Efficient one-pot production of 5-hydroxymethylfurfural from inulin in ionic liquids†

Xinhua Qi,*[a,b] Masaru Watanabe,[b] Taku M. Aida[b] and Richard L. Smith Jr.*[b]

Received 24th May 2010, Accepted 11th August 2010
DOI: 10.1039/c0gc00141d

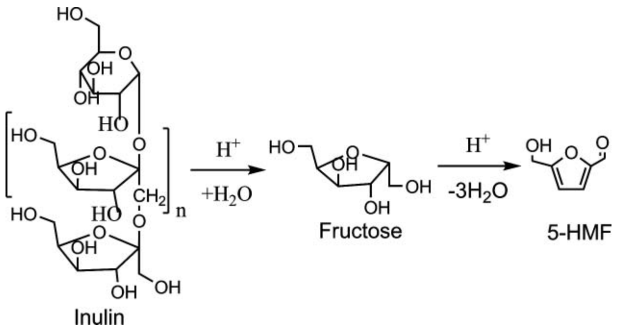
An efficient one pot, two-step process was developed for the preparation of 5-hydroxymethylfurfural (5-HMF) from inulin in ionic liquids under mild conditions. In the first step, the ionic liquid 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]) was used as both solvent and catalyst for the rapid hydrolysis of inulin into fructose with 84% fructose yield in 5 min reaction time. In the second step, 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) and a strong acidic cation exchange resin were added to the mixture to selectively convert fructose into 5-HMF, giving a 5-HMF yield of 82% in 65 min at 80 °C, which is the highest 5-HMF yield reported by thus far for an inulin feedstock.

1. Introduction

With the growing interest in developing carbohydrate chemistry for product sustainability, increasing attention has been recently devoted to the transformation of various chemicals from biomass resources.[1] Among the many possible biomass-derived chemicals, 5-hydroxymethylfurfural (5-HMF) is expected to become a substitute for the building block that is presently derived from petrochemicals and used in plastics, pharmaceuticals, fine chemicals and biofuels.[2,3] The most convenient method for the preparation of 5-HMF is the acid-catalyzed dehydration of fructose by eliminating three moles of water molecules, and this pathway has been well studied.[4–16] However, fructose is normally produced from glucose isomerization by isomerase in industry, and glucose is generally produced by hydrolysis of starch, which results in competition with food supplies. Processes for the production of 5-HMF from non-digestible carbohydrate resources are needed to be compatible with human development.

Inulin, also called fructan, is a carbohydrate consisting of fructose units that range in their degree of polymerization (DP) from 2 to 60, or higher, and the fructosyl units in inulin are linked by β(2→1) linkages with the polymer chains terminating in a glucose unit.[17] Inulin is used by some plants as a means of storing energy and exists in many plants such as chicory root and artichoke tuber. Most plants that synthesize and store inulin do not store other materials such as starch. Due to the beta-configuration of the anomeric C-2 in their fructose monomers, inulin-type fructans resist hydrolysis by intestinal digestive enzymes and so they are classified as carbohydrates that are non-digestible by human beings.[18]

The hydrolysis of inulin to fructose followed by the dehydration of fructose to produce 5-HMF is a possible two-step reaction pathway. Because both reaction steps are catalyzed by acid catalysts, it is interesting to consider the production of 5-HMF from inulin as a one pot reaction, since this would avoid the separation of fructose in the intermediate step (Scheme 1). The preparation of 5-HMF from inulin in one pot has been carried out in different systems. Carlini *et al.* studied the reaction in water at 80–100 °C with heterogeneous niobium catalysts or a vanadium based catalyst, but the 5-HMF yields were below 40%.[19,20] When the reaction was conducted in water-dimethylsulfoxide or water-acetone mixtures at 170–180 °C in the presence of mineral acids such as HCl and H_2SO_4, the 5-HMF yield was improved to *ca.* 70%, but the reaction conditions were very harsh.[7,21] Hu *et al.*[22] developed a process for the direct conversion of inulin to 5-HMF in choline chloride (ChoCl)/oxalic acid and ChoCl/citric acid ionic liquids (ILs), for which a 5-HMF yield of 56% was obtained at relatively low temperatures (80 °C). When a biphasic system with IL and ethyl acetate was used for the *in situ* extraction of 5-HMF, the 5-HMF yield was enhanced to 64%.[22] Wu *et al.*[23] developed a process where the inulin was converted in highly compressed water in the presence of high pressure of CO_2, and a 5-HMF yield of 53% was obtained in 1.5 h reaction time at 180 °C at a CO_2 pressure of 6 MPa.



Scheme 1 The pathways for acid-catalyzed hydrolysis and dehydration of inulin to 5-hydroxymethylfurfural.

---

[a] *Key Laboratory of Pollution Processes and Environmental Criteria (Ministry of Education), College of Environmental Science and Engineering, Nankai University, Tianjin, 300071, China. E-mail: qixinhua@scf.che.tohoku.ac.jp*
[b] *Research Center of Supercritical Fluid Technology, Tohoku University, 6-6-11 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan. E-mail: smith@scf.che.tohoku.ac.jp; Fax: +81 022-795-5864*

† Electronic supplementary information (ESI) available: Effect of reaction temperature, resin dosage and amount of added water on inulin conversion, acidity of different Brønsted ionic liquids in [BMIM][Cl]. See DOI: 10.1039/c0gc00141d

In this work, we used the characteristics of two kinds of ionic liquids to develop an efficient process for the direct conversion of inulin to 5-HMF in one pot with two reaction steps. 1-Butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]) was used for the hydrolysis of inulin as both solvent and catalyst, followed by the dehydration of fructose to 5-HMF in the presence of 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) and a strong acidic ion exchange resin. With the catalytic system, a high 5-HMF yield of above 80% was obtained under mild conditions.

2. Experimental

2.1 Materials

Inulin from dahlia tubers, with a degree of polymerization of 36 was purchased from Fluka Company. Fructose and 5-hydroxymethylfurfural were obtained from Wako Pure Chemical Company. The 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]), 1-methyl imidazolium hydrogen sulfate ([HMIM][HSO_4]), 1-ethyl-3-methyl imidazolium hydrogen sulfate ([EMIM][HSO_4]), 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]) and Amberlyst® 15 ion exchange resin (concentration of acid sites: 4.7 eq/kg) was purchased from Sigma-Aldrich Company. All chemicals were used without further purification.

2.2 Typical experimental procedure

In a typical reaction, 0.05 g of inulin (0.3 mmol fructose units), 0.054 g (3 mmol) of water, and a known amount of ionic liquid were added into the reactor with or without a catalyst. The reaction mixture was agitated with electromagnetic stirring to keep the resin particles suspended at 80 °C for the desired time in the oil bath. After reaction, each sample was cooled and diluted with 10 g of ultra pure water before analysis. The product yields were analyzed with high performance liquid chromatograph (HPLC).

2.3 Analyses

An HPLC equipped with a refractive index detector (HPLC-RI, SH 1011 column) was employed for the analysis of the liquid samples. Column oven temperature was 60 °C, and 0.5 mM sulfuric acid aqueous solution as mobile phase a flow rate of 1 ml min^{-1}.

2.4 Definitions

The fructose yield (mol%) and 5-HMF yield (mol%) were calculated on the basis of total moles of fructose and glucose units in the loaded inulin as shown below:

Fructose yield (mol %):

$$X = \left(\frac{\text{Fructose moles in product}}{\text{Total moles of fructose and glucose units in the loaded inulin}}\right) \times 100\% \tag{1}$$

5-HMF yield (mol %):

$$Y = \left(\frac{\text{5-HMF moles in product}}{\text{Total moles of fructose and glucose units in the loaded inulin}}\right) \times 100\% \tag{2}$$

3. Results and discussion

3.1 Catalytic conversion of inulin in [BMIM][Cl] by different acid catalysts

As a green solvent, ionic liquids have been identified that are able to completely dissolve inulin,[22] and both hydrolysis of inulin and dehydration of fructose are known to be catalyzed by acid catalysts. Thus, the conversion of inulin in ionic liquid [BMIM][Cl] catalyzed by different acid catalysts was studied. Here, we used three kinds of acidic ionic liquids 1-methyl imidazolium hydrogen sulfate ([HMIM][HSO_4]), 1-ethyl imidazolium hydrogen sulfate ([EMIM][HSO_4]), 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]), and one solid acid catalyst Amberlyst® 15 ion exchange resin as catalyst. Results are given in Fig. 1, which shows that the conversion of inulin to fructose and 5-HMF in [BMIM][Cl] was effective with similar profiles for all of these catalysts. When the reaction was carried out in [BMIM][Cl] catalyzed by [BMIM][HSO_4] at 80 °C, fructose was produced slowly with a maximum yield of about 44% in 60 min and then steadily decreased with increasing 5-HMF yield. When [EMIM][HSO_4] and [HMIM][HSO_4] were used as catalyst, the decrease of the alkyl chain length (BMIM, EMIM, HMIM) in the cation of the ionic liquids caused the acidity of the ionic liquid to increase (Table S1†), and the reaction time required for the fructose yield reached a peak value that was shortened leading to an increase in the 5-HMF

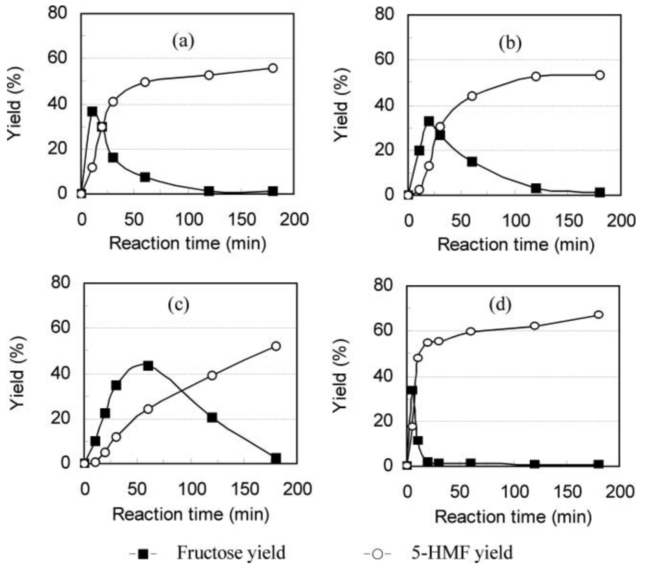


Fig. 1 Catalytic conversion of inulin to fructose and 5-HMF in [BMIM][Cl] with different additives: (a) [HMIM][HSO_4]; (b) [EMIM][HSO_4]; (c) [BMIM][HSO_4]; (d) Amberlyst 15 resin. Reaction conditions: 0.05 g inulin (0.3 mmol fructose units), 1 g [BMIM][Cl], 0.1 mmol Brønsted acidic ionic liquid or 0.05 g Amberlyst 15 resin, 3 mmol water, 80 °C.

formation rate. The 5-HMF yields catalyzed by these ionic liquid catalysts reached comparable values of about 53% in 180 min reaction time. For the case of strong acidic exchange resin catalyst, 34% of fructose was produced within 5 min, and the fructose was quickly dehydrated into 5-HMF. Then, the fructose yield sharply decreased to 1% and contributed to a high 5-HMF yield of 55% within 20 min, and the 5-HMF yield increased to 67% in 180 min. To improve the 5-HMF yield, catalytic conversion of inulin to 5-HMF was investigated in detail by changing the reaction temperature, resin dosage and amount of water and these results are provided in Electronic Supporting Information (ESI†, Fig. S1, S2 and S3). By varying the reaction parameters, a maximum 5-HMF yield of 69% could be obtained.

It is well known that in the acid-catalyzed hydrolysis, inulin is decomposed to the fructofuranosyl cation first, and the fate of this cation depends on the conditions of its generation.[24,25] When it is generated in a strongly acidic atmosphere or at high temperatures under dry conditions, it can rapidly dehydrate to 5-HMF, or react with nucleophiles such as amino acids if present. However, if the fructofuranosyl cation is generated under the conditions of dilute or weak acid and at low temperatures, it will mainly be transformed to fructose due to its fast reaction with water that is followed by a slow dehydration to 5-HMF from fructose.[24] As shown in Fig. 1, inulin was rapidly converted into 5-HMF with a high yield in [BMIM][Cl] with ion-exchange resin catalyst (Fig. 1d), and was transformed at a relatively slower rate by [BMIM][HSO_4] (Fig. 1c) and at a moderate rate by [EMIM][HSO_4] and [HMIM][HSO_4] (Fig. 1a, Fig. 1b).

3.2 Catalytic conversion of inulin in acidic ionic liquids acting as solvents and catalysts

Brønsted acidic ionic liquids, [HMIM][HSO_4], [EMIM][HSO_4] and [BMIM][HSO_4] were found to be effective catalysts for the inulin conversion to fructose and 5-HMF in [BMIM][Cl] solvent. We expected that it might be possible to improve the 5-HMF yield or reaction rate by increasing the concentration of acid sites in the system. Therefore, we studied inulin conversion in these acidic ionic liquids that act as both solvents and catalysts (Fig. 2). It can be seen in Fig. 2, that inulin was rapidly converted to fructose in the ionic liquids at 80 °C. In [HMIM][HSO_4], the fructose and 5-HMF yields were 55% and 10%, respectively within 3 min. The fructose yield reached 82% in [EMIM][HSO_4] with 2% of 5-HMF yield within 3 min. When [BMIM][HSO_4] was used for the inulin conversion, the fructose yield increased to 84% with a low 5-HMF yield of 1% within 5 min.

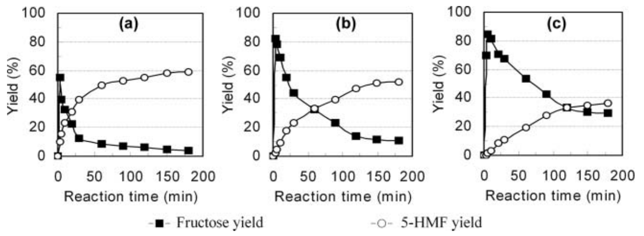


Fig. 2 Different Brønsted acidic ionic liquids used that act as both solvent and catalyst for conversion of inulin to fructose and 5-HMF: (a) [HMIM][HSO_4]; (b) [EMIM][HSO_4]; (c) [BMIM][HSO_4]. Reaction conditions: 0.05 g of inulin (0.3 mmol fructose units), 1 g of Brønsted acidic ionic liquid, 3 mmol water, 80 °C.

After fructose formed, the fructose was immediately dehydrated to 5-HMF in [HMIM][HSO_4], and 49% of 5-HMF yield was achieved in 60 min at 80 °C (Fig. 2a). The formed fructose was converted at a relatively slower rate in [EMIM][HSO_4] and [BMIM][HSO_4], and 52% and 37% of 5-HMF yields were obtained at a reaction time of 180 min in [EMIM][HSO_4] and [BMIM][HSO_4], respectively (Fig. 2b, Fig. 2c). Compared with the 5-HMF formation from inulin in [BMIM][Cl] in the presence of these acidic ionic liquids as catalysts, the 5-HMF yields did not increase. It can be concluded that these ionic liquids are excellent solvents and catalysts for inulin conversion to fructose, and the stability of formed fructose seems to be related to the acidity of the ionic liquids. The ionic liquids having low acidity seemed to promote slow dehydration of fructose to 5-HMF. The reverse is true for high acidity ionic liquids. Although these ionic liquids are probably not the best for promoting 5-HMF formation from inulin, they did promote the formation of fructose from inulin, especially for [EMIM][HSO_4] and [BMIM][HSO_4]. From the above results, it can be seen that the strong acidic cation exchange resin in [BMIM][Cl] was effective for promoting conversion of both inulin and fructose to 5-HMF. Thus, we considered a second step that would add [BMIM][Cl] ionic liquid and ion exchange resin catalyst with the hope of obtaining high 5-HMF yields.

3.3 Catalytic conversion of inulin in [EMIM][HSO_4] and [BMIM][HSO_4] in the presence of resin

First, the inulin was treated in [EMIM][HSO_4] and [BMIM][HSO_4] at 80 °C for 5 min reaction time, and 79% and 84% of fructose yield were obtained, respectively. Then, 0.05 g of resin was added and the reaction was allowed to continue at 80 °C (Table 1). It can be seen that the 5-HMF yield increased with increasing reaction time, and correspondingly, the fructose yield decreased. It should be noted that in this case, the sum of the 5-HMF and fructose yields decreased as the reaction time progressed, which implies that by-products were generated as fructose underwent conversion. The levulinic acid and formic acid yield were always below 1%, and no other primary by-products could be detected. The reaction mixture became a deeper brown, indicating that the losses in the sum of fructose and 5-HMF yields should result due to the formation of solvent soluble humins that often form as 5-HMF forms.[26] These brown soluble humins at present could not be quantified and their amount could only be assessed by the occurrence and deepness of their brown color.[27,28]

To improve the reaction rate for fructose dehydration and increase the 5-HMF yield, after inulin was hydrolyzed in [EMIM][HSO_4] or [BMIM][HSO_4] for 5 min, we added resin catalyst into the ionic liquids and raised the reaction temperature to 100 °C. It was found that a higher temperature promoted the formation of the 5-HMF, and the 5-HMF yield increased to 65% with almost all of the formed fructose being converted for the ionic liquid [EMIM][HSO_4] for 20 min reaction time. We examined the inulin conversion to 5-HMF in [EMIM][HSO_4] and [BMIM][HSO_4] with one step. The resin was added into the ionic liquids, together with inulin at the beginning of the reaction, and the reaction temperature of the reaction mixture was directly elevated to 100 °C (Table 1). This procedure

Table 1 The conversion of inulin to fructose and 5-HMF in single ionic liquids system (0.05 g inulin, 1 g of IL, 3 mmol of water, 0.05 g of resin)

IL	$T/°C$	Time/min	5-HMF yield (%)	Fructose yield (%)	Conditions
[EMIM][HSO$_4$]	80	5	4	79	No resin addition
[BMIM][HSO$_4$]	80	5	1	84	
[EMIM][HSO$_4$]	80/80[a]	5/10	18	51	Resin added at second time and temperature
		5/20	33	29	
		5/30	38	22	
	80/100[a]	5/5	60	3	
		5/10	65	1	
		5/20	62	1	
[BMIM][HSO$_4$]	80/80[a]	5/10	9	67	
		5/20	22	49	
		5/30	32	33	
	80/100[a]	5/5	54	12	
		5/10	56	1	
		5/20	48	1	
[EMIM][HSO$_4$]	100[b]	5	65	3	Resin added at the beginning of reaction
		10	59	2	
		20	54	1	
[BMIM][HSO$_4$]	100[b]	5	54	18	
		10	61	3	
		20	56	1	

[a] Entries with two temperatures means that the reaction mixtures were first stirred at the former temperature in the absence of resin for 5 min, then stirred at latter temperature for 5, 10, 20 or 30 min after resin was added in. [b] Entries were stirred at 100 °C for 5, 10 or 20 min in the presence of resin.

gave 5-HMF yields of 65% in 5 min and 61% in 10 min for [EMIM][HSO$_4$] and [BMIM][HSO$_4$] ionic liquids, respectively.

3.4 Highly efficient formation of 5-HMF from inulin with two-step process

The reaction rate for the fructose dehydration in [EMIM][HSO$_4$] and [BMIM][HSO$_4$] even after the addition of resin was much slower than that in [BMIM][Cl] in the presence of resin (Table 1, Fig. 1d). The difference between [BMIM][Cl] and [BMIM][HSO$_4$] is only their cationic counter ions ([Cl] *vs.* [HSO$_4$]). Thus, it seems that the chloride ion in the ionic liquid [BMIM][Cl] played an important role in accelerating the reaction rate for fructose (or inulin) conversion for 5-HMF and improving the 5-HMF yield. Binder *et al.*[26] studied the influence of halides on the yield and rate in 5-HMF formation from fructose in ionic liquids and found that weakly ion-paired halide ions favor the reaction. They proposed that the occurrence of halide ions favor the fructofuranosyl oxocarbenium ion to deprotonate at C-1 to form an enol through nucleophilic or basic mechanisms,[26] so that the enol can be thought of as being a key intermediate for 5-HMF formation.[29] Binder *et al.* concluded that the rate of 5-HMF formation has a first-order dependence on halide concentration.[26]

As discussed above, ionic liquids, [EMIM][HSO$_4$] and [BMIM][HSO$_4$] were found to be highly efficient for inulin hydrolysis to fructose within short reaction times, and the formed fructose was relatively stable in the ionic liquids. On the other hand, the dehydration of fructose to 5-HMF in [BMIM][Cl] in the presence of strong acidic cation exchange resin has been shown to be fast with high 5-HMF yields under mild conditions.[9] Therefore, we tried to conduct the reaction for the conversion of inulin to 5-HMF in two steps: effective hydrolysis of inulin to fructose in [BMIM][HSO$_4$], followed by the dehydration of fructose to 5-HMF promoted by the addition of [BMIM][Cl] and the resin (Fig. 3). The inulin was reacted first in [BMIM][HSO$_4$] for 5 min at 80 °C, and a fructose yield of 84% with 1% 5-HMF yield was obtained. Then, the given amount of [BMIM][Cl] and resin were added into the reaction mixture and allowed to react at 80 °C. Upon the addition of [BMIM][Cl] and the resin, the formed fructose was quickly consumed and almost an equal amount of 5-HMF produced. After 35 min of reaction time, in which 5 min was allowed for the hydrolysis of inulin, a

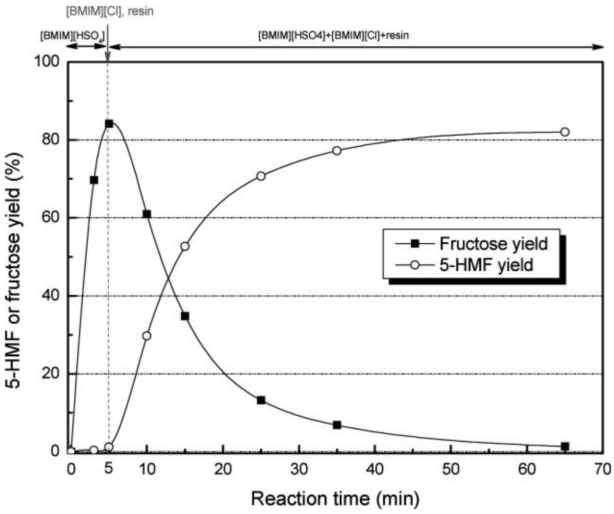


Fig. 3 Effective conversion of inulin to 5-HMF with two-step process. (0.05 g inulin and 6 mmol water were firstly added into 1 g [BMIM][HSO$_4$] and stirred at 80 °C for 5 min, and then 1 g [BMIM][Cl] and 0.05 g resin were added into for reaction of another 5–60 min.).

5-HMF yield of 77% was obtained with a 7% of fructose yield. When the reaction time was extended to 65 min, the 5-HMF yield increased to 82% with only a small amount of fructose remaining (1% fructose in yield), indicating that fructose conversion was highly selective.

3.5 By-products and carbon balance

In this study, besides fructose (1 to 85% yield), the main by-products are glucose (3 to 5% yield), formic acid (<1% yield), levulinic acid (<0.5% yield), humic acids (soluble polymers), and probably some di-D-fructose dianhydrides. The di-D-fructose dianhydrides are easily formed from inulin under acidic conditions, and there are at least 14 kinds of di-D-fructose dianhydrides that are generated from inulin hydrolysis.[22,30] The analysis of these di-D-fructose dianhydrides was not conducted due to its complexity as it was not the key point of this work. The formed soluble humic acids (soluble polymers) are not easily quantified at present, but could be assessed for their occurrence from the mixture color,[27,28] and there were no solid humins observed for the reaction conditions studied in this work.

Since inulin is a biopolymer, the quantitative determination of inulin is generally based on acidic or enzymatic hydrolysis of inulin and quantification of released fructose and glucose employing high-performance liquid chromatograph with refractometer detection (HPLC-RI).[31,32] Fructose and glucose are intermediate products (by-products) in this reaction, hence, the quantitative method mentioned above for conversion is not applicable for the inulin analysis in this work and the inulin concentration during the reaction is not easily quantified. The 5-HMF and fructose yields can be quantified since these are end products. Therefore, in most cases, it was difficult to obtain a reliable carbon balance calculated from HPLC-RI analysis due to the lack of inulin concentration data in the reaction mixture. However, in the two-step process where inulin was quickly converted to fructose, about 90–95% of carbon balance was obtained according to HPLC-RI analysis.

3.6 Conceptual process and recycling

At first sight, the process of mixing two high boiling liquids together as a method to improve reaction yields for a chemical product (fructose, 5-HMF) might seem to be counterproductive. However, we can show that their separation and recycling can be done with established methods that can be considered to be green, as illustrated in Fig. 4, which shows the 1-pot reaction (dashed box), hydrolysis and dehydration that is followed by extraction and filtration separation. The key to the recycling of the ionic liquids is to note that the cations are the same for the ionic liquids used, [BMIM][Cl] and [BMIM][HSO_4]. The effluent from the filtration step is a mixture of [BMIM][Cl] and [BMIM][HSO_4] that is readily converted to [BMIM][Cl] through ion exchange (left side). It should be noted that it is not necessary to convert all of this mixture to [BMIM][Cl] but rather only half of the stream, thus the stream from the filtration step is split. One half of the stream must be converted to [BMIM][HSO_4]. This is also readily accomplished since [BMIM][HSO_4] is derived from [BMIM][Cl]. Namely, addition of sodium bisulfate will cause reaction and precipitation of NaCl to give [BMIM][HSO_4]. The ratio of the split is determined by the ratio of the ionic liquids used in the 1-pot reaction. The ion exchange resin used for converting [BMIM][HSO_4] to [BMIM][Cl] can be regenerated in the usual ways (HCl). The NaCl can be used with H_2SO_4 to generate $NaHSO_4$ and HCl. Thus, there is substantial chemical recycling.

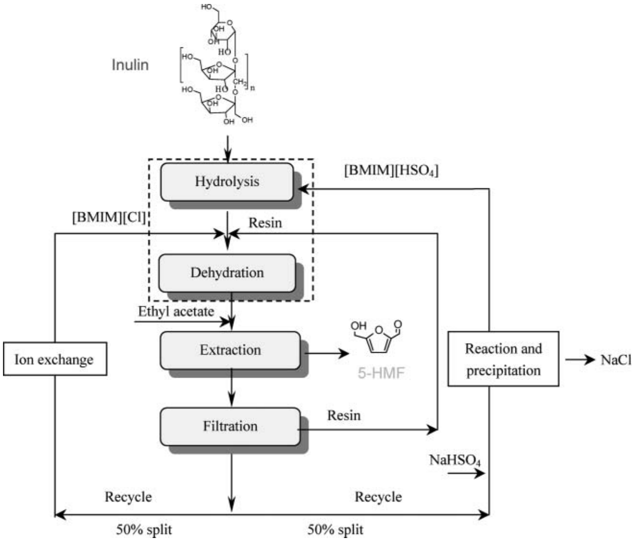


Fig. 4 Proposed process for conversion of inulin to 5-HMF with recycling of mixed ionic liquids. The 1-pot, 2-step reaction is enclosed in the dashed box.

The resin used as catalyst in the dehydration reaction has already been studied for its recyclability,[9] and the ethyl acetate used in the extraction process can be easily removed from the IL mixture after filtration by a liquid–liquid separator that is followed by either flash vaporization of the ethyl acetate from the ionic liquid mixture or gas stripping. In the proposed process, the ionic liquid, resin, catalyst, ethyl acetate, and the supplied chemicals are internally recycled and represent an efficient method for producing 5-HMF from inulin.

4. Conclusions

In this work, inulin conversion was studied with several kinds of ionic liquid solvents as a one pot reaction under mild conditions. The combination of [BMIM][Cl] and strong acidic cation exchange resin was found to transform inulin into 5-HMF rapidly, and a 5-HMF yield of 55% was obtained in 20 min reaction time. Brønsted acidic ionic liquids, [EMIM][HSO_4] and [BMIM][HSO_4] acting both as solvent and catalyst, were found to be highly effective for inulin hydrolysis to fructose with short reaction times, and the formed fructose was relatively stable in the ionic liquids. On the basis of these results, direct conversion of inulin to 5-HMF was implemented in two steps in which [BMIM][HSO_4] was used for the conversion of inulin to fructose, and [BMIM][Cl] and ion exchange resin was used to promote the dehydration of fructose to 5-HMF. A 5-HMF yield of 82% was obtained in 65 min reaction time at 80 °C with the mixed ionic liquid system. For using common cation ionic liquids [BMIM][Cl] and [BMIM][HSO_4], recycling is simplified and the process is green and efficient.

Acknowledgements

The authors gratefully acknowledge the financial supports by the National Natural Science Foundation of China (NSFC, No. 20806041) and the Japan Society for the Promotion of Science (JSPS).

References

1 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
2 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.
3 Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen and A. Riisager, *ChemSusChem*, 2009, **2**, 672–675.
4 H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600.
5 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *ChemSusChem*, 2009, **2**, 944–946.
6 C. Moreau, R. Durand, A. Roux and D. Tichit, *Appl. Catal., A*, 2000, **193**, 257–264.
7 M. Bicker, J. Hirth and H. Vogel, *Green Chem.*, 2003, **5**, 280–284.
8 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
9 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2009, **11**, 1327–1331.
10 C. Lansalot-Matras and C. Moreau, *Catal. Commun.*, 2003, **4**, 517–520.
11 Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
12 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2008, **10**, 799–805.
13 F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger and B. Konig, *Green Chem.*, 2009, **11**, 1948–1954.
14 T. S. Hansen, J. M. Woodley and A. Riisager, *Carbohydr. Res.*, 2009, **344**, 2568–2572.
15 C. Sievers, I. Musin, T. Marzialetti, M. B. V. Olarte, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2009, **2**, 665–671.
16 J. Y. G. Chan and Y. G. Zhang, *ChemSusChem*, 2009, **2**, 731–734.
17 S. Sirisansaneeyakul, N. Worawuthiyanan, W. Vanichsriratana, P. Srinophakun and Y. Chisti, *World J. Microbiol. Biotechnol.*, 2007, **23**, 543–552.
18 M. Verghese, L. T. Walker, L. Shackelford and C. B. Chawan, *Nutr. Res.*, 2005, **25**, 859–868.
19 C. Carlini, P. Patrono, A. M. R. Galletti and G. Sbrana, *Appl. Catal., A*, 2004, **275**, 111–118.
20 C. Carlini, M. Giuttari, A. M. R. Galletti, G. Sbrana, T. Armaroli and G. Busca, *Appl. Catal., A*, 1999, **183**, 295–302.
21 J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
22 S. Q. Hu, Z. F. Zhang, Y. X. Zhou, J. L. Song, H. L. Fan and B. X. Han, *Green Chem.*, 2009, **11**, 873–877.
23 S. X. Wu, H. L. Fan, Y. Xie, Y. Cheng, Q. A. Wang, Z. F. Zhang and B. X. Han, *Green Chem.*, 2010, **12**, 1215–1219.
24 C. P. Locas and V. A. Yaylayan, *J. Agric. Food Chem.*, 2008, **56**, 6717–6723.
25 T. L. Mega and R. L. Vanetten, *J. Am. Chem. Soc.*, 1988, **110**, 6372–6376.
26 J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979–1985.
27 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2007, **46**, 7703–7710.
28 B. F. M. Kuster, *Starch/Staerke*, 1990, **42**, 314–321.
29 C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros and G. Avignon, *Appl. Catal., A*, 1996, **145**, 211–224.
30 T. J. Christian, M. Manley-Harris, R. J. Field and B. A. Parker, *J. Agric. Food Chem.*, 2000, **48**, 1823–1837.
31 A. Bohm, I. Kaiser, A. Trebstein and T. Henle, *Eur. Food Res. Technol.*, 2005, **220**, 466–471.
32 S. Vendrell-Pascuas, A. I. Castellote-Bargallo and M. C. Lopez-Sabater, *J. Chromatogr., A*, 2000, **881**, 591–597.