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Influence of reaction atmosphere on the liquefaction and depolymerization of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride

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Abstract The influence of reaction atmosphere on the liquefaction and depolymerization of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), has been systematically studied. The wood samples were treated with [C2mim][Cl] at 120°C under various atmospheres such as oxygen, nitrogen, and carbon dioxide, both dried and humidified. The percentage of residue after the treatment shows that oxygen considerably accelerates the liquefaction of wood in [C2mim][Cl], and humidity hardly affects liquefaction under any atmosphere. Gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC) analyses on the solubilized compounds in [C2mim][Cl] indicate that oxygen and humidity enhance the depolymerization of the wood component. Thus, the reaction atmosphere was revealed to influence, and be capable of controlling, the reaction of wood in [C2mim][Cl].

Key words Wood · Ionic liquid · Reaction atmosphere · Liquefaction · Depolymerization

Introduction

The efficient utilization of renewable, carbon-neutral biomass has been anticipated for decades, with the goal of achieving a sustainable society. Biomass has the potential to replace conventional fossil fuel as an energy resource or starting material for the production of useful chemicals.

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Although some biomass crops, corn and sugarcane, for example, are already in practical use as bioethanol, cultivation space is limited and some serious food problems have arisen. Lignocellulosics such as wood, on the other hand, account for more than 90% of biomass in the world and are unrelated to the food supply. The key to using lignocellulosics in an effective manner lies in its conversion technology. Much research has been conducted, such as acid hydrolysis,¹ enzymatic saccharification,² and pyrolysis.^{3,4} However, an efficient method has not yet been established.

One of the encouraging novel alternative methods is ionic liquid treatment. Ionic liquids are salts with low melting points around ambient temperature.⁵ Because of their many unique characteristics, such as negligible vapor pressure, thermal stability, reusability, and nonflammability, ionic liquids are said to be a “green solvent.” Based on the fact that some ionic liquids can dissolve cellulose,⁶ which is the most abundant renewable natural organic compound on the earth, many studies regarding applications of ionic liquids for cellulose have been conducted.^{7–10} Research to understand its dissolution mechanisms has been also carried out.^{11,12} Very recently, ionic liquids came to be applied to wood.^{13–15} Xie and Shi reported that the liquefaction of wood with ionic liquids is much more rapid compared to conventional liquefaction with phenol/H₂SO₄.¹³ It is also revealed that wood can be dissolved not only in ionic liquids but also in a co-solvent of ionic liquids and dimethylsulfoxide.¹⁴ Kilpeläinen et al. demonstrated that wood dissolved in ionic liquids can be regenerated as an amorphous mixture of its original components, and the cellulose of the regenerated wood is efficiently hydrolyzed by cellulase.¹⁵ Our previous work showed that as wood components are liquefied, they are decrystallized and depolymerized.¹⁶ Additionally, the difference between the reaction behavior of two different wood species against an ionic liquid was also studied. The resulting significant difference in lignin liquefaction behavior was found to be explained by the difference in the chemical structure of the lignin of the two species.¹⁷

Regarding the parameters that may influence the ionic liquid treatment of wood, Seddon et al. reported that impurities of ionic liquids, including water, alter their physical

properties considerably.¹⁸ Although many studies on ionic liquids have already conducted, the influence of the reaction atmosphere has garnered little attention so far. In this research, therefore, the influence of reaction atmosphere on the liquefaction of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride, was studied. In this article, the decrease of wood residue by ionic liquid treatment is described as liquefaction of wood.

Materials and methods

Samples and chemicals

Wood flour from Western red cedar (*Thuja plicata*) (80- μm sieve pass) was extracted with ethanol/benzene (1:2 v/v) for 8 h in a Soxhlet apparatus. The extracted wood flour was dried in an oven at 105°C for 24 h before use. As an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) was purchased from Tokyo Kasei Kogyo. Dehydrated dimethylsulfoxide (DMSO) was purchased from Wako Chemicals.

Treatment with [C2mim][Cl] and separation

As shown in Fig. 1a, 3 g [C2mim][Cl] and 0.09 g wood sample were separately put into a 100-ml glass flask. As pretreatment, the flask was heated at 120°C for 30 min under vacuum to dehydrate its interior. The reaction was then started by mixing wood flour with [C2mim][Cl], and the specific gas was directed to flow into the flask (Fig. 1b). Flow rate was set at 10 ml/min. During this procedure, extra care was taken to ensure no moisture remained and that no other gases were mixed in. The gases used in this research were nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), pseudo-air (O_2/N_2 , 21:79 (v/v)) (air); those humidified were ($\text{N}_2 + \text{H}_2\text{O}$), ($\text{O}_2 + \text{H}_2\text{O}$), ($\text{CO}_2 + \text{H}_2\text{O}$), and ($\text{air} + \text{H}_2\text{O}$). The gases were confirmed to be 0% RH at 17°C. The humidity was contained in gas flow by having it pass through distilled water in midflow, which was 99% RH at 17°C. The relative

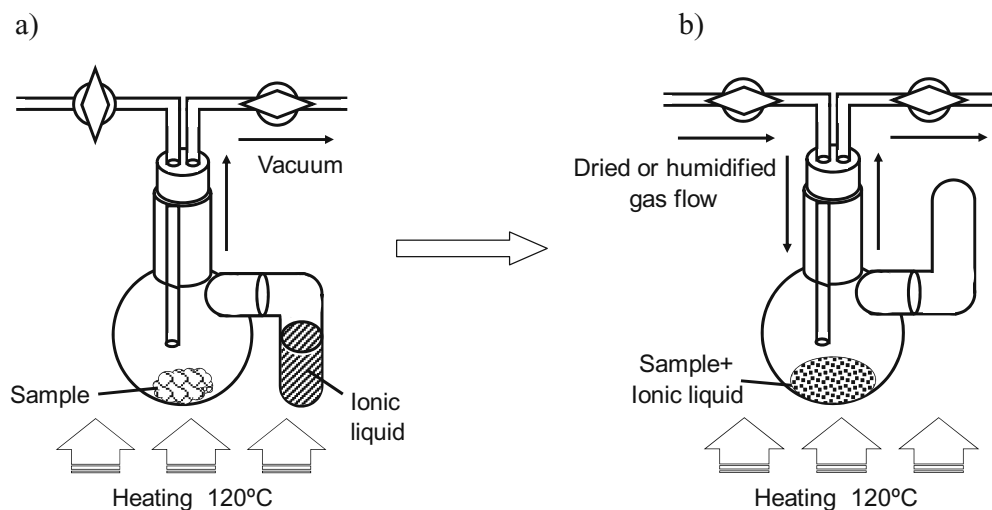
humidity and temperature were measured by a humidity sensor HM70 (Vaisala). In addition, a vacuum condition (vacuum) was conducted. The vacuum condition was maintained with a rotary pump that is capable of decompression to 6.7×10^{-2} Pa. After treatment with magnetic stirring for 3 or 24 h, 30 ml DMSO was poured into the flask to halt the reaction and stirring continued for 2 h at room temperature. The solution was filtered by a membrane filter with a 0.45- μm pore size, and the obtained [C2mim][Cl] insoluble residue was washed with DMSO and then distilled water several times. The [C2mim][Cl] insoluble residue was then dried in an oven at 105°C for 24 h and weighed to calculate its residue percentage.

Evaluation methods

The content of lignin, cellulose, and hemicellulose in the [C2mim][Cl] insoluble residue was determined to be Klason lignin,¹⁹ as described by Wise et al.²⁰ X-ray diffractograms of the [C2mim][Cl] insoluble residue were obtained by RINT2000 (Rigaku Denki) under $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1524$ nm) using a $\text{K}\beta$ filter, operating at 40 kV and 30 mA. The residue amounts obtained by the 24-h treatment under O_2 and $\text{O}_2 + \text{H}_2\text{O}$ were negligible, and thus they were excluded from determination of the content and the analysis by X-ray diffractometer.

Gel permeation chromatographic (GPC) analysis was carried out for the solubilized compounds in [C2mim][Cl] to determine molecular weight (MW) distribution. The samples for the analysis were prepared as follows. After 3- or 24-h treatment for wood in [C2mim][Cl], as already described, 125 μl reaction media was homogeneously mixed with 125 μl DMSO and then filtrated by a 0.45- μm filter. The obtained filtrates were analyzed under the following conditions: column, Shodex SB-803 HQ; eluent, DMSO; flow rate, 0.3 ml/min; detector, refractive index detector (RID), and photodiode array detector (PDA) set at 280 nm; column temperature, 60°C. Pullulan (Shodex standard P-82) was used as a standard for molecular weight distribution.

Fig. 1. Diagrams of the experimental apparatus. **a** Dehydration of ionic liquid and wood sample at 120°C under vacuum for 30 min. **b** Reaction began by twisting the handle and mixing ionic liquid and wood sample without exposure to any other gases



The solubilized compounds in [C2mim][Cl] were also analyzed by high performance liquid chromatography (HPLC). The samples for the analysis were prepared as follows. After 3 or 24 h of treatment, 10 μ l reaction media was homogeneously mixed with 90 μ l water and then filtrated by a 0.45- μ m filter. The obtained filtrates were analyzed under the following conditions: column, Aminex HPX-87P; eluent, distilled water; flow rate, 0.6 ml/min; detector, RID, and PDA set at 280 nm; column temperature, 85°C.

Results and discussion

[C2mim][Cl] insoluble residue

The changes in [C2mim][Cl] insoluble residue and composition as treated by [C2mim][Cl] for 3 or 24 h under various atmospheres are shown in Fig. 2. Under all atmospheres, the residues at 24-h treatment are found to be less than those at 3-h treatment, indicating the liquefaction of wood proceeds as the [C2mim][Cl] treatment continues. The

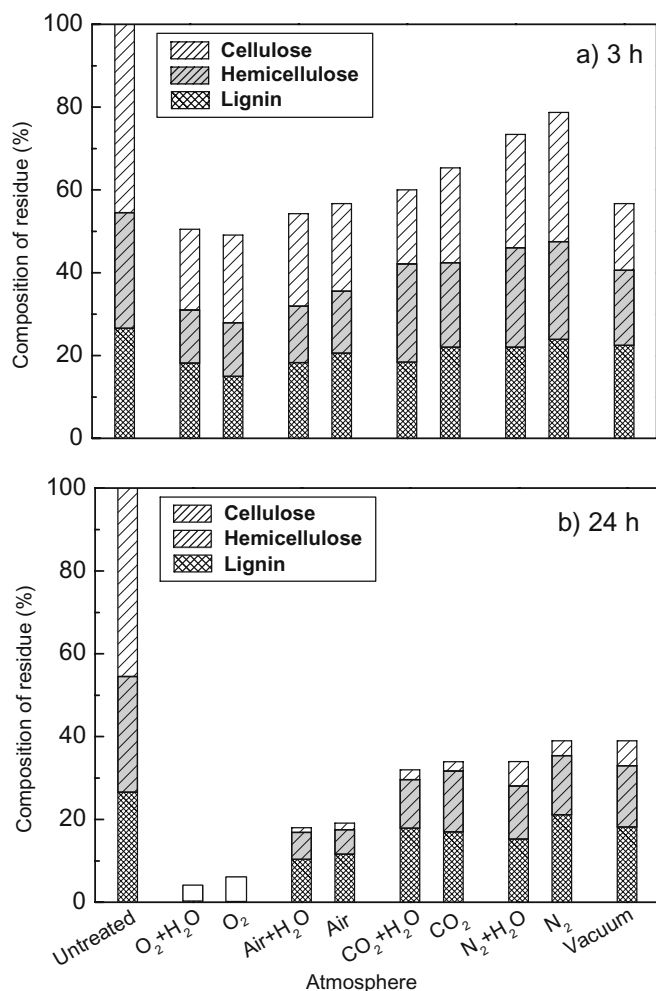


Fig. 2. Changes in residue and composition as treated by 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) for 3 h (a) and 24 h (b) under various atmospheres

samples treated for 24 h under O₂ + H₂O and O₂ drop to 4% and 6%, respectively, while those under CO₂, N₂, and vacuum remain above 35%. The samples treated under air + H₂O and air, which contain 21% oxygen, drop to 18% and 19%, respectively. These results reveal that oxygen accelerates the liquefaction of wood in [C2mim][Cl] considerably. Under all atmospheres, no significant difference in the percentages of residue can be observed between the samples treated under gases that were dried and humidified. The presence of humidity in the reaction atmosphere hardly affects the liquefaction of wood in [C2mim][Cl]. The percentage of the residue under vacuum condition falls to 57%, which is markedly lower compared to that under the other inactive gases such as N₂ and CO₂ that were dried and humidified. Under vacuum, it is known that more liquid can penetrate into wood compared to that under atmospheric conditions. Then, the expanding contact area between the ionic liquid and wood increases the liquefaction rate of wood. This rapid liquefaction under vacuum condition at 3 h could suggest that the penetration of ionic liquid into wood plays an important role in its liquefaction at the initial stage of the reaction. As already mentioned, active gases such as O₂ and air accelerate the liquefaction of wood in [C2mim][Cl] considerably. However, even under inactive gases such as N₂ and CO₂, or under a vacuum condition, the liquefaction of wood is found to proceed. These results indicate that [C2mim][Cl] itself has the ability to liquefy wood.

From Fig. 2, on the other hand, it seems that cellulose is easily liquefied compared to hemicellulose and lignin. Thus, based on the results in Fig. 2, the changes of the percentages for each component relative to the untreated sample were calculated as shown in Fig. 3 to make a comparison between liquefaction rates of each component under various atmospheres. Cellulose and hemicellulose are carbohydrates, although their chemical components differ. Xylan, which is a major component of hemicellulose in hardwood, was reported to be dissolved in [C2mim][Cl] the same as cellulose.²¹ However, it is obvious from Fig. 3 that hemicellulose remains relatively higher than cellulose. It was also found that cellulose decreases much more than lignin under all atmospheres. Cellulose is thought to exist independently without covalent bonds with hemicellulose and lignin in the wood structure. However, some amounts of hemicellulose and lignin are reported to exist as high polymers linked together through covalent bonds, which is called the lignin carbohydrate complex (LCC).^{22,23} Thus, it is inferable that such a high polymer becomes liquefied in the ionic liquid with difficulty and remains as an insoluble residue after the ionic liquid treatment. On the other hand, the presence of humidity does not influence the composition in the residue significantly under any atmosphere.

Figure 4 shows the X-ray diffractograms of the [C2mim][Cl] insoluble residue obtained under various atmospheres. The untreated wood sample shows the two typical peaks from crystals of cellulose around 15° and 22°. These peaks are weakened and broadened after the [C2mim][Cl] treatment for both 3 h and 24 h under all atmospheres, which indicates that there are few crystals of

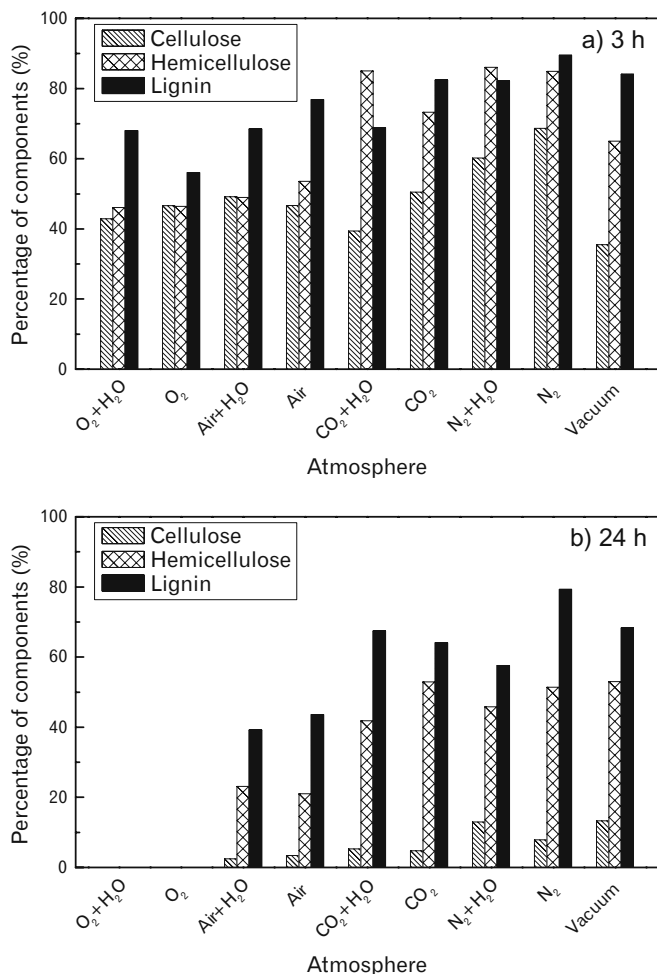
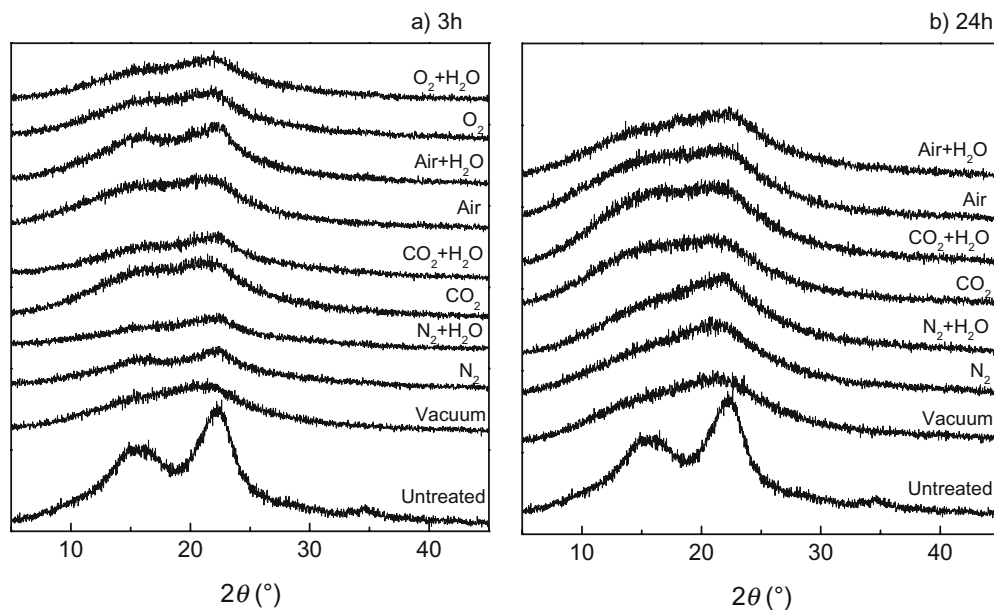


Fig. 3. Percentage changes for each component as treated by [C2mim][Cl] for 3 h (a) and 24 h (b) under various atmospheres. Each value is calculated as the percentage of each component in the untreated sample

Fig. 4. X-ray diffractograms of the residue as treated by [C2mim][Cl] for 3 h (a) and 24 h (b) under various reaction atmospheres



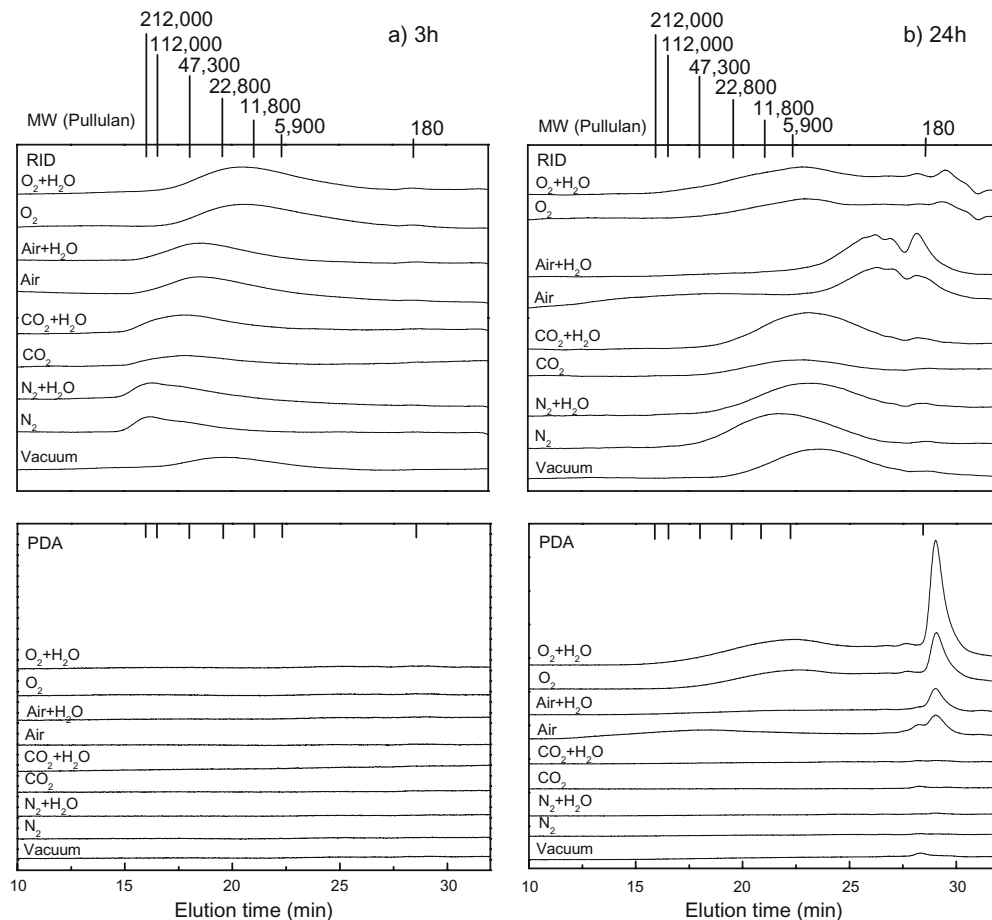
cellulose in the residue. Cellulose has been largely removed from wood after the 24-h treatment (Fig. 3b). Thus, no peak is observed in the diffractograms. On the other hand, around 40%–60% of cellulose still remains after 3-h treatment (see Fig. 3a), which means the crystals of cellulose inside of wood are decrystallized without liquefying from wood. In contrast, a significant influence on the decrystallization of cellulose cannot be observed among various atmospheres when dried and humidified.

Solubilized compounds in [C2mim][Cl]

The GPC chromatograms of the solubilized compounds in [C2mim][Cl] under various atmospheres are shown in Fig. 5. The peaks for [C2mim][Cl] occur around 58 min in elution time and thus are excluded from this figure. At 3 h in RID, the samples treated under O₂ + H₂O and O₂ show broad peaks around a few tens of thousands of daltons in MW whereas those under N₂ + H₂O and N₂ show a MW of a few hundred thousand daltons. In general, the samples treated under active gases show a lower MW and those under inactive gases have a higher MW. The sample treated under vacuum, which is the inactive condition, has a notably lower MW. On the other hand, no peaks are detected in PDA for all atmospheres.

The MW of the solubilized compounds in [C2mim][Cl] decreases as the treatment continues. After 24 h in RID, for example, the samples treated under air + H₂O and in air drop in MW and show peaks around 180 daltons, which is equivalent to that of a hexose. These results show that the wood components are depolymerized in [C2mim][Cl]. The depolymerization rates of the samples treated under inactive gas and vacuum are so slow that the MW becomes a few thousand daltons at 24 h. In PDA at 24 h, the samples treated under inactive gas have no sharp peaks. Because the

Fig. 5. Gel permeation chromatography (GPC) chromatograms for the solubilized compounds in [C2mim][Cl] obtained by treatment for 3 h (a) and 24 h (b) under various reaction atmospheres. *Top*, refractive index detector (RID); *bottom*, photodiode array (PDA) detector. Column, Shodex SB-803 HQ; eluent, dimethylsulfoxide; flow rate, 0.3 ml/min; column temperature, 60°C. MW, molecular weight



corresponding peaks to the major peaks of RID cannot be seen in the PDA, the depolymerization of wood components under inactive gas in Fig. 5 is thought to be caused mainly by the depolymerization of polysaccharides. On the other hand, the samples treated under active gases show peaks below 180 in MW. Lignin-derived compounds and the degradation compounds of cellulose and hemicelluloses could possibly exist in those low-MW compounds. The peak for those low-MW compounds in $O_2 + H_2O$ is much larger than that in O_2 , indicating that humidity influences the depolymerization of wood components under active gases.

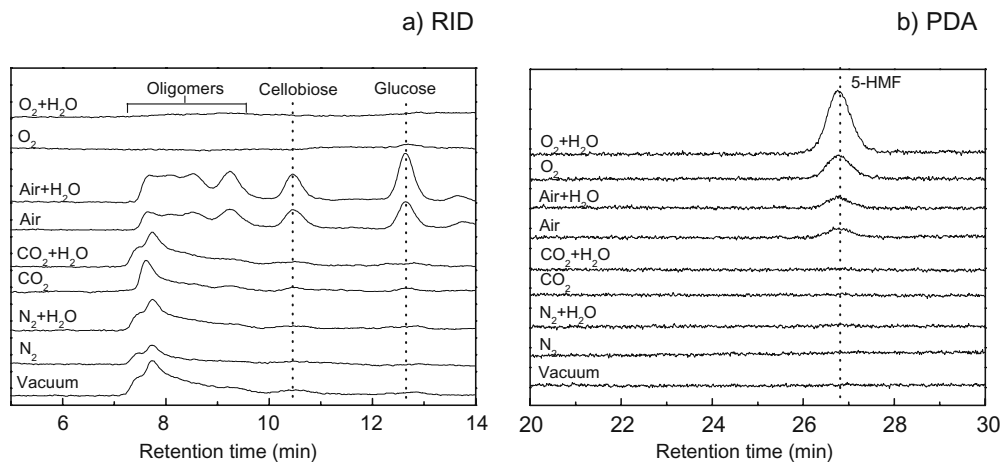
There is no gas or humidity under vacuum. However, in such a reaction condition, it is found that the MW of wood components solubilized in [C2mim][Cl] decreases as the treatment time is prolonged. These results indicate that [C2mim][Cl] itself has the ability to depolymerize the wood components. Additionally, this depolymerization by [C2mim][Cl] can be accelerated with O_2 and humidity in the reaction atmosphere.

For further investigation of the low-MW compounds observed in Fig. 5, HPLC analyses were carried out. Figure 6 shows the chromatograms by RID and PDA, respectively. In Fig. 6a, samples treated both under air + H_2O and under air show peaks at around 10.5 and 12.5 min in retention time, which correspond to cellobiose and glucose, respectively. The complex peaks observed between 7.5 and 9.5 min in retention time are thought to be oligomers. The samples

treated under inactive gases are degraded to oligomers and those treated under air + H_2O and air are degraded to glucose. Those under $O_2 + H_2O$ and O_2 , which show no clear peaks in Fig. 6a, do show large peaks at 27 min retention time in PDA in Fig. 6b. This peak corresponds to 5-hydroxymethyl furfural (5-HMF). This result implies that the samples treated under $O_2 + H_2O$ and O_2 are degraded to monosugars such as glucose first, after which these monosugars are degraded into lower MW compounds such as 5-HMF. These results coincide with the results in Fig. 5b. Ogata et al. reported that glucose oxidatively decomposes to 5-HMF in aqueous solution by heating a glucose solution at 100°C under oxygen atmosphere.²⁴ However, the solvent is different from our experiment. It is not certain that the role of oxygen in the mechanism for the decomposition of glucose to 5-HMF is the same in each reaction system.

Consequently, it is clarified that reaction atmosphere influences the liquefaction of wood with [C2mim][Cl]. Although the presence of O_2 in the reaction atmosphere accelerates the liquefaction of wood, humidity does not affect this process significantly. Also, the depolymerization of wood components liquefied in [C2mim][Cl] is also understood to be influenced by the reaction atmosphere. The presence of O_2 and humidity enhances the depolymerization. We conclude that the reaction atmosphere is an important factor for the liquefaction of wood with [C2mim][Cl].

Fig. 6. High performance liquid chromatography (HPLC) chromatograms of the solubilized compounds in [C2mim][Cl] obtained by 24-h treatment under various reaction atmospheres: **a** refractive index detector (RID); **b** photodiode array detector (PDA). Column, HPX-87P; eluent, distilled water; flow rate, 0.6 ml/min; column temperature, 85°C



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