ORIGINAL ARTICLE

Hisashi Miyafuji · Kenji Miyata · Shiro Saka
Fumio Ueda · Midori Mori

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

Abstract Reaction of Japanese beech (*Fagus crenata*) in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), which can dissolve cellulose, was investigated. Although both lignin and polysaccharides such as cellulose and hemicelluloses can be liquefied at a treatment temperature of around 100°C, the liquefaction of polysaccharides mainly occurs at the beginning of the treatment with [C2mim][Cl]. Cellulose crystallinity in the wood was gradually broken down as the treatment continued. The solubilized polymers were depolymerized to low molecular weight compounds. The results indicate that [C2mim][Cl] is an effective solvent and reagent for the liquefaction of wood components and subsequent depolymerization of them.

Key words Wood · Ionic liquid · 1-Ethyl-3-methylimidazolium chloride · Reaction behavior · Depolymerization

Introduction

Energy and environmental issues such as the exhaustion of fossil resources and global warming are major concerns. As a result, increased attention has been focused on biomass resources as alternatives to fossil resources due to their environmentally benign nature: they are renewable and are carbon neutral. Among various biomasses, wood is thought to be a promising resource because of its huge stocks and inedible character, which means that its utilization poses no threat to food supply. However, to utilize it for producing various useful chemicals, effective conversion technology must be applied. Various studies on wood treatment have been performed such as acid hydrolysis,[1] enzymatic saccharification,[2] hot-compressed water treatment,[3] supercritical fluid treatment,[4,5] pyrolysis,[6,7] and others.

Much attention has been focused on ionic liquids as solvents for chemical reactions.[8] Ionic liquids are salts that have melting points at around ambient temperature. It is known that they are nonvolatile and have good solvation power for various chemical species. It has also been found that some ionic liquids when used as reaction solvent can be recycled several times without negative effects such reduced yield of products.[9] Therefore, the use of ionic liquids as solvent is expected to attain "green chemistry" status for various chemical reactions. Recently, some ionic liquids have been used in the chemical conversion of cellulose or wood. It has been revealed that some ionic liquids can dissolve cellulose[10] and can be utilized as solvent to produce cellulose films[11] or to derivatize cellulose in processes such as acetylation,[12–15] carbanilation,[15,16] carboxymethylation,[12] succination,[17] and phthalation.[18] In those research studies, the ionic liquids studied were mainly composed of imidazolium cation and chloride anion. These ionic liquids were also applied to the liquefaction of wood, and found to liquefy not only cellulose but also lignin in wood.[19–21] However, detailed behavior for the liquefaction of wood in ionic liquids has not been clarified as yet. In this study, therefore, we investigated the reaction behavior of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride, which can dissolve cellulose. The difference of reactivity toward lignin and polysaccharides, such as cellulose and hemicellulose, was studied.

H. Miyafuji (✉) · K. Miyata · S. Saka
Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
Tel. +81-75-753-9116; Fax +81-75-753-9116
e-mail: miyafuji@energy.kyoto-u.ac.jp

F. Ueda · M. Mori
Vehicle Engineering Group, Toyota Motor Corporation, Toyota, Aichi 471-8572, Japan

Materials and methods

Samples and chemicals

Wood flours from Japanese beech (*Fagus crenata*) were extracted with ethanol/benzene (1/2, v/v) for 8 h in a Soxhlet
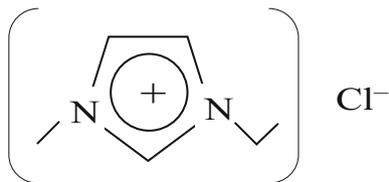
Fig. 1. The chemical structure of 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl])

apparatus. The extracted wood flours were used for all experiments after oven drying at 105°C for 24 h. 1-Ethyl-3-methylimidazolium chloride ([C2mim][Cl]) was purchased from Tokyo Kasei Kogyo. The chemical structure of [C2mim][Cl] is shown in Fig. 1. 1,3-Dimethyl-2-imidazolidinone (DMI) and dehydrated dimethylsulfoxide (DMSO) was purchased from Wako.

Treatment with [C2mim][Cl]

Three grams of solid [C2mim][Cl] was heated at 90°, 100°, 110°, and 120°C in a 100-ml glass flask. After melting of the [C2mim][Cl], 0.09 g of wood flour was added into the flask to start the reaction. The reaction media were gently stirred.

Evaluation methods

For characterization of [C2mim][Cl]-insoluble residue, 30 ml of DMI was poured into the flask at the specified time to quench the reaction. After stirring for 24 h at room temperature, the wood flour mixture was filtered. The obtained residues were washed with DMI and then washed several times with distilled water. The washed [C2mim][Cl]-insoluble residue was then dried in an oven at 105°C for 24 h and weighed to calculate yield. X-Ray diffractograms of the [C2mim][Cl]-insoluble residue were obtained with a RINT2000 diffractometer (Rigaku) under Cu-K$_\alpha$ radiation ($\lambda = 0.1524$ nm) with a K$_\beta$ filter, operating at 40 kV and 30 mA. The lignin content in the [C2mim][Cl]-insoluble residue was determined as Klason lignin.[22] Based on this lignin content, the total of cellulose and hemicelluloses in the [C2mim][Cl]-insoluble residue was calculated. In addition, the amounts of constituent monosaccharides in the [C2mim][Cl]-insoluble residue were determined by high-performance liquid chromatography (HPLC) for the clear filtrate from acid hydrolyzates in Klason lignin determination 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. Mannose, galactose, and xylose could not be separated on this column and so were analyzed as a single peak.

To analyze the molecular weight distribution of compounds that were soluble in [C2mim][Cl], other experiments were carried out. After starting the treatment of wood flour with [C2mim][Cl] by the procedure described above, 125 µl of the reaction media was withdrawn at a specified reaction time. To this sampled reaction media, 125 µl of DMSO was added and mixed well. The mixture was filtered through a 0.45-µm filter. The obtained filtrate was applied to a gel permeation chromatography (GPC) under the following conditions: column, Shodex SB-803 HQ; flow rate, 0.3 ml/min; eluent, DMSO; detector, RID and photodiode array (PDA) detector set at 280 nm; column temperature, 60°C. Pullulan (Shodex standard P-82) was used as a standard for the molecular weight distribution.

Another 125 µl of the reaction media prepared by the same procedure as described above was sampled to observe the morphological change of the [C2mim][Cl]-insoluble residue by light microscope.

Results and discussion

[C2mim][Cl]-insoluble residue

Figure 2 shows the changes in the chemical composition of cellulose, hemicellulose, and lignin in the [C2mim][Cl] residue of beech woods treated with [C2mim][Cl] at various temperature between 90° and 120°C. The yield of the residue was around 95% for up to 16 h at 90° and 100°C. However, after 24 h of treatment the yield of residue was reduced to 80% and 45% at 90° and 100°C, respectively. At both treatment temperatures, the decrease of lignin was negligible. Therefore, the decrease in residue yield was caused mainly by the decreases of cellulose and hemicellulose in wood. For treatment at 110°C, although the residue yield decreased in a similar fashion as in the 100°C treatment and with a shorter treatment time, the lignin in the residue also started to decrease after 8 h. This trend was observed over a much shorter treatment time at 120°C. The residue yield decreased to about 5% after treatment at 120°C for 24 h. These results indicate that much of the different components of wood can be liquefied in [C2mim][Cl] with high temperature and long treatment time. It is also found that although both lignin and polysaccharides such as cellulose and hemicelluloses can be liquefied, the liquefaction of the latter occurs mainly at the beginning of the reaction with [C2mim][Cl].

Figure 3 shows HPLC chromatograms of the acid hydrolyzates in Klason lignin determination of the [C2mim][Cl]-insoluble residue obtained at 120°C with various treatment times. For comparison, the result for untreated wood is also shown. In untreated wood, the intensity of the glucose peak was stronger than the peaks of the other sugars. This glucose peak gradually weakened with prolonged treatment time, and became much lower compared than those of the other sugars (mannose, galactose, and xylose) after 8 h of treatment. Glucose and the other sugars are thought to be obtained mainly from cellulose and hemicelluloses in the [C2mim][Cl]-insoluble residue, respectively. Therefore, the results in Fig. 3 indicate that in [C2mim][Cl] treatment of wood, the liquefaction of cellulose precedes that of hemicelluloses.

Fig. 2a–d. Products composition of wood treated by [C2mim][Cl] at **a** 90°C, **b** 100°C, **c** 110°C, and **d** 120°C
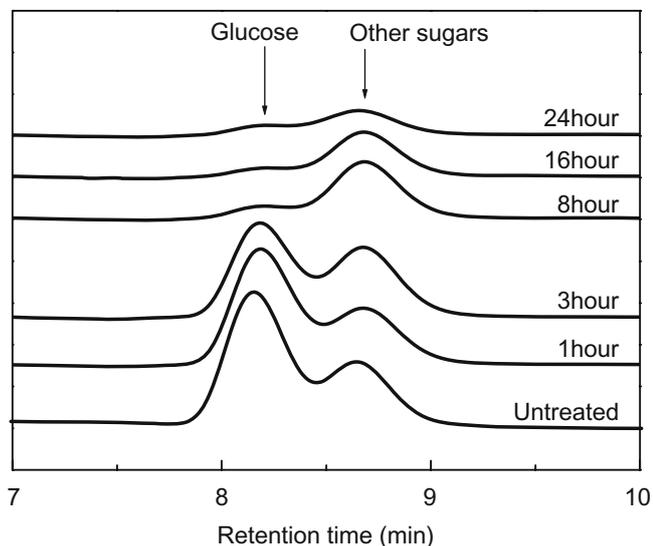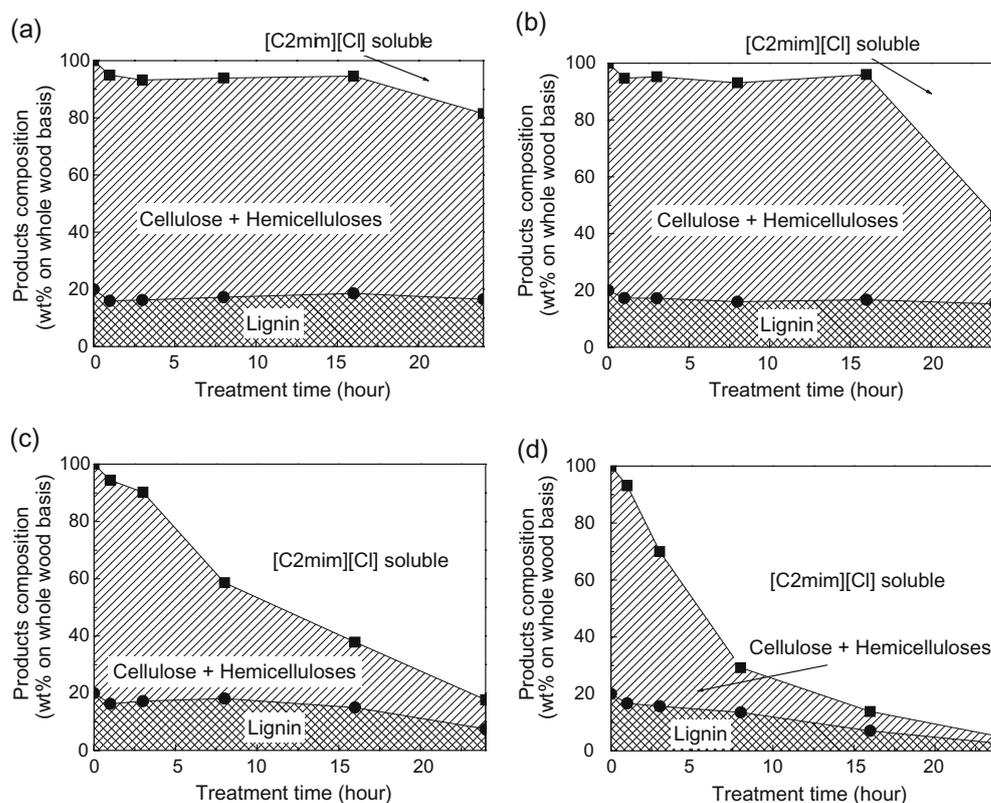

Fig. 3. High-performance liquid chromatography (HPLC) chromatograms of the acid hydrolyzates in Klason lignin determination of [C2mim][Cl]-insoluble residues obtained at 120°C with various treatment times. Column, Shodex Sugar KS-801; flow rate, 1 ml/min; eluent, H₂O; detector, refractive index detector (RID); temperature, 80°C. *Other sugars*, combined mannose, galactose, and xylose

Figure 4 shows the light micrographs of the residues after treatment with [C2mim][Cl] at 120°C with various treatment times. The brightness due to the birefringence of cellulose can be observed on whole samples in the polarization image for 0 h treatment. The bright parts decrease gradually as the treatment time extends and are invisible at 8 h treat-

ment, although the tissue of wood still remained. A similar phenomenon on the decrystallization of cellulose in wood by ionic liquid treatment was reported previously,[23] although the ionic liquid and size of the sample used were different from those used in this study. From these results, it is clear that the crystalline structures of cellulose in the insoluble residue were destroyed although the polysaccharides still remained in the residue as shown in Fig. 2.

Figure 5 shows X-ray diffractograms of the residues obtained at 100° and 120°C with various treatment times. For comparison, the result for the untreated wood is also shown. In the diffractogram for untreated wood, two peaks at around 15° and 22° due to the crystals of cellulose can be seen. These peaks were observed to weaken and broaden with prolonged treatment time. In particular, after 8 h at 120°C, the prominent peaks disappeared and a broad peak became apparent, which is in accordance with the light microscope observations as in Fig. 4. The results in Figs. 4 and 5 reveal that the decrystallization of cellulose in wood by [C2mim][Cl] treatment proceeds gradually.

Solubilized compounds in [C2mim][Cl]

The molecular weight distribution of the solubilized compounds in [C2mim][Cl] was studied by GPC (see Fig. 6). Peaks from [C2mim][Cl] are not visible in Fig. 6 due to their long elution time of around 80 min. Therefore, Fig. 6 essentially displays the molecular weight distribution of wood components solubilized in [C2mim][Cl]. From the chromatogram obtained by RID for treatment at 100°C, the

Fig. 4. Light microscopy images of the [C2mim][Cl]-insoluble residues treated at 120°C with various treatment times (*upper*) and their polarization microscopy images (*lower*)
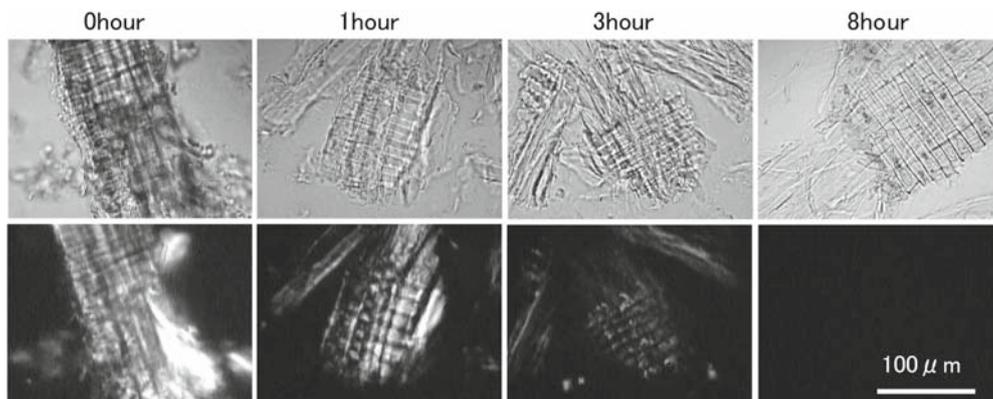

Fig. 5a, b. X-Ray diffractograms of the [C2mim][Cl]-insoluble residues treated at **a** 100°C and **b** 120°C with various treatment times
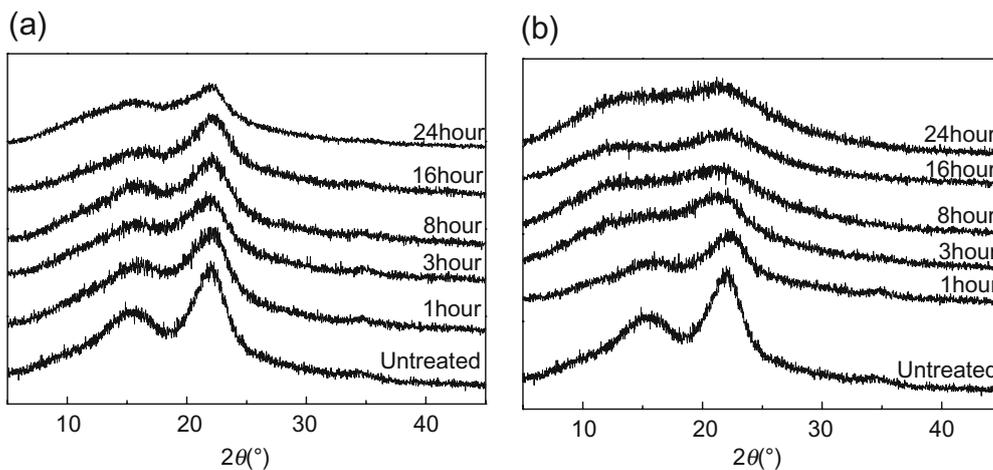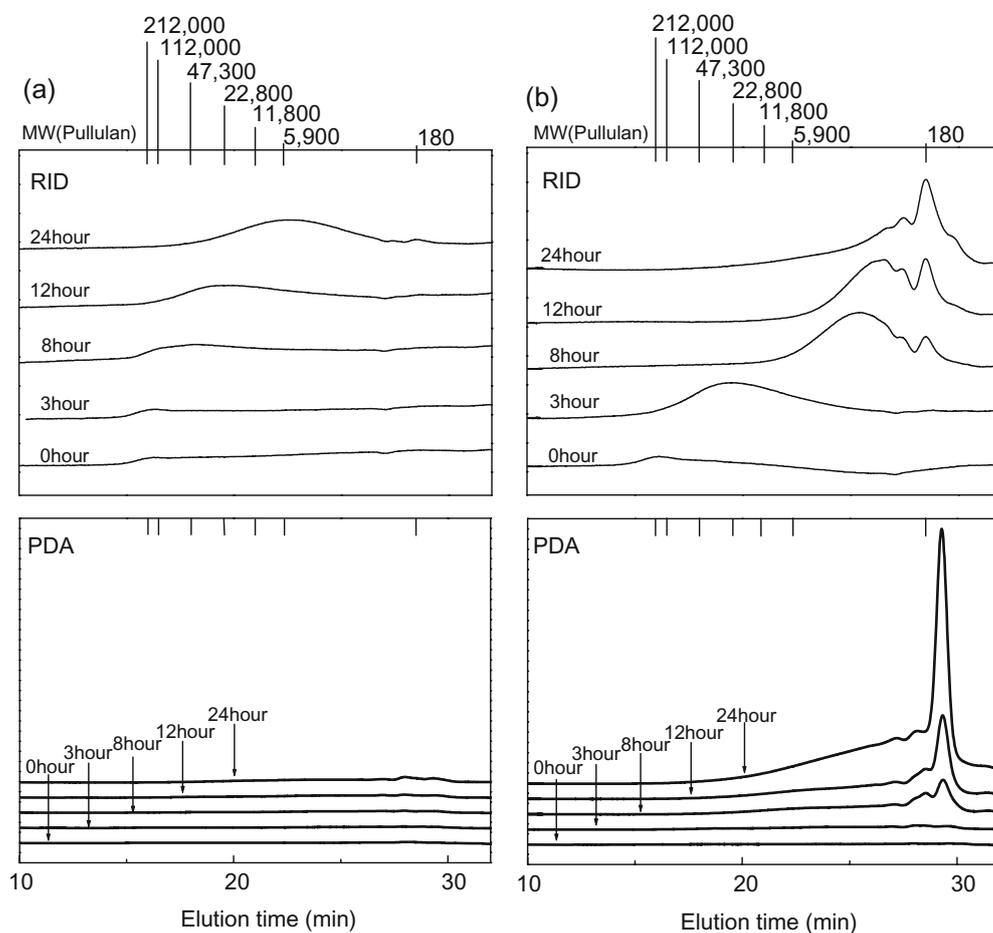

Fig. 6a, b. Gel permeation chromatograms for the solubilized compounds in [C2mim][Cl] at **a** 100°C and **b** 120°C with various treatment times. *Top*, refractive index detector (*RID*); *bottom*, photodiode array (*PDA*) detector. Column, Shodex SB-803 HQ; flow rate, 0.3 ml/min; eluent, dimethylsulfoxide; temperature, 60°C. *MW*, molecular weight

mean molecular weight was found to decrease as the treatment time was extended. On the other hand, no prominent peaks are observed in the chromatogram obtained with PDA detection. These results indicate that wood components solubilized in [C2mim][Cl] are not lignin-derived compounds but polysaccharides, and depolymerization of the polysaccharides occurred in [C2mim][Cl].

Such depolymerization was even more enhanced at 120°C as shown in the chromatogram obtained by RID (Fig. 6). In the chromatogram for 24 h of treatment, a peak is observed for a molecular weight (MW) around 180, which is the MW of hexose. It is also observed in the chromatograms obtained by PDA detection that low molecular weight compounds with MW below 180 were obtained. These results probably indicate the presence of lignin-derived compounds because lignin can be liquefied in [C2mim][Cl] at 120°C, as shown in Fig. 2. More detailed investigations, however, are necessary to elucidate the mechanism of the depolymerization of wood components in [C2mim][Cl].

Reaction mechanisms of [C2mim][Cl] in treatment of wood

Based on the results obtained, possible reaction mechanisms in the treatment of wood with [C2mim][Cl] are proposed. At the initial stage of the reaction, [C2mim][Cl] penetrates into wood and mainly liquefies polysaccharides such as cellulose and hemicellulose, although both lignin and polysaccharides can be liquefied simultaneously (Fig. 2). However, this reaction does not destroy the cellulose crystallinity straight away, but breaks down the crystal structure gradually as the treatment continues (Figs. 4 and 5). During these reactions, the liquefaction of cellulose precedes that of hemicellulose (Fig. 3). Lignin then starts to be liquefied with [C2mim][Cl] before all polysaccharides are eluted from wood. Subsequently, [C2mim][Cl] liquefies the polysaccharides and lignin together (Fig. 2). Meanwhile, the dissolved polysaccharides and lignin in [C2mim][Cl] are depolymerized. Consequently, these wood components can be converted to the low molecular weight compounds with the same molecular weights as monosaccharides (Fig. 6).

Conclusions

We demonstrated that [C2mim][Cl], which can dissolve cellulose, liquefies wood components with subsequent depolymerization of them. It is concluded from the observed results that [C2mim][Cl] can work not only as a solvent for wood components but also as a reagent for converting them to low molecular weight compounds. This finding suggests that [C2mim][Cl] can be used for the chemical conversion of wood to obtain useful chemicals.

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