

Reaction behavior of wood in an ionic liquid, 1-ethylpyridinium bromide

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Abstract The reactions of Japanese cedar and Japanese beech in a pyridinium-based ionic liquid, 1-ethylpyridinium bromide ([EtPy][Br]) were studied. Japanese beech was more easily liquefied than Japanese cedar. Hemicellulose is liquefied rapidly, lignin more slowly, while cellulose is partially liquefied. X-ray diffraction analyses on the [EtPy][Br]-insoluble residues revealed that the crystalline structure of cellulose is maintained even after treatment. The difference in liquefaction can be explained by chemical structural differences between softwood and hardwood lignins and hemicelluloses.

Keywords Wood · Ionic liquid · 1-Ethylpyridinium bromide · Liquefaction · Reaction behavior

Introduction

We have achieved a comfortable life by making advances in science and technology. Since the Industrial Revolution, use of fossil fuel resources such as oil and coal has enhanced our standard of living. However, mass consumption of fossil fuels affects the global environment and causes global warming. Serious energy problems are also associated with the depletion of fossil fuel resources.

Recently, increased attention has been focused on biomass resources as alternatives to fossil resources. Wood is thought to be a promising biomass resource for energy because of its huge stocks and inedible nature, which

means that its use poses no threat to food supply. Various studies have been performed so far with respect to chemical conversion of wood using techniques such as acid hydrolysis [1], enzymatic saccharification [2], hot-compressed water treatment [3], pyrolysis [4, 5], and supercritical fluid treatment [6].

In recent years, much attention has been focused on processing wood using ionic liquids. Ionic liquids are salts that have melting points near ambient temperature. They are regarded as novel green solvents because of their unique characteristics such as negligible vapor pressure, high thermal and chemical stability, nonflammability, and ability to dissolve many substances. In addition, some ionic liquids can be recycled several times when used as solvents [7]. Many studies have been conducted on chemical synthesis using ionic liquids as reaction media [8–10] or catalysts [11–13]. Ionic liquids have also been applied for the extraction of chemical substances [14–16].

Because some ionic liquids are reported to be able to dissolve cellulose [17], much attention has been focused on reactions between ionic liquids and wood (which is made up of cellulose, hemicellulose, and lignin) [18–28]. 1-Ethyl-3-methylimidazolium chloride ([C2mim][Cl]) was found to liquefy all the above-mentioned constituents of wood [29]. The polymers solubilized in [C2mim][Cl] are depolymerized to low-molecular-weight compounds such as glucose, mannose, levoglucosan, and 5-hydroxymethylfurfural. It was also revealed that the atmosphere in the reaction system affects the reaction behavior of wood in ionic liquids [30]. Moreover, differences in reaction behavior between wood species have been reported [31].

Although many studies on the reaction of wood in ionic liquids have been conducted, imidazolium-based ionic liquids have been used in those studies. There are fewer reports on other ionic liquids. In this paper, therefore, we

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investigated the reaction behavior of wood in a pyridinium-based ionic liquid, 1-ethylpyridinium bromide. The differences in reactivity of cellulose, hemicellulose, and lignin were studied. In addition, we investigated the reaction behavior of two different wood species.

Materials and methods

Samples and chemicals

Wood flours from Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) were extracted with ethanol/benzene (1/2, v/v) for 8 h in a Soxhlet apparatus. The extracted wood flour was oven dried at 105 °C for 24 h prior to use. The ionic liquid 1-ethylpyridinium bromide ([EtPy][Br], chemical structure shown in Fig. 1), was purchased from Tokyo Chemical Industry. Dimethyl sulfoxide (DMSO), acetonitrile, sodium hydroxide aqueous solution, sulfuric acid, sodium sulfate, and potassium bromide were purchased from Wako Pure Chemical Industries. *N,O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) was purchased from Sigma-Aldrich and pyridine was purchased from Nacalai Tesque.

Treatment with [EtPy][Br]

Three grams of [EtPy][Br] was heated at 120 °C in a 100-mL flask. After melting the [EtPy][Br], 0.09 g of wood flour was added into the flask to start the reaction. The reaction media were gently stirred in the atmosphere.

Evaluation methods

Thirty milliliters of DMSO was poured into the flask to stop the reaction at a predetermined time. After stirring for 24 h at room temperature, the solution was filtered. The obtained [EtPy][Br]-insoluble residue was washed with DMSO and then washed several times with distilled water. The washed [EtPy][Br]-insoluble residue was then dried in an oven at 105 °C for 24 h and weighed to calculate yield.

X-ray patterns of the [EtPy][Br]-insoluble residue were obtained with an Ultima IV diffractometer (Rigaku) using

Cu-K α radiation ($\lambda = 0.1524$ nm) with a K β filter, operating at 40 kV and 30 mA. The relative crystallinity of the [EtPy][Br]-insoluble residue at each treatment time was calculated from the obtained patterns.

Fourier transform infrared (FT-IR) spectra of the [EtPy][Br]-insoluble residue (in KBr pellets) were recorded using a Shimadzu 8200PC spectrophotometer over a spectral range of 4000–400 cm $^{-1}$ with 20 accumulations.

The lignin content in [EtPy][Br]-insoluble residue was determined as Klason lignin and acid-soluble lignin [32]. Based on these lignin contents, the total amount of cellulose and hemicelluloses in the [EtPy][Br]-insoluble residue was calculated. Furthermore, the amounts of the constituent monosaccharides in the [EtPy][Br]-insoluble residue were determined by high-performance liquid chromatography (HPLC) for the filtrate from the acid hydrolyzates in Klason lignin under the following conditions: column, Shodex Sugar KS-801; flow rate, 1 mL/min; eluent, H $_2$ O; detector, refractive index detector (RID); column temperature, 80 °C. The ratio of cellulose and hemicelluloses in the [EtPy][Br]-insoluble residue was calculated from the obtained amounts of constituent monosaccharides.

The molecular weight distributions of the compounds solubilized in [EtPy][Br] were analyzed during the treatment, by taking 150- μ L aliquots of the reaction media at specified reaction times. These aliquots were mixed with 150 μ L of DMSO until homogeneous and then filtered through a 0.45- μ m filter. The filtrate was analyzed by gel permeation chromatography (GPC) under the following conditions: column, Shodex SB-803 HQ; flow rate, 0.3 mL/min; eluent, DMSO; detectors, RID and photodiode array detector set at 280 nm; column temperature, 60 °C. Pullulan (Shodex standard P-82) was used as a molecular weight standard.

Gas chromatography mass spectrometer (GC-MS) analysis was used to identify low-molecular-weight products solubilized in [EtPy][Br]. During the treatment of wood with [EtPy][Br], 20- μ L aliquots of the reaction media were taken at specified reaction times. This sampled media was mixed with 240 μ L of acetonitrile homogeneously. After dehydration with sodium sulfate, 120 μ L of filtrate was silylated with 60 μ L of BSTFA mixed with 5 μ L of pyridine at room temperature. The obtained samples were analyzed by GC-MS under the following conditions: column, Shinwa HR-52; temperature program 60 °C (0–1 min), 60 °C \rightarrow 230 °C (1–9.5 min), 230 °C (9.5–24.5 min); carrier gas, He; column flow rate, 1 mL/min.

The compounds solubilized in [EtPy][Br] were also analyzed by HPLC. At specified reaction times, 20 μ L of the reaction media was taken and homogeneously mixed with 180 μ L of distilled water. These mixtures were then filtered through a 0.45- μ m filter and the filtrates analyzed under the following conditions: column, Shodex Sugar KS-

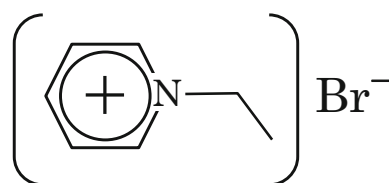
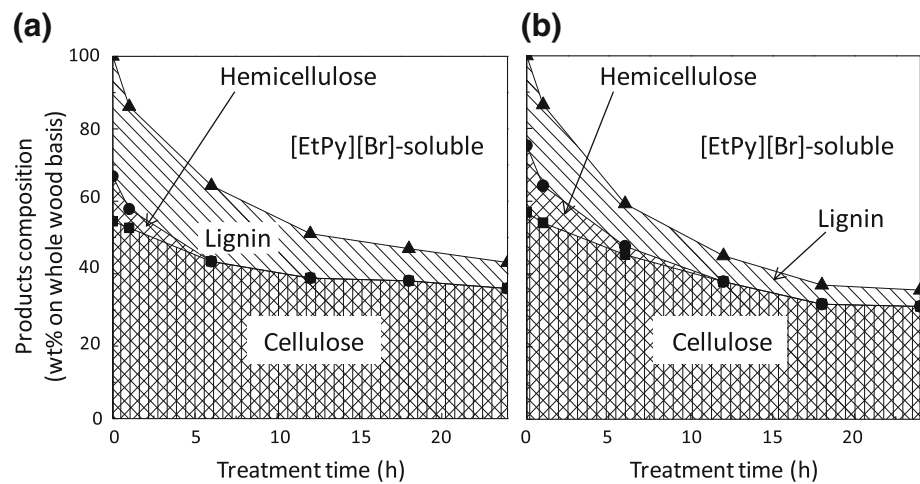


Fig. 1 The chemical structure of 1-ethylpyridinium bromide ([EtPy][Br])

Fig. 2 Compositions of products of **a** Japanese cedar and **b** Japanese beech treated with [EtPy][Br]



801; flow rate, 1 mL/min; eluent, H₂O; detector, RID; column temperature, 80 °C.

Results and discussion

[EtPy][Br]-insoluble residue

Figure 2 shows the changes in the chemical composition of Japanese cedar and Japanese beech as they are treated with [EtPy][Br]. After 24 h of treatment, the residual fractions for Japanese cedar and Japanese beech were 43 and 36 %, respectively. For both woods, the contents of cellulose, hemicellulose, and lignin decreased with treatment. In particular, during the early stages of treatment, for Japanese cedar and Japanese beech hemicellulose was essentially removed from the residues after 6 and 12 h of treatment, respectively. Lignin was also materially reduced with treatment. However, cellulose decreases much less than hemicellulose and lignin, meaning that the decrease in yield of residue was caused mainly by decreases in the amounts of hemicellulose and lignin in the wood. These results indicate that more hemicellulose and lignin are easily liquefied than cellulose, although all components of wood can be liquefied in [EtPy][Br].

To investigate the denaturation of lignin, Fig. 3 shows the ratios of acid-soluble lignin to Klason lignin in the [EtPy][Br]-insoluble residues for both wood samples. If denaturation of lignin does not occur, the ratio shown in Fig. 3 is constant independently of treatment time. However, the ratio for Japanese cedar increases with increasing treatment time, and the ratio for Japanese beech reaches a maximum at 6 h of treatment. From these results, the contents of acid-soluble lignin or Klason lignin (acid-insoluble lignin) in the residue are found to vary during [EtPy][Br] treatment, indicating the denaturation of lignin

occurs. This result means that reactivity of acid-soluble lignin to [EtPy][Br] is different from that of Klason lignin. Moreover, it is found that the denaturation behavior of Japanese cedar and Japanese beech is different. This must be because of the structural differences between softwood and hardwood lignin.

Figure 4 shows infrared spectra for the [EtPy][Br]-insoluble residues. For the residue from Japanese cedar, as shown in Fig. 4 a, The peak at 1740 cm⁻¹, derived from the C=O of the acetyl group in hemicellulose, also becomes weaker as the [EtPy][Br] treatment continues. This is not caused by denaturation of hemicellulose from the [EtPy][Br]-insoluble residues but instead by the dissolution of hemicellulose (and thus its removal from the residues) by the [EtPy][Br]. The peaks at 1510 cm⁻¹, derived from aromatic rings, are found in all residues. The peak at 1270 cm⁻¹, derived from the methoxy groups in guaiacyl lignin and C=O stretch, becomes weaker as the treatment time is extended. Because lignin is present in the [EtPy][Br]-insoluble residues as shown in Fig. 2, the weakening of this peak is not caused by reduction of lignin but instead by the chemical change of lignin by [EtPy][Br] treatment. Similar results were obtained for Japanese beech, as shown in Fig. 4 b. From the results shown in Figs. 3 and 4, it is clarified that [EtPy][Br] denatures lignin in wood.

To investigate the crystalline structure in wood after [EtPy][Br] treatment, X-ray diffractograms of the [EtPy][Br]-insoluble residues are shown in Fig. 5. Untreated wood samples of both species show the typical two peaks of crystalline cellulose at around 15° and 22° (2θ). After 24 h of treatment, these two peaks are still detected in both species, which indicates that the crystalline structure of cellulose in wood is maintained even after [EtPy][Br] treatment. Figure 6 shows the changes in relative crystallinity of cellulose in [EtPy][Br]-insoluble

Fig. 3 Ratios of acid-soluble lignin to Klason lignin of [EtPy][Br]-insoluble residues from **a** Japanese cedar and **b** Japanese beech

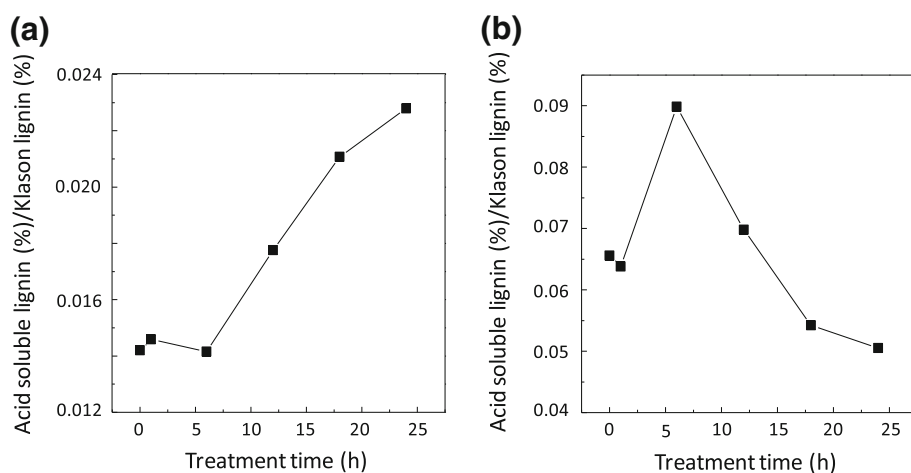
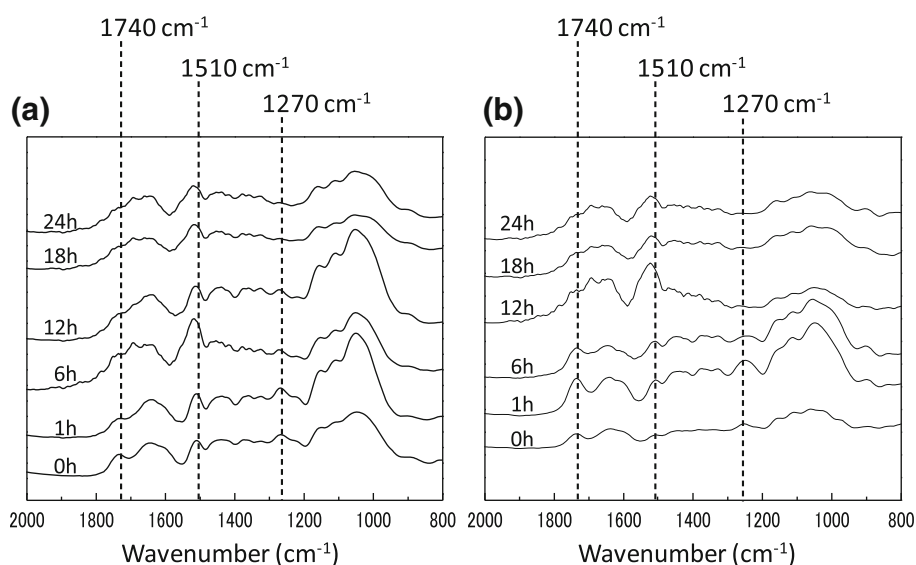


Fig. 4 FT-IR spectra of [EtPy][Br]-insoluble residues from **a** Japanese cedar and **b** Japanese beech



residues. The relative crystallinity of the residues for both species increases with increasing treatment time. As shown in Fig. 2, the amounts of hemicellulose and lignin, which are amorphous regions in wood, decrease with [EtPy][Br] treatment; this in turn causes the relative crystallinity to increase.

Solubilized compounds in [EtPy][Br]

From GC–MS analysis, glucose, mannose, xylose, galactose, and arabinose were determined as solubilized low-molecular-weight products in [EtPy][Br]. Levoglucosan, levomannosan, and 5-hydroxymethylfurfural (5-HMF) were also found in the [EtPy][Br] extract by HPLC. However, levomannosan was obtained only from Japanese cedar. This difference between Japanese cedar and Japanese beech is due to the difference in constitution of hemicelluloses. Although the main component

of hemicelluloses in Japanese beech is xylan, that in Japanese cedar is galactoglucomanan. Thus, levomannosan is thought to be produced by the decomposition of galactoglucomanan in Japanese cedar. Figure 7 shows changes in the yields of these compounds from wood treated with [EtPy][Br]. The “monosaccharides” in the figure are the total yield of glucose, mannose, xylose, galactose, and arabinose. For Japanese cedar, the yield of monosaccharides at 1 h was 6 %, which was the highest among the various compounds. The maximum yields of levoglucosan, levomannosan, and 5-HMF were found after 6 h. These compounds are thought to arise from decomposition of the hemicellulose, which was liquefied in the early stages of [EtPy][Br] treatment. For Japanese beech, similar trends can be seen. Monosaccharides reached their maximum at 6 h and showed much higher yields compared with those obtained for other compounds.

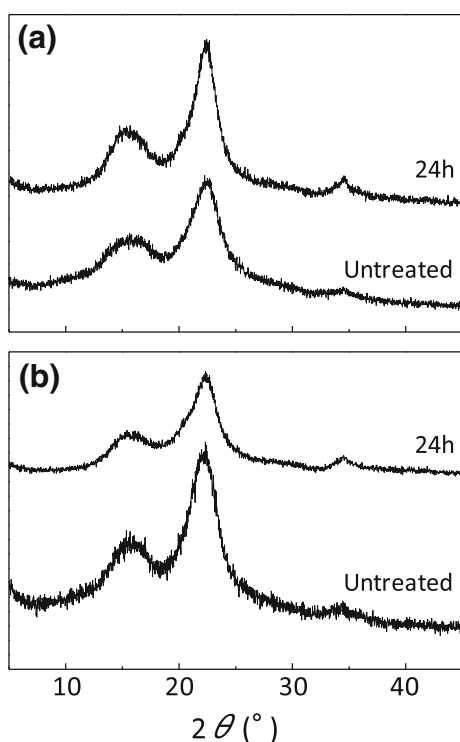


Fig. 5 X-ray diffractograms of [EtPy][Br]-insoluble residues from **a** Japanese cedar and **b** Japanese beech treated for 24 h

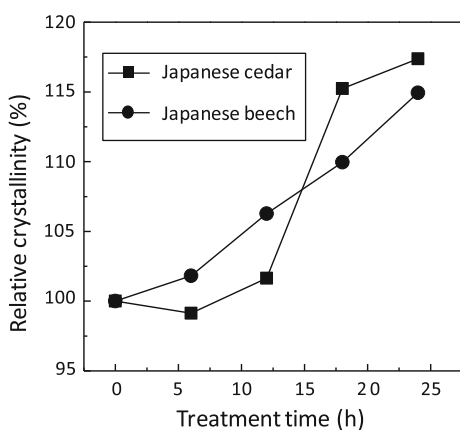


Fig. 6 Changes in relative crystallinity of [EtPy][Br]-insoluble residue from Japanese cedar and Japanese beech

The molecular weight distributions of the compounds solubilized in [EtPy][Br] were studied by GPC, as shown in Fig. 8. Peaks from [EtPy][Br] are not visible in this figure because of their long elution time (~ 40 min). In the chromatogram for Japanese cedar obtained by the RID, a peak at molecular weight (MW) $>212,000$ is observed at a longer treatment time. This result indicates that some wood components that have not depolymerized are present in [EtPy][Br]. Similar peaks are observed in the chromatogram

obtained with the ultraviolet (UV) detector. Hemicellulose can be decomposed easily during the early stages of treatment with [EtPy][Br], as described above. Thus, these peaks in the chromatogram indicate the presence of lignin-derived polymers in [EtPy][Br]. For both RID and UV, the peaks are consistently found at MW $>212,000$, indicating that the lignin-derived polymers are stable in [EtPy][Br]. Japanese beech (Fig. 8b) gave results similar to those obtained for Japanese cedar.

Comparison with results obtained using other ionic liquids

A previous paper on liquefaction of Japanese beech and Western red cedar by 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) reported that [C2mim][Cl] can liquefy polysaccharides such as cellulose and hemicellulose in priority. The crystalline structure of cellulose was also found to be destroyed by [C2mim][Cl] treatment [24, 25]. The polymers solubilized in [C2mim][Cl] were depolymerized to low-molecular-weight compounds such as glucose, mannose, xylose, levoglucosan, and 5-HMF [24, 25]. Conversely, 1-ethyl-3-methylimidazolium acetate ([C2mim][Ac]) can completely liquefy wood flour of southern yellow pine and red oak, and lignin in those woods was liquefied before the polysaccharides [22]. Xie et al. [18] reported that dawn redwood can be rapidly liquefied by 3,3'-ethane-1,2-diylbis(1-methyl-1*H*-imidazol-3-ium) dichloride and 3,3'-ethane-1,2-diylbis(1-methyl-1*H*-imidazol-3-ium)dichloroaluminate treatment at 120 °C in 25 min. It is also reported that 1-allyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-3-methylimidazolium methylsulfate can extract lignin from maple wood flour [20, 33, 34].

In contrast to these ionic liquids, the [EtPy][Br] studied in this paper can liquify lignin and hemicelluloses in priority. Cellulose was partially liquefied, and its crystalline structure is maintained in the residues after [EtPy][Br] treatment. It is reported that imidazolium-based ionic liquid disrupts crystalline structure of cellulose in eucalyptus and sugarcane bagasse more efficiently than pyridinium-based ionic liquid [35]. Similar results are obtained in our research. The solubilized polysaccharides in [EtPy][Br] were partially depolymerized to low-molecular-weight compounds. Hemicellulose can be decomposed easily during the early stages of treatment. GPC chromatograms indicate that lignin-derived polymers are stable in [EtPy][Br]. These findings are characteristics of [EtPy][Br] treatment. Consequently, the reaction behavior of wood in [EtPy][Br] is significantly different from that in several imidazolium-based ionic liquids, as described

Fig. 7 Changes in yield of various compounds from **a** Japanese cedar and **b** Japanese beech. 5-HMF; 5-hydroxymethyl furfural

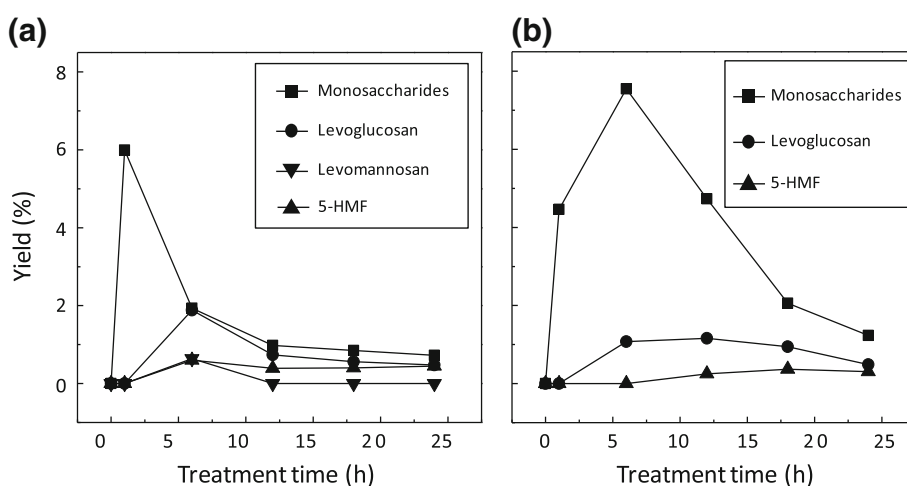
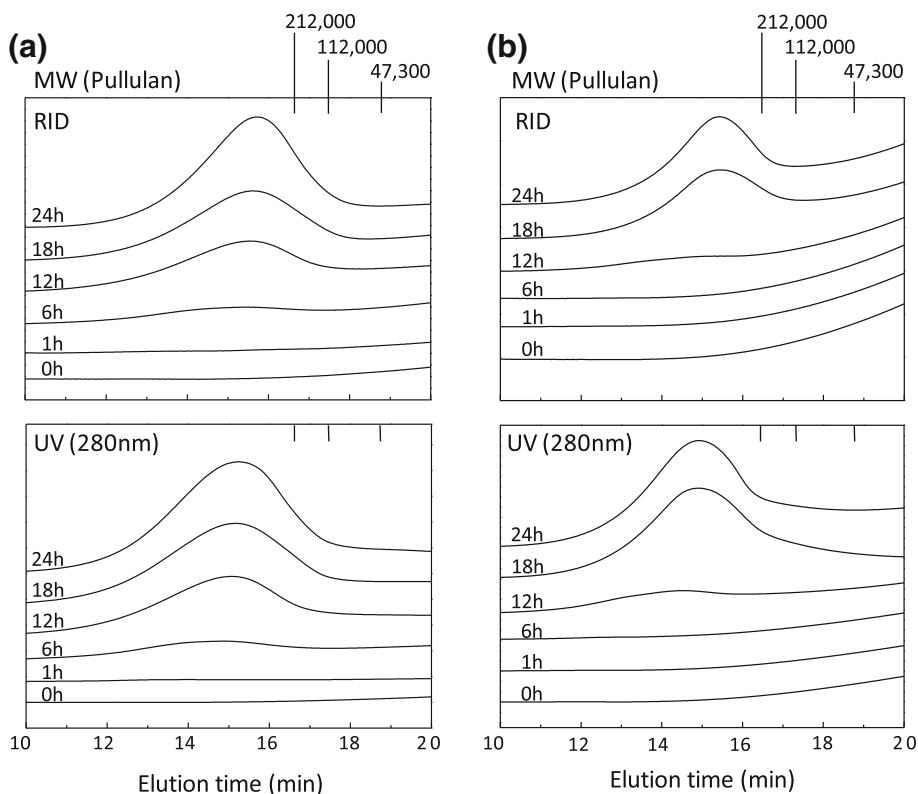


Fig. 8 GPC chromatograms of the solubilized compounds in [EtPy][Br] from **a** Japanese cedar and **b** Japanese beech for various treatment times. *Top* refractive index detector (RID), *bottom* UV detector ($\lambda = 280$ nm)



above. These differences are assumed to be due to the reactivity of cations to wood although much further research is necessary.

Conclusions

In this study, Japanese cedar and Japanese beech were selected as representative of Japanese softwood and hardwood, respectively. We demonstrated that 1-ethylpyridinium bromide, [EtPy][Br], can liquefy wood components.

Liquefaction of hemicellulose was rapid and complete, while lignin also liquefied rapidly. Cellulose and lignin were partially liquefied. Japanese beech was more easily liquefied than Japanese cedar. A significant difference was seen in the denaturation of lignins from Japanese beech and Japanese cedar, which is believed to be because of differences in the chemical structures of softwood and hardwood lignins and hemicelluloses. The reaction behavior shown in this study is quite different from the results of previous studies of wood in imidazolium-based ionic liquids. We conclude that the combination of wood and ionic liquid is

an important factor in the effective use of wood via liquefaction through treatment with ionic liquids.

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