

Production of 5-hydroxymethylfurfural from wood by ionic liquid treatment

Ryoya Ito¹ · Hisashi Miyafuji¹ · Yuya Miyazaki² · Takuya Kawai²

Received: 15 January 2016 / Accepted: 28 March 2016 / Published online: 19 April 2016
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Abstract 5-Hydroxymethylfurfural (5-HMF) is one of the most important platform intermediates for the future synthesis of liquid transportation biofuel and other valuable compounds. This study aimed to identify ionic liquids that can convert wood into 5-HMF without catalysts. Glucose was converted into 5-HMF without catalysts in ionic liquids that contain sulfonyl groups, such as 1-ethyl-3-methylimidazolium hydrogensulfate ([EMIM]HSO₄) and 1-ethyl-3-methylimidazolium *p*-toluenesulfonate ([EMIM]Tos). However, [EMIM]Tos produced less 5-HMF from cellulose and wood, compared with [EMIM]HSO₄. This is due to the difference of ability to decompose cellulose and wood between these ionic liquids. Consequently, among various ionic liquids studied, [EMIM]HSO₄ achieved the highest yield of 5-HMF from wood and cellulose at 4.5 and 10.2 wt% yields, respectively, after 10 h at 140 °C.

Keywords Japanese cedar · Cellulose · Glucose · 5-Hydroxymethylfurfural · Ionic liquid

Introduction

In recent years, biomass has attracted attention as a raw material for the production of liquid fuels and fine chemicals, because fossil resources are in danger of running out [1]. Crops, such as corn and sugarcane, have been transformed into liquid fuels, such as ethanol. However, the use of edible biomass can lead to soaring prices and global scarcity of food [2]. Thus, the use of inedible biomass, such as wood, should be promoted for the production of liquid fuels and fine chemicals [3, 4]. However, it is difficult to convert wood into such products inexpensively [5]. Among the various chemicals that can be produced from wood, 5-hydroxymethylfurfural (5-HMF) is an important platform intermediate for synthesizing liquid transportation biofuels and other valuable compounds [6–8]. However, 5-HMF is not yet produced on an industrial scale mainly because of its high production cost [9, 10]. To overcome this problem, ionic liquid technology has attracted significant attention.

Ionic liquids are organic salts that are composed of cations and anions that give melting points near ambient temperature. They are thermally stable and have low vapor pressures, low toxicities, and extensive solvation capabilities [11]. Because some ionic liquids can dissolve the major wood components, cellulose, hemicellulose, or lignin, it is suggested that they can be used in biorefineries or chemical processing of wood [12–15]. In particular, their solvation capabilities can be applied to the production of 5-HMF from wood and its components.

Zhao et al. [16] studied reaction systems using the ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), with chromium (II) chloride (CrCl₂) as a catalyst. This system enabled the conversion of glucose into 5-HMF with yields of 70 mol%, and their results have encouraged conversion of disaccharides, cellulose, and lignocellulosics

✉ Hisashi Miyafuji
miyafuji@kpu.ac.jp

¹ Division of Environmental Sciences, Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Hangi-cho, Shimogamo, Sakyo-ku, Kyoto 606-8522, Japan

² Project Planning Group, Project Development Department, Plant Project Center, Energy and Plant Operations, IHI Corporation, Toyosu IHI Building, 1-1, Toyosu 3-chome, Koto-ku, Tokyo 135-8710, Japan

to 5-HMF in ionic liquids [17–22]. These studies suggest that 5-HMF can be produced from lignocellulosics without requiring preprocessing steps, such as delignification and hydrolysis.

In the reports described above, however, production of 5-HMF from biomass in ionic liquids has included the use of catalysts [23]. In such reaction system, production of 5-HMF is mainly due to the catalysts, and ionic liquids are thought to be a solvent. Our previous study revealed that some ionic liquids are multifunctional reagent to dissolve and decompose cellulose. In this study, therefore, we studied the formation of 5-HMF from Japanese cedar (*Cryptomeria japonica*) in various ionic liquids without the use of catalyst to clarify their potential to produce 5-HMF from lignocellulosics. In particular, the reactions of cellulose and glucose were investigated.

Materials and methods

Samples and chemicals

Table 1 lists the ionic liquids that were used in this study. 5-HMF, glucose, fructose, cellobiose, cellotriose, levoglucosan, 1,6-anhydro- β -D-glucofuranose (AGF), acetonitrile, sodium sulfate, and acetic acid were purchased from Wako Pure Chemical Industries (Osaka, Japan). *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and dehydrated dimethyl sulfoxide were purchased from Sigma-Aldrich (St Louis, MO, USA). Sodium chlorite and pyridine were purchased from Kanto Chemicals (Tokyo, Japan). Cellulose sample (Whatman CF1) was dried in an oven at 105 °C for 24 h before use. Wood flours from Japanese cedar (*C. japonica*) (90–180 μ m) were extracted

Table 1 Ionic liquids used in this study

Ionic liquids	Abbreviations	Manuf.
1-Methylimidazolium bis(trifluoromethylsulfonyl)imido	[MIM]NTf ₂	Sigma-Aldrich
1-Ethylimidazolium nitrate	[EIM]NO ₃	IoLiTec
1,3-Dimethylimidazolium dimethyl phosphate	[DMIM]DMP	IoLiTec
1,3-Dimethylimidazolium bis[oxalato(2-)-O,O']borate	[DMIM]BOB	Merck
1-Ethyl-3-methylimidazolium chloride	[EMIM]Cl	TCI
1-Ethyl-3-methylimidazolium hydrogensulfate	[EMIM]HSO ₄	TCI
1-Ethyl-3-methylimidazolium methylphosphate	[EMIM]MPO ₄	Kanto Chemical
1-Ethyl-3-methylimidazolium acetate	[EMIM]Ac	Sigma-Aldrich
1-Ethyl-3-methylimidazolium hexafluorophosphate	[EMIM]PF ₆	TCI
1-Ethyl-3-methylimidazolium tetrachloroaluminate	[EMIM]AlCl ₄	Sigma-Aldrich
1-Ethyl-3-methylimidazolium tetracyanoborate	[EMIM]TCB	Merck
1-Ethyl-3-methylimidazolium <i>p</i> -toluenesulfonate	[EMIM]Tos	TCI
1-Ethyl-3-methylimidazolium methanesulfonate	[EMIM]Mes	IoLiTec
1-Butyl-3-methylimidazolium thiocyanate	[BMIM]SCN	TCI
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM]BF ₄	TCI
1-Butylpyridinium bis(fluorosulfonyl)imido	[BPr]FSI	Kanto Chemical
1-Buthylpyridinium hexafluorophosphate	[BPr]PF ₆	TCI
1-Methyl-1-propylpyrrolidinium hexafluorophosphate	[MPPyr]PF ₆	IoLiTec
1-Methyl-1-propylpiperidinium hexafluorophosphate	[MPPip]PF ₆	IoLiTec
Tetrabutylammonium chloride	[N ₄₄₄₄]Cl	TCI
Tetrabutylammonium bromide	[N ₄₄₄₄]Br	TCI
Tetrabutylammonium dichlorobromide	[N ₄₄₄₄]Cl ₂ Br	TCI
Tetrabutylammonium azide	[N ₄₄₄₄]N ₃	TCI
Tetrabutylammonium salicylate	[N ₄₄₄₄]Sal	TCI
Tributylethylphosphonium diethylphosphate	[P ₄₄₄₂]DEP	IoLiTec
Trihexyltetradecylphosphonium hexafluorophosphate	[P ₁₄₋₆₆₆]PF ₆	IoLiTec
Trihexyltetradecyl decanoate	[P ₁₄₋₆₆₆]Dec	IoLiTec
Choline dihydrogen citrate	[Choline]Cit	TCI
Acetylcholine perchlorate	[Accholine]ClO ₄	TCI
1-Hexyl-1,4-diaza[2,2,2]bicyclooctanium bis(trifluoromethylsulfonyl)imide	[HDABCO]NTf ₂	IoLiTec

Manuf manufacturer, TCI Tokyo Kasei Kogyo

with ethanol/benzene (1/2, v/v) for 24 h in a Soxhlet apparatus. The extractive-free wood flour was oven-dried at 105 °C for 24 h before use.

Treatment with ionic liquids

In a typical experiment, 3 g of ionic liquid was heated at 120 °C. A 0.09 g portion of sample (wood flours, cellulose, cellobiose, and glucose) was then added to the ionic liquid, and the reaction media gently stirred. Zero hour of treatment was defined as the time the sample was added to the ionic liquid.

Evaluation method

The products from samples treated by ionic liquids were analyzed by high-performance liquid chromatography (HPLC). HPLC was carried out on a Shimadzu Prominence (Shimadzu, Kyoto, Japan) equipped with a pump (LC-20AD), a column oven (CTO-20A), a refractive index detector (RID-10A), and an ultraviolet–visible detector (SPD-M20A). The samples for this analysis were prepared as follows: 40 μ L of the reaction medium was mixed with 360 μ L of distilled water and then filtered through a 0.45- μ m filter. The filtrates were analyzed under the following conditions: column, Shodex Sugar KS-801 (Showa Denko, Tokyo, Japan); flow rate, 1 mL/min; eluent, ultrapure water; column temperature, 80 °C; and detector, refractive index detector and ultraviolet–visible detector set at 280 nm.

The yield (wt%) of products was calculated using the following equation:

$$\text{Yield (wt\%)} = \left(\frac{\text{weight of product}}{\text{weight of charged sample}} \right) \times 100.$$

The yield (mol%) of product was calculated using the following equation:

$$\text{Yield (mol\%)} = \left(\frac{\text{moles of product}}{\text{moles of hexose unit in charged material}} \right) \times 100.$$

The moles of hexose units in Japanese cedar were determined as follows. The Japanese cedar was added to distilled water, and sodium chlorite was added to give a final concentration of 0.09 M, along with a small quantity of acetic acid. The obtained reaction mixture was heated at 80 °C, and further sodium chlorite and acetic acid were added to the reaction mixture every hour for 4 h. The mixture was then filtered, to recover the holocellulose residue, which was then oven-dried at 105 °C for 24 h and weighed. The moles of hexose units were calculated on the basis of holocellulose recovered and the reported component ratio of hexose and pentose in Japanese cedar [24].

The monosaccharides in ionic liquid were analyzed by a Shimadzu GC-2014 gas chromatography (GC), with samples prepared as follows. The reaction medium (20 μ L) was homogeneously mixed with 200 μ L of acetonitrile and 20 μ L of pyridine. After drying with sodium sulfate, the obtained mixture was filtered using a 0.45- μ m filter. The filtrate (150 μ L) was silylated at room temperature by mixing with 100 μ L of BSTFA. The silylated sample was then analyzed by GC using an InertCap 17 capillary column (GL Sciences, Tokyo, Japan). The temperature program was 60 °C (0 \rightarrow 1 min); 60 \rightarrow 250 °C (1 \rightarrow 10.5 min); and 250 °C (10.5 \rightarrow 40 min). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The temperatures of flame ionization detector and injector were 250 and 230 °C, respectively.

Samples of Japanese cedar treated in ionic liquids were examined by light microscopy (BH-2, OLYMPUS, Tokyo, Japan) to investigate the reactivity of wood samples.

Results and discussion

Prior to studying the conversion of wood or cellulose into 5-HMF in various ionic liquids without a catalyst, we investigated the conversion of glucose, which is a constituent of cellulose. HPLC chromatograms of glucose treated in [P₄₄₄₂]DEP and [EMIM]Cl at 120 °C for 24 h are

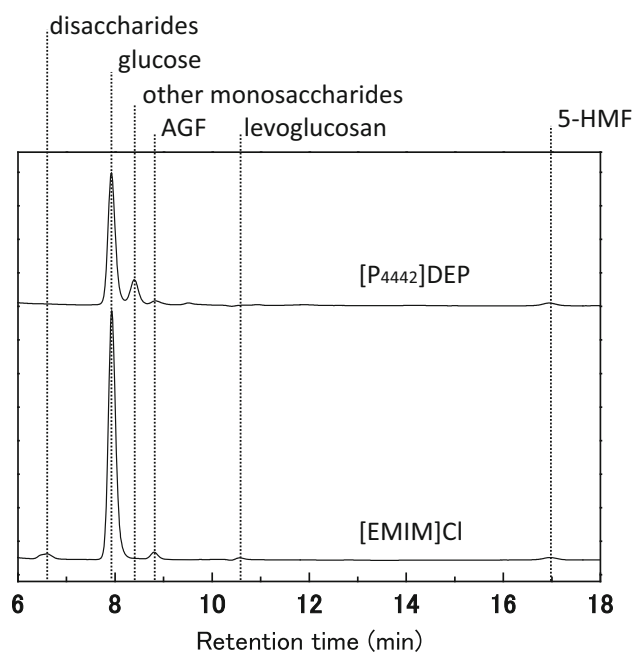


Fig. 1 HPLC chromatograms of glucose treated in [P₄₄₄₂]DEP (upper) and [EMIM]Cl (lower) for 24 h at 120 °C, detected by refractive index detector. Other mono saccharides other than glucose, AGF 1,6-anhydro- β -D-glucopyranose, and 5-HMF 5-hydroxymethylfurfural

shown in Fig. 1. Various compounds were detected, including 5-HMF, levoglucosan, and AGF as decomposition products. In addition, disaccharides were formed in [EMIM]Cl. In a previous study, Ohno and Miyafuji [25] showed that glucose is polymerized to disaccharides, such as maltose, nigerose, gentiobiose, and isomaltose in [EMIM]Cl. These disaccharides are thought to comprise the broad peak seen in the chromatogram in Fig. 1. On the other hand, monosaccharides other than glucose, which are referred to as “other monosaccharides” (OMS), were formed in [P₄₄₄₂]DEP. GC analysis on OMS revealed the

production of fructose. Therefore, it is possible that glucose was isomerized to fructose in ionic liquids.

Table 2 shows the yields of products from glucose after the treatments with ionic liquids at 120 °C. [EMIM]AlCl₄ and [N₄₄₄₄]N₃ solidified and evaporated, respectively, during treatment, while [Choline]Cit becomes abnormally high in viscosity upon heating. Thus, data for these three ionic liquids could not be obtained. The results in Table 2 suggest that 5-HMF was formed from glucose without catalyst in [EMIM]HSO₄, [EMIM]Tos, and [EMIM]Mes, which contain the sulfonyl group. Closer investigations

Table 2 Yield (wt%) of products from glucose in various ionic liquids at 120 °C

Ionic liquids	OMS		LG		AGF		5-HMF		Disaccharides	
	1 h	24 h	1 h	24 h	1 h	24 h	1 h	24 h	1 h	24 h
[MIM]NTf ₂	n.d.	n.d.	15.0	12.0	2.2	1.5	0.0	0.0	n.d.	n.d.
[EIM]NO ₃	n.d.	1.5	4.7	2.0	2.3	1.5	0.0	0.0	6.5	n.d.
[DMIM]DMP	4.8	1.1	0.6	0.7	n.d.	0.6	n.d.	n.d.	n.d.	n.d.
[DMIM]BOB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	n.d.	n.d.
[EMIM]Cl	n.d.	n.d.	n.d.	0.6	n.d.	1.2	0.1	1.3	0.3	1.7
[EMIM]HSO ₄	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	6.4	n.d.	n.d.
[EMIM]MPO ₄	n.d.	5.8	1.9	2.7	n.d.	n.d.	0.0	0.0	n.d.	n.d.
[EMIM]Ac	1.8	n.d.	0.1	0.4	0.4	0.5	n.d.	n.d.	n.d.	n.d.
[EMIM]PF ₆	n.d.	n.d.	n.d.	n.d.	n.d.	11.8	n.d.	n.d.	n.d.	n.d.
[EMIM]AlCl ₄	^a	^a	^a	^a	^a	^a	^a	^a	^a	^a
[EMIM]TCB	n.d.	n.d.	n.d.	3.5	n.d.	0.3	n.d.	n.d.	n.d.	6.1
[EMIM]Tos	n.d.	n.d.	n.d.	n.d.	22.2	n.d.	4.3	3.2	13.2	n.d.
[EMIM]Mes	1.3	n.d.	18.7	1.4	8.8	0.9	1.2	2.6	10.1	0.7
[BMIM]SCN	n.d.	3.1	n.d.	n.d.	n.d.	n.d.	0.0	0.0	n.d.	n.d.
[BMIM]BF ₄	0.8	0.9	19.8	23.2	n.d.	n.d.	0.0	0.0	n.d.	n.d.
[BPr]FSI	n.d.	n.d.	n.d.	0.3	n.d.	0.1	n.d.	n.d.	0.3	2.3
[BPr]PF ₆	n.d.	n.d.	n.d.	n.d.	1.3	2.7	0.0	0.1	n.d.	n.d.
[MPPyr]PF ₆	n.d.	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
[MPPip]PF ₆	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
[N ₄₄₄₄]Cl	n.d.	n.d.	n.d.	0.8	n.d.	1.6	n.d.	0.0	n.d.	1.3
[N ₄₄₄₄]Br	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	n.d.	0.3	n.d.	0.2
[N ₄₄₄₄]Cl ₂ Br	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
[N ₄₄₄₄]N ₃	^b	^b	^b	^b	^b	^b	^b	^b	^b	^b
[N ₄₄₄₄]Sal	12.6	9.8	n.d.	n.d.	n.d.	0.9	0.0	0.1	n.d.	n.d.
[P ₄₄₄₂]DEP	1.1	7.0	n.d.	0.3	0.1	0.6	0.0	1.4	n.d.	n.d.
[P _{14,666}]PF ₆	n.d.	0.8	n.d.	n.d.	n.d.	0.1	n.d.	0.1	n.d.	n.d.
[P _{14,666}]Dec	1.8	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.
[Choline]Cit	^c	^c	^c	^c	^c	^c	^c	^c	^c	^c
[Accholine]ClO ₄	1.3	2.1	0.4	0.5	n.d.	n.d.	n.d.	0.0	n.d.	n.d.
[HDABCO]NTf ₂	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0	0.0	n.d.	n.d.

OMS monosaccharides except for glucose, LG levoglucosan, AGF 1,6-anhydro-β-D-glucopyranose, 5-HMF 5-hydroxymethylfurfural, n.d. not detected

^a Solidified during treatment

^b Evaporated during treatment

^c Viscosity becomes abnormally high upon heating

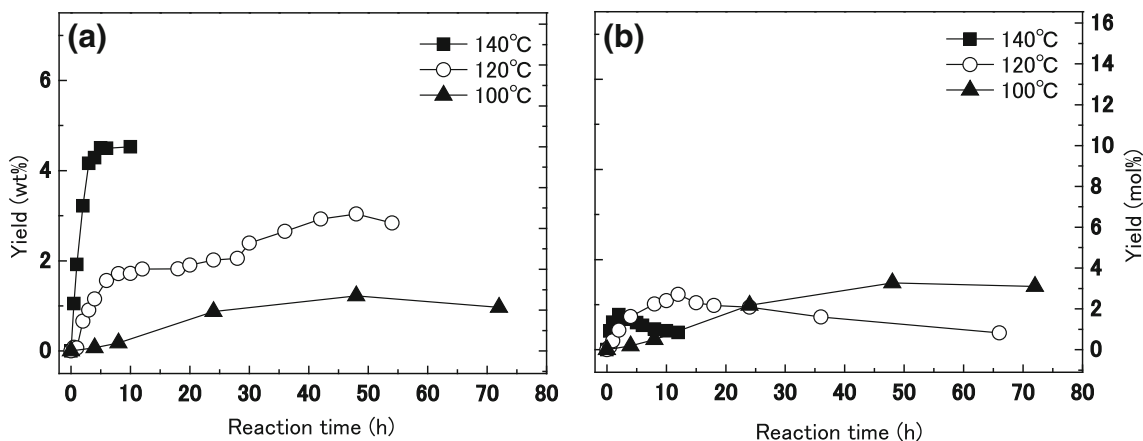


Fig. 2 Changes in 5-HMF yield from Japanese cedar treated in **a** [EMIM]HSO₄ and **b** [EMIM]Tos at various reaction temperatures

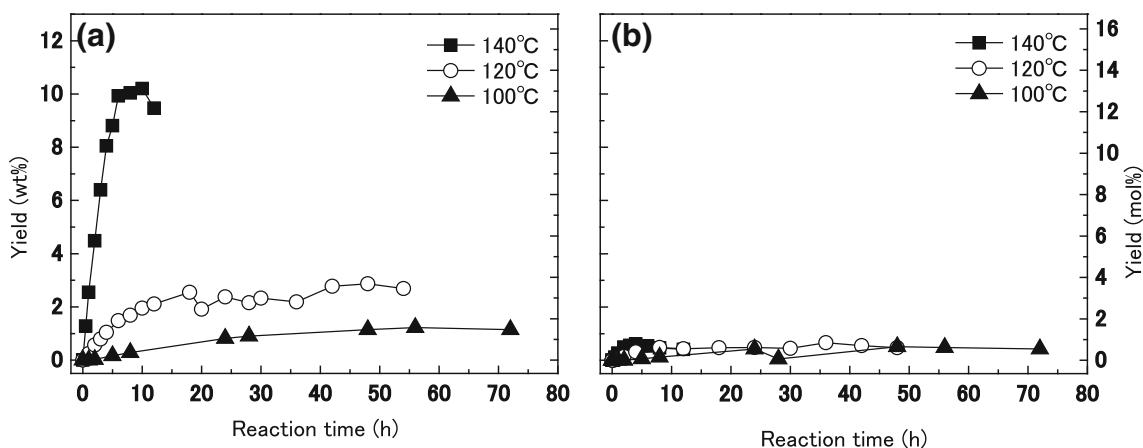


Fig. 3 Changes in 5-HMF yields from cellulose treated in **a** [EMIM]HSO₄ and **b** [EMIM]Tos at various reaction temperatures

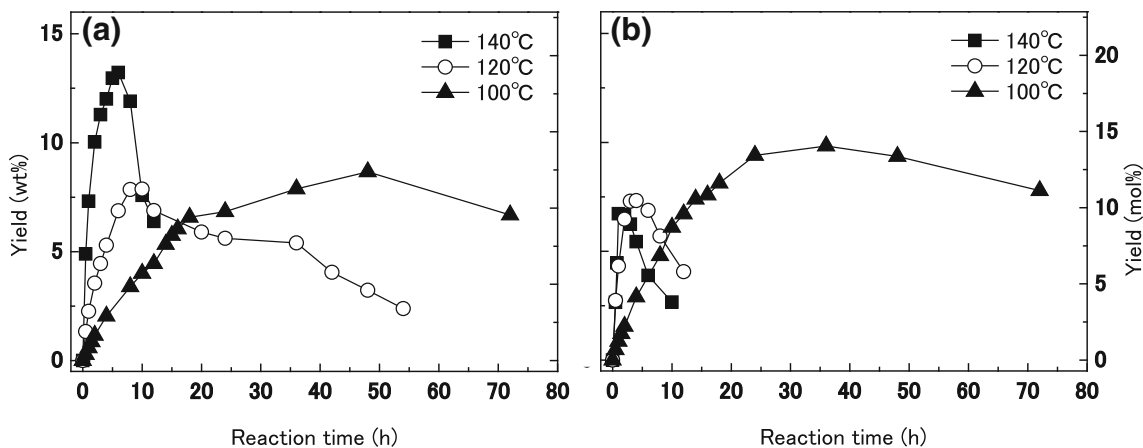


Fig. 4 Changes in 5-HMF yields from glucose treated in **a** [EMIM]HSO₄ and **b** [EMIM]Tos at various reaction temperatures

show that glucose was sparingly converted into the various chemicals listed in Table 2 in hydrophobic ionic liquids, such as [BPr]FSI, [P_{14,666}]Dec, and [HDABCO]NTf₂.

[DMIM]DMP and [N₄₄₄₄]Sal effectively converted glucose into other monosaccharides, while glucose was polymerized to disaccharides in [EMIM]NO₃, [EMIM]Tos, and

[EMIM]Mes, [BMIM]BF₄ and [EMIM]Tos can convert glucose into levoglucosan and AGF with high yields, respectively. These reactions of glucose in various ionic liquids are interesting, and future research to optimize the production of these compounds is necessary.

Based on the results shown above, conversions of wood into 5-HMF in [EMIM]HSO₄ and [EMIM]Tos were studied. Changes in 5-HMF yield from wood (Japanese cedar) in [EMIM]HSO₄ and [EMIM]Tos at various reaction temperatures are shown in Fig. 2a, b, respectively. In the case of [EMIM]HSO₄, the yield of 5-HMF reached a maximum at 4.5 wt% with treatment for 10 h at 140 °C. At 120 °C, the yield gradually increased to 2.5 wt%. However, 5-HMF was formed below a 1.0 wt% yield at 100 °C. The 5-HMF yield thus increased with temperature for [EMIM]HSO₄, but it was below 2 wt% in [EMIM]Tos at all reaction temperatures, as shown in Fig. 2b. It was found that wood was poorly converted into 5-HMF in [EMIM]Tos when compared with its conversion in [EMIM]HSO₄.

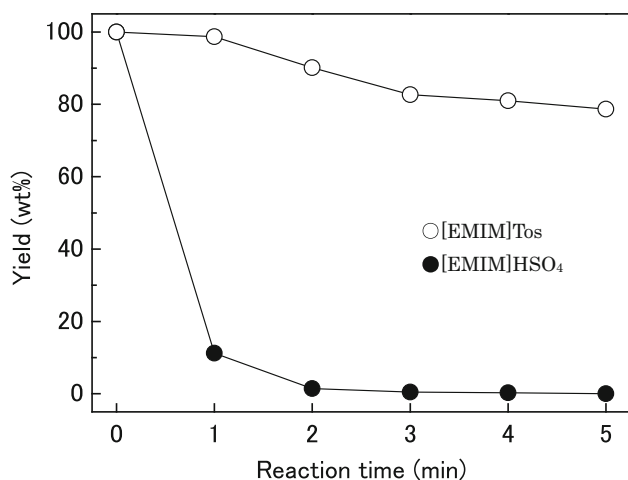


Fig. 5 Changes in cellobiose yields during the treatment with [EMIM]Tos and [EMIM]HSO₄ at 120 °C

Cellulose and glucose were treated in [EMIM]HSO₄ and [EMIM]Tos to investigate the difference in their 5-HMF yields. Changes in 5-HMF yields for cellulose treated in [EMIM]HSO₄ and [EMIM]Tos at various reaction temperatures are shown in Fig. 3. The yield of 5-HMF reached a maximum at 10.2 wt% with treatment in [EMIM]HSO₄ for 10 h at 140 °C, as shown in Fig. 3a. At 100 and 120 °C, the yields increased slightly from 1.2 to 2.5 wt%, respectively, with prolonged reaction time. 5-HMF was also found to be effectively produced from cellulose in [EMIM]HSO₄ at 140 °C but was not produced in significant quantities in [EMIM]Tos at any reaction temperature, as shown in Fig. 3b. Figure 4 shows the changes in 5-HMF yield from glucose treated in [EMIM]HSO₄ and [EMIM]Tos at various reaction temperatures. The yield reached a maximum of 13.2 wt% with treatment in [EMIM]HSO₄ for 6 h at 140 °C, as shown in Fig. 4a. However, the yields were 8.6 wt% after 48 h at 100 °C and 7.8 wt% after 10 h at 120 °C, respectively. Thus, although glucose can be converted into 5-HMF in [EMIM]HSO₄ at all reaction temperatures, yields can be increased with higher reaction temperatures and shorter reaction times. It was also found that the yield decreased more quickly at higher reaction temperature, because 5-HMF in [EMIM]HSO₄ is thought to be unstable and decomposes easily as the reaction temperature increases. Meanwhile, the yield of 5-HMF from glucose in [EMIM]Tos reached a maximum of 9.8 wt% through treatment for 36 h at 100 °C, as shown in Fig. 4b. At 120 and 140 °C, the maximum yields were 7.3 and 6.7 wt%, respectively. 5-HMF was formed at all reaction temperatures when glucose was treated in [EMIM]Tos, but it readily decomposes as the reaction temperature increases.

These results show that wood and cellulose are only slightly converted into 5-HMF in [EMIM]Tos, although glucose can be converted. Previous studies reported that wood is converted into 5-HMF through hexoses, such as

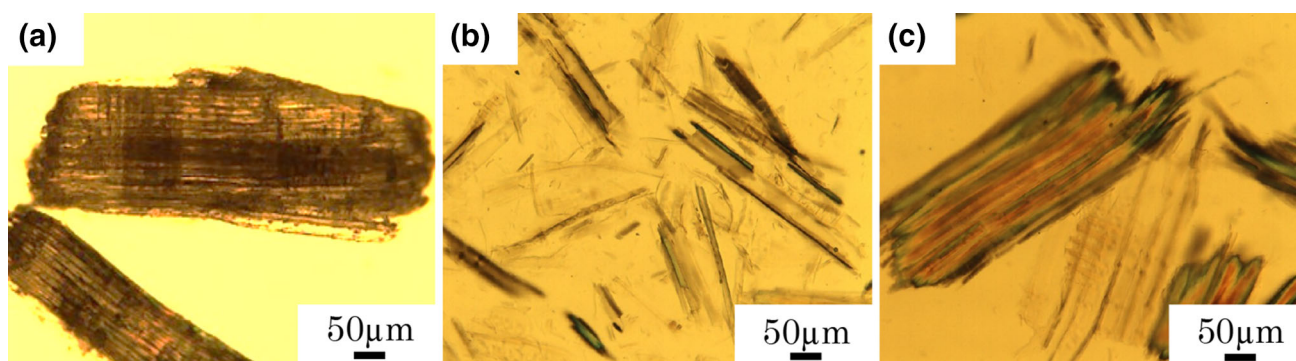


Fig. 6 Light microscope images of wood treated with ionic liquid for 4 h at 120 °C, **a** untreated, **b** [EMIM]HSO₄, and **c** [EMIM]Tos

glucose [26–28]. Thus, it is possible that [EMIM]Tos can only partially decompose polysaccharides. To investigate the ability of [EMIM]Tos and [EMIM]HSO₄ for decomposition, cellobiose was treated in [EMIM]Tos and [EMIM]HSO₄ at 120 °C. Changes in cellobiose yields are shown in Fig. 5. It is found that cellobiose is much stable in [EMIM]Tos, although it disappears quickly in [EMIM]HSO₄. These results suggest that 5-HMF is difficult to produce from wood using [EMIM]Tos, because it has a low ability for decomposing cellulose.

To investigate the reaction of wood in [EMIM]HSO₄ and [EMIM]Tos, wood particles samples were treated in these ionic liquids for 4 h at 120 °C and examined by light microscopy, as shown in Fig. 6. Wood particles treated with [EMIM]HSO₄ decreased in size, as shown in Fig. 6b, but those treated with [EMIM]Tos maintained their original sizes, as shown in Fig. 6c. These results suggest that solubility and reactivity of wood in [EMIM]HSO₄ is higher than in [EMIM]Tos. Thus, we believe that the yield of 5-HMF from wood in [EMIM]HSO₄ will be higher than that in [EMIM]Tos.

Conclusion

Glucose can be converted into 5-HMF without a catalyst in ionic liquids that contain sulfonyl groups, such as [EMIM]HSO₄ and [EMIM]Tos. However, wood and cellulose were poorly converted into 5-HMF in [EMIM]Tos, because it has a low ability to decompose wood and cellulose. Among various ionic liquids tested, [EMIM]HSO₄ was notable for its ability to convert wood and cellulose into 5-HMF at 140 °C without a catalyst, probably because it has a superior ability to solubilize wood.

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