Applied Catalysis A: General 403 (2011) 98–103

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

A process for efficient conversion of fructose into 5-hydroxymethylfurfural in ammonium salts

Quan Cao[a], Xingcui Guo[a], Jing Guan[a], Xindong Mu[a,*], Dongke Zhang[a,b,**]

[a] Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, People's Republic of China
[b] Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

ARTICLE INFO

Article history:
Received 19 April 2011
Received in revised form 11 June 2011
Accepted 18 June 2011
Available online 24 June 2011

Keywords:
Ammonium salts
Biphasic system
Dehydration
Fructose
5-Hydroxymethylfurfural (HMF)
Tetraethyl ammonium chloride (TEAC)

ABSTRACT

Low melting systems consisting of ammonium salts and highly concentrated fructose were used for the conversion of fructose into 5-hydroxymethylfurfural (HMF). Not only acting as solvents, at sufficiently high temperatures, the ammonium salts themselves could also catalyse the dehydration of fructose to HMF. Among those salts, tetraethyl ammonium chloride (TEAC) was found to be the most efficient solvent-catalyst, demonstrated by its ability to achieve 81.3% HMF yield with 33.3 wt% fructose concentration at 120 °C. 79.2% HMF yield was obtained with 50 wt% fructose concentration in the TEAC/fructose system using 5 mol% $NaHSO_4{\cdot}H_2O$ as a co-catalyst. A semi continuous biphasic system of TEAC/fructose/$NaHSO_4{\cdot}H_2O$ melt using tetrahydrofuran (THF) to recover HMF was proposed and demonstrated in a laboratory scale process operating at 120 °C. The impurities in the HMF recovered, involving TEAC and $NaHSO_4{\cdot}H_2O$, were determined using ^{1}H NMR, elemental analysis and ICP-OES.

1. Introduction

Carbohydrates derived from biomass are one of the most abundant renewable resources and possess a great potential to become raw materials for the production of many high value products [1–4]. Among those products, 5-hydroxymethylfurfural (HMF), which can be produced by the dehydration of hexose [5–13], has attracted much attention. By oxidation, hydrogenation, hydrogenolysis, HMF can be further transformed into useful chemicals such as 2,5-furandicarboxylic acid, 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl)tetrahydrofuran which can be used as monomers in the synthesis of new polymeric materials, and dimethylfuran [8,13,14] which is suitable to be used as a liquid transportation fuel.

An alternative, more convenient and efficient way to produce HMF is acid-catalysed dehydration of fructose, because of the similar conformation between the furanose form of fructose and HMF. However, due to the simultaneous side reactions of fructose and HMF [15], the selectivity of HMF in the fructose dehydration is limited. In an effort to achieve a high HMF yield, a great deal of work has been reported in the literature, using various mediums, such as water [10,16–19], highly polarised organic solvents [7,9,12,20–23] and ionic liquids [11,24–27]. HMF produced under acidic aqueous conditions is partially rehydrated to form levulinic acid and formic acid [28], leading to a comparably low HMF yield. Although excellent yields of HMF can be achieved in some high-boiling point organic solvents such as dimethyl sulfoxide (DMSO) [9,12,22,23] and dimethylacetamide (DMA) [20], the disadvantage of using those solvents is the high energy consumption during separation [2]. Satisfactory yields can also be obtained in ionic liquids in the presence of acidic additives [25,28–30] or metal catalysts [11,24,25,31]. Furthermore, the choline chloride (ChoCl)/citric acid melt [32] has been reported to exhibit excellent catalytic activity in fructose dehydration.

A high substrate concentration is usually preferred to improve the efficacy of the process. However, most of the aforementioned catalytic systems are only tolerant towards low to moderate fructose concentrations (not more than 30 wt%) with very few exceptions. A low melting system of ChoCl/fructose [15] containing 40 wt% of fructose has been developed, where 67% HMF yield was achieved in the presence of a catalyst. An aqueous acidic system with up to 50 wt% fructose has also been shown to give a HMF yield of approximately 70%, where DMSO and polyvinylpyrrolidinone (PVP) were added to suppress the side reactions [2].

The present contribution reports a new approach to the conversion of fructose to HMF using relatively cheap ammonium salts and high fructose loadings. The tetraethyl ammonium chloride (TEAC)/fructose low melting mixtures with high substrate contents

---

* Corresponding author. Tel.: +86 532 8066 2723; fax: +86 532 8066 2724.
** Corresponding author at: Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia. Tel.: +61 8 6488 7600; fax: +61 8 6488 7235.
E-mail addresses: muxd@qibebt.ac.cn (X. Mu), Dongke.Zhang@uwa.edu.au (D. Zhang).

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.06.018

were shown to efficiently catalyse the fructose dehydration solely or by using $NaHSO_4 \cdot H_2O$ as a catalyst. The partitioning of HMF from the highly concentrated TEAC/fructose/$NaHSO_4 \cdot H_2O$ melt at 120 °C and the recycling of TEAC were also demonstrated by continuously adding THF as an extracting phase.

2. Experimental

2.1. Materials and experimental procedures

Tetramethyl ammonium chloride (TMAC) (analytical grade), tetraethyl ammonium chloride (TEAC) (98%), benzyltrimethylammonium chloride (BeTMAC) (98%), benzyltriethylammonium chloride (BeTEAC) (98%), trimethylphenylammonium chloride (PhTMAC) (98%), trimethylamine hydrochloride (TMHC) (chemically pure), and choline chloride (ChoCl) (analytical grade) were purchased from Aladdin Reagent (China) Co., Ltd. Tetrabutyl ammonium chloride (TBAC) (analytical grade), dimethylamine hydrochloride (DMHC) (99.0%) were purchased from Tianjin Institute of Fine Chemicals Retrocession. Fructose ($\geq$99%) was purchased from Solarbio Science & Technology Co., Ltd. and used as a standard. $CrCl_3 \cdot 6H_2O$ ($\geq$99%), anhydrous ferric chloride ($\geq$97%) and $CuCl_2 \cdot 2H_2O$ (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) (99%) was purchased from Tianjin Fuyu Fine Chemicals Co., Ltd. $NaHSO_4 \cdot H_2O$ ($\geq$98.5%) was purchased from Guangdong Guanghua chemical reagent Co., Ltd. Aluminum chloride anhydrous was purchased from Tianjin Bodi Chemical Co., Ltd. $MoCl_3$ (99.5%) was purchased from Alfa Aesar. 5-Hydroxymethylfurfural ($\geq$99%) was obtained from Wujiang Yingchuang Chemical Reagent Co., Ltd. and used as a standard. Anhydrous glucose (analytical grade) was obtained from Guangdong Guanghua Chemical Reagent Co., Ltd.

In a typical experiment, a 25 mL reaction tube was charged with 1.0 g TEAC, 0.5 g fructose and 0.074 g $CrCl_3 \cdot 6H_2O$ (10 mol% corresponding to 0.5 g fructose) in a glovebox and then sealed. The reaction mixture was heated in an oil bath preset at 100 °C for 70 min and then cooled to room temperature.

The biphasic reaction was carried out in an autoclave vessel lined with Teflon. 1.0 g TEAC, 1.0 g fructose, 0.038 g $NaHSO_4 \cdot H_2O$ (5 mol% corresponding to 1.0 g fructose) and 10 mL THF were added into the vessel. The vessel was sealed and heated at 120 °C with magnetic stirring in an oil bath for 30 min and then cooled to room temperature to refresh the THF for the next batch. The THF layer recovered from the reactor vessel after each batch was flashed in vacuum to remove the volatile components for reuse. The residue was then analysed using HPLC to determine the content of HMF. For batch run 1, the residue containing HMF in the reactor vessel was subsequently analysed using ^1H NMR. Nitrogen and sulphur contained in the residue was further analysed using an elemental analyser (Vario EL cube, ELEMENTAL) and an inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista Axial CCD Simultaneous), respectively.

2.2. Analytical methods

HMF was quantified using a Waters HPLC with an UV detector at 284 nm and a SunFire^{TM} C_{18} column (4.8 mm × 150 mm) at 35 °C. A mixture of methanol and water at a volumetric ratio of 1:4 was used as the carrying solvent. The flow rate was 0.6 mL/min. The amount of HMF was calculated using the external standard as described in Section 2 above.

The fructose concentration was analysed using a high performance ion-exchange chromatograph with a pulsed amperometric detector (Dionex, ICS-3000) and a CarboPac^{TM} PA10 column (4 mm × 250 mm) at 30 °C. The eluent used was 7.5 mM NaOH aqueous solution with a flow rate of 1.0 mL/min. The amount of fructose was determined using the external standard.

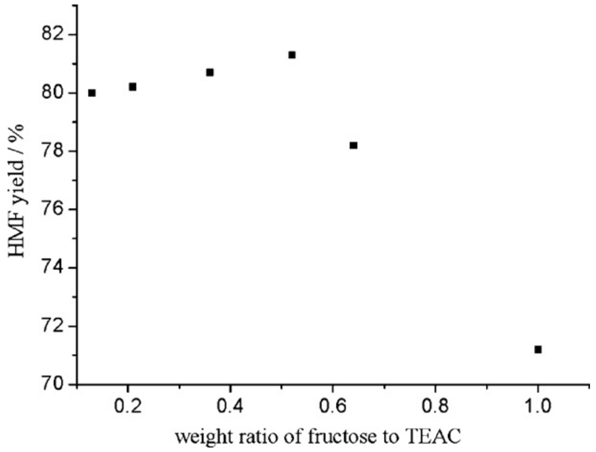

Fig. 1. HMF yield in the fructose/TEAC system as a function of the fructose to TEAC weight ratio. Conditions: TEAC 1 g, 120 °C, 70 min reaction time, fructose conversion 100%.

^1H NMR spectra were recorded by using a Bruker AVANCE III NMR spectrometer (600 M Hz) and $CDCl_3$ as the solvent.

3. Results and discussion

3.1. The reactivity of fructose in the TEAC/fructose systems

Low melting systems have already been obtained by mixing ChoCl with fructose [15] or other polar organic components like carboxylic acids [32,33]. The formation of the TEAC/fructose low melting mixtures is not unexpected because of the similar structures between ChoCl and TEAC. However, the conversion of fructose to HMF in the TEAC/fructose mixtures without a catalyst at 120 °C as shown in Fig. 1 is new. While some solvent-catalysts in fructose dehydration do exist, such as DMSO [22,34], DMA [20], 1-ethyl-3-methylimidazolium chloride (EmimCl) [24] and BmimCl [28], the chemical structure of TEAC is very different from those of these solvents. A novel type of solvent-catalyst has therefore been introduced in this work.

The reactivity of fructose in TEAC was first investigated by changing the weight ratio of fructose to TEAC at 120 °C. Fig. 1 shows that over 80% HMF yield could be achieved when the fructose to TEAC weight ratio was less than 0.52. As the fructose concentration was further increased, a gradual decrease in the HMF yield occurred. This observation may be attributed to the fact that higher fructose concentration would lead to a higher local HMF concentration, causing undesired side reactions [15]. The side reactions, such as the formation of insoluble humins or soluble polymers [28], lead to products in addition to HMF, thus causing a decrease in the HMF yield. Speculation as to why TEAC, a neutral compound, can catalyse the fructose dehydration, it has been known that Cl^- does not play a significant role in fructose dehydration as observed by Zhao et al. [24]. It is therefore hypothesised that the catalytic effect of TEAC is due to the $N^+(CH_2CH_3)_4$ cation which interacts with the fructose molecule leading to the dehydration of fructose. This mechanism warrants further studies in the future.

Temperature is a significant parameter influencing the rates of reactions [29]. In the conversion of fructose to HMF, increasing the reaction temperature not only speeds up the reaction of HMF formation, but also the competing side reactions [24,35,36]. Thus, an optimal temperature should be determined for a fixed reaction time. Visual inspection of the reaction systems confirmed that in the temperature range from 100 to 140 °C, homogeneous phase

Table 1
Effect of reaction temperature on the HMF yield in the fructose/TEAC system.[a]

Temperature (°C)	HMF yield (%)[b]	Conversion (%)[b]	Selectivity (%)
100	33.2	58.2	57.0
110	71.6	96.3	74.3
120	81.3	100	81.3
140	74.6	100	74.6

[a] Conditions: TEAC 1 g, fructose 0.5 g, 70 min reaction time.
[b] The HMF yield and fructose conversion were determined by HPLC.

could be formed by fructose and TEAC in the reactor vessel. The relationship between temperature and HMF yield is presented in Table 1. It can be seen that 120 °C was the ideal temperature for a constant reaction time of 70 min to obtain the highest selectivity towards HMF.

Fig. 2 shows the yield of HMF as a function of reaction time at 120 °C. It can be seen that the HMF yield rapidly reached 77.1% within the first 35 min and slowly increased to a maximum yield of 81.3% after 70 min. As seen from Fig. 1, when the reaction proceeded for 70 min, fructose was completely converted. Therefore, 70 min was probably the optimal reaction time under the experimental conditions in Fig. 2.

3.2. Fructose conversion in different ammonium salts

The excellent catalytic activity of TEAC observed prompted a comparison of the fructose reactivity in different ammonium salts. Nine ammonium salts were examined in this work. Those salts can be divided into two categories. One is quaternary ammonium chlorides (TMAC, TEAC, TBAC, BeTMAC, PhTMAC, BeTEAC and ChoCl) and the other is alkylamine hydrochlorides (TMHC and DMHC). Based on the results with TEAC, the reaction temperature of 120 °C, the fructose to TEAC weight ratio at 1:2 and 70 min reaction time were employed to evaluate the catalytic performance of the different ammonium salts. The results are shown in Fig. 3.

As with TEAC, all nine ammonium salts examined melt with fructose to form a homogeneous solution and fructose conversion took place in all of them. It can be seen from Fig. 3, only the use of TEAC was able to achieve over 80% HMF yield while the use of TMAC, BeTMAC, ChoCl, TMHC and DMHC produced about 70% HMF yields and the other salts gave about 60% HMF yields. The HMF yield follows the order TEAC > TMAC > TMHC > BeTMAC ≈ ChoCl > DMHC > BeTEAC > TBAC > PhTMAC as observed in this study. Although it is reasonable to speculate that the varying catalytic activities of those salts can be attributed to their alkyl variation attached to N$^+$, the relationship between alkyl chain length or alkyl volume and the HMF yield does not follow a conclusive trend. Although, TEAC was superior in fructose dehydration to the other ammonium salts investigated under the experimental conditions, the catalytic ability of other ammonium salts still needs further exploration by changing the reaction conditions. Compared to the literature reports [22,24,28,34] where DMSO, DMA, 1-ethyl-3-methylimidazolium chloride (EmimCl) and BmimCl were used both as solvents and catalysts in fructose dehydration as well, TEAC has achieved a higher HMF yield than the aforementioned solvents at higher fructose concentrations. Thus, TEAC has proven to be the most efficient solvent-catalyst reported so far.

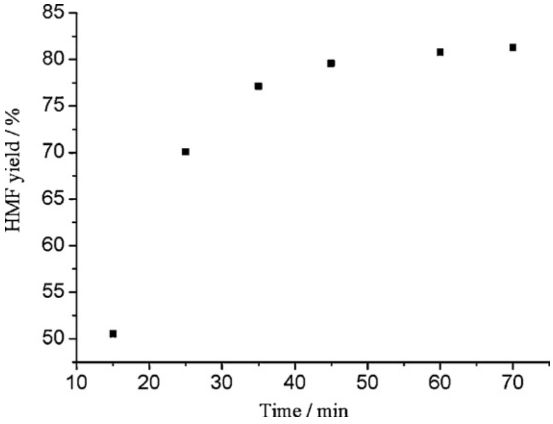

Fig. 2. HMF yield as a function of reaction time. Conditions: TEAC 1 g, fructose 0.5 g, 120 °C.

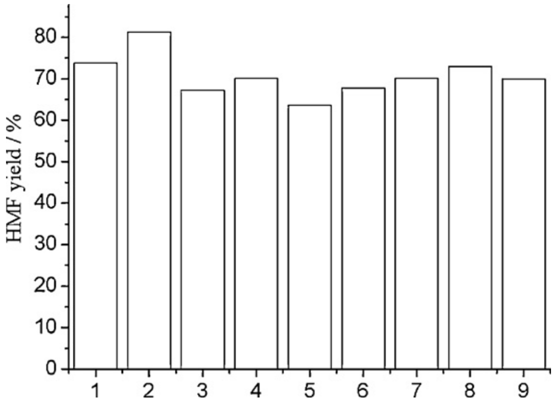

Fig. 3. HMF yield in various ammonium salts. Conditions: ammonium salts 1.0 g, fructose 0.5 g, 70 min reaction time, 120 °C, fructose conversion 100%. The number of *x*-coordinate represents: 1 TMAC; 2 TEAC; 3 TBAC; 4 BeTMAC; 5 PhTMAC; 6 BeTEAC; 7 ChoCl; 8 TMHC; 9 DMHC.

3.3. Effect of co-catalysts in the TEAC/fructose system

The above analysis only revealed that TEAC was an efficient solvent-catalyst at 120 °C, achieving more than 80% HMF yield. At 100 °C, however, only 33.2% HMF yield was obtained suggesting a weak catalytic ability under this condition. Therefore, 10 mol% additional catalysts, or co-catalysts were added to the TEAC/fructose system to assist the fructose dehydration with the results shown in Fig. 4. The use of a co-catalyst may be beneficial in limiting undesired side reactions, especially in high fructose concentration systems. Six co-catalysts, namely, $CrCl_3{\cdot}6H_2O$, $FeCl_3$, $CuCl_2{\cdot}2H_2O$, $MoCl_3$, $AlCl_3$, and $NaHSO_4{\cdot}H_2O$, were selected and respectively used in the TEAC/fructose system as an additional catalyst. With 100% fructose conversion and 82.7% HMF yield, $NaHSO_4{\cdot}H_2O$ was shown to be the most efficient co-catalyst under

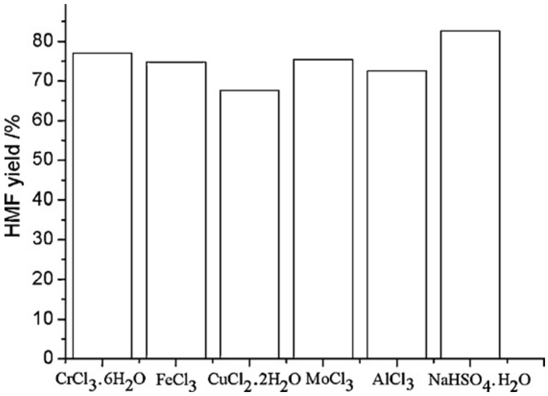

Fig. 4. HMF yield in TEAC in the presence of catalysts. Conditions: TEAC 1.0 g, fructose 0.5 g, 100 °C, 70 min reaction time, catalyst loading 10 mol% based on sugar, fructose conversion 100%.

Table 2
Conversion of fructose using $NaHSO_4\cdot H_2O$ as a co-catalyst.[a]

Fructose concentration (wt%)	$NaHSO_4\cdot H_2O$ loading (mol%)	HMF yield (%)[b]
50	5	79.2
50	10	78.3
60	10	73.3

[a] Reaction conditions: TEAC, 1.0 g; reaction time 70 min; 120 °C; fructose conversion 100%.
[b] The HMF yield and fructose conversion were determined using HPLC.

the experimental conditions The other five metal chloride catalysts can only produce ca 70% HMF yields or less.

The metal chlorides examined in this work displayed almost the same catalytic activity in fructose dehydration as that reported in the literature [24] in which EmimCl was used as the solvent. However, the fructose concentration (33.3%) in this work was much higher than that in the literature (9.1%). The higher fructose concentration is preferred in practical HMF production processes.

Efficient conversion of highly concentrated fructose to HMF is preferred to achieve greater productivity of a practical process, measured in the amount of HMF produced per unit reactor volume and thus a more favourable process economics. However, high fructose concentrations would result in acceleration of undesired side reactions [15,35]. In this work, $NaHSO_4\cdot H_2O$ was added into the highly concentrated TEAC/fructose system to assist in the dehydration of the highly concentrated fructose with the results given in Table 2. It can be seen from Table 2 that 79.2% HMF yield was achieved at 50 wt% fructose concentration. When the fructose concentration was further increased to 60 wt%, only 73.3% HMF yield was obtained. Compared to the literature report of highly concentrated low melting systems [15], where 67% HMF yield was obtained in a fructose/ChoCl (4:6) mixture using p-TsOH as the catalyst, the present catalytic system achieved a much greater HMF yield at higher substrate concentrations.

Although TEAC itself could exhibit excellent catalytic ability in fructose dehydration, it was unable to synthesize HMF from glucose as seen from Table 3. In the presence of 10 mol% $CrCl_3\cdot 6H_2O$ as catalyst, 51.4% HMF yield could be achieved. However, the added $NaHSO_4\cdot H_2O$ has no obvious catalytic activity in glucose dehydration. Like ChoCl [15], EmimCl [24] and BmimCl [28], TEAC was only a solvent in glucose dehydration.

3.4. Separation of HMF by THF extraction

Separation of HMF from the reaction system is another challenge that has to be solved and the recycling of the solvent should also be considered to reduce the HMF production cost. Extraction is widely applied in the separation and purification of HMF [2,3,29,32] as the solubility of HMF in several organic solvents is high. To be used as an extracting reagent, the organic solvent must not only be immiscible with the reactive catalytic system but also possess a low boiling point, which will facilitate its separation from the extracted HMF via evaporation. THF with its boiling point of only 66 °C was reported to be a good choice in the extraction of HMF. Moreover, its miscibility with water takes the generated water away from the reaction system, preventing the side reactions due to the presence of water molecules [29]. In this work, THF was screened as an HMF extraction solvent. Because the TEAC/fructose/$NaHSO_4\cdot H_2O$ system was most reactive at 120 °C, a temperature far above the boiling point of THF, a high pressure autoclave vessel with teflon lining was utilized to prevent the evaporation of THF. When THF was added into the reaction system, the HMF produced can be extracted into the THF layer, which can be recovered for HMF separation, forming a THF-TEAC biphasic system for semi continuous HMF production. Note that at 120 °C, the viscosity of the melt is very low, favouring the mass transfer. With THF refreshed and fructose added at a regular interval, a semi continuous process for the conversion of fructose into HMF can be conducted in a THF-TEAC biphasic system as shown in Fig. 5(a). A series of operations of the semi continuous THF-TEAC biphasic system were conducted to demonstrate the efficacy of the HMF production process at a laboratory scale and the experimental results are displayed in Fig. 5(b).

Table 3
Conversion of glucose in TEAC with and without catalyst.[a]

Temperature (°C)	Catalyst	HMF yield (%)[b]
120	No catalyst	0
140	No catalyst	5.0
120	$NaHSO_4\cdot H_2O$	10.5
120	$CrCl_3\cdot 6H_2O$	51.4

[a] Conditions: TEAC 1 g; glucose 0.5 g; catalyst loading 10 mol%; 70 min reaction time.
[b] The HMF yield was determined using HPLC.

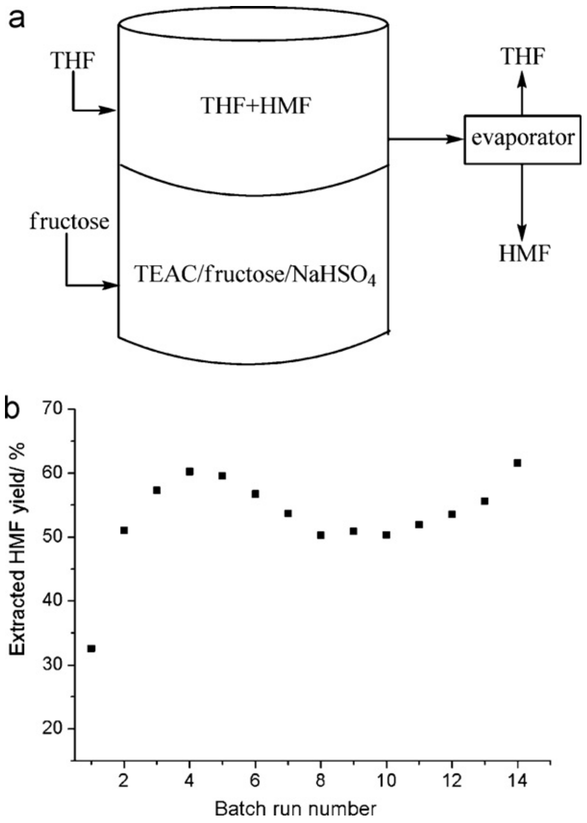

Fig. 5. (a) A schematic of the semi continuous process for the conversion of fructose to HMF in a THF-TEAC/$NaHSO_4\cdot H_2O$/fructose biphasic system. The lower phase contains TEAC, fructose and $NaHSO_4\cdot H_2O$, whereas the upper phase contains THF. HMF is extracted into the THF phase and separated through an evaporation step. Fructose and THF were added to the system at the beginning of each consecutive batch of the operation. (b) The extracted yield of HMF from the semi continuous process using a THF-TEAC biphasic system. The extracted HMF yield was calculated by dividing the number of moles of HMF extracted with THF by the number of moles of fructose added into the reaction system. One batch lasted for 30 min with 10 mL THF refreshed for the next batch. Reaction conditions for the batch runs 1 and 2 are: fructose 1.0 g, TEAC 1.0 g, $NaHSO_4\cdot H_2O$ 0.038 g. 0.50 g fructose was added from batch runs 3 to 8. In batch run 9, 0.50 g fructose and 0.025 g $NaHSO_4\cdot H_2O$ were added. In batch run 10, 0.50 g fructose was added. From batch runs 11 to 14, 0.5 g fructose and 0.025 g $NaHSO_4\cdot H_2O$ were added in each batch. T = 120 °C.

It can be seen from Fig. 5(b) that the yield of HMF increased from batch run 1 to 4, indicating that the reaction system remained active during those processes. From batch run 4 to 8, a gradual decrease in the HMF yield occurred, which may be attributed to

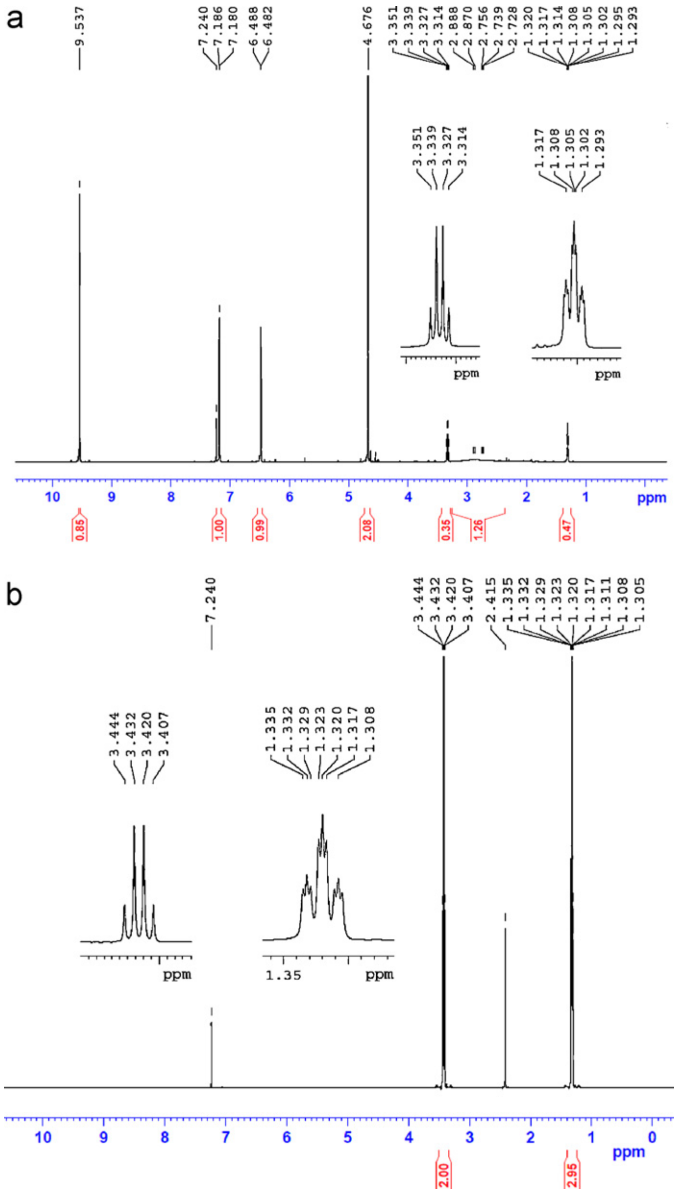

Fig. 6. (a) ^{1}H NMR spectra of the extracted HMF after batch run 1 and (b) ^{1}H NMR spectra of TEAC. The solvent used was $CDCl_3$.

the deactivation of the catalyst or build-up of by-products. Therefore, in batch run 9, a small amount of $NaHSO_4{\cdot}H_2O$ (0.025 g) was added and the HMF yield increased accordingly. However, in batch run 10, the HMF yield decreased again without further addition of $NaHSO_4{\cdot}H_2O$, suggesting there was a loss of the catalytic activity of the system. Thus, from batch run 11 to 14, 0.025 g $NaHSO_4{\cdot}H_2O$ was added in each batch and the HMF yield increased gradually to 61.6% in batch run 14. The reaction was stopped after batch run 14.

The amounts of the residual HMF and fructose in the reaction phase were analysed using HPLC to be 0.21 g and 0.67 g, respectively. In the whole process operation, a total of 7.0 g fructose was added into 1 g of TEAC and 90.4% of the fructose was reacted. The selectivity towards HMF was 73.1% and 3.0 g HMF was isolated by the THF extraction, corresponding to 93.5% of the HMF produced during the whole process. Although the process experiment was terminated after batch run 14, the reaction system remained active and was capable of producing more products. Compared with the THF/BmimCl/WCl_6 [29] and the THF/BmimCl/HCl [37] systems reported in the literature, 1 g TEAC could afford much more HMF product in a much shorter time than 1 g BmimCl using the same or less THF, and offer a highly efficient alternative route for HMF production in large scales. Although the work by Dumesic et al. [2] demonstrated that methyl isobutyl ketone (MIBK) and a mixture of MIBK and 2-butanol could effectively separate HMF from the acidic aqueous solution of fructose modified by DMSO and PVP and further increase the selectivity of fructose conversion towards HMF to as high as 85%, the boiling point of MIBK (117 °C) is considered too high. The separation of HMF from MIBK would be very energy-inefficient. In the present work, the evaporation of THF (boiling point 66 °C) is less energy intense than that of MIBK, offering an advantage over the previous system.

To analyse the impurities of the HMF recovered from the reaction system, ^{1}H NMR analysis, elemental analysis and ICP-OES analysis were performed on the extracted HMF after batch run 1. The ^{1}H NMR spectra shown in Fig. 6(a) clearly demonstrated that the peaks at about 1.3 and 3.3 ppm are attributed to some impurities. When compared with the ^{1}H NMR spectra of the pure TEAC in Fig. 6(b), it is obvious that the main impurity in the extracted HMF was TEAC, which may be soluble in the water generated. From the peak areas of 6.4 ppm and 1.3 ppm in Fig. 6(a), which correspond to the C-4 hydrogen of furan ring and the CH_3 hydrogen of TEAC, respectively, the content of TEAC in the HMF was estimated to be 4.9 wt%, suggesting that 1.14 wt% of the total mass of TEAC was taken into the THF phase. The elemental analysis further indicated that the amount of nitrogen in the HMF recovered was only 0.23 wt%, corresponding to 2.5 wt% of TEAC in the HMF. The content of sulphur in the HMF recovered, as determined using the ICP-OES, was only 0.01 wt% corresponding to 0.038 wt% $NaHSO_4$ in the HMF. The loss of TEAC together with the $NaHSO_4$ is considered a reason for the deactivation of the system in batch runs 5–8 shown in Fig. 5(b). Although a very small amount of TEAC existed in the separated HMF, further purification of HMF may be feasible by the extraction of diethyl ether. Because HMF was soluble in diethyl ether while TEAC and water were not soluble in it.

4. Conclusions

Low melting mixtures have been formed by mixing fructose and various ammonium salts, which have then been used as both solvent and catalyst in fructose dehydration. TEAC proved to be the most effective solvent-catalyst among those salts. The TEAC/fructose system was tolerant towards as high as 33.3 wt% fructose concentration to produce approximate 81.3% HMF yield without the use of a co-catalyst. The TEAC/fructose/$NaHSO_4{\cdot}H_2O$ system produced 79.2% HMF yield at 50 wt% fructose concentration. Using the TEAC/fructose/$NaHSO_4{\cdot}H_2O$ catalytic system not only improved its tolerance towards high fructose concentrations but also attained high selectivities. A biphasic reaction containing THF and the reactive TEAC/fructose/$NaHSO_4{\cdot}H_2O$ system was conducted at 120 °C, which allowed for not only an efficient conversion of highly concentrated fructose but also the separation of HMF from the reaction system by the extraction of the THF. Impurities in the HMF recovered were identified to involve TEAC and $NaHSO_4{\cdot}H_2O$, explaining the reasons for partial deactivation of the system.

Acknowledgements

This work is supported by the National High Technology Research and Development Program of China (No. 2009AA05Z410), the Natural Science Foundation of China (No. 20803038, 21003146), the Key Science and Technology Program of Shandong Province (No. 2008GG20002038), the Natural Science Foundation of Shandong Province (No. ZR2010BQ014) and China's World One Thousand Chinese Talents Award.

References

[1] B. Kamm, Angew. Chem. Int. Ed. 46 (2007) 5056–5058.
[2] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, Science 312 (2006) 1933–1937.
[3] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982–985.
[4] R.M. West, Z.Y. Liu, M. Peter, J.A. Dumesic, ChemSusChem 1 (2008) 417–424.
[5] J.N. Chheda, Y. Román-Leshkov, J.A. Dumesic, Green Chem. 9 (2007) 342–350.
[6] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411–2502.
[7] M. Ohara, A. Takagaki, S. Nishimura, K. Ebitani, Appl. Catal. A 383 (2010) 149–155.
[8] X. Tong, Y. Ma, Y. Li, Appl. Catal. A 385 (2010) 1–13.
[9] K.B. Sidhpuria, A.L. Daniel-da-Silva, T. Trindade, J.A.P. Coutinho, Green Chem. 13 (2011) 340–349.
[10] T.S. Hansen, J. Mielby, A. Riisager, Green Chem. 13 (2011) 109–114.
[11] Z. Zhang, Q. Wang, H. Xie, W. Liu, Z. Zhao, ChemSusChem 4 (2011) 131–138.
[12] Y. Zhang, V. Degirmenci, C. Li, E.J.M. Hensen, ChemSusChem 4 (2011) 59–64.
[13] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, Green Chem. 13 (2011) 754–793.
[14] G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Science 308 (2005) 1446–1449.
[15] F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger, Green Chem. 11 (2009) 1948–1954.
[16] F.S. Asghari, H. Yoshida, Ind. Eng. Chem. Res. 45 (2006) 2163–2173.
[17] F.S. Asghari, H. Yoshida, Ind. Eng. Chem. Res. 46 (2007) 7703–7710.
[18] M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, Appl. Catal. A 295 (2005) 150–156.
[19] C.V. McNeff, D.T. Nowlan, L.C. McNeff, B. Yan, R.L. Fedie, Appl. Catal. A 384 (2010) 65–69.
[20] J.B. Binder, R.T. Raines, J. Am. Chem. Soc. 131 (2009) 1979–1985.
[21] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Ind. Eng. Chem. Res. 47 (2008) 9234–9239.
[22] K. Shimizu, R. Uozumi, A. Satsuma, Catal. Commun. 10 (2009) 1849–1853.
[23] X. Tong, Y. Li, ChemSusChem 3 (2010) 350–355.
[24] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597–1600.
[25] S. Lima, P. Neves, M.M. Antunes, Appl. Catal. A 363 (2009) 93–99.
[26] Y. Su, H.M. Brown, X. Huang, X. Zhou, J.E. Amonette, Z.C. Zhang, Appl. Catal. A 361 (2009) 117–122.
[27] Y. Su, H.M. Brown, G. Li, X. Zhou, J.E. Amonette, J.L. Fulton, D.M. Camaioni, Z.C. Zhang, Appl. Catal. A 391 (2011) 436–442.
[28] C. Sievers, I. Musin, T. Marzialetti, ChemSusChem 2 (2009) 665–671.
[29] J.Y.G. Chan, Y. Zhang, ChemSusChem 2 (2009) 731–734.
[30] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Green Chem. 11 (2009) 1327–1331.
[31] G. Yong, Y. Zhang, J.Y. Ying, Angew. Chem. Int. Ed. 47 (2008) 9345–9348.
[32] S. Hu, Z. Zhang, Y. Zhou, B. Han, Green Chem. 10 (2008) 1280–1283.
[33] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, J. Am. Chem. Soc. 126 (2004) 9142–9147.
[34] A.S. Amarasekara, L.D. Williams, C.C. Ebede, Carbohydr. Res. 343 (2008) 3021–3024.
[35] F. Őrsi, J. Therm. Anal. 5 (1973) 329–335.
[36] T. Tuercke, S. Panic, S. Loebbecke, Chem. Eng. Technol. 32 (2009) 1815–1822.
[37] L. Lai, Y. Zhang, ChemSusChem 3 (2010) 1257–1259.