Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 1220

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Published on 07 March 2012 on http://pubs.rsc.org | doi:10.1039/C2GC16671B

Entrainer-intensified vacuum reactive distillation process for the separation of 5-hydroxylmethylfurfural from the dehydration of carbohydrates catalyzed by a metal salt–ionic liquid†

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Received 26th December 2011, Accepted 30th January 2012
DOI: 10.1039/c2gc16671b

As more and more novel catalyst systems are being developed for the dehydration of carbohydrates, especially glucose, an effective way to separate the dehydration product 5-hydroxylmethylfurfural (5-HMF) is also required for industrial manufacturing. In this paper, for the first time, we have developed a process called EIVRD (entrainer-intensified vacuum reactive distillation) to separate 5-HMF from the dehydration solutions of carbohydrates catalyzed by a metal chloride/1-methyl-3-octyl imidazolium chloride ([OMIM]Cl) ionic liquid, in which high vacuity and entrainers were applied to intensify the distillation of 5-HMF as well as the dehydration of fructose or glucose. In such an EIVRD process, the average recoveries of 5-HMF dehydrated from fructose and glucose are around 93% and 88%, respectively. The recycling of the catalyst system in the EIVRD process is so convenient that the recovery and actual yield of 5-HMF is successfully repeated during the whole five recycled reactions.

Introduction

In recent years, the efficient utilization of biomass has received increasing attention as a promising alternative to petroleum for the production of fuels and chemicals.[1–4] Among the many possible biomass-derived chemicals, 5-hydroxylmethylfurfural (5-HMF) prepared from the dehydration of carbohydrates is considered to be a key bio-based platform compound, as it can be converted to 2,5-furandicarboxyl acid, 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl) tetrahydrofuran, dimethylfuran, and other liquid alkanes by oxidation, hydrogenation, hydrogenolysis or aldol condensation.[1,2,5–10]

Being the basic building units of the carbohydrates such as sucrose, inulin, cellulose and other polysaccharoses, fructose and glucose are always applied as model substrates for the dehydration of carbohydrates into 5-HMF. A lot of catalysts, including mineral acids (such as HCl, H_2SO_4 and H_3PO_4),[11–14] organic liquid acids (such as oxalic acid, levulinic acid and maleic acid),[15–17] metal salts and metal oxides (such as γ-TiP, C-ZrP_2O, TiO_2, $HTiNbO_5$–MgO, $NbOPO_4$ and ZrP),[18–23] ion exchange resins,[12,24,25] zeolites,[12,16,26,27] as well as ionic liquids[28–30] have been applied for the dehydration of carbohydrates.

Additionally, the selection of a suitable reaction solvent is of the same importance. Water,[12,18,19,22,23] organic solvents (such as acetonitrile, dimethylsulphoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA)),[5,24,26,31,32] organic–water mixtures (such as water–acetone, water–butanol and water–DMSO mixtures)[21,25,32] as well as ionic liquids[28–30] have been mainly studied for carbohydrate dehydration. From the ecological and technological point of view, aqueous processes are the most favored but, unfortunately, are inefficient, because 5-HMF can further react with water to form levulinic acid and formic acid.[17,33,34] Whereas in an ionic liquid medium, the formed amounts of levulinic acid and formic acid are very low, thus make it possible to obtain a high selectivity to 5-HMF. Moreover, the ionic liquid is likely to serve as a co-catalyst, especially in the dehydration of glucose which is catalyzed by $CrCl_2$ and $SnCl_4$.[30,35] By far, many ionic liquids, especially imidazolium-based ionic liquids have been demonstrated to be the most effective catalyst–solvent system for the conversion of fructose and glucose into 5-HMF,[24,30] owing to their outstanding characteristic properties such as low vapor pressure, good thermal stability and a range of tunable hydrophobicity/hydrophilicity. For example, a record yield of 5-HMF as high as 92% from fructose is achieved within 15–45 minutes at 90 °C using 1-*H*-3-methylimidazolium chloride ([HMIM]Cl) as the catalyst–solvent system.[36] Compared with the dehydration of fructose, the dehydration of glucose is rather difficult. However, such a problem has been overcome by Zhang's group, who have obtained a high 5-HMF yield of *ca.* 80% from glucose for the first time using $CrCl_2$–1-ethyl-3-methyl-imidazolium chloride ([EMIM]Cl) as the catalyst–solvent system.[30,37] Afterwards, an even higher yield of 5-HMF is obtained from glucose using a *N*-heterocyclic carbene complexed with $CrCl_2$/3-octyl-1-methyl imidazolium chloride ([OMIM]Cl) as a catalyst/solvent.[38] This

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2gc16671b

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new methodology enables high 5-HMF yields of 96% and 81% form fructose and glucose, respectively. Hu *et al.*[35] have found that $SnCl_4$ in 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM]BF_4$) is also effective for the conversion of glucose and glucose unit-containing carbohydrates.[11,30,39] Although the catalytic mechanism remains elusive, some insights on the reaction indicate that the special ionic liquid forms complexes with the metal chloride to promote rapid mutarotation of α-glucose to β-glucose, and leads to isomerization of glucose to fructose, while the latter can be much easier transformed to 5-HMF.[30,35,40]

In spite of many advantages in the dehydration of carbohydrates, the use of ionic liquids for the production of 5-HMF in industry has been impracticable up to now. The main problems are the separation of the products as well as the recycling of the ionic liquid-containing reaction medium. Similar to the conventionally used solvent such as DMSO and DMF, ionic liquids always have very high boiling points, however, 5-HMF is thermally sensitive. Therefore, it is neither economical nor technically feasible to separate the products out by simple solvent distillation. Alternatively, the extraction of 5-HMF from ionic liquids using organic solvents has been frequently reported.[35–38] Authors claimed that such a solvent extraction method can recover more than 90% of 5-HMF and the ionic liquid can be reused more than 5 times. For example, Moreau *et al.*[36] reported that 5-HMF can be completely extracted in a continuous manner with diethyl ether (50 ml for 8 h for 0.5 g of 5-HMF in 2 g of ionic liquid) or in a stepwise manner (6 × 150 ml for 1.2 g of 5-HMF in 2 g of ionic liquid), and the yield of 5-HMF decreases little, while the ionic liquid is reused for five times. Yu *et al.*[37] used methyl isobutyl ketone (MIBK) to recover 5-HMF from $CuCl_2/CrCl_2/[EMIM]Cl$ at 100 °C. Three successive 8 h runs were conducted, and more than 90% of 5-HMF is recovered. Hu *et al.*[5] conducted the dehydration of fructose in ethyl acetate/choline chloride (ChoCl)-based ionic liquid to promote the yield of 5-HMF by continuously extracting it from the ionic liquid phase. These solvent extraction processes are both time-consuming and require large amounts of solvent, which prevents their industrial use. Besides, the applied ionic liquids are always viscous and miscible with 5-HMF, therefore it is not as easy to extract 5-HMF as expected; the researchers themselves claim that such a method "is difficult, at the present time, to be transposed on a pilot scale".[36] So far, exploring an effective separation method is much more urgent in order to industrially manufacture 5-HMF from the dehydration of carbohydrates in ionic liquids.

Reactive distillation is a combination of chemical reaction and product separation by a distillation process within a single unit, and it has a wide range of industrial applications.[41–43] Inspired by our previous study on the Fischer esterification reactions catalyzed by ionic liquid in which we have easily separated the ester products and recovered the ionic liquid by distillation process,[44] the objective of the present study is focused on the reactive distillation process for the separation of 5-HMF from the metal chloride–ionic liquid catalyst system. Considering that 5-HMF has a much higher boiling point (114–116 °C, 133.3 Pa), two conventional chemical engineering strategies have been applied: (1) a vacuum pump is added to accelerate the evaporation of 5-HMF; (2) nitrogen and other organic vapours are used as entrainers to increase the evaporation efficiency. As reported, imidazolium ionic liquids with shorter carbon side chains show higher reactivity for the dehydration of carbohydrates. However, in order to avoid being distilled out together with 5-HMF under vacuum, ionic liquids having longer carbon side chains are more suitable to the distillation process. Based on the thermodynamic formula proposed by Valderrama and Robles,[45] the boiling point of [OMIM]Cl and [BMIM]Cl are estimated as 638.9 K and 548.9 K, respectively. Considering that the boiling point of 5-HMF is *ca.* 564 K,[6] it is rational to choose [OMIM]Cl as the reaction medium for the dehydration of carbohydrates in our following distillation process.

Experimental

Materials

Anhydrous [OMIM]Cl was synthesized from *n*-octyl chloride and 1-methylimidazole according to the literature.[46] Its structure was confirmed by FT-IR and ^1H-NMR analysis, the same as our previous study.[47] Fructose (purity: 99%) and glucose (purity: 99%) were bought from Sino-pharm chemical reagent Co. Ltd. Standard 5-HMF was bought from Tengzhou Runlong Flavours & Fragrances Co. Ltd (>99.9%). Iridium trichloride was bought from Shanxi Kaida Chemical Engineering Co. Ltd (molecular formula: $IrCl_3{\cdot}(1–2)H_2O$, iridium content ≥58.3%). $CrCl_3{\cdot}6H_2O$ and the organic solvents were all bought from Sino-pharm chemical reagent Co. Ltd.

A sliding-vane rotary vacuum pump (2XZ-2) was bought from Zhejiang Huangyan Qiujing Vacuum pump Co. Ltd. The vacuum pressure sensor (Model 760) for vacuity measurement was bought from Setra Systems, Inc.

Typical work-up procedure

The reaction set-up is shown in Fig. 1. Dehydration of the carbohydrates was carried out in a 100 ml magnetically stirred flask at

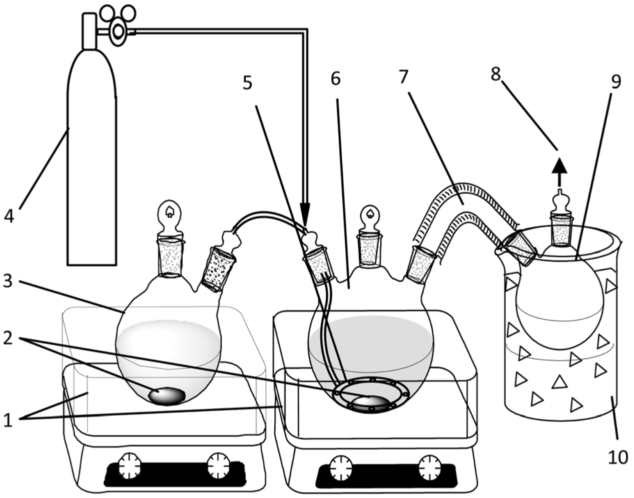

Fig. 1 Experimental set-up for the vacuum reactive distillation of the fructose and glucose dehydrations. Codes: 1) oil bath heater; 2) magnetic rotator; 3) two-neck flask for vapor generation; 4) nitrogen cylinder; 5) ring-type gas distributor; 6) three-neck flask; 7) connector with heat keeping jacket; 8) to vacuum oil pump; 9) two-neck flask for product collection; 10) ice bath.

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different temperatures (Fig. 1, code: 6). In a typical experiment, 7% (mol ratio based on fructose or glucose) of $CrCl_3$ or $IrCl_3$ and 20 g of [OMIM]Cl were successively added into the flask (Fig. 1, code: 6) and heated to the predetermined temperature by an oil bath. Then, fructose or glucose was added to initiate the reaction. A vacuum pump and an accurate pressure sensor were used to depressurize the system and record the value. The entrainer was introduced to the bottom of the flask (Fig. 1, code: 6) from the left inlet with a ring-type gas distributor (Fig. 1, code: 5). A nitrogen cylinder with a stable outlet pressure of 0.1 MPa was used as a nitrogen entrainer supplier. While hexane or MIBK were used as entrainers, *ca.* 150 ml of the corresponding liquid solvent was loaded in a 500 ml flask (Fig. 1, code: 3) and heated to its ambient boiling point (69 °C for hexane and 118 °C for MIBK) to generate saturated vapor with 0.1 MPa pressure, and was then introduced to the gas distributor (Fig. 1, code: 5). The flow rate of the gas is controlled by the working power of the vacuum pump. The generated 5-HMF was vaporized and entrained out, and settled down on the inner surface of the connector (Fig. 1, code: 7) and flask (Fig. 1, code: 9). Two samples were analyzed for carbohydrates and 5-HMF after the reaction was terminated: one is the 5-HMF in the ionic liquid reaction solution in flask (Fig. 1, code: 6) and the other one is the 5-HMF powder in connector (Fig. 1, code: 7) and flask (Fig. 1, code: 9) after rinsing with pure water.

Analysis

Carbohydrates were analyzed by HPLC (Detector: Waters 410 Differential Refractometer; Aminex® HPX-87H column 9 μm, 300 × 7.8 mm), using 5 mmol l^{-1} H_2SO_4 in ultrapure water as mobile phase at a flow rate of 0.6 ml min^{-1} and a column temperature of 60 °C. 5-HMF was analyzed by HPLC (UV Detector: Waters 2487; wavelength: 284 nm; Sunfire™ C18 column 5 μm; 250 × 4.6 mm), using 70% methanol in ultrapure water as mobile phase at a flow rate of 1 ml min^{-1} and a column temperature of 35 °C.

Recovery of 5-HMF was defined as the molar ratio of the 5-HMF collected in the connector (Fig. 1, code: 5) and the flask (Fig. 1, code: 6) to the total 5-HMF that added or could theoretically produced from. The yield of 5-HMF was defined as the molar ratio of the total amount of formed 5-HMF to the carbohydrates added.

Results and discussion

Thermal stability of 5-HMF in $IrCl_3$–[OMIM]Cl and $CrCl_3$–[OMIM]Cl

$IrCl_3$ and $CrCl_3$ were adopted as catalysts respectively for the dehydration of fructose and glucose in [OMIM]Cl, as they have been demonstrated to be the most effective metal salts for the same catalytic reactions in our previous study,[44,47] as well as in other reports.[30,48] $IrCl_3$ and $CrCl_3$ are regarded as singularly thermal stabilizers for 5-HMF at 100–120 °C,[30,47] which may inhibit the unwanted degradation of 5-HMF during the following vacuum distillation process. Since the vacuum reactive distillation experiment will be carried out at 150 °C or 180 °C, it is necessary to further study the thermal stability of 5-HMF at those higher temperatures first.

As shown in Fig. 2, 5-HMF is quite thermally unstable at 120 °C in [OMIM]Cl when no metal salt is added, with only 68% recovery after heating for 3 hours. In contrast, it tends to be much more stable in the presence of either 7 mol% of $IrCl_3$ or $CrCl_3$, in which only 1–3% degradation is found. Unfortunately, when the temperature increases, 5-HMF starts to degrade again despite the metal chloride being present. For $IrCl_3$–[OMIM]Cl, about 85% and 75% of 5-HMF are recovered after 3 hours of heating at 150 °C and 180 °C, respectively. 5-HMF appears to

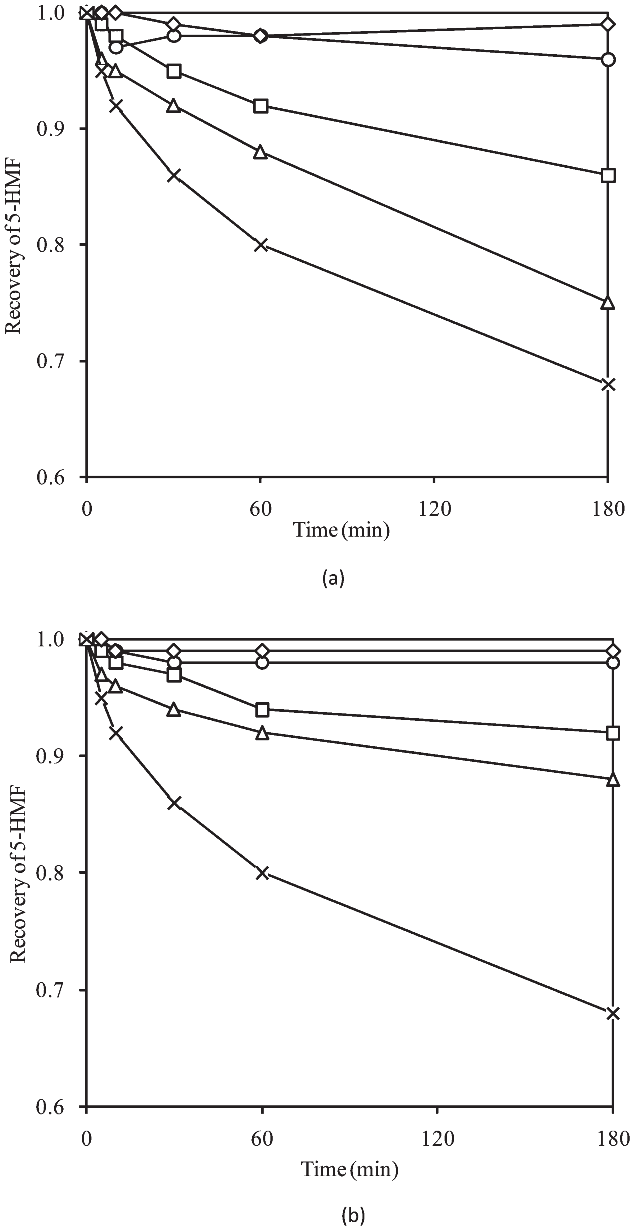

Fig. 2 Thermal stability of 5-HMF in $IrCl_3$–[OMIM]Cl (a) and $CrCl_3$–[OMIM]Cl (b) catalyst systems at 100 °C (◯), 120 °C (□), 150 °C (□) and 180 °C (△). × is 5-HMF in only [OMIM]Cl at 120 °C for comparison. Reaction conditions: 2.0 g of [OMIM]Cl and 7 mol% of $IrCl_3$ or $CrCl_3$ (or added only [OMIM]Cl for comparison) were first heated to the predetermined temperature, and then 140 mg of 5-HMF was added.

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Table 1 Vacuum distillation of 5-HMF from $IrCl_3$–[OMIM]Cl without entrainer

			Mass of 5-HMF (mg)			
Entry	Temp. (°C)	Time (min)	Residue in IL phase	Distilled out	Recovery (%)	Vacuity (Pa)
1	120	15	334	152	30.4	20–50
2		30	217	271	54.2	
3	150	15	255	224	44.7	90–120
4		30	135	343	68.5	
5	180	15	195	277	55.4	150–180
6		30	40.4	431	86.1	
7[a]	120	<5	ND	195	97.5	130–150
8[b]	120	<5	ND	487	97.4	130–150

Operation conditions: 0.5 g 5-HMF and 0.065 g $IrCl_3 \cdot (1–2)H_2O$ (*ca.* 7 mol% based on 5-HMF) dissolved in 20 g [OMIM]Cl. The vacuity is the as-shown value while the vacuum pump was running at its full capacity. [a] 0.2 g 5-HMF. [b] 0.5 g 5-HMF heated with the vacuum pump running at its full capacity; ND is the abbreviation of not detected.

be more stable in $CrCl_3$–[OMIM]Cl than in $IrCl_3$–[OMIM]Cl, in which nearly 90% of 5-HMF can be recovered in the former when heated at 180 °C for 3 hours. It can be seen from Fig. 2, that the degradation of 5-HMF can be controlled within 5%, in the range of experimental temperatures, if the heating time is less than 30 minutes. These results give a guide to estimate the degradation amount of 5-HMF during the following vacuum distillation process.

Vacuum distillation of pure 5-HMF from $IrCl_3$–[OMIM]Cl

In the first stage, pure 5-HMF, instead of the carbohydrate, was introduced into the $IrCl_3$–[OMIM]Cl system, in order to test the feasibility of the distillation process. Since the saturated vapor pressure of 5-HMF is rather low (*e.g.* 133.3 Pa at 114–116 °C), and the fraction of 5-HMF in [OMIM]Cl is always less than 10% in the dehydration of carbohydrate, leading to even lower partial vapor pressure in the gas phase, it is therefore necessary to add a vacuum pump to intensify the distillation. Compared with the distillation of pure 5-HMF, extra forces are needed to be overcome besides the intermolecular force of 5-HMF for successful distillation of 5-HMF from the $IrCl_3$–[OMIM]Cl system, *i.e.* the interaction forces between 5-HMF and [OMIM]Cl, as well as those between 5-HMF and $IrCl_3$. As a result, the distillation process should be much more difficult than that of pure 5-HMF.

As expected, only 54.2% of 5-HMF is distilled from the $IrCl_3$–[OMIM]Cl system at 120 °C in 30 minutes when 0.2 g of 5-HMF was boiled and evaporated rapidly in a few minutes at 120 °C at a vacuity of 130–150 Pa (Table 1, entries 2 and 7). Higher recoveries of 5-HMF are obtained at higher temperatures: *i.e.* 68.5% at 150 °C and 86.1% at 180 °C in 30 minutes, as increasing the temperature can raise the partial vapor pressure of 5-HMF. These recoveries are fairly satisfying. However, in consideration of the generally less than 50% yield of 5-HMF from the dehydration of glucose, the final recovery of 5-HMF would be even less by the reactive distillation process. Therefore, in order to obtain a satisfactory recovery of 5-HMF or to operate the process at milder conditions, we attempted to add an entrainer to improve the efficiency of the vacuum distillation process.

The idea of adding entrainers originated from the classic refinery industry of edible oil, which uses high-temperature water steam or nitrogen to remove the substances with lower boiling points from triglycerides such as long-chain fatty acids, steroids and odor components.[49–52] Principally, the addition of an entrainer can increase the gas–liquid contact area, which will enhance the mass transfer of the target component from the liquid phase to the gas phase. Besides, the affinity from the entrainer may also accelerate the distillation of the target component. As a result, a higher recovery of the target component could be obtained in the gas phase at milder operation conditions. As shown in Table 2, with the addition of nitrogen as an entrainer, the recoveries of 5-HMF from $IrCl_3$–[OMIM]Cl are remarkably higher than those when no entrainer was introduced (Table 1). Furthermore, a higher recovery of 5-HMF can be obtained at a lower temperature with a longer degassing time and at a higher temperature with a lower degassing time. For example, 95.5% of 5-HMF is recovered at 150 °C in 30 minutes with nitrogen as an entrainer (Table 2, entry 6) while a similar higher value, 94.7% of 5-HMF recovery is obtained at 180 °C in 10 minutes with the same entrainer (Table 2, entry 8). An excessive distillation time of 30 minutes is unnecessary for improving the recovery (Table 2, entry 9), indicating that a gas–liquid equilibrium of 5-HMF has already been reached in

Table 2 Vacuum distillation of 5-HMF from $IrCl_3$/[OMIM]Cl with nitrogen as an entrainer

			Mass of 5-HMF (mg)		
Entry	Temp. (°C)	Time (min)	Residue in IL phase	Distillated out	Recovery (%)
1	120	5	287	203	40.5
2		10	167	322	64.2
3		30	66	428	85.5
4	150	5	204	288	57.5
5		10	55.7	438	87.5
6		30	8.5	478	95.5
7	180	5	90.5	403	80.5
8		10	5.5	474	94.7
9		30	2.5	469	93.8

Operation conditions: 0.5 g of 5-HMF and 0.065 g of $IrCl_3 \cdot (1\text{-}2)H_2O$ (ca 7 mol% based on 5-HMF) were dissolved into 20 g of [OMIM]Cl. Nitrogen was introduced from the left neck of the three-neck flask (code 4 in Fig. 1). The vacuity is controlled at *ca.* 300 Pa.

Table 3 Vacuum Reactive distillation of 5-HMF from the dehydration of carbohydrates with different entrainers

Entry	Carbohydrate	Entrainer	Temp. (°C)	Time (min)	Recovery (%)	Yield (%)
1	Frustose	N_2	180	10	90.6	94.4
2			150	30	89.4	93.2
3		Hexane	180	10	94.6	93.8
4			150	30	93.6	93.7
5		MIBK	180	10	95.0	95.1
6			150	30	93.6	94.6
7[a]		—	180	10	—	92.5
8[a]		—	150	30	—	90.8
9[a]		—	120	20	—	89.0
10	Glucose	N_2	180	10	88.3	68.5
11			150	30	85.3	65.2
12		Hexane	180	10	87.5	70.4
13			150	30	88.6	64.8
14		MIBK	180	10	88.2	71.8
15			150	30	88.4	66.2
16[a]		—	180	10	—	51.3
17[a]		—	150	30	—	42.1
18[a]		—	100	180	—	35.1

Operation conditions: 2 g of fructose/glucose and 0.065 g of $IrCl_3\cdot(1\text{-}2)H_2O$/0.049 g of $CrCl_3\cdot 6H_2O$ (ca 7 mol% based on fructose) were dissolved into 20 g of [OMIM]Cl. Nitrogen or organic vapor was introduced from the left neck of the three-neck flask (code 4 in Fig. 1). The vacuity is controlled at *ca.* 300 Pa. [a] Reaction carried out without vacuum distillation.

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10 minutes, and further degassing time leads to the decomposition of 5-HMF.

These results demonstrate that the distillation of 5-HMF from the metal salt–[OMIM]Cl system under vacuum is feasible, and the favorable operation conditions are at 150 °C for 30 minutes and 180 °C for 10 minutes.

Entrainer-intensified vacuum reactive distillation (EIVRD) for 5-HMF

As vacuum distillation with an entrainer is effective in the recovery of 5-HMF, as mentioned above, the next step was to apply the EIVRD process to the dehydration reactions of the carbohydrates in the metal chloride–[OMIM]Cl system. For either fructose or glucose, three entrainers, *i.e.* nitrogen, hexane, and MIBK, were tried. The results are shown in Table 3.

As can be seen from Table 3, the EIVRD process is quite effective for the recovery of 5-HMF from the dehydration reaction bulk. Within the experimental range, the averaged recoveries of 5-HMF dehydrated from fructose and glucose are around 93% and 88%, respectively. These results are very exciting as they report, for the first time, the separation of the 5-HMF product from the reaction bulk with high recoveries. Use of a high temperature (180 °C) can increase the dehydration rate and the vapor pressure of 5-HMF, as a result, the reaction is almost complete within 10 minutes and the maximum recovery is obtained. However, it seems that the contribution of a higher temperature can be compensated by prolonging the reaction time at a lower temperature, as it can be seen that similar recoveries are reached in 30 minutes while the reaction was carried out at 150 °C.

It is generally known that glucose can be converted to 5-HMF by two steps, *i.e.*, isomerization into fructose, and subsequent dehydration to 5-HMF.[27,39,53] As a result, the dehydration of glucose is more difficult than that of fructose. It is the same case based on our results (Table 3). However, compared with the dehydration reactions without vacuum distillation, the yields of 5-HMF from glucose in our EIVRD process are greatly increased by more than 20% (*e.g.* Table 3, entries 11 *vs.* 17). This could be explained that the EIVRD process removes 5-HMF out from the reaction bulk soon after it generates, which (1) avoids further decomposition of the produced 5-HMF; (2) avoids the cross-reactions between the reactive aldehyde groups in 5-HMF, fructose and glucose which was mentioned in our previous work,[43] and (3) depletes fructose much more rapidly and therefore pushes the right shift of the isomerization equilibrium reaction of glucose to fructose. Only a few types of catalyst (base[39] or enzyme[53]), which promote the isomerization of glucose to fructose and are effective in the dehydration of glucose to 5-HMF have been reported, so it is exciting that we have reached the goal by the simple entrainer-intensified vacuum reactive distillation process.

When fructose was used as a substrate, the yield of 5-HMF can be as high as 95% with our EIVRD process.

As shown in Table 3, the type of the entrainers used in this work has little effect on the recovery and the yield of 5-HMF. We therefore deduce that the distillation of 5-HMF in our case, is controlled by the surface area of the liquid–gas interface while the entrainer is bubbled in, rather than the affinity force between the entrainer and 5-HMF. In all of the entries in Table 3, the conversion of fructose or glucose is close to 100%.

Recycle of $IrCl_3$–[OMIM]Cl system

Compared with the reported laboratory solvent-extraction method for 5-HMF removal,[35–38] the recycling of the catalytic systems in our EIVRD process is quite convenient. After one batch of the reaction is completed, 2 g of fructose or glucose is added directly into the flask reactor to initiate the next reaction. As shown in Table 4, both the recovery and the yield of 5-HMF

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Table 4 Recycling of the catalyst system in the dehydration of fructose and glucose

	Fructose used as reactant			Glucose used as substrate		
Entry	Recovery	Yield	Purity of obtained HMF	Recovery	Yield	Purity of obtained HMF
1	88.6	91.4	94.5	86.2	65.1	93.2
2	86.7	92.2	95.1	87.1	63.8	92.9
3	87.5	91.1	94.8	84.5	65.4	94.6
4	88.6	93.5	93.7	82.6	66.7	94.1
5	89.3	93.1	94.1	84.8	64.8	92.9

Note: the reaction conditions were similar to those of entry 2 for fructose and entry 11 for glucose in Table 3.

are well repeated during the five cycles of $IrCl_3$–[OMIM]Cl for the dehydration of either fructose or glucose. Small amounts of an insoluble solid is found at the bottom of the reactor, which may be ascribed to the formation of by products such as humins, carbon and other polymers at high temperature. Such a solid, however, can be easily discarded by filtration after several runs when the amount is no longer negligible.

The purity of the obtained 5-HMF by HPLC detection is around 92.9–95.1%, indicating that 4.9–7.1% of [OMIM]Cl (most probably) is stripped out with 5-HMF. This can also be seen from its ^{1}H NMR spectrum (Fig. 5s†) in which several small impurity peaks are visible. However, a crystallization and re-crystallization process can be easily carried out to further purify the 5-HMF.

Discussion

As we know, dehydration of fructose is rather easier than that of glucose. Therefore the first step to achieve the final goal of the dehydration of biomass is to dehydrate glucose efficiently. The EIVRD process can improve the yield of glucose remarkably. More excitingly, it can effectively separate 5-HMF out from the reaction bulk with high recovery. From an industrial point of view, the EIVRD process is simple and easy to operate.

Comparing Tables 1–3, one can see that the direct vacuum distillation could separate 5-HMF to certain extent, while the introduction of an entrainer, yet independent of its polarity, enabled the distillation to be performed much more efficiently, indicating that increasing the surface area of the gas–liquid phase is the main reason for using an entrainer to improve the separation of 5-HMF. Consequently, a reactor that can produce a high surface area of the reaction liquid may have the same effect for the separation of 5-HMF. Conceptual reaction/separation equipment that is similar to the existing molecular distillation equipment[54] may be a good choice. In such an equipment, the dehydration of carbohydrates in the ionic liquid is conducted within the narrow and high-speed rotating cylinders. The reaction liquid therefore forms a very thin layer with large specific surface areas adhering to the inner wall of the outer cylinder, in which 5-HMF having higher vapor pressure will be evaporated under heat and vacuum and form light components or the final product, while the metal salt and ionic liquid, having ignorable vapor pressures, will not be distilled and consequently form the heavier component. The heavier component can be re-entered into the cylinder reactor with more carbohydrates to make the reaction consecutive.

As reported, the imidazolium ionic liquid, that has shorter carbon side chains, shows higher reactivity for the dehydration of carbohydrates. However, in order to avoid being distilled out together with 5-HMF under vacuum, ionic liquids having longer carbon side chains are more suitable to this distillation process. Based on the thermodynamic formula proposed by Valderrama and Robles,[45] the boiling point of 3-octyl-1-methyl imidazolium chloride ([OMIM]Cl) and 3-butyl-1-methyl imidazolium chloride ([BMIM]Cl) are estimated as 638.9 K and 548.9 K, respectively. Considering the boiling point of 5-HMF is *ca*. 564 K,[6] it is rational to choose [OMIM]Cl as the reaction medium for the dehydration of carbohydrate in our following distillation process.

The amount of [OMIM]Cl used has a large impact on the mass transfer efficiency between the gas and liquid phases during the EIVRD process. We found that it was very hard to distribute the entrainer gas uniformly in the liquid phase ([OMIM]Cl) when only 2 g of [OMIM]Cl was used as the reaction medium during the first stage of the experiment. When the amount of [OMIM]Cl was increased to 20 g, a simple ring-type gas distributor could be introduced to the bottom of the reaction flask to intensify the blending of the entrainer gas and the [OMIM]Cl,which worked efficiently. However, we did not optimize the economic amount in the present work.

Conclusions

In this paper, for the first time, we have developed a process called the entrainer-intensified vacuum reactive distillation (EIVRD) process, which can be used to separate 5-HMF from the dehydration solutions of carbohydrates catalyzed by a metal chloride–[OMIM]Cl system. A high vacuity and an entrainer were applied to intensify the dehydration of fructose or glucose. The following main conclusions can be drawn:

(1) 5-HMF is thermally instable at 150 °C and 180 °C, while the presence of $IrCl_3$ or $CrCl_3$ can decrease its degradation to within 5% if the heating time is less than 30 minutes.

(2) Vacuum distillation is effective to separate 5-HMF from [OMIM]Cl. Additionally, the introduction of nitrogen as an entrainer can accelerate the distillation of 5-HMF, by which 95.5% and 94.7% recovery of 5-HMF can be achieved at 150 °C in 30 minutes and at 180 °C in 10 minutes, respectively.

(3) The EIVRD process used in this study can improve the dehydration of glucose remarkably. More excitingly, it can effectively separate 5-HMF out from the reaction bulk with high recovery. In the EIVRD process, the average recoveries of

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Published on 07 March 2012 on http://pubs.rsc.org | doi:10.1039/C2GC16671B

5-HMF dehydrated from fructose and glucose are around 93% and 88%, respectively. The affinity of the entrainer has little effect on the recovery of 5-HMF.

(4) Recycling of the $IrCl_3$–[OMIM]Cl catalyst system in the EIVRD process is very convenient. Recovery of the catalyst system and the actual yield of 5-HMF are repeated rather well during all five recycled reactions of the dehydration of either fructose or glucose.

Acknowledgements

This research was supported by the Zhejiang Provincial Natural Science Foundation of China (Y4090304, Y4100671) and National Natural Science Foundation of China (21106134, 20936005).

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