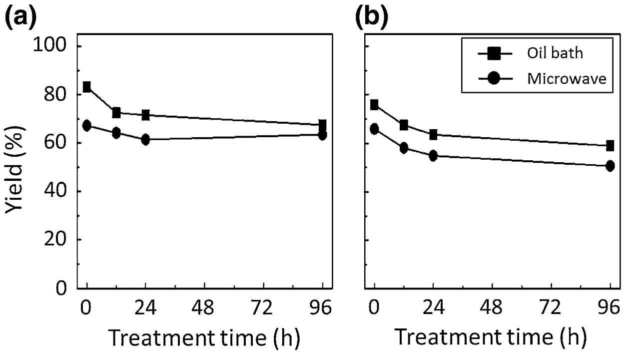

**Fig. 5** Changes in the water-insoluble portion yield for the MWL of Japanese cedar (**a**) and Japanese beech (**b**) treated with an oil bath and by microwave in [C2mim][Cl] at 120 °C

### Characterization of the water-insoluble portions

To characterize the water-insoluble portions, we carried out a Fourier transform infrared spectroscopic analysis as illustrated in Fig. 6. For the MWL from Japanese cedar shown in Fig. 6a, a peak is present at 1,705 cm$^{-1}$ for the water-insoluble portions obtained by heating in an oil bath. This peak was not observed in the MWL. This peak derives from C=O stretching and it increases with an increase in treatment time. The peak at 1,415 cm$^{-1}$ is due to C–H in-plane deformation with aromatic ring stretching. This peak decreased slightly as the treatment time increased. These changes were also confirmed for treatment with microwave irradiation, as shown in Fig. 6c. For the MWL from Japanese beech, as shown in Fig. 6b, a similar change was observed for the peak at 1,415 cm$^{-1}$, as shown in Fig. 6a, for the

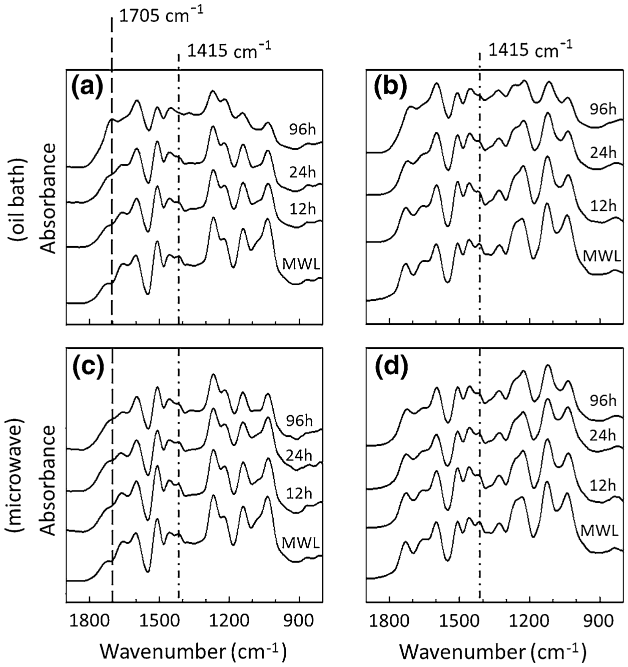

**Fig. 6** Fourier transform infrared spectra of the water-insoluble portions obtained from the MWL of Japanese cedar (**a**, **c**) and Japanese beech (**b**, **d**) treated in [C2mim][Cl] at 120 °C. *Top* oil bath, *Bottom* microwave

water-insoluble portions obtained by oil bath heating. A change occurred for this peak upon microwave irradiation, as shown in Fig. 6d. The peak at 1,730 $\mathrm{cm}^{-1}$ is due to C=O with acetyl group in hemicellulose or uronic acid ester, and it is reported to be remarkably seen in MWL from hardwood [21]. In Fig. 6b, d, this peak slightly decreased by treatment with [C2mim][Cl] but did not disappear. From these results, chemical bond transformations are apparent in the MWL upon [C2mim][Cl] treatment. However, differences in these transformations for the oil bath and microwave irradiation heating methods were not confirmed.

For further characterization, an EDX spectroscopic analysis of the water-insoluble portion was obtained for the MWL of Japanese cedar that was treated in an oil bath for 24 h in [C2mim][Cl]. The obtained spectrum is shown in Fig. 7 and it shows the results for the MWL of Japanese cedar. Chlorine peaks were found in the water-insoluble portion although it was not observed in the MWL. To quantify the amount of chlorine in the water-insoluble portions, the oxygen flask combustion method was used to analyze the MWL water-insoluble portion for the MWL obtained from Japanese cedar and from Japanese beech. The obtained results are shown in Fig. 8. As the treatment time increased, the chlorine content was found to increase in both Japanese cedar and in Japanese beech. At 96 h, the chlorine content of the water-insoluble portion from the MWL of Japanese cedar and Japanese beech was 5.9 and 5.1 %, respectively. This result suggests that chlorine from [C2mim][Cl] was incorporated into the MWL water-insoluble portion.

[C2mim][Cl] can be removed from the water-insoluble portions by washing because it dissolves easily in water. Nitrogen from [C2mim][Cl] was not detected by EDX analyses, as shown in Fig. 7. From the results in Figs. 7 and 8, the chlorine of [C2mim][Cl] was found to be covalently bound to the MWL during [C2mim][Cl] treatment. It is known that hydrogen on the aromatic ring of lignin is substituted easily by a halogen, such as chlorine [22]. Because [C2mim][Cl] has chloride anion, it is assumed that chlorine of [C2mim][Cl] was incorporated into MWL although the imidazolium cation of [C2mim][Cl] was not present in the water-insoluble portions.

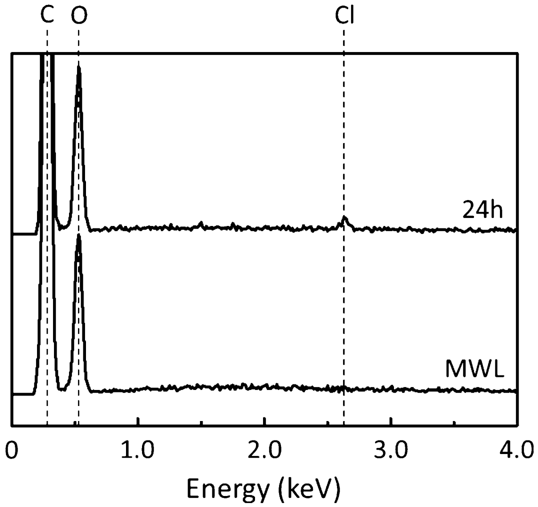

**Fig. 7** Energy dispersive X-ray spectra of the water-insoluble portion obtained from the MWL of Japanese cedar treated for 24 h in an oil bath and in [C2mim][Cl] at 120 °C

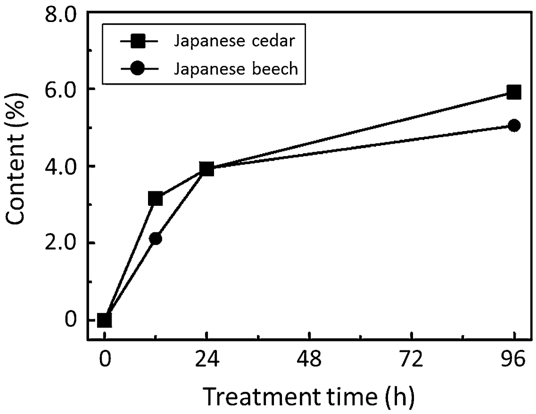

**Fig. 8** Changes in the Cl content of the water-insoluble portions obtained from the MWL of Japanese cedar and Japanese beech treated at 120 °C in an oil bath

### Reaction behavior of the MWL in [C2mim][Cl]

Based on the results obtained in this study, the reaction behavior of MWL from Japanese cedar and Japanese beech in [C2mim][Cl] is discussed below. Initially, both the MWLs dissolved completely in [C2mim][Cl]. The solubilized MWL depolymerized slightly with the production of a few low molecular weight compounds such as vanillin, coniferylaldehyde, syringaldehyde and sinapylaldehyde. The reason for the stability of the MWL in [C2mim][Cl] is the aggregation of MWL molecules without independent dispersion in [C2mim][Cl].

Chemical bond transformations occurred in the MWL and the chlorine of [C2mim][Cl] bound chemically to the MWL during treatment with [C2mim][Cl]. No significant difference in the reaction behavior of the MWLs from Japanese cedar and that from Japanese beech was found. We studied differences in the reaction behavior in both the oil bath and microwave irradiation heating methods; however, no remarkable differences were observed.

## Conclusion

We used MWL as a model lignin because it is regarded as having the least modifiable chemical structure to study the reaction behavior of lignin in [C2mim][Cl]. [C2mim][Cl] is a multifunctional reagent for the MWL. [C2mim][Cl] can dissolve and decompose the MWL although the decomposition is limited. Moreover, it transforms some chemical bonds of the MWL and [C2mim][Cl] reacts with the MWL. This finding is important for the effective use of lignocellulosics in ionic liquid treatments.

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