

Decomposition of cellulose in an ionic liquid, 1-ethyl-3-methylimidazolium chloride

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Abstract We investigated the decomposition of cellulose upon heating in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), in air and we studied the reactions of various cellulose decomposition compounds such as cellobiose, cellobiosan, glucose and levoglucosan. We propose two possible decomposition pathways for cellulose during [C2mim][Cl] treatment in air. One pathway is the hydrolysis of cellulose to cellobiose and glucose because [C2mim][Cl] can retain water even at higher than 100 °C, the boiling point of water. The other pathway is the depolymerization of cellulose to cellobiosan by a reaction of the hydroxy group at the C6 position in the glucose residue to form a glycosidic bond. The obtained cellobiosan is then depolymerized to two molecules of levoglucosan by a similar reaction of the hydroxy group at the C6 position. The levoglucosan produced is further hydrolyzed to glucose. Therefore, several products from cellulose decomposition are converted to glucose, which is the final hydrolyzed product. Furthermore, the obtained glucose can be further dehydrated to 5-HMF.

Keywords Cellulose · Ionic liquid · 1-Ethyl-3-methylimidazolium chloride · Decomposition reaction

Introduction

Recently, several energy and environmental problems from the use of fossil resources have been identified. To solve

these problems and establish a sustainable society based on renewable resources, the efficient use of biomass is required.

Among the various types of biomass, lignocellulosics such as wood account for more than 90 % of the biomass in the world. Lignocellulosics are renewable and do not compete with food resources. To produce various useful materials from lignocellulosics, methods such as acid hydrolysis [1], enzymatic saccharification [2], pyrolysis [3, 4] and supercritical fluid treatment [5] have been studied. These methods, however, require severe conditions for treatment such as high temperatures and high pressures.

Recently, much attention has been given to treatment using ionic liquids as an attractive novel technology for the conversion of lignocellulosics. Ionic liquids are organic salts with low melting points around ambient temperatures [6] and they are electrochemically stable [7]. They are only composed of cations and anions. By the modification of these cations and/or anions, a wide range of potential ionic liquids can be tailored to display a wide variety of solvent properties. Furthermore, ionic liquids are regarded as “green solvents” because of their negligible vapor pressure, non-flammability and recyclability.

Cellulose is the main component of wood and its solubility in various solvent systems has been investigated [8–11]. Recently, it has been revealed that some ionic liquids can dissolve cellulose [12]. They are expected as green solvent because of their many unique characteristics, such as negligible vapor pressure, thermal stability, reusability, and non-flammability.

Many fundamental and applied studies have focused on various ionic liquid treatments of cellulose for chemical conversion since Swatloski et al. [12] revealed that imidazolium-based ionic liquids can dissolve cellulose. Ionic liquids comprising imidazolium cations and chloride or

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acetate anions are often used in cellulose research. Vitz et al. [13] reported that cellulose dissolves in 1-butyl-3-methylimidazolium chloride ([C4mim][Cl]) and 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), but that [C4mim][Cl] gives a higher degree of cellulose degradation than [C2mim][Cl]. The influence of water on the dissolution of cellulose in 1-ethyl-3-methylimidazolium acetate ([C2mim][Ac]) was analyzed by Le et al. [14]. They reported that cellulose does not completely dissolve in [C2mim][Ac], if it contains more than 15 wt% water. The dissolution of cellulose is greatly affected by the source of cellulose [15], the water content [16], the series of ionic liquids used [17–19] and other conditions such as the heating method and the temperature. The dissolution mechanism of cellulose in ionic liquids has been partly determined. NMR analysis suggests that the solubilization of cellulose in ionic liquids is mainly caused by hydrogen bonding between the hydroxyl groups of cellulose and the chloride or acetate anions and very little interaction exists with the imidazolium cations [20–22]. These interactions were also investigated by molecular dynamics simulations [23, 24].

Cellulose solubilized in [C4mim][Cl] or [C2mim][Ac] can be recovered as amorphous cellulose by the addition of anti-solvents for cellulose (such as water) [25, 26]. These regenerated celluloses show enhanced activity during enzymatic hydrolysis by cellulase, compared with native cellulose [26, 27]. Regenerated cellulose can be obtained as films and these films contain crystals of cellulose II, which are different from native cellulose [28, 29]. Nitrogen is not detected in dried films obtained from 1-allyl-3-methylimidazolium chloride [30] and [C2mim][Cl] [31] upon the addition of distilled water.

Ionic liquids have also been used as alternative solvents for the derivatization of cellulose such as acetylation [32, 33], carboxymethylation [34], tritylation [17] and succination [35], since conventional organic solvents have limitations because of volatility, toxicity and difficulties of recovery. In addition, much work has been done to determine the most efficient reaction conditions for cellulosic conversion to 5-hydroxymethylfurfural [36–39] and sorbitol [40] in ionic liquids.

A higher cellulose depolymerization rate during ionic liquid dissolution occurs in [C4mim][Cl] and [C2mim][Cl] compared with [C2mim][Ac] [15]. [C2mim][Cl] can dissolve and decompose cellulose into cellobiose, cellobiosan, glucose, levoglucosan and 5-hydroxymethylfurfural. In addition, [C2mim][Cl] can also react with the compounds produced by cellulose to form new polymers [31]. However, the detailed reaction decomposition behavior of cellulose in ionic liquids remains unclear.

In this study, therefore, the decomposition behavior of cellulose in [C2mim][Cl] was examined in detail by

studying the reaction behavior of low molecular compounds such as cellobiose, cellobiosan, glucose and levoglucosan in [C2mim][Cl]. This fundamental information is crucial in understanding the reaction behavior of wood polysaccharides and applying ionic liquids to the effective use of wood.

Materials and methods

Samples and chemicals

Cellobiose, glucose, levoglucosan and 5-hydroxymethylfurfural (5-HMF) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Cellobiosan was purchased from Carbosynth Ltd., Berkshire, UK. All compounds were dried in an oven at 105 °C for 24 h before use. Water-¹⁸O as stable isotopes (SI) (purity 99.99 %) was purchased from Taiyo Nippon Sanso, Tokyo, Japan. The ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan.

Treatment with [C2mim][Cl]

The 3 g of [C2mim][Cl] was heated at 100 °C in a 100-ml glass flask. The reaction atmosphere in the flask was controlled by vacuum, nitrogen (N₂) flow or air flow. After melting the [C2mim][Cl], 0.09 g of cellobiose, cellobiosan, glucose and levoglucosan were added to the flask and the reaction media were gently stirred. The point where the reaction media became transparent without any particles in the flask was defined by 0 h of treatment. It took several minutes before the reaction media became transparent at 100 °C.

Evaluation methods

Fourier transform infrared (FT-IR) spectra of [C2mim][Cl] were recorded using an IRAffinity-1 spectrophotometer (Shimadzu, Kyoto, Japan), over a spectral range of 4000–400 cm⁻¹ with 32 accumulations. A GladiATR Vision Diamond Crystal Plate (ST Japan INC.) was used as a stage heater. Dry nitrogen (N₂) gas was directed to flow to the sample stage. In case of making N₂ gas humidify, the humidity was contained in N₂ gas flow by having it pass through distilled water in midflow. The temperature program was 20 °C/min from 37.5 to 120 °C.

To determine the influence of water on the reaction of cellulose in [C2mim][Cl], a Shimadzu GCMS-QP2010 ultra gas chromatography–mass spectrometer (GC–MS) was used. The samples for GC–MS analysis were prepared as follows: 20 µl of the reaction media were

homogeneously mixed with 240 μl of acetonitrile. After drying with sodium sulfate, the obtained mixture was filtered using a 0.45- μm filter. The 120 μl of the filtrate was silylated at room temperature using 60 μl of BSTFA mixed with 10 μl pyridine. The obtained silylated samples were analyzed by GC–MS. The capillary column was a ULBON HR-52 (diameter 0.25 mm) from Shinwa Chemical Industries Ltd., Kyoto, Japan. The temperature program was 60 $^{\circ}\text{C}$ (0 \rightarrow 1 min), 60 \rightarrow 230 $^{\circ}\text{C}$ (1 \rightarrow 21 min) and 230 $^{\circ}\text{C}$ (21 \rightarrow 50 min). Helium was used as a carrier gas at a flow rate of 1.0 ml/min. The injector and detector temperatures were 250 and 230 $^{\circ}\text{C}$, respectively.

The compounds solubilized in [C2mim][Cl] were analyzed by high performance liquid chromatography (HPLC). HPLC was carried out on a Shimadzu Prominence, equipped with pump (LC-20AD), column oven (CTO-20A) and refractive index detector (RID-10A). The samples for this analysis were prepared as follows: at a specific reaction time, 20 μl reaction medium was homogeneously mixed with 180 μl distilled water and then filtered through a 0.45- μm filter. The filtrates were analyzed as follows: column, Shodex Sugar KS-801 (SHOWA DENKO, Tokyo, Japan); flow rate, 1 ml/min; eluent, distilled water; detector, refractive index detector (RID); column temperature, 80 $^{\circ}\text{C}$.

Results and discussion

Water in [C2mim][Cl]

In our previous work [31], we found that the hydrolysis of cellulose occurred in [C2mim][Cl] at 100–140 $^{\circ}\text{C}$, which is higher than the boiling point of water, and we identified various hydrolyzed products of cellulose such as cellooligosaccharides, cellobiose and glucose. Thus, the presence of water in [C2mim][Cl] was studied under various conditions.

Figure 1 shows the infrared spectra for [C2mim][Cl] under various conditions. The atmospheric and temperature conditions were changed as shown in Fig. 1a. The temperature program was 37.5 \rightarrow 120 $^{\circ}\text{C}$ (0 \rightarrow 5 min) and 120 $^{\circ}\text{C}$ (5 \rightarrow 35 min). The atmosphere consisting of humidified nitrogen (0 \rightarrow 15 min) is indicated as “N₂ + H₂O”, and dry nitrogen (15 \rightarrow 25 min) is indicated as “N₂” followed by humidified nitrogen (25 \rightarrow 35 min). The IR spectra were recorded under various conditions as indicated by (1), (2), (3) and (4). The spectra measured under N₂ + H₂O at 37.5 $^{\circ}\text{C}$ (condition (1)) show a water peak at 3400 cm^{-1} , as shown in Fig. 1b. The obvious peak at 3400 cm^{-1} is present despite heating at 120 $^{\circ}\text{C}$ under N₂ + H₂O (condition (2)). This result reveals that the water in [C2mim][Cl] under N₂ + H₂O remains even at

120 $^{\circ}\text{C}$, which is higher than the boiling point of water. The spectrum obtained for condition (3) does not show a peak at 3400 cm^{-1} . Therefore, under dry N₂ [C2mim][Cl] the water in [C2mim][Cl] can be evaporated. Although noise peaks over 3400 cm^{-1} can be seen, it is not clear why these peaks appeared. For N₂ + H₂O (condition (4)), the peak at 3400 cm^{-1} is present. These results indicate that [C2mim][Cl] can absorb moisture from the reaction atmosphere and retain it, even at 120 $^{\circ}\text{C}$, which is higher than the boiling point of water.

Influence of water on hydrolysis in [C2mim][Cl]

To study the influence of the water absorbed by [C2mim][Cl] from the atmosphere on hydrolysis by [C2mim][Cl], cellobiose was treated in [C2mim][Cl] at 100 or 120 $^{\circ}\text{C}$ with the experimental apparatus shown in Fig. 2. N₂ was directed into a flask containing water-¹⁸O, and then humidified N₂ gas (N₂ + water-¹⁸O) was flowed into the reaction flask that contained [C2mim][Cl] and cellobiose to fill the reaction atmosphere with N₂ + water-¹⁸O. After treatment at 100 or 120 $^{\circ}\text{C}$, the glucose produced from cellobiose was analyzed by HPLC and GC–MS. Under this reaction, cellobiose is hydrolyzed to produce two molecules of glucose. Water is used for cleavage of glycosidic bond in cellobiose, and ¹⁸O can be included in either glucose produced.

Figure 3 shows the mass spectrum of the trimethylsilyl derivative of the glucose produced from the cellobiose treated in [C2mim][Cl] at 100 $^{\circ}\text{C}$ for 48 h (a) or at 120 $^{\circ}\text{C}$ for 24 h (b) under N₂ + water-¹⁸O flow. This was compared with that produced under humidified N₂ gas flow with normal water (N₂ + water-¹⁶O). In spectrum (c), the characteristic ions are present at m/z 271, 291, 345, 361, 393 and 454. These are typical ions for trimethylsilylated glucose. In spectra (a) and (b), however, not only those ions but also ions at 273, 293, 347, 363, 395 and 456 were detected. The difference in m/z between the former and latter is two, which corresponds to the difference in the molecular weight for water-¹⁸O and water-¹⁶O. Thus, water-¹⁸O in the reaction atmosphere was used for the hydrolysis of cellobiose in [C2mim][Cl]. From the results in Figs. 1 and 3, [C2mim][Cl] absorbs moisture even at higher than 100 $^{\circ}\text{C}$, and this absorbed water can induce hydrolysis in [C2mim][Cl].

Reaction pathway for the production of cellobiosan from cellulose by [C2mim][Cl] treatment

In our previous paper, cellulose was found to decompose into cellobiosan during [C2mim][Cl] treatment [31]. Two reaction pathways are proposed to explain the formation of cellobiosan from cellulose, as shown in Fig. 4. Pathway 1

Fig. 1 FT-IR spectra for [C2mim][Cl] under various conditions. **a** Time program for the temperature and atmospheric conditions, **b** FT-IR spectra

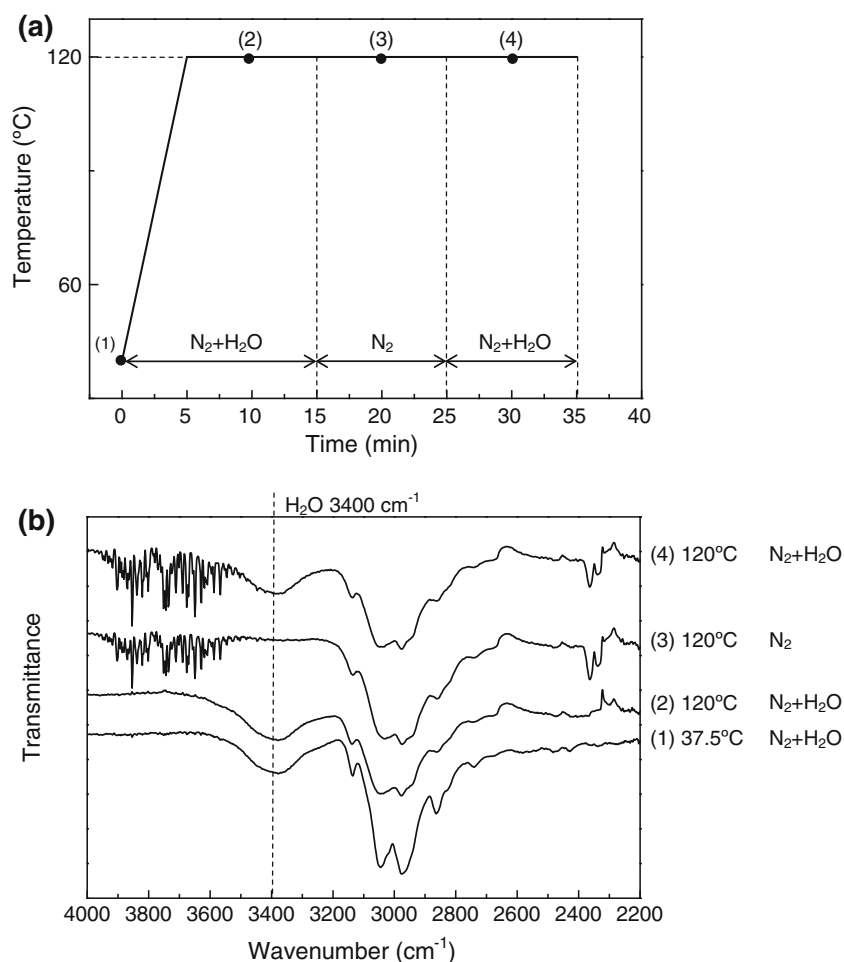
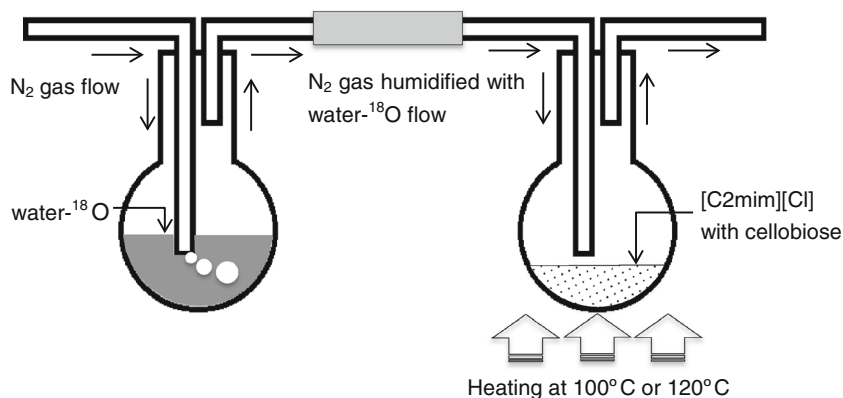


Fig. 2 Diagram showing the experimental apparatus



shows the dehydration of cellobiose, which is produced by the hydrolysis of cellulose. Conversely, pathway 2 shows that cellulose is directly decomposed to cellobiosan. The hydroxy group at the C6 position of the glucose residue interacts with the glycosidic bond and the glycosidic linkages cleave to form cellobiosan.

To confirm pathway 1, as shown in Fig. 4, the reaction behavior of cellobiose during [C2mim][Cl] treatment was

studied. HPLC analyses were performed for the compounds obtained from cellobiose after the treatment of cellobiose at 100 °C under air. Figure 5 shows changes in the yields of the various compounds produced. The yield of cellobiose decreases as the treatment time is extended. In contrast, the yields of glucose, levoglucosan and 5-hydroxymethylfurfural (5-HMF) increase with prolonged treatment time.

Fig. 3 Mass spectrum of the trimethylsilyl derivative of glucose produced from cellobiose treated at 100 °C for 48 h (a) and 120 °C for 24 h (b) under N₂ + water-¹⁸O flow, and compared with that treated at 100 °C for 24 h under N₂ + water-¹⁶O flow (c)

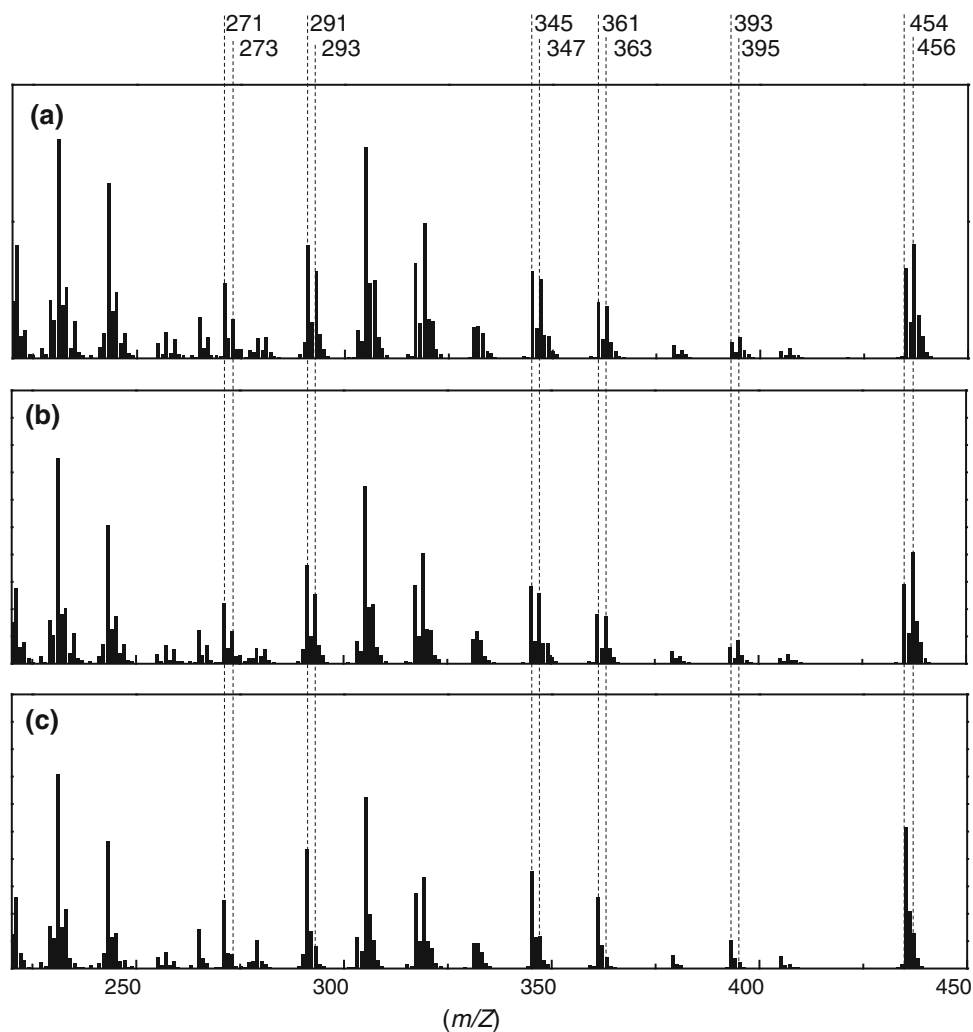
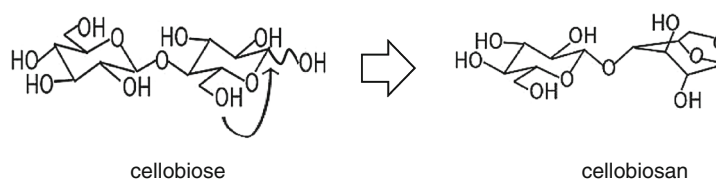
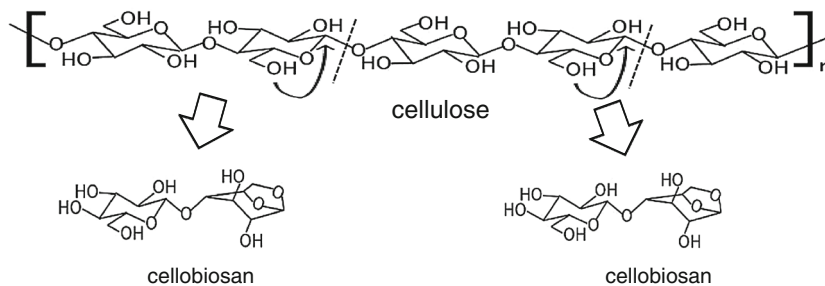


Fig. 4 Possible pathways for the production of cellobiosan from cellulose during [C2mim][Cl] treatment

(Pathway 1)



(Pathway 2)



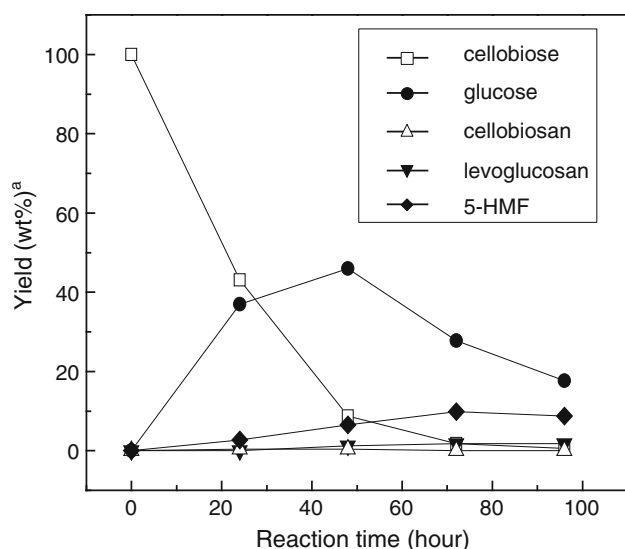


Fig. 5 Changes in the yields of various compounds from cellobiose treated at 100 °C under air. ^a The yield was calculated from the following equation: $\text{Yield (wt\%)} = W_1/W_0 \times 100$, where W_0 is the amount of charged cellobiose, and W_1 is the weight of products

Table 1 Yields of various products from cellobiose treated at 100 °C for 48 h under vacuum or N₂

Material	Products	Yield (wt%) ^a	
		Vacuum	N ₂
Cellobiose	Cellobiose	98.9	23.9
	Cellobiosan	n.d.	n.d.
	Glucose	2.9	63.1
	Levoglucosan	n.d.	n.d.
	5-HMF	n.d.	1.9

n.d. not detected, *5-HMF* 5-hydroxymethylfurfural

^a The yield was calculated from the following equation: $\text{Yield (wt\%)} = W_1/W_0 \times 100$, where W_0 is the amount of charged cellobiose, and W_1 is the weight of products

The yield of cellobiosan was negligible even after 48 h, indicating that cellobiosan cannot be produced through the dehydration of cellobiose as shown in pathway 1, but may be produced through pathway 2. To study the detailed decomposition of cellobiose, the treatment of cellobiose with [C2mim][Cl] was performed under vacuum or N₂ gas flow to create a reaction atmosphere with less humidity.

Table 1 shows the yields of various products from cellobiose. Under vacuum, cellobiose decomposes partially to glucose without dehydrating to cellobiosan despite the lower humidity in the reaction atmosphere. The decomposition of cellobiose under N₂ on the other hand is much faster than that under vacuum. Glucose as well as 5-HMF

Table 2 Yields of various products from cellulose treated at 100 °C for 72 h under various reaction atmospheres

Material	Products	Yield (wt%) ^a		
		Air [31]	Vacuum	N ₂
Cellulose	Cellobiose	17.0	2.2	5.1
	Cellobiosan	2.8	1.1	1.3
	Glucose	39.4	0.7	4.1
	Levoglucosan	2.4	n.d.	n.d.
	5-HMF	3.4	n.d.	0.6

n.d. not detected, *5-HMF* 5-hydroxymethylfurfural

^a The yield was calculated from the following equation: $\text{Yield (wt\%)} = W_1/W_0 \times 100$, where W_0 is the amount of charged cellulose, and W_1 is the weight of products

was quantified as decomposition products of cellobiose. 5-HMF is a dehydration product of glucose indicating that water can be produced in [C2mim][Cl]. Because of the higher yield of glucose under N₂ compared with that under vacuum, the water produced is thought to remain in [C2mim][Cl] as mentioned above and can be used for the hydrolysis of cellobiose to glucose although it can be immediately removed from [C2mim][Cl] under vacuum. It is confirmed that 5-HMF is unstable and disappears during heating in [C2mim][Cl] (data are not shown). This may be why the yield of 5-HMF is much lower than that of glucose.

Reaction behavior of cellulose during [C2mim][Cl] treatment

Table 2 shows the yields of various products from the cellulose treated with [C2mim][Cl] at 100 °C for 72 h under various reaction atmospheres. Cellobiose, cellobiosan, glucose, levoglucosan and 5-HMF are present in [C2mim][Cl]. Cellobiosan was confirmed to be present under all reaction atmospheres, indicating that the reaction proposed as pathway 2 in Fig. 4 occurs under all reaction atmospheres. Under N₂, cellobiose and glucose, which are the hydrolyzed products of cellulose, are produced in higher quantities compared with the reaction under vacuum. As described above, water can be produced during the decomposition of cellobiose. Thus, in the case of cellulose, the water produced during the decomposition of cellulose promotes the hydrolysis of cellulose in [C2mim][Cl]. Under air, water from cellulose and moisture from the air dissolve in [C2mim][Cl], as shown in Fig. 1. The water in [C2mim][Cl] under air is thought to accelerate the hydrolysis of cellulose. Therefore, a higher yield of various products was obtained under air, as listed in Table 2.

Table 3 Yields of various compounds from cellobiosan treated at 100 °C for 48 h under various reaction atmospheres

Material	Products	Yield (wt%) ^a		
		Air	Vacuum	N ₂
Cellobiosan	Cellobiose	3.2	n.d.	3.2
	Cellobiosan	64.0	95.3	76.8
	Glucose	16.3	0.5	6.4
	Levoglucosan	14.8	3.6	12.5
	5-HMF	1.2	n.d.	0.4

n.d.:not detected, *5-HMF* 5-hydroxymethylfurfural

^a The yield was calculated from the following equation: Yield (wt%) = $W_1/W_0 \times 100$, where W_0 is the amount of charged cellobiosan, and W_1 is the weight of products

Reaction behavior of cellobiosan during [C2mim][Cl] treatment

Table 3 shows the yields of various products from cellobiosan treated with [C2mim][Cl] at 100 °C for 48 h under various reaction atmospheres. Under air, where a significant amount of water is present in [C2mim][Cl], cellobiosan decomposes to various products. The yield of glucose is equivalent to that of levoglucosan. This suggests that cellobiosan is hydrolyzed with water in [C2mim][Cl] to form glucose and levoglucosan. Under N₂, where less water is present than under air, the yield of levoglucosan is higher than that of glucose under vacuum. Under vacuum, where only a small amount of water is present, the decomposed products are mainly composed of levoglucosan. The reaction where the glycosidic bond in cellobiosan is cleaved is shown in Fig. 4 and this is thought to occur to form two molecules of levoglucosan from cellobiosan. Because some cellobiose can be obtained from cellobiosan under air or N₂, the hydrolysis of the levoglucosan residue in cellobiosan also occurs as a minor reaction.

Reaction behavior of glucose and levoglucosan during [C2mim][Cl] treatment

Table 4 shows the yields of various products from glucose treated with [C2mim][Cl] at 100 °C for 48 h under various reaction atmospheres. Under air and N₂, the main product from glucose is 5-HMF, but 5-HMF was not detected under vacuum. This decomposition of glucose to 5-HMF was accelerated under air because the yield of glucose is less than that under vacuum or N₂. The dehydration of glucose also occurs to form levoglucosan. The yield of levoglucosan and 5-HMF under air is higher than those under vacuum or N₂. This is due that much glucose decomposed under air compared with under vacuum or N₂. However, the yields of all products under air are low. As described

Table 4 Yields of various compounds from glucose treated at 100 °C for 48 h under various reaction atmospheres

Material	Products	Yield (wt%) ^a		
		Air	Vacuum	N ₂
Glucose	Glucose	11.8	91.6	81.6
	Levoglucosan	2.6	0.7	1.9
	5-HMF	6.3	n.d.	4.7

n.d. not detected, *5-HMF* 5-hydroxymethylfurfural

^a The yield was calculated from the following equation: Yield (wt%) = $W_1/W_0 \times 100$, where W_0 is the amount of charged glucose, and W_1 is the weight of products

Table 5 Yields of various compounds from levoglucosan treated at 100 °C for 48 h under various reaction atmospheres

Material	Products	Yield (wt%) ^a		
		Air	Vacuum	N ₂
Levoglucosan	Glucose	18.5	0.1	4.9
	Levoglucosan	63.4	99.3	92.8
	5-HMF	1.6	n.d.	0.1

n.d. not detected, *5-HMF* 5-hydroxymethylfurfural

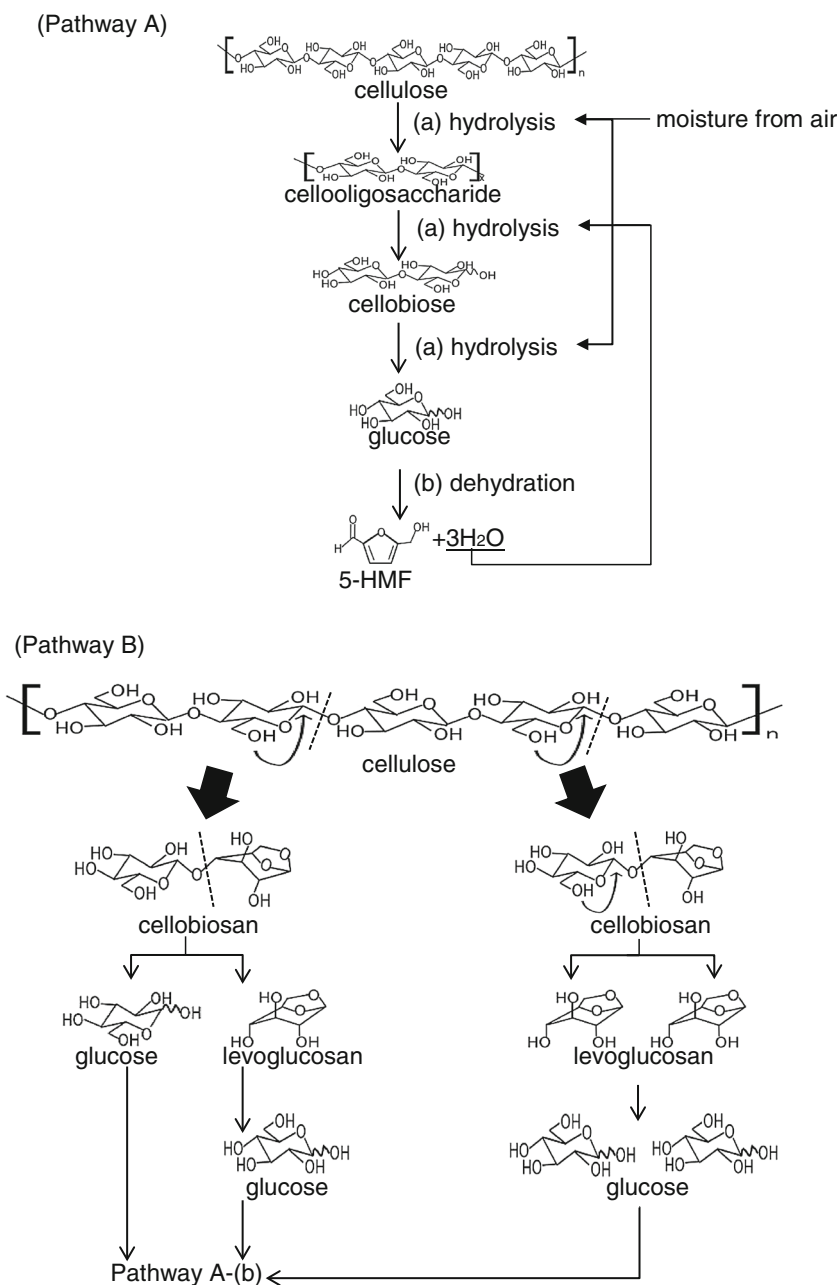
^a The yield was calculated from the following equation: Yield (wt%) = $W_1/W_0 \times 100$, where W_0 is the amount of charged levoglucosan, and W_1 is the weight of products

above, 5-HMF is not stable in [C2mim][Cl]. Thus, produced 5-HMF is thought to be decomposed further during heating in [C2mim][Cl] although the products from 5-HMF are still unknown. Table 5 shows the yields of various products from the levoglucosan treated with [C2mim][Cl] at 100 °C for 48 h under various reaction atmospheres. The main product from levoglucosan is glucose, indicating that the hydrolysis of levoglucosan occurred. However, some levoglucosan remains even after 48 h of treatment under all reaction atmospheres. These results indicate that levoglucosan is more stable in [C2mim][Cl] than glucose. Under air and N₂, 1.6 and 0.1 % 5-HMF were produced from glucose, respectively, because the dehydration of glucose occurred during treatment with [C2mim][Cl].

Decomposition pathway of cellulose in [C2mim][Cl]

Based on the results obtained in this study, two possible decomposition pathways for cellulose during [C2mim][Cl] treatment under air are shown in Fig. 6. The pathways A and B in this figure show not only the decomposition to cellobiosan as in pathways 1 and 2 in Fig. 4 but also whole decomposition pathway of cellulose including the

Fig. 6 Proposed reaction pathway for cellulose in [C2mim][Cl]



decomposition to cellobiosan. In pathway A, cellulose is depolymerized to cellobiosan, cellobiose and glucose upon hydrolysis with the moisture absorbed by [C2mim][Cl] from the air. The obtained glucose is converted to 5-HMF with the production of water. This water further reacts and contributes to the depolymerization of cellulose, cellobiosan and cellobiose. In pathway B, cellulose is depolymerized to cellobiosan by the reaction of the hydroxy group at the C6 position in the glucose residue to give a glycosidic bond. The obtained cellobiosan is depolymerized into two molecules of levoglucosan by a

similar reaction of the hydroxy group at the C6 position. The levoglucosan produced is further hydrolyzed to glucose. As for the other reaction of cellobiosan, it is hydrolyzed to glucose and levoglucosan, which is further hydrolyzed to glucose as mentioned above. The produced glucose is converted to 5-HMF, as shown in pathway A. However, the reaction of the hydroxyl group at the C6 position shown in pathway B is expected to occur randomly in cellulose. Therefore, cellobiosan in addition to several 1,6-anhydro-β-D-cellobiosan such as cellotriosan, cellotetraosan and cellopentaosan must be

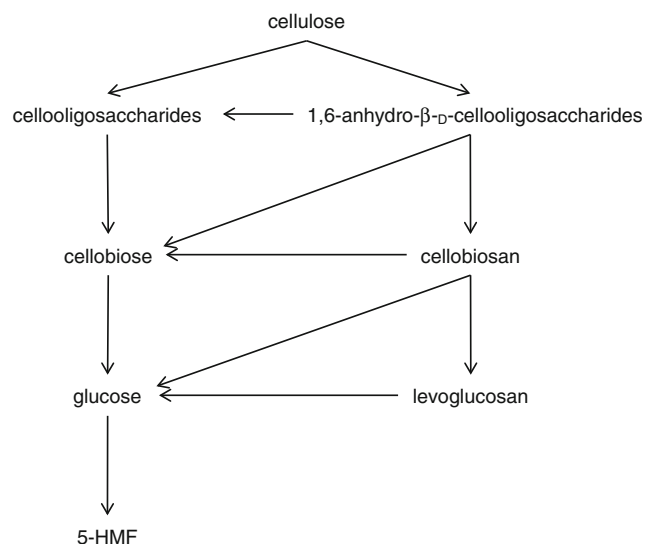


Fig. 7 Proposed decomposition pathway for cellulose in [C2mim][Cl]

produced. Considering these aspects and all results shown above, a decomposition pathway of cellulose in [C2mim][Cl] is proposed as shown in Fig. 7.

Conclusions

The decomposition of cellulose by heating in [C2mim][Cl] under various atmospheres was studied, and a decomposition pathway is proposed. Although a pathway for the production of anhydrosugars exists, hydrolysis is superior because [C2mim][Cl] can retain water, even at higher than 100 °C, the boiling point of water. Several products from cellulose were found to be converted to glucose, which was the final hydrolyzed product. Furthermore, the obtained glucose was further dehydrated to 5-HMF. Consequently, hydrolysis coexists with dehydration during the decomposition of cellulose in [C2mim][Cl] under air. The conclusion in this study implies that water content in the reaction system of [C2mim][Cl] is important to control the reaction of cellulose in [C2mim][Cl]. Under the reaction condition with much water content, the hydrolysis of cellulose can be accelerated to obtain several useful low molecular weight compounds. Under less water content, on the other hand, cellulose can be dissolved in [C2mim][Cl] without decomposition.

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