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Qi *et al.*
Conversion of fructose to 5-hydoxymethylfurfural

Melero *et al.*
Heterogeneous acid catalysts for biodiesel production

Clark *et al.*
Expanding the potential for waste PVA

Krause and Winter
Towards sustainable homogeneous gold catalysis

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Efficient process for conversion of fructose to 5-hydroxymethylfurfural with ionic liquids†

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An efficient process for the dehydration of fructose into 5-hydroxymethylfurfural (5-HMF) in ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) by using a sulfonic ion-exchange resin as catalyst was developed. A fructose conversion of 98.6% with a 5-HMF yield of 83.3% was achieved in 10 min reaction time at 80 °C. When the reaction temperature was increased to 120 °C, a 5-HMF yield of 82.2% was obtained in only 1 min for essentially 100% fructose conversion. No large decrease in 5-HMF selectivity occurred for initial fructose concentrations of up to 20 wt.%. Water content of up to 5% in the [BMIM][Cl] had no effect on the fructose conversion rate and 5-HMF yield, but water content higher than 5 wt.% led to lower conversions and yields. The ionic liquid and sulfonic ion-exchange resin could be recycled and exhibited constant activity for 7 successive trials. The proposed process of using an ionic liquid with ion-exchange resin catalyst greatly reduces the reaction time required over previous works for converting fructose to 5-HMF.

1. Introduction

As a valuable biomass-derived intermediate for plastics, pharmaceuticals, fine chemicals and liquid fuel, the preparation of 5-hydroxymethylfurfural (5-HMF) through dehydration of fructose has received increasing attention.[1–14] In the past few years, water,[10,12,15–18] organic solvents[3,16,19–21] and organic–water mixtures[2,8,13,22] have been mainly studied with some of the drawbacks being low 5-HMF selectivities or environmental problems with solvent recycling. The application of ionic liquids as green solvents has been proposed,[1,4–6,9,23] and several kinds of ionic liquids in the presence of an appropriate catalyst have been demonstrated to be effective for the conversion of fructose to 5-HMF. Thus far, high 5-HMF yields (80–95%) have been obtained at moderate reaction temperatures of 80 to 100 °C, but these required long reaction times on the order of hours and the use of relatively toxic chromium catalysts.

Lansalot-Matras *et al.*[23] studied the acid-catalyzed dehydration of fructose in 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM][PF_6]) with dimethyl sulfoxide (DMSO) as co-solvent in the presence of Amberlyst® 15 sulfonic ion-exchange resin as catalyst to obtain a high 5-HMF yield of 87% at 80 °C for 32 h reaction time. Zhao *et al.*[6] studied the catalytic conversion of fructose and glucose into 5-HMF in an ionic liquid solvent (1-ethyl-3-methylimidazolium chloride) with metal halides. It was found that chromium (II) chloride is the most effective catalyst, leading to the conversion of fructose and glucose to 5-HMF with a yield of 83% and 70%, respectively at a temperature of 80 °C for a reaction time of 3 h. The $CrCl_3^-$ anion seems to play a role in proton transfer, facilitating the mutarotation of glucose in [EMIM][Cl] as noted by these authors.[6] Hu *et al.*[4] investigated the conversion of fructose to 5-HMF in choline chloride/citric acid at 80 °C, and obtained a 5-HMF yield of 77.8% without in situ extraction and a yield of 91.4% when continuous extraction with ethyl acetate was used for a 1 h reaction time. Yong *et al.*[1] studied the production of 5-HMF from fructose and glucose in 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) using $CrCl_2$ as catalyst, and 5-HMF yields of 96% and 81% were achieved at 100 °C for 6 h reaction time for fructose and glucose, respectively. Those authors considered that NHC/$CrCl_x$ (NHC = N-heterocyclic carbene) complexes played the key role in glucose dehydration in [BMIM][Cl]. Additionally, in the $CrCl_2$/EMIM system, a NHC/Cr complex could be formed under the reaction conditions and therefore serves as a catalyst.[1]

In this work, we developed an efficient catalytic process for the conversion of fructose into 5-HMF, in which the ionic liquid, 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]), was used as solvent with a strong acidic ion exchange resin as catalyst. With the given catalytic process and fructose as the starting material, a 5-HMF yield of 85.9% could be achieved at 80 °C for a reaction time of 10 minutes. The ionic liquid and catalyst could be recycled and the catalyst exhibited constant activity over 7 cycles of evaluation.

2. Experimental

2.1 Materials and experimental methods

Fructose (purity: 99%), 5-hydroxymethylfurfural, H_2SO_4, HCl, H_3PO_4, acetic acid, $CuCl_2$, and $PdCl_2$ were purchased from

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† Electronic supplementary information (ESI) available: Arrhenius plot for the dehydration of fructose in [BMIM]Cl (Fig. S1). See DOI: 10.1039/b905975j

Wako Pure Chemical Company, 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl], purum grade, purity: 98%), Amberlyst® 15 ion exchange resin and Dowex® 50WX8 resin were purchased from Sigma-Aldrich Company, all of them were used without further purification.

In a typical reaction, 0.100 g of fructose (0.556 mmol) was dissolved in 1 g of [BMIM][Cl] firstly, and 0.05 g Amberlyst® 15 ion exchange resin catalyst was added. The reaction mixture was heated to 80 °C and kept for 10 min in the water bath. The experiments that used reaction temperatures above 100 °C were conducted with microwave heating. After reaction, each sample was diluted with 10 g of ultra pure water before analysis. For the recycling of ionic liquid and catalyst, 5-HMF was extracted out from the mixture 5 times with 8 ml of ethyl acetate after 0.5 g of water was added. After extraction, the ionic liquid was heated at 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate. The ionic liquid was then used directly for the next run by adding fructose.

2.2 Analyses

For analysis of solutions, a high performance liquid chromatograph equipped with a refractive index detector (HPLC-RI, SH 1011 column) was employed. The column oven temperature was 60 °C, and mobile phase was a 0.5 mM sulfuric acid aqueous solution that had a flow rate of 1 ml/min.

2.3 Yield and selectivity definitions

The fructose conversion (mol%), the 5-HMF yield (mol%) and selectivity (mol%) were evaluated on a carbon basis as shown below:

Fructose conversion (mol%):

$$X = \left(1 - \frac{\text{Fructose concentration in product}}{\text{Fructose concentration in the loaded sample}}\right) \times 100\% \qquad (1)$$

5-HMF yield (mol%):

$$Y = \frac{\text{Moles of carbon in 5-HMF}}{\text{Moles of carbon in the loaded as fructose}} \times 100\% \qquad (2)$$

5-HMF selectivity (mol%):

$$S = \frac{\text{Yield of 5-HMF}}{\text{Fructose conversion}} \qquad (3)$$

3. Results and discussion

3.1 Fructose conversion in [BMIM$^+$]Cl$^-$ treated with catalysts

[BMIM][Cl] is one of the most common ionic liquids, which is used broadly as the starting material for the production of other ionic liquids. We studied the conversion of fructose to 5-HMF in [BMIM][Cl] with catalysts at 80 °C for 10 min. The catalysts included mineral acids (H_2SO_4, HCl, H_3PO_4), organic acids (acetic acid), Lewis acids ($CuCl_2$, $PdCl_2$) and solid acid ion-exchange resins (Dowex® 50WX8 and Amberlyst® 15). As shown in Fig. 1, it can be seen that H_3PO_4 and acetic acid exhibited little or no catalytic activity under the experimental conditions, whereas HCl and $PdCl_2$ had weak activity. On the other hand, H_2SO_4, $CuCl_2$ and the ion-exchange resins had very high catalytic activity for the conversion of fructose to 5-HMF. Under the experimental conditions, Amberlyst® 15 resin gave a 99.6% fructose conversion and 83.3% 5-HMF yield at 80 °C for 10 min reaction time. Since results were most favorable for Amberlyst® 15 resin, this catalyst was chosen to study in detail.

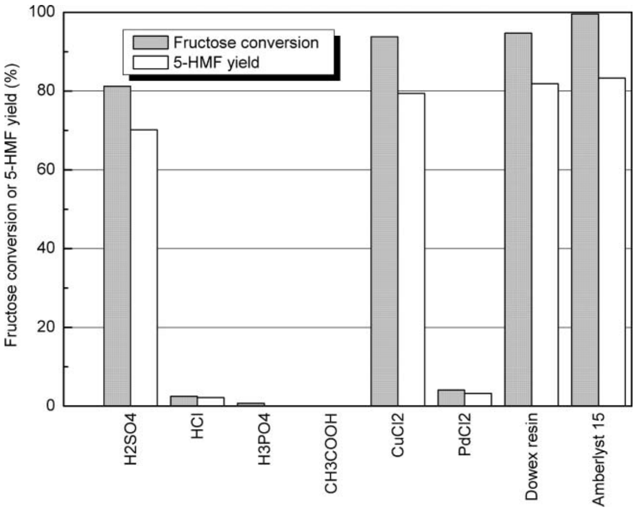


Fig. 1 Conversion of fructose to 5-HMF in [BMIM][Cl] in the presence of catalysts. Conditions: fructose 0.05 g, [BMIM][Cl] 1 g, 80 °C, 10 min reaction time, catalyst loading 18 mol% based on sugar, 0.05 g for Amberlyst® 15 ion exchange resin and Dowex® 50WX8 resin.

3.2 Effect of catalyst dosage on fructose conversion and 5-HMF yield

Fig. 2 shows the effect of the catalyst dosage on fructose conversion and 5-HMF yield. The amount of resin used was 0.02, 0.04, 0.08 and 0.1 g respectively. In the absence of catalyst, at a reaction temperature of 80 °C, no fructose conversion was observed for a reaction time of 20 min (not shown). In the presence of catalyst (0.02 g), formation of 5-HMF occurred. When the catalyst dosage increased from 0.02 to 0.04 g, the 5-HMF yield remarkably increased at 80 °C for a reaction

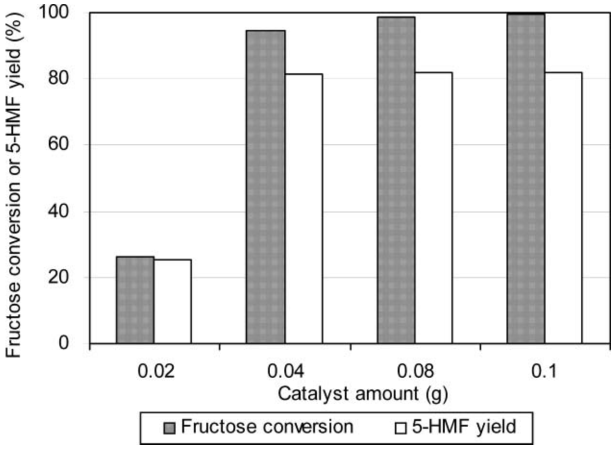


Fig. 2 Effect of catalyst dosage on fructose and 5-HMF yield (Amberlyst® 15 ion exchange resin, fructose 0.05 g, [BMIM][Cl] 1 g, 80 °C, reaction time 5 min).

Table 1 Effect of reaction temperature on the conversion of fructose to 5-HMF (conditions: 0.05 g fructose, 1 g [BMIM][Cl], 0.05 g Amberlyst resin)

Reaction temperature (°C)	Reaction time (min)	Fructose conversion (%)	5-HMF yield[a] (%)	5-HMF selectivity (%)
70	3	10.2	9.9	97.2
	5	52.9	49.2	93.0
	10	93.4	81.3	87.0
	20	98.6	83.1	84.3
80	3	31.9	31.6	99.1
	5	90.7	79.3	87.4
	7	97.3	82.0	84.3
	10	98.6	83.3	84.5
90	1	52.2	47.1	90.4
	3	91.5	79.0	86.3
	5	98.7	83.5	84.6
	7	99.4	83.2	83.7
100	2	93.0	79.2	85.2
	3	98.1	81.6	83.2
120	0.33	77.6	66.8	86.1
	0.5	96.5	81.2	84.1
	1	99.3	82.2	82.8

[a] Byproduct yields: glucose ⩽2%, levulinic acid ⩽1%, formic acid ⩽2%.

time of 5 min, from 25.5% to 81.6%. However, when the amount of resin was increased from 0.04 to 0.1 g, there was little change in fructose conversion and 5-HMF yield. As the fructose conversion and 5-HMF yield did not change with further catalyst dosage over 0.04 g, this implies that there are sufficient catalytic sites (*ca.* 0.2 mmol sulfonic acid sites for 0.04 g resin) available for the substrate fructose (0.278 mmol) in the system at the experimental conditions.

3.3 Effect of reaction temperature

Table 1 shows the effect of reaction temperature on fructose conversion. The use of ionic liquid as solvent in the acid catalytic dehydration of fructose significantly reduced the temperature required for the reaction compared with aqueous or organic solvents.[2,3,8,13] The fructose conversion was 98.6% for a 5-HMF yield of 83.3% at 80 °C for 10 min reaction time. In our previous work, the fructose conversion and 5-HMF yield were 95.1% and 73.4%, respectively, at 150 °C for 15 min in 70:30 (w/w) acetone–water mixture in the presence of resin as catalyst.[2] Compared with that work, the reaction temperature could be reduced from 150 °C to 80 °C for a similar fructose conversion but at shorter reaction times (Table 1).

The reaction temperature had a large effect on both the fructose conversion and 5-HMF yield. When the reaction temperature was 70 °C, the fructose conversion was 52.9% for a 5-HMF yield of 49.2% for 5 min reaction time. The 5-HMF yield increased from 49.2% to 83.5% when conditions changed from 70 °C to 90 °C for a 5 min reaction time. For a reaction temperature of 120 °C, a 5-HMF yield of 82.2% was obtained for 1 min.

Many works reported a reaction order of one for the dehydration of fructose to 5-HMF.[2,3,13,14] According to this, the kinetic analysis of the dehydration of fructose in ILs was performed. Plots of $\ln(1 - X)$ (X is fructose conversion) *versus* reaction time (t) were made to obtain first order kinetic constants. With those constants, an Arrhenius plot was generated as shown in the ESI (Fig. S1†) and an activation energy of 65.2 kJ/mol was determined. The value of this work was lower than that of previous values (*ca.* 100 kJ/mol) reported in the literature, which may be attributed to the reaction occurring in organic solvents.[2,13] The analysis shows that the activation energy of fructose dehydration to 5-HMF is lower in ionic liquids than in organic solvents.

Also, for comparison, results that other authors have achieved with ionic liquids for fructose conversion to 5-HMF are summarized in Table 2. The results of this work show that the present process is more efficient than previous works as evident from the shorter reaction times. The efficiency of fructose dehydration mainly depends on the reaction media and catalyst employed. Compared with organic solvents such as DMSO, ionic liquids as solvents could effectively increase the reaction rate,[9] and it has been reported that there is an obvious relationship between activity and catalyst acidity in the reaction, and that high catalyst acidity leads to high reaction activity.[5] The higher acidity of the strong sulfonic ion-exchange resin over that of the other catalysts such as CrCl$_2$ and citric acid should probably be responsible for its higher catalytic activity in this work.

3.4 Effect of reaction time

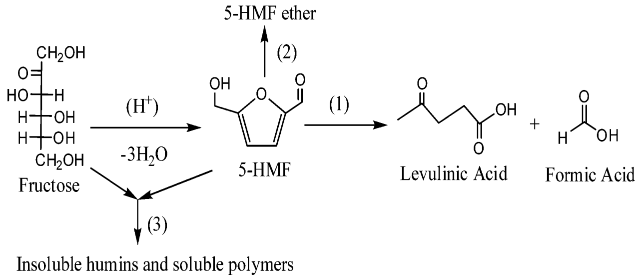
As listed in Table 1, almost all of the fructose was converted into 5-HMF, and the 5-HMF selectivity was as high as 95% at the beginning of the reaction. The selectivity decreased as the reaction proceeded, and went below 85% as the fructose conversion reached about 99.5%. As the reaction proceeded, the color of the solution changed to deep brown, which is evidence for the decomposition of the formed 5-HMF.

There are three pathways for the decomposition of 5-HMF in acid catalyzed dehydration of fructose,[24,25] as depicted in Scheme 1. The first pathway is the rehydration of 5-HMF into levulinic acid and formic acid; the second pathway is

Table 2 Comparison of fructose conversion efficiencies in different ionic liquids

Solvents	Catalyst	Reaction temperature (°C)	Reaction time	Fructose conversion (%)	5-HMF yield (%)	Ref.
[EMIM][Cl]	CrCl$_2$	80	3 h	—	83	6
DES[a]	Citric acid	80	1 h	93.2	77.8	4
				94.2	86.8[b]	4
[BMIM][Cl]	NHC-CrCl$_2$	100	6 h	—	96	1
[BMIM][Cl]	Amberlyst® 15 resin	80	10 min	98.6	83.3	This work
		100	3 min	98.1	81.6	This work

[a] Deep eutectic solvent. [b] With ethyl acetate in situ extraction.



Scheme 1 5-Hydroxymethylfurfural formation from fructose and 5-HMF decomposition pathways.

the self-polymerization between 5-HMF molecules; and the third pathway is the cross-polymerization between 5-HMF and fructose.[7,14,24] In non-aqueous systems 5-HMF rehydration can be suppressed, and in this work, the levulinic acid yield was always lower than 1.0% since there was only a limited amount of water in the system that results from the dehydration of fructose and from any impurities in [BMIM][Cl]. Thus, it is unlikely that the rehydration pathway causes the 5-HMF selectivities to decrease.

Self- or cross-polymerization reactions of 5-HMF can occur and lead to brown soluble polymers and insoluble humins.[14] We tested the self-polymerization of 5-HMF in the system at 80 °C by adding 0.05 g of 5-HMF and 0.05 g resin into 1 g of [BMIM][Cl] in the absence of fructose. After a reaction time of 20 min, 99.6% of 5-HMF could be recovered, indicating that the self-polymerization between 5-HMF molecules did not occur in the system, and that the 5-HMF was stable at the experimental conditions in the absence of fructose.

The byproducts that could be analyzed with HPLC in this work were glucose, levulinic acid and formic acid; the yields were below 2%, 1% and 2%, respectively. The color of the reacted solutions was brown, and the brown color remained even after yellow 5-HMF was extracted from the mixture with ethyl acetate. The brown products appearing in acid catalyzed dehydration of fructose are thought to be soluble polymers and humins, and at present these soluble polymers have not been able to be quantified.[14,24] In this work, the decrease in 5-HMF selectivity with reaction time is supposed to be due to the polymerization between 5-HMF and fructose to form humins, which consume the initial fructose and form 5-HMF, and hence reduce the 5-HMF selectivity.

3.5 Effect of initial fructose concentration

In acid catalytic dehydration of fructose, initial fructose concentration has a large effect on 5-HMF yield and selectivity. As discussed above, 5-HMF can combine with fructose, and cross-polymerize to form humins.[14] In aqueous systems including aqueous mixture systems, losses due to humin formation can be as high as 35% for 18 wt.% fructose solution, although this value decreases to 20% for 4.5 wt.% fructose solutions.[14]

The effect of initial fructose concentration on fructose conversion and 5-HMF selectivity in [BMIM][Cl] is illustrated in Fig. 3. When the fructose/[BMIM][Cl] weight ratio increased from 0.01 to 0.05, the 5-HMF selectivity changed slightly from 86% to 85.2%. As the fructose/[BMIM][Cl] weight ratio increased from 0.05 to 0.1, the 5-HMF selectivity decreased by about 5%. Additional increases in the fructose/[BMIM][Cl] weight ratio did not lead to significant lowering of the 5-HMF selectivity, which is similar to the trends noted by Yong *et al.* for the conversion of fructose in [BMIM][Cl] with NHC/$CrCl_2$ (NHC = N-heterocyclic carbene) complexes as catalysts.[1] It can be seen that ionic liquids other than aqueous or aqueous mixtures can inhibit the formation of humins in fructose conversions.

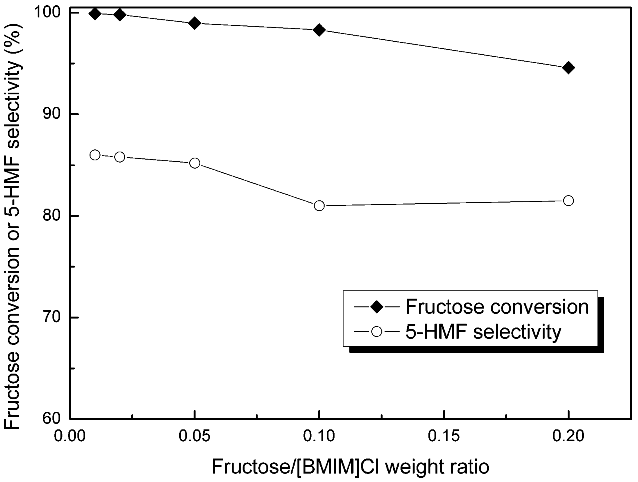


Fig. 3 Effect of substrate loading on 5-HMF yield from fructose (80 °C, [BMIM][Cl] 1 g, resin 0.05 g, 10 min).

3.6 Effect of water content in [BMIM$^+$]Cl$^-$ on fructose conversion

Water is generally thought to has a negative effect on the dehydration of fructose to 5-HMF.[2,4] Since [BMIM][Cl] is a hydroscopic ionic liquid, the influence of water content in [BMIM][Cl] on fructose dehydration was studied. As shown in Fig. 4, when the water content in [BMIM][Cl] was below 5 wt.%, it had little effect on the fructose conversion and 5-HMF yield. However, as water content increased to above 5 wt.%, the fructose conversion and 5-HMF yield decreased significantly. Zhao *et al.* added water or organic solvents such as glycerol to

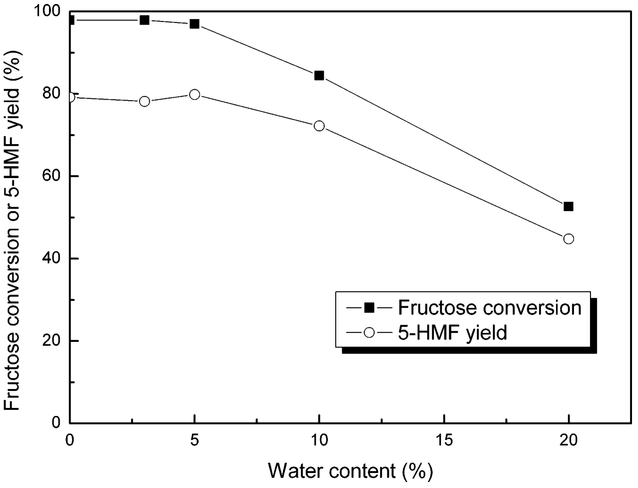


Fig. 4 Influence of water content in [BMIM][Cl] on fructose conversion (80 °C, 0.01 g fructose, 1 g [BMIM][Cl], 0.05 g resin, 10 min).

[EMIM][Cl] and proposed that lowering the dielectric constant of the reaction media would result in the loss of catalytic activity.[6]

3.7 Recycling of [BMIM][Cl] and catalyst

In the principles of green engineering,[26,27] recycling of both solvent and catalyst is essential so these were examined. Experiments were conducted at 80 °C for a reaction time of 10 min. The product 5-HMF was separated from the solvent mixture after reaction by extracting 5 times with 8 ml of ethyl acetate after 0.5 g of water was added, similar to other procedures in the literature.[1,4] [BMIM][Cl] and fructose were found to be insoluble in ethyl acetate and 5-HMF was the sole product in the ethyl acetate phase similar to that noted by Hu *et al.*[4] We examined the amount of 5-HMF in ethyl acetate that represents the total amount of 5-HMF obtained after separation. The reaction mixture after extraction was heated at 60 °C for 24 hours in a vacuum oven to remove water and residual ethyl acetate. It was then used directly in the next run by adding an equal amount of fructose. It can be seen in Fig. 5 that the recycled reaction ionic liquid and catalyst gave comparable amounts of 5-HMF showing that the catalyst retained a very high activity for the conversion of fructose into 5-HMF. The 5-HMF yield in the recycled system was even higher in some cases than that in the system with the fresh ionic liquid and resin, which might be due to the retention of some 5-HMF and unreacted fructose in the previous cycle.

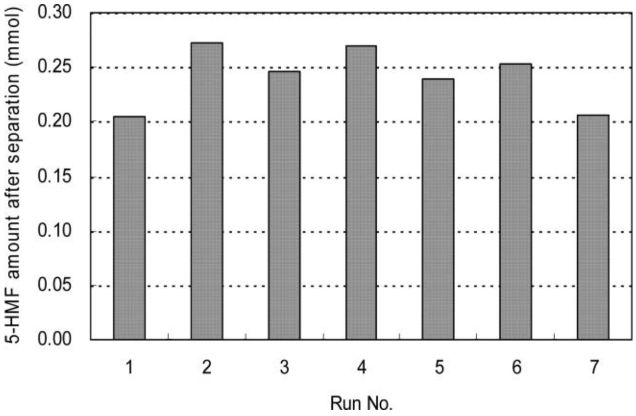


Fig. 5 Recycling of [BMIM][Cl] and catalyst (80 °C, 50 mg (0.278 mmol) fructose, 1 g [BMIM][Cl], 0.05 g resin, 10 min).

4. Conclusions

Catalytic dehydration of fructose to 5-HMF using a strong acid cation exchange resin as catalyst in ionic liquid [BMIM][Cl] was investigated. The process we developed was shown to be efficient, and a fructose conversion of 98.6% with 83.3% of 5-HMF yield was obtained at 80 °C for a relatively short reaction time of 10 min. When the reaction temperature increased to 120 °C, 99.3% of fructose conversion with 82.2% of 5-HMF yield was achieved at a reaction time of 1 min. Initial concentrations of up to 20 wt.% of fructose in the system did not lead to a lowering in 5-HMF selectivity. Water content below 5% in [BMIM][Cl] had little effect on the fructose conversion rate and 5-HMF yield, but water content above 5% caused a significant decrease in the fructose conversions and 5-HMF yields. The ionic liquid [BMIM][Cl] and resin could be recycled without loss of activity after the product 5-HMF was separated with ethyl acetate.

Although the process developed is efficient for the conversion of fructose to 5-HMF, further work is required to improve the 5-HMF yields.

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