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REVIEW ARTICLE

Application of ionic liquids for effective use of woody biomass

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Abstract Ionic liquids are salts that have melting points around ambient temperature and unique characteristics, such as high solubility, extremely low volatility, incombustibility and low viscosity. Application of ionic liquids in wood processing technology has attracted attention and is expected to promote further use of wood. They are effective as wood-preserving agents to enhance decay-resistance and also improve fire resistance of wood. Ionic liquids have been used as reaction solvents for preparing various cellulose derivatives or composites with other materials. Attempts have been made to use ionic liquids in pretreatments for enzymatic hydrolysis when producing bio-ethanol from cellulose or wood. Ionic liquids also have been shown to be effective for dissolution of cellulose or wood, forming the basis for studies into the separation of cellulose, hemicellulose and lignin from wood. The effective separation of these components is essential for chemical use of wood, and ionic liquid treatment thus has potential as an enabling technique in biorefineries. Moreover, ionic liquids induce depolymerization of solubilized wood polymers, which may be applicable to the production of useful chemicals from wood polymers such as cellulose, hemicellulose and lignin.

Keywords Ionic liquid · Woody biomass · Cellulose · Preservation · Biorefinery

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Introduction

While global environmental problems such as global warming and depletion of energy resources have become increasingly serious, the use of biomass resources that are carbon-neutral, sustainable and cause smaller environmental burdens is expected to offer ways to resolve such problems. It is considered critical to promote the use of a woody biomass resource that is abundant, non-edible and does not compete with land use for growing foods to provide post-fossil resources and realize a low-carbon society. Thus, this paper aims to introduce recent research and developments in ionic liquid treatment technology, which is new and expected to promote the use of woody biomass.

Woody biomass is a material that has been available to humankind since ancient times; we also use it in various ways today. Methods of its use can be roughly classified into three categories: (1) material use, (2) chemical use, and (3) thermal use. Material use refers to methods that use woody biomass as a material by changing its size for usability by physical machining. Chemical use aims to use the cellulose, hemicellulose and lignin components of woody biomass and the wide variety of useful chemicals that can be obtained from them by performing certain chemical or biochemical treatments. Thermal use uses woody biomass as a fuel through combustion. Ionic liquid treatment has attracted attention as a new technology related to both material and chemical use.

What is an ionic liquid?

An ionic liquid is a salt that has a melting point near normal temperature (below approximately 100 °C) and has unique characteristics such as excellent solubility, extremely low volatility, incombustibility and low viscosity. Application of ionic liquids has advanced in various fields and, in particular, they come under the spotlight as favorable solvents in terms of green chemistry, with low environmental impact, in the context of using them as chemical reaction solvents because they can be recycled for repeated use [1]. However, effective purification process is indispensable for actual recycling of them. The first important characteristic of ionic liquids to be identified from the perspective of applying it to using woody biomass is that it can dissolve cellulose, which is the most abundant organic resource on earth and is contained in woody biomass. Figure 1 shows the structural formula of 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), as an example of an ionic liquid that is capable of dissolving cellulose, and Fig. 2 shows typical cations and anions for ionic liquids. Because ionic liquids are salts, as described above, they provide numerous combinations of anions and cations; it is therefore possible to prepare a variety of ionic liquids that vary in physical properties such as a melting point, viscosity, and polarity by varying such combinations.

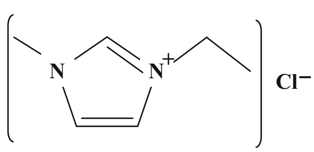
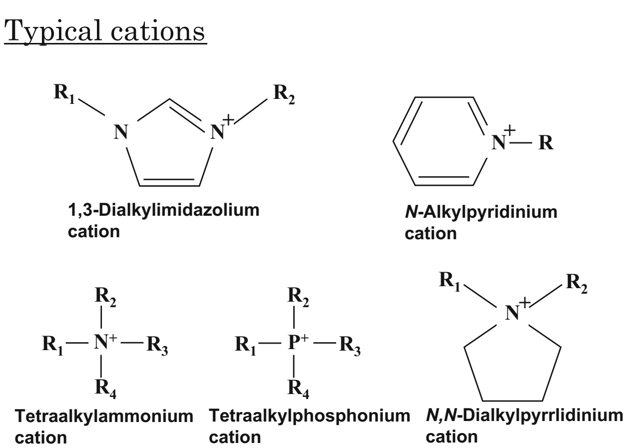


Fig. 1 1-Ethyl-3-methylimidazolium chloride ([C2mim][Cl])



Typical anions

Cl^-, Br^-, I^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)N^-$, CH_3COO^-, $HCOO^-$

Fig. 2 Typical ionic liquid cations and anions

Ionic liquid treatment technology for woody biomass

Application in material use

In the use of woody biomass as construction materials, its susceptibilities to decay and combustion have been regarded as defects, so various chemical agents are often used to reduce these. However, ionic liquids have been shown to be effective as wood-preserving agents. The treatment of wooden materials with the ionic liquids dimethyldidecylammmonium D,L-lactate and benzalkonium D,L-lactate has been reported to result in unsatisfactory decay-resistant performances against *Coniophora puteana*, which belongs to brown-rot fungi, and *Trametes versicolor*, which belongs to white-rot fungi [2]. However, an agar medium test demonstrated that both 1-methyl-3-octyloxymethylimidazolium tetrafluoroborates and 1-methyl-3-nonyloxymethylimidazolium tetrafluoroborates exhibit the same decay-resistant performances as commercially available chemical agents [3]. Moreover, as a result of examining the decay-resistance of wood treated with various ionic liquids containing pyridinium cations, 1-decyloxymethyl-4-dimethylaminopyridinium chloride and 1-decyloxymethyl-4-dimethylaminopyridinium acesulfamate were reported to confer satisfactory decay-resistance [4].

Figure 3 shows the result of an experiment comparing the combustion of wood treated with ionic liquids, obtained by impregnating samples with the ionic liquid, 1-ethyl-3-methylimidazolium hexafluorophosphate. The left side shows untreated wood and the right side shows wood treated with ionic liquids; both are shown approximately 5 s after exposure to flames at their centers. The untreated wood was almost entirely burned, whereas that treated with ionic liquid was burned only at the portion directly contacting the fire, and flames did not spread. This demonstrates that ionic liquids are effective anti-combustion agents for wood [5].

Fig. 3 Fire-resistance test on wood treated with ionic liquid (*right*) compared with untreated wood (*left*)

These findings imply that ionic liquid treatment can improve the performance of wood and enhance its function. Further research and development is expected to yield a novel wood treatment technology that enables the use of wood at locations where it is not currently feasible because of its decay and flammability properties, leading to the prevention and mitigation of disasters in houses and various buildings.

Application in chemical use

Dissolution and component separation

Fundamental research has advanced in dissolution of cellulose and wood in ionic liquids since it was reported by Swatloski et al. [6] that a certain type of ionic liquid dissolves cellulose. It should be noted that many research reports related to ionic liquid treatment technologies have used two terms, i.e., "Dissolution" and "Liquefaction", both of which refer to the phenomena whereby solid cellulose or wood samples become invisible in ionic liquids; thus, this paper uses these terms interchangeably.

With regard to an ionic liquid that is capable of dissolving cellulose, ionic liquids that possess imidazolium cations, shown in Fig. 1, have often been used in research. However, it has recently been reported that various kinds of ionic liquids having different structures from this can also dissolve cellulose; furthermore, numerous findings have been reported regarding the effects of cation and anion structures on cellulose solubility and the relationship between conditions such as temperature or heating time and the solubility of cellulose [7–12]. Nuclear magnetic resonance (NMR) analysis [13–15] and analyses using molecular dynamics simulations [16–18] have been conducted on dissolution mechanisms, which have reported that dissolution progresses when ionic liquids dissociate the intramolecular and intermolecular hydrogen bonds of cellulose and generate interactions with its hydroxyl groups [19]. Additionally, it has been posited that the anions in ionic liquid molecules have a significant effect on the solubility of cellulose [20]. Is has also been reported that carbon–carbon bonds are formed as a result of reactions between imidazolium cations in the ionic liquid and the hydroxyl groups at the C2 position of the reducing ends in cellulose [21].

An examination of the reactivity of each type of ionic liquid with wood, focusing mainly on the ionic liquid having the ability to dissolve cellulose showed that the selection of adequate reaction conditions ensures the complete liquefaction of all components, including lignin, hemicellulose, and cellulose, irrespective of whether hardwood or softwood used [22–27]. However, cellulose and hemicellulose are easier to liquefy than lignin [28–30].

Figure 4 shows an example of fluctuations in the residue rate, as well as changes in the total amounts of cellulose and hemicellulose within a residue and the amount of lignin when treating beech wood at 120 °C using [C2mim][Cl]. It was found that the residue decreases, and that lignin, cellulose and hemicellulose decrease with increasing treatment time. Moreover, there have been studies aimed at separating cellulose, hemicellulose, and lignin from woody biomass, leveraging this property [31, 32]. The cellulose and hemicellulose that comprise woody biomass are types of polysaccharide, and their chemical structures and characteristics differ greatly from lignin, which is a type of aromatic polymer. Therefore, effective separation of these components is essential for their chemical use and ionic liquid treatment offers the potential for use as a fundamental technique in biorefineries. This is a highly likely and anticipated application of ionic liquids.

Effects at the cellular level have also been examined to evaluate reactions between wood and ionic liquids. It has been demonstrated that when [C2mim][Cl] is used to treat Japanese cedar, separation and destruction of wood cells occur selectively in latewood, and that cellulose within wood is amorphized while maintaining the tissue structure of wood [33, 34]. This behavior is attributable to the significant swelling that occurs after an ionic liquid treatment has been performed; this swelling is caused by the presence of thicker tracheid cell walls in latewood compared with those in earlywood. However, in cases where hardwood samples such as beech wood, were similarly treated, destruction similar to those observed in Japanese cedar were not observed, although the swelling behaviors of vessels and wood fibers were found to differ from one another [35, 36]. Additionally, in cases where 1-ethyl-3-methylimidazolium acetate [C2mim][Ac] was used, similar changes were observed in the wood samples [37]. Moreover, when Japanese cedar was treated with [C2mim][Cl],

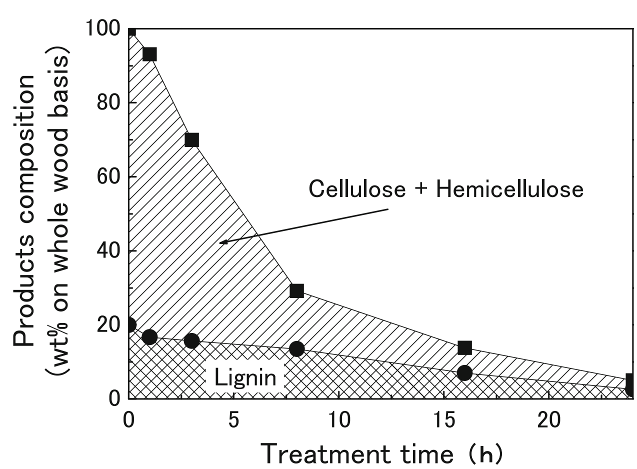


Fig. 4 Product composition of beech wood treated with [C2mim][Cl] at 120 °C [24]

topochemical evaluations based on Raman microscopy clarified that although cellulose and hemicellulose in wood cells could be relatively uniformly dissolved, lignin in the cell walls was dissolved first and the lignin in the compound middle lamellae and cell corners was stabilized and remained as a residue [38]. Raman microscopy has also been used to observe changes in the wood cells of a poplar tree after treatment with [C2mim][Ac] [39].

Derivatization and preparation of composites

Apart from the basic studies related to dissolution described above, there have been studies related to chemical processing, aimed at advanced applications of cellulose materials. There have also been reports on the use of ionic liquids as reaction solvents to prepare various derivatives such as cellulose acetate and cellulose succinate [40–48] or various composites of cellulose with different types of materials such as TiO_2 and wool [49–53]. Additionally, some studies attempted to derivatize wood or compound wood with other materials after liquefaction in an ionic liquid. The octanoylation [54], acetylation [55], benzoylation [55], and carbanilation [55] of wood that was completely liquefied were performed in 1-butyl-3-methylimidazolium chloride, whereas other studies produced composites with polystyrene, as well as products of lauroylation and benzylation treatments of samples [56]. In these studies, although the effects of various reaction conditions were examined, it was inferred that uniform materials were obtained through short reactions in the cases of both cellulose and wood, which represents an excellent reaction system compared with other, previously investigated reaction solvents, because they were derivatized or combined with other materials in a homogeneous dissolution system.

Pretreatment for bio-ethanol production

Attempts have been made at using ionic liquids in pretreatments before enzymatic hydrolysis to produce bioethanol from cellulose, on the premise that the amorphization of cellulose is possible when the treatment is performed using ionic liquids that are capable of solubilizing cellulose. After cellulose is dissolved in an ionic liquid, water is added as a poor solvent for cellulose (referred to as an "anti-solvent" technique) and cellulose collected as a precipitate. It was apparent that the glucose yield could be improved by markedly increasing the reactivity of enzymes such as cellulase towards the obtained amorphous cellulose [57–59]. It was also apparent that the rate of glucose generation could be increased by applying cellulase to wood components that were precipitated from ionic liquids through water addition after ionic liquid treatment [60–69]. Additionally, it has been shown that cellulase retains its catalytic activity in an ionic liquid–water mixture system, whereas it is not functional in pure ionic liquids that are capable of dissolving cellulose [70–73]. Other studies have been conducted on the separation of glucose obtained after enzymatic hydrolysis using ionic liquids and enzymes [74, 75].

Depolymerization and conversion to useful chemicals

When ionic liquid treatments are performed over short periods of time, ionic liquids can function as solvents not only for cellulose but also for hemicellulose and lignin. However, long-period treatments induce depolymerization of the solubilized polymers within the ionic liquid. Currently, studies are actively being conducted on ionic liquid treatment techniques for producing useful chemicals from cellulose or wood using the afore-mentioned properties.

Figure 5 shows the results of gel permeation chromatography analysis of solubilized wood components from ionic liquids after treatment of wood by [C2mim][Cl]. Results obtained using a refractive index detector (RID), showed that low-molecular-weight compounds were formed with increasing treatment time, although during the initial stages of the reaction, some components exhibiting relatively large molecular weights were observed. A peak was observed around the molecular weight of 180 Da after a 24-h treatment, indicating that depolymerization progresses to the monomer level. Additionally, although compounds that absorb ultraviolet light were detected using a photodiode array (PDA) detector, large peaks appeared at molecular weights of 180 Da or less, from which it is believed that degradation compounds of sugars such as 5-hydroxymethylfurfural (5-HMF) or low-molecular-weight compounds from lignin were contained in the ionic liquids [24]. Additionally, depolymerization has been confirmed to be accelerated under environments with high concentrations of water and oxygen [76]. In contrast, reactions using 1-ethylpyridinium bromide were found to undergo less progressive depolymerization compared with the reaction using [C2mim][Cl] [77].

By analyzing the solubilized compounds in [C2mim][Cl] after treating western red cedar and beech wood at 120 °C, the amount of sugars such as glucose, xylose, mannose, galactose, and arabinose was confirmed to increase with increasing reaction time [29]. Conventional chemical conversion techniques such as acid hydrolysis or hot-compressed water treatment require the use of acid catalysts or a high-temperature (200 °C) treatment, whereas new chemical conversion techniques using ionic liquids can convert cellulose or woody biomass to various useful chemicals without catalysts, at relatively low temperatures (120 °C).

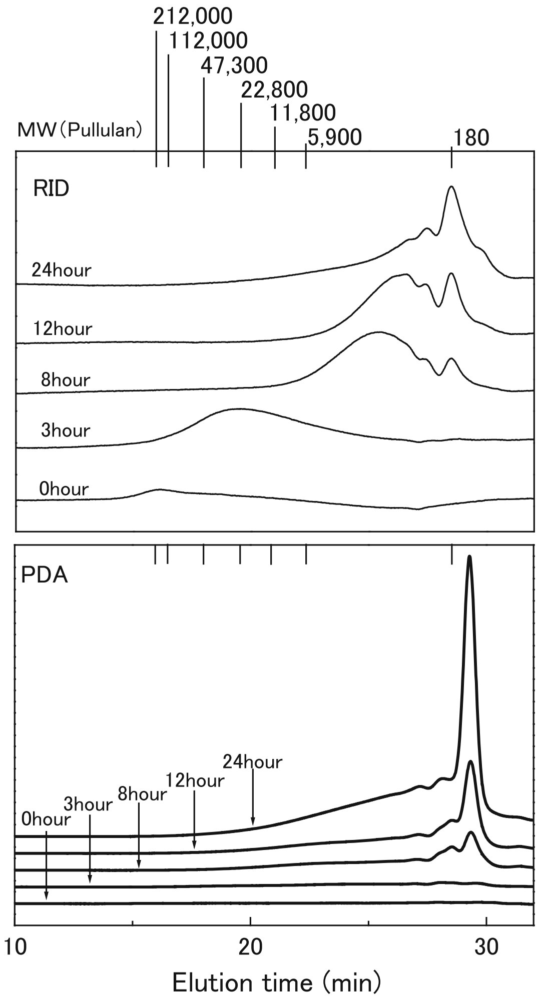


Fig. 5 Gel-permeation chromatograms for compounds produced from beech wood solubilized in [C2mim][Cl] at 120 °C at various treatment times [24]. *RID* refractive index detector, *PDA* photodiode array

More detailed investigations on the reaction of cellulose in ionic liquids have been carried out. Cellulose that undergoes heat processing at 120 °C in the presence of [C2mim][Cl] can be converted into useful chemicals such as glucose, cellobiosan, 5-HMF and levoglucosan via cellobiose and cello-oligosaccharide through reaction pathways that produce anhydrosugars and hydrolysis with water, which is produced by degradation of cellulose or is present in the reaction environment. These various compounds are further decomposed and low-molecular-weight compounds produced then react to form new kinds of polymers that are completely different from cellulose. In such processes, the [C2mim][Cl] moiety is incorporated into the polymers [78, 79]. In addition, during these reactions, inversion of a portion of glucose occurs, to produce various disaccharides such as maltose, nigerose, kojibiose, laminaribiose, isomaltose, and gentiobiose [80]. [C2mim][Cl] is an interesting reaction solvent that induces two different types of reactions (depolymerization of cellulose and the formation of new polymers). Furthermore, although the same types of reaction are thought to occur with cellulose in ionic liquids with the pyridinium cation as those observed to occur in [C2mim][Cl], the reaction rate is faster in cases where the anions are Cl^- compared with Br^- [81].

Some researchers have claimed that lignin that has been extracted from wood using [C2mim][Ac] can be degraded by treatment with [C2mim][Cl] [82]. Depolymerization mechanisms of lignin in ionic liquids are gradually being elucidated through detailed experiments with various types of lignin model compounds [83–85].

The literature contains reports regarding the treatment of cellulose in ionic liquids with acid catalysts to promote depolymerization and produce useful chemicals [86]; other research is related to the kinetics of cellulose depolymerization using an acid catalyst [87]. Researchers have reported the ability to obtain 5-HMF and glucose by rapid hydrolysis of cellulose dissolved in an ionic liquid at 100 °C, using acid catalysts such as sulfuric acid or hydrochloric acid [88–91]. Other researchers have mentioned production of various types of sugars, such as glucose and xylose, by performing acid hydrolysis of wood in ionic liquids containing various acid catalysts such as sulfuric, hydrochloric or trifluoroacetic acid [92–94]. It was also found that 5-HMF and furfural, which are decomposition products of sugars promising raw materials for polymer production, can be obtained during such hydrolysis reactions. Other research describes the production of these furan compounds from wood using various catalysts such as chromium oxide [95–97]. Furthermore, some researchers have reported the hydrolysis of cellulose in ionic liquids using solid acids [98, 99]. The aim of this research was to improve the reactivity of wood by creating homogenous reaction systems through its liquefaction with ionic liquids.

It is reported that various compounds can be produced by various reaction system with ionic liquids as described above. However, those products are difficult to recover from ionic liquids. Separation or recovery of such products derived from woody biomass is thought to be an important future research subject for the practical application.

Summary

Because ionic liquids are currently expensive, it will be necessary to recycle them for repeated use or establish simple treatment processes to push the technology introduced in this article towards practical implementation. In addition, there are numerous types of ionic liquids whose basic reactions with cellulose or wood remain unclear. On the basis of the mechanisms identified so far, it is apparent that ionic liquids possess the potential to offer unique technologies for the use of woody biomass that distinctly differ from previous technologies. I hope that this article will provide hints for research and development directions, which will help promote use of wood.

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