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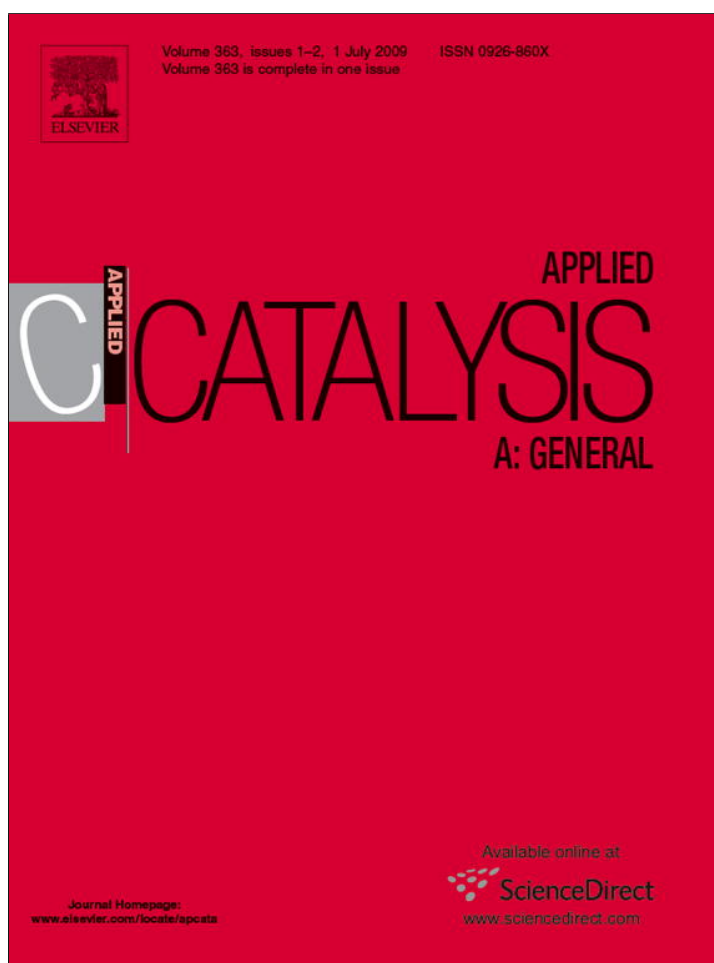University of Aveiro
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Conversion of mono/di/polysaccharides into furan compounds using 1-alkyl-3-methylimidazolium ionic liquids

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ABSTRACT

The one-pot hydrolysis/dehydration of mono/di/polysaccharides into furfural (FUR) or 5-hydroxy-methyl-2-furaldehyde (HMF) in the presence of an acidic ionic liquid, 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO$_4$]), at 100 °C, was investigated and the results were compared with those using 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), with or without CrCl$_3$ or H$_2$SO$_4$. The ionic liquid [EMIM][HSO$_4$] is effective in converting xylose and fructose or related polysaccharides into FUR (e.g. from xylose: 84% yield at 6 h) or HMF (e.g. from fructose: 88% yield at 30 min), but not glucose and polymers containing these units, which contrasts to that observed for the [BMIM][Cl]/CrCl$_3$ system. The latter is quite effective in converting glucose and related disaccharides into HMF, but not the polysaccharides cellulose and starch. For the latter feedstocks, the addition of H$_2$SO$_4$ or [EMIM][HSO$_4$] to cellulose/[BMIM][Cl]/CrCl$_3$ enhances HMF yields, presumably by accelerating the hydrolysis step, although the selectivity of the dehydration of glucose monomers seems rather poor (HMF yield < 13 wt.%). In the case of the xylose to FUR conversion in [EMIM][HSO$_4$], two systems involving the reaction and simultaneous separation of the target product were investigated, namely reaction/solvent extraction and reaction/evaporation systems, and for both the ionic liquid could be recovered and reused without a significant drop in FUR yield in recycling runs.

1. Introduction

Economic and geopolitical factors (high prices of fossil fuels and commodity chemicals, environmental concerns, such as CO$_2$ emissions and climate change, and supply instability) together with the increasing energy demand by society are prompting policy-makers to put added emphasis on renewable energy sources [1]. Vegetable biomass, an abundant, relatively inexpensive renewable source, is a promising alternative for the sustainable supply of valuable intermediates to the chemical industry, relieving, at least to a certain extent, the industry's reliance on petroleum [2–5].

Carbohydrates are among the most abundant organic compounds on earth and represent the major portion of the world's annually renewable biomass. Sources of carbohydrates include conventional forestry, wood processing by-products, agricultural crops and surpluses, and plants grown on degraded soils. The bulk of the carbohydrate-biomass comprises di/oligo/polysaccharides (e.g. hemicelluloses, cellulose, starch, inulin and sucrose), which by hydrolysis form sugars, such as xylose, arabinose, glucose and fructose. The partial dehydration of monosaccharides can form furfural (FUR) from pentoses (e.g. xylose) and 5-hydroxymethyl-2-furaldehyde (HMF) from hexoses (e.g. fructose and glucose) [6]. These reactions may be selectively accelerated by the use of Brönsted or Lewis acid catalysts. Currently, FUR is used both as a solvent (e.g. in oil refining) and as a building block for the preparation of pharmaceuticals, agrochemicals, fragrances, tetrahydrofuran and other furan-based chemicals; similarly, HMF has a broad, versatile application profile [7]. Thus the manufacture of HMF and FUR may constitute primary processes for generating a variety of non-petroleum derived products from saccharides. While FUR is currently produced on an industrial scale (often using H$_2$SO$_4$ as catalyst) [8], HMF is not yet a high-volume chemical, partly due to the currently high production costs [3,6].

Recent studies have demonstrated the potential of hydrophilic ionic liquids (ILs) for the conversion of saccharides into FUR and HMF. Moreau firstly reported on the dehydration of fructose in the presence of Amberlyst-15 or para-toluene sulfonic acid as catalysts, using solvent mixtures of dimethylsulfoxide (the latter enhanced dissolution of fructose in the IL medium) and

[BMIM][BF$_4$] or [BMIM][PF$_6$], which gave 75–80% HMF yield within 24 h, at 80 °C [9]. In another study, the dehydration of fructose in 1-H-3-methylimidazolium chloride gave 92% HMF yield within 15–45 min at 90 °C [10]. The acidic IL 3-allyl-1-(4-sulforylchloride butyl)imidazolium trifluoromethanesulfonate was also effective in converting fructose into HMF, using DMSO as solvent, at 100 °C, under microwave radiation: ca. 85% HMF yield was reached within 4 min [11]. Immobilisation of this IL in silica gel gave an effective and reusable solid catalyst, with no decay in HMF yields after seven runs.

Zhang and co-workers [12] reported on the use of several metal chlorides in 1-alkyl-3-methylimidazolium chloride ([AMIM][Cl], A = alkyl) ILs for the dehydration of glucose, a more demanding saccharide than fructose for HMF production, at 100 °C. These authors found that CrCl$_2$ in [EMIM][Cl] (E = ethyl) was a singularly effective catalytic system, affording up to 70% HMF yield at ca. 95% glucose conversion (3 h reaction), and negligible amounts of levulinic acid were formed. Several explanations for the high HMF yields achieved in imidazolium chloride ILs have been put forward, such as the low concentration of water present in the reaction medium (avoiding the subsequent hydration of HMF to levulinic acid), the formation of complexes between the IL and the sugar (decreasing the activation barrier for HMF formation) [10], and the formation of complexes between the sugar and metal chlorides in the ILs [12]. Xie and co-workers [13] reported on the dehydration of fructose in IL/ethyl acetate biphasic systems: the choline chloride/citric acid/ethyl acetate system gave more than 90% HMF yield and could be recycled successfully.

The above examples are representative of the literature in that most of the published work on the use of ILs for the conversion of saccharides has focused on the hexose monosaccharides fructose and glucose. Based on studies such as that by Rogers and co-workers in Ref. [14], where it was shown that cellulose dissolves in [BMIM][Cl] under conventional (100 °C) or microwave-assisted heating, it may be possible to use ILs for the conversion of di/polysaccharides. Herein, we report on the dehydration of pentose and hexose monosaccharides, and the one-pot hydrolysis of di/polysaccharides and subsequent dehydration of the corresponding monosaccharides into FUR or HMF, using the acidic IL 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO$_4$]), at 100 °C. A comparative study with 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) or [EMIM][HSO$_4$]/[BMIM][Cl] mixtures was also carried out and the effect of adding chromium chloride was investigated, with the aim of enhancing the selectivity of the dehydration of glucose into HMF.

2. Experimental

2.1. Materials and methods

Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer. The solid state ^{13}C NMR spectrum was recorded at 11.75 T on a Bruker DRX 500 spectrometer operating at 125.76 MHz, using a 4 mm BL CP MAS VTN probe. The sample was spun at 9.0 kHz and the contact time was 8 ms. Chemical shifts are quoted in ppm from TMS. Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer.

[EMIM][HSO$_4$] was supplied by Merck KGaA. ^{1}H NMR (300.13 MHz, 20 °C, DMSO-d$_6$, TMS): δ = 1.41 (t, 3H, CH_3CH$_2$), 3.86 (s, 3H, N–CH$_3$), 4.20 (q, 2H, N–CH$_2$), 7.72 (s, 1H, CH), 7.81 (s, 1H, CH), 9.19 (s, 1H, CH). ^{13}C NMR (75.47 MHz, 20 °C, DMSO-d$_6$, TMS): δ = 15.2 (CH$_3$CH$_2$), 35.7 (N–CH$_3$), 44.1 (N–CH$_2$), 122.0 (CH), 123.6 (CH), 136.4 (CH). All remaining starting materials were purchased from commercial sources and used as received: [BMIM][Cl] (≥98.0%), D-(+)-cellobiose (≥99%), inulin, D-(+)-sucrose (≥99%) and phenol (≥99.5%) from Fluka, D-(+)-glucose and toluene (≥99.9%) from Sigma–Aldrich, sulfuric acid (95–97%) and metha-

nol (≥99.8%) from J.T. Baker, isobutylmethyl ketone (≥99.9%) and chromium(III) chloride hexahydrate (≥99.5%) from Merck, D-xylose (99%), D-(−)-fructose (>99%) and D-(−)-ribose (98%) from Aldrich, cellulose (powder D natural) and D-(+)-maltose monohydrate from Riedel-de Haën, and starch from Panreac.

2.2. Catalytic experiments and product analysis

The catalytic experiments were performed batch-wise using magnetically stirred (≅600 rpm) glass micro-reactors, which were heated with a thermostated oil bath. Zero time was taken to be the instant the micro-reactor was immersed in the oil bath. Each sample was taken from an individual batch run after a certain reaction time and, in general, two or three replicates were obtained for each point. The experimental error in these values is estimated to be about 5%. Two methods were used to facilitate the immediate separation of the target product upon formation: (i) use of an extracting solvent [toluene (T) or isobutylmethyl ketone (IBMK)], immiscible/poorly soluble with the IL, or (ii) the reaction was carried out under reduced pressure, using a water aspirator, to evaporate FUR/HMF from the IL. For separation method (i), the catalytic experiments were performed under nitrogen (autogeneous pressure) using micro-reactors with a pear-shaped bottom and equipped with a valve for gas purging. The reactors were typically charged with 30 mg mono/di/polysaccharide (or 36 mg for the hexoses; monosaccharide concentration in the IL was kept constant at 0.67 M), IL (0.3 mL) and in some cases with co-solvent (0.7 mL T or IBMK), and heated at 100 °C. The setup for separation method (ii) consisted of a round-bottomed glass reactor (25 mL capacity), which was charged with xylose (900 mg) and [EMIM][HSO$_4$] (5 g), and connected to a Liebig condenser with circulating water cooled to ca. 15 °C. The quasi-horizontally positioned condenser was connected through a vacuum adapter to a 10 mL round-bottomed flask for collection, which was cooled with liquid nitrogen-frozen ice. The fed reactor was degassed under vacuum and placed in a water-filled ultrasound bath (50 W, 40 kHz) for ca. 15 min at room temperature prior to immersion in the oil bath and heating at 100 °C for 4 h.

The samples were analysed by HPLC in isocratic mode. The products present in the IL phase were analysed using a Knauer K-1001 HPLC pump and a PL Hi-Plex H 300 mm × 7.7 mm (i.d.) ion exchange column (Polymer Laboratories Ltd., UK), coupled to a Knauer 2300 differential refractive index detector (for sugar) and a Knauer 2600 UV detector (280 nm, for FUR and HMF). The mobile phase was 0.01 M H$_2$SO$_4$. Analysis conditions: flow rate 0.6 mL min^{-1}, column temperature 65 °C. The products present in the organic phase were quantified using a Gilson 306 HPLC pump and a Spherisorb ODS S10 C18 column, coupled to a Gilson 118 UV–vis detector (280 nm). The mobile phase consisted of 30% (v/v) methanol in an aqueous solution with 10% methanol (flow rate 0.7 mL min^{-1}). Authentic samples of reagents and products were used as standards and calibration curves were used for quantification. Some by-products were identified by gas chromatography–mass spectrometry (Trace GC 2000 Series (Thermo Quest CE Instruments) – DSQ II (Thermo Scientific)), equipped with a capillary column (DB-1MS, 30 m × 0.32 mm), using He as carrier gas.

3. Results and discussion

3.1. Dehydration of monosaccharides in ionic liquids

3.1.1. Xylose/[EMIM][HSO$_4$] reaction system under nitrogen atmosphere and IL recyclability

The reaction of xylose in [EMIM][HSO$_4$] (0.67 M) at 100 °C gives 86% conversion and 72% FUR selectivity at 30 min (Table 1). These

Table 1
Conversion of mono/disaccharides into FUR and/or HMF in the ionic liquids [EMIM][HSO4] or [BMIM][Cl].

Substrate	IL/co-solvent/temperature	Conc.[a] (g dm^{-3} IL)	T[b] (h)	Conv.[c] (%)	%Yield FUR[d]	%Yield HMF[d]
Xylose	[EMIM][HSO4]/none/100 °C	100	0.5	86	62	–
	[EMIM][HSO4]/T/100 °C	100	0.5	80	33	–
		100	4	95	82	
		100	6	96	84	
		33	4	71	71	–
		167	4	93	60	
	[EMIM][HSO4]/T/120 °C	100	0.5	100	58	–
	[BMIM][Cl]/T/100 °C	100	4	0	–	–
	[BMIM][Cl]/T/100 °C + H2SO4	100	4	83	44	–
Fructose	[EMIM][HSO4]/T/100 °C	120	0.5	100	–	79
	[EMIM][HSO4]/IBMK/100 °C	120	0.5	100	–	88
	[BMIM][Cl]/T/100 °C	120	0.5	23	–	16
Glucose	[EMIM][HSO4]/T/80 °C	120	0.5	86	–	1
			4	95	–	3
			24	97	–	8
	[EMIM][HSO4]/T/100 °C	120	0.5	95	–	3
			4	95	–	9
	[BMIM][Cl]/T/100 °C	120	4	0	–	–
	[BMIM][Cl]/T/100 °C + CrCl3[e]	120	4	91	–	91
	[BMIM][Cl]/IBMK/100 °C + CrCl3[e]	120	4	79	–	79
	[BMIM][Cl]/none/100 °C + CrCl3[e]	120	4	83	–	81
Sucrose	[BMIM][Cl]/IBMK/100 °C + CrCl3[e]	120		–	–	100
Cellobiose	[BMIM][Cl]/IBMK/100 °C + CrCl3[e]	120		–	–	50

[a] Initial concentration expressed as g feedstock/dm^3 ionic liquid.
[b] Reaction time.
[c] Conversion at time T.
[d] FUR or HMF yield at the specified reaction time.
[e] 0.04 M CrCl3.

results are fairly good, for example, in comparison to that reported for the reaction of xylose carried out in the presence of Keggin-type heteropolytungstates (ca. 0.007 M) or sulfuric acid (0.01 M), using dimethylsulfoxide as solvent (a commonly used solvent to promote selectivity to the furan derivative [6]). After 4 h at 140 °C, these reaction systems gave 58–63% FUR yield [15]. When toluene (T) is used as a co-solvent with [EMIM][HSO4], a liquid–liquid biphasic system is obtained, which gives approximately half of the FUR yield (33%) achieved without a co-solvent (62%), at 30 min. However, the FUR yield for the biphasic system reaches 84% at 6 h (Fig. 1, Table 1), which is higher than the maximum

Fig. 1. Xylose conversion (○) and FUR yield (+) versus time, for the reaction carried out in [EMIM][HSO4]/toluene at 100 °C.

observed without a co-solvent (62% at 30 min). In contrast to that observed for the biphasic system, without a co-solvent FUR yield decreases with time, reaching 40%/28% after 4/6 h. These results parallel those reported in the literature for reactions of saccharides in aqueous phase, concerning the beneficial effect of using a co-solvent for improving FUR and HMF yields [16,17].

Increasing the xylose concentration from 0.22 to 0.67 M (or 33 to 100 g dm^{-3} IL) leads to an increase in conversion after 4 h reaction from 71 to 95%, and in FUR yield from 71 to 82%, under biphasic conditions (Table 1). A further increase in the amount of xylose to 1.11 M (167 g dm^{-3} IL) results in a decrease in FUR yield at high conversions (60% at 93% conversion, compared with 82% at 95% conversion for 0.67 M xylose).

Increasing the reaction temperature from 100 to 120 °C (for 0.67 M xylose in [EMIM][HSO4]/T) accelerates the reaction, giving 100% conversion within 30 min, and a FUR yield of 58% (Table 1). At higher reaction temperatures the reaction is probably so fast that the effect of the co-solvent on product selectivity becomes less pronounced. As the reaction proceeds the mixture becomes darker and increasingly viscous, which may result in mass transfer limitations that affect the overall reaction. Several side reactions may contribute to the loss of FUR, such as condensation reactions between furfural and intermediates of the xylose-to-furfural conversion to give furfural pentose and difurfural xylose [8]. No by-products of the xylose reaction in [EMIM][HSO4]/T were detected by HPLC (using a diode array detector) and GC–MS analysis showed a few very weak peaks, which were not clearly identified. Thus, we postulate that the by-products are mainly heavier products resulting from condensation reactions.

For comparative purposes the reaction of xylose was carried out in [BMIM][Cl], using toluene as co-solvent at 100 °C, with or without H2SO4. No reaction takes place in [BMIM][Cl]/T without H2SO4, at least until 4 h (Table 1). These results show that the Brönsted acidity associated to the anion in [EMIM][HSO4] is responsible for xylose dehydration into FUR. The reaction of xylose in aqueous H2SO4 (0.4 M, approximately equivalent to half the
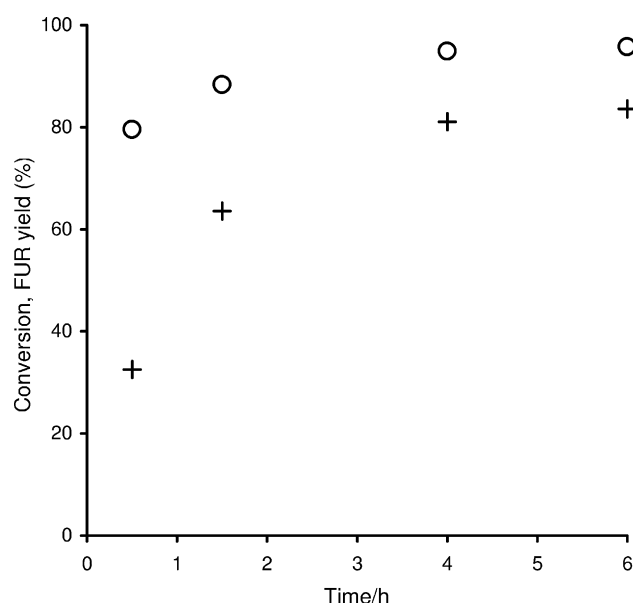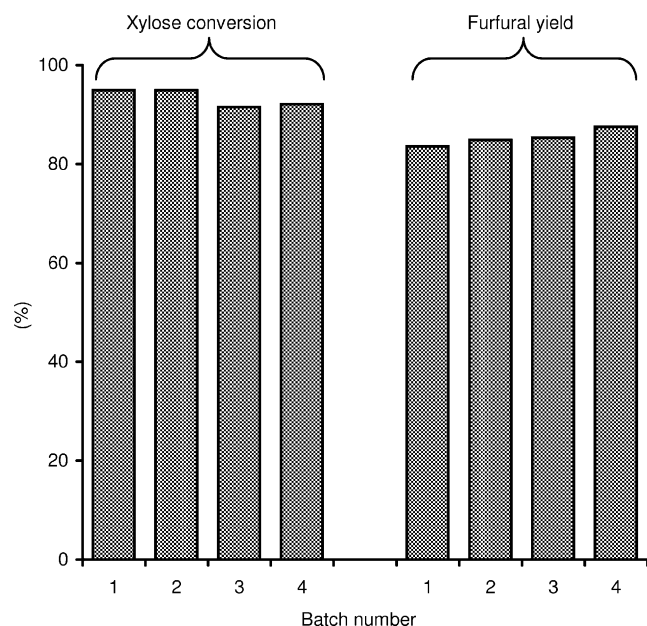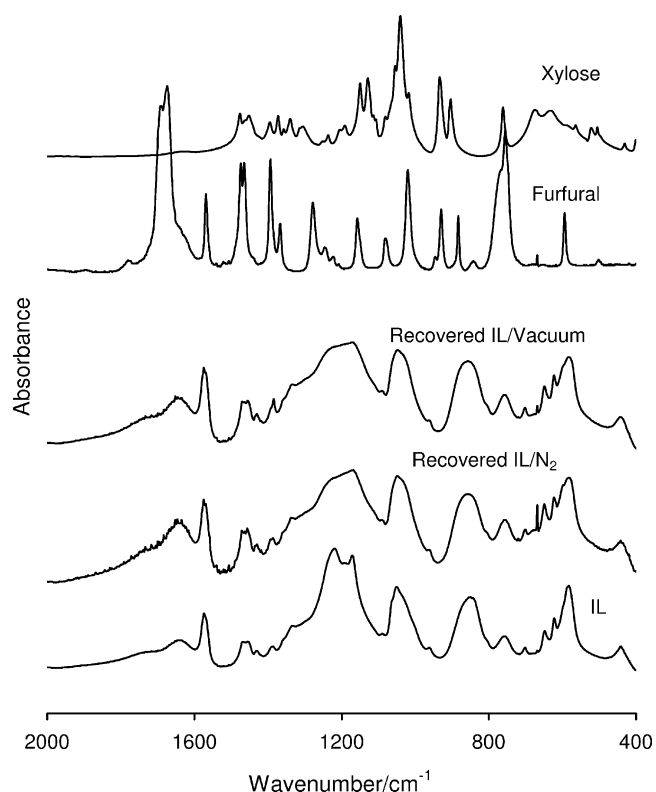
Fig. 2. Conversion of xylose into furfural in [EMIM][HSO$_4$]/T, for four consecutive 4 h runs at 100 °C, using the same ionic liquid charged initially to the reaction vessel.

Fig. 3. IR spectra of pure [EMIM][HSO$_4$] (IL) and the ionic liquid recovered from the reaction of xylose carried out in [EMIM][HSO$_4$]/T under nitrogen or in [EMIM][HSO$_4$] under reduced pressure. The spectra of xylose and furfural are given for comparison. The weak, sharp peak at ca. 650 cm^{-1} in the spectrum of the recovered IL is attributed to a residual amount of acetonitrile that was not completely separated from the IL during the work-up procedure.

number of moles of charged [EMIM][HSO$_4$]) gives less than 5% FUR yield at 38% conversion, after 4 h at 100 °C. When H$_2$SO$_4$ (0.04 M) is added to the [BMIM][Cl]/T mixture, 83% conversion and 44% FUR yield are reached after 4 h. For the same residence time [EMIM][HSO$_4$]/T gives 81% FUR yield (Fig. 1): furfural selectivity increases with time possibly due to the fact that the reaction mechanism involves a series of elementary steps [15].

The recyclability of the [EMIM][HSO$_4$]/T system was investigated by recovering and reusing the IL in four consecutive runs at 100 °C (100 g xylose dm^{-3} IL). Prior to each reuse of the IL, the two liquid phases were separated by decantation. Acetonitrile (miscible with [EMIM][HSO$_4$]) was added to the IL phase with stirring, which facilitated the subsequent separation of dark residues by centrifugation. Acetonitrile and water were removed from the solution by evaporation under reduced pressure, giving the recovered IL free of furfural as detected by HPLC. Xylose conversion and FUR yield at 4 h remained nearly constant at ca. 93 and 85% in the four consecutive runs (Fig. 2). Recycling of the [EMIM][HSO$_4$]/T system using 167 g xylose dm^{-3} IL gave a turnover number of 1.25 after seven runs at 100 °C. The CNS microanalyses, IR (Fig. 3), ^{1}H and ^{13}C NMR spectra of fresh (Section 2.1) and recovered IL were very similar. These results demonstrate that [EMIM][HSO$_4$] can be efficiently recycled, under the reaction conditions used.

3.1.2. Xylose/[EMIM][HSO$_4$] reaction system under reduced pressure and IL recyclability

The downside to using volatile solvents for extraction of the target furan compounds are the inherent dangers involved in working with these chemicals. Extraction using supercritical CO$_2$ or reduced pressure for evaporation seems cleaner [18–20]. The former method requires special equipment for containment and pressure. In this work, we used a simple reaction-vacuum evaporation setup for performing the reaction of xylose in [EMIM][HSO$_4$] without a co-solvent at 100 °C. A control experiment carried out at 100 °C using the IL without xylose showed that only residual water was distilled out of the IL. The IR spectra of the IL before and after the control experiment were similar, and no colour changes were observed, indicating that the IL is stable under the applied reaction conditions. After 4 h reaction of xylose in [EMIM][HSO$_4$], 84% conversion and 15% FUR selectivity were

obtained. The initially transparent mixture of IL and xylose became gradually darker and more viscous with increasing residence time, suggesting the formation of heavy products. In order to recycle the IL, the reaction mixture was cooled to room temperature after 4 h, and water was added to promote the precipitation of by-products. Black residues were separated by centrifugation and membrane filtration, leaving a transparent, pale yellow liquid. Excess water (and possibly other volatile products) in the IL was distilled off under reduced pressure. The amount of xylose in the recovered IL was ca. 1 wt.% (measured by HPLC) of the initial amount of xylose charged to the reactor. The IR spectra (Fig. 3) and the elemental analysis data of pure and recovered IL were similar. For both runs, the distillate consisted of two separate colourless liquids, which were identified by IR spectroscopy as being furfural and water. For the second run, 81% conversion and 22% FUR selectivity were reached. The similar results for both runs suggest that the IL is recyclable, as observed for the reactions carried out under nitrogen. However, the applied IL/vacuum system used is not as efficient as that carried out under nitrogen: furfural yields at 4 h are 12–18% for the reduced pressure system compared with 40% for the IL without toluene, and 81% for the IL/T biphasic system.

The exact nature of the black residue mentioned above is unknown at present. Elemental analysis revealed C, H, N and S contents of 45.7, 4.9, 4.8 and 8.0 wt.%, respectively (C:N:S mole ratio of 15:1.4:1), suggesting that the residue contains the IL or an insoluble derivative thereof. However, the calculated values for the pure IL are different: C, 34.6; H, 5.8; N, 13.45; S, 15.4% (C:N:S mole ratio of 6:2:1). The solid state ^{13}C CP MAS NMR spectrum of the recovered solid showed a complex series of overlapping resonances between 0 and 200 ppm (not shown): δ = 23.1, 44.3, 53.0, 89.5, 120.0, 131.5, 144.2 and 159.0. The signals up to 53 ppm are

presumably due to methyl and/or methylene carbon atoms, while those in the range 90–160 ppm are likely to arise from the carbon atoms of furan and/or imidazole/imidazolium rings. An alternative assignment for the peak at 90 ppm is a CH or CH$_2$ carbon bonded to two oxygen atoms, while the peak at 159 ppm may be due to the carbonyl group of an ester (since the IR spectrum showed a new absorption band at ca. 1700 cm^{-1} that is attributed to a carbonyl stretching vibration]. A full investigation of the nature of this residue may be carried out in future work.

3.1.3. Hexoses/[EMIM][HSO$_4$]/co-solvent reaction system under nitrogen atmosphere

The efficiency of the [EMIM][HSO$_4$]/T system was further investigated for the reaction of the hexoses, glucose and fructose, using the same initial concentration as that used for xylose (0.67 M, or 120 g dm^{-3} IL). The reactivity of the monosaccharides (based on conversion at 30 min, Table 1) follows the order: fructose (100%) > glucose (95%) > xylose (80%). As mentioned above, FUR yield from xylose increases up to 84%, reached at 6 h (Fig. 1). The reaction of fructose gives 79% HMF yield within 30 min. When [BMIM][Cl]/T is used instead of [EMIM][HSO$_4$]/T, the reaction of fructose gives 16% HMF yield at 30 min, under similar conditions. Hence, the Brönsted acidity associated to [EMIM][HSO$_4$] plays a major role in the dehydration of fructose, similar to that observed for xylose. Recently, Xie and co-workers reported 56% HMF yield in [EMIM][HSO$_4$] without a co-solvent, at 80 °C [13]. For the glucose/ [EMIM][HSO$_4$]/T system, HMF selectivity is very low (<9% up to 100% conversion, reached within 6 h). Decreasing the reaction temperature from 100 to 80 °C leads to lower glucose conversion at 30 min (86%, compared with 95% at 100 °C, Table 1), and HMF yield is less than 8% up to 97% conversion (reached within 24 h). Levulinic and formic acids, which are common by-products formed in aqueous phase under acidic conditions (via acid hydrolysis of HMF), were not detected by HPLC (using a diode array detector) in the reactions of the hexoses in [EMIM][HSO$_4$]/T.

While HMF may be formed in significant amounts from the reaction of fructose in [EMIM][Cl] at 100–120 °C, previous studies have shown that the same does not apply for the reaction of glucose in this IL, under similar reaction conditions [12]. These results were reproduced in this work for [EMIM][Cl] at 100 °C (Table 1). Moreau et al. [10] reported that the reaction of sucrose in 1-H-3-methylimidazolium chloride ([HMIM]Cl) at 90 °C resulted in the very rapid cleavage of the disaccharide into fructose and glucose. However, while fructose was selectively dehydrated into HMF in a consecutive pathway, glucose practically did not react. It has been postulated that the efficient in situ isomerization of glucose to fructose is important to obtain high HMF yields [12]. In the case of the glucose/[EMIM][HSO$_4$]/T system, no fructose was detected by HPLC, suggesting that glucose–fructose isomerization hardly takes place, which may explain the much lower HMF selectivities from glucose than from fructose (notwithstanding the similar reactivity of both hexoses). The decomposition of glucose may give several by-products, such as other sugars (e.g. mannose) via isomerization, C–C bond scission via reverse aldol condensation, and non-furan cyclic ethers via dehydrations [12,21]. However, we have not identified related products formed in the glucose/[EMIM][HSO$_4$]/T system. GC–MS analysis was performed to identify any volatile by-products. The chromatograms presented a few very weak peaks, which could not be fully and clearly identified. In the reaction of fructose, 5,5′-oxy-dimethylene-bis(2-furaldehyde), a symmetric ether of HMF, was detected, which may be formed via condensation of HMF [22]. This product has also been detected in the thermal decomposition of HMF [23]. Possibly, the by-products are mainly heavy/non-volatile compounds.

Zhang et al. obtained outstanding results for the conversion of glucose into HMF (nearly 70% HMF yield after 3 h at 100 °C) by adding CrCl$_2$ (0.04 M) to [EMIM][Cl] without a co-solvent; a series of other metal halides was tested, but the results were much poorer [12]. The authors proposed that a chromium chloride anion facilitates mutarotation of glucose (from α-glucopyranose to β-glucopyranose anomer) in the IL, followed by isomerization into fructofuranose via a chromium enolate intermediate [11]. For comparative purposes, the reaction of glucose was carried out in [BMIM][Cl]/T/CrCl$_3$ at 100 °C. CrCl$_3$ was chosen instead of CrCl$_2$ since it is more stable and easily handled under air, much cheaper, and, on the other hand, it is very likely that Cr^{2+} is oxidized to Cr^{3+} in the IL system containing dissolved air and water (at least from the dehydration reaction). After 4 h at 100 °C, the glucose/ [BMIM][Cl]/CrCl$_3$ system (i.e., no co-solvent) gives 81% HMF yield, which is comparable to that reported by Zhang and co-workers [12]. The use of toluene as a co-solvent further improved HMF yield at 4 h to 91% (Table 1).

The influence of using IBMK instead of toluene as the extracting co-solvent was investigated for the fructose/[EMIM][HSO$_4$] and glucose/[BMIM][Cl]/CrCl$_3$ systems. The mixtures of these ILs with T or IBMK are biphasic. Control experiments performed without monosaccharide did not reveal the formation of products due to solvent decomposition, under the applied conditions (ascertained by GC–MS and HPLC). Whereas the use of IBMK instead of toluene leads to a higher HMF yield in the fructose/[EMIM][HSO$_4$] reaction system, the opposite occurs for the glucose/[BMIM][Cl]/CrCl$_3$ system (Table 1). These results may be due to differences in the solubility of the co-solvent in each IL (may not be totally immiscible) and the distribution ratio of the target product in the two liquid phases.

3.2. One-pot hydrolysis/dehydration of di/polysaccharides in ionic liquids

The efficiency of the [EMIM][HSO$_4$]/co-solvent and [BMIM][Cl]/ IBMK/CrCl$_3$ systems was further investigated in the one-pot conversion of different renewable feedstocks, namely the disaccharides sucrose and cellobiose, and the polysaccharides xylan, inulin, starch and cellulose, into HMF or FUR under nitrogen, using conditions which were chosen on the basis of preliminary tests and to facilitate comparative studies (for xylose and di/polysaccharide, 100 g feedstock dm^{-3} IL; for hexoses, 120 g feedstock dm^{-3} IL). The results are shown in Fig. 4 and are calculated on the basis of wt.% yield of FUR or HMF, and for comparative purposes the values were also calculated for the monosaccharides: the theoretical yields (TY) are approximately 64 wt.% FUR for xylose, 70 wt.% HMF for fructose or glucose, 74 wt.% HMF for sucrose, maltose or cellobiose, ca. 73 wt.% FUR for the xylose precursor xylan, and ca. 78 wt.% HMF for the fructose precursor inulin. The xylan/ [EMIM][HSO$_4$]/T reaction system gives nearly half the FUR TY at 4 h, and inulin/[EMIM][HSO$_4$]/IBMK gives nearly the full HMF TY at 30 min (Fig. 4). These results are somewhat congruent with the observed higher reactivity of fructose in comparison to xylose in [EMIM][HSO$_4$] (Table 1, Fig. 1).

For the [BMIM][Cl]/IBMK/CrCl$_3$ system, the reaction of sucrose (a disaccharide with a β(1 → 2) glycosidic bond between a glucose and a fructose molecule) gives the full HMF TY at 4 h. The reactions of maltose (a disaccharide with two glucose molecules linked by a α(1 → 4) glycosidic bond) and cellobiose (a disaccharide with two glucose molecules linked by a β(1 → 4) glycosidic bond) in [BMIM][Cl]/IBMK/CrCl$_3$ give approximately half of the HMF TY; negligible amounts of the glucose were detected. The reactions of starch (a polymer of glucose units containing α(1 → 4) glycosidic bonds in a linear fashion and α(1 → 6) in a branched fashion) and cellulose (a polymer of glucose units linked by β(1 → 4) glycosidic bonds) in [BMIM][Cl]/IBMK/CrCl$_3$ give negligible HMF yields, for residence times up to 4 h. No hydrolysis products were detected
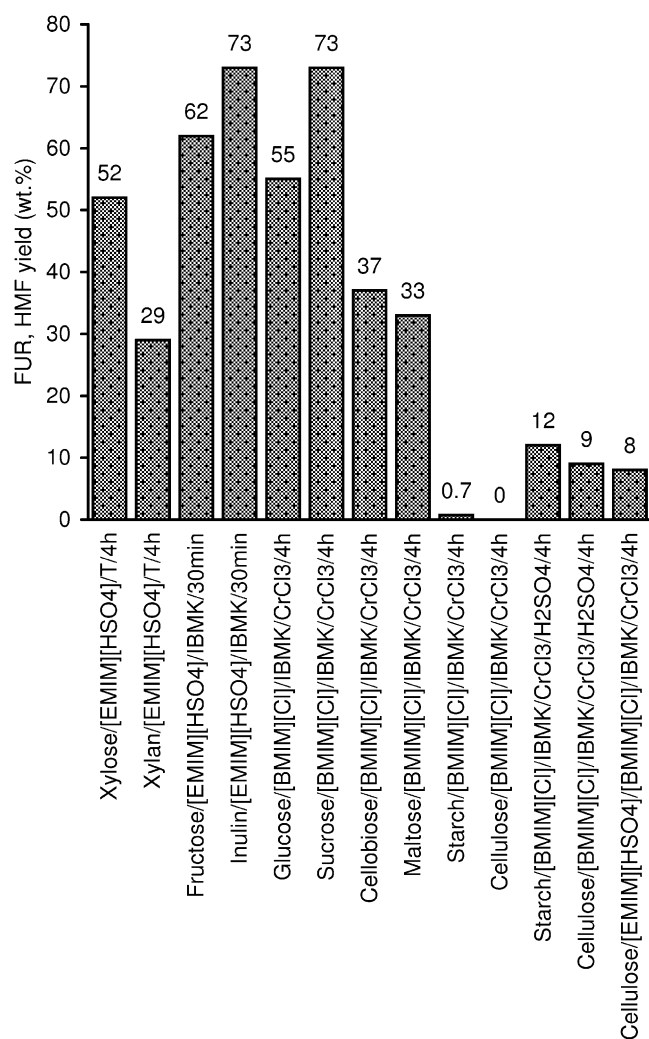
Fig. 4. FUR (from xylose/xylan) or HMF (from the remaining substrates) yields obtained in ionic liquid–co-solvent biphasic systems at 100 °C (initial concentration expressed as g feedstock/L ionic liquid = 100, except for hexoses, 120). In general, theoretical quantitative yields vary between 70 and 80 wt.%.

and the appearance of the reaction mixture remained unchanged, suggesting that practically no reaction of these polysaccharides took place.

The dissolution of cellulose in [AMIM]Cl ILs is greatly assisted by the high chloride ion concentration, which effectively breaks the extensive hydrogen bonding network present in its macro-structure [14,24–26]. Accordingly, the sluggish reaction for cellulose/[BMIM][Cl]/IBMK/CrCl$_3$ is probably not due entirely to solubility limitations. A possible explanation is that the hydrolysis step is rate limiting and demands a stronger acidity (Brönsted rather than Lewis type). Zhao and Li reported that cellulose hydrolysis takes place in [BMIM][Cl] in the presence of HCl or H$_2$SO$_4$ as catalysts, at 100 °C, under atmospheric pressure and without pretreatment [27]. After stirring the IL/cellulose mixtures for 5 min at 100 °C, a solution is obtained in the case of [EMIM][HSO$_4$] (and the mixture is light brown), whereas a heterogeneous mixture is obtained for [BMIM][Cl] (apparently cellulose does not completely dissolve, and no colour change in the reaction mixture is observed), suggesting that cellulose dissolves better in [EMIM][HSO$_4$]. It is worth noting that prior to the reaction at 100 °C, the mixtures were treated in an ultrasound bath (50 W, 40 kHz) for 15 min, at room temperature. Based on these findings and those by Zhang and co-workers [12], an attempt was made to

simultaneously enhance the hydrolysis reaction rate of cellulose ([EMIM][HSO$_4$] for enhanced polysaccharide solubility and acidity, i.e., of the Brönsted type) and selectively dehydrate glucose into HMF ([BMIM][Cl]/IBMK/CrCl$_3$) in a single reactor, at 100 °C, by using a mixed IL system consisting of [BMIM][Cl]/[EMIM][HSO$_4$] (2:1, v/v)/IBMK/CrCl$_3$. The HMF yield after 4 h at 100 °C was 8% (Fig. 4). Similar results are obtained when H$_2$SO$_4$ (0.04 M) is added to the [BMIM][Cl]/IBMK/CrCl$_3$ system: 9 and 12% HMF yield for the reactions of cellulose and starch, respectively. Starting the reaction from glucose in [EMIM][HSO$_4$]/T/CrCl$_3$ gives 96% conversion and 7% HMF yield at 4 h, which is similar to that observed for [EMIM][HSO$_4$]/T (wt.% yield of 6%). Hence, the rather low HMF yields for the cellulose reaction in the [BMIM][Cl]/[EMIM][HSO$_4$] (2:1, v/v)/IBMK/CrCl$_3$ system may be due to the lack of selectivity in the dehydration of the glucose monomers. The CrCl$_2$/[BMIM][Cl] system reported by Zhang and co-workers [12] was successful in converting glucose into HMF due to the formation of a higher halogenated anion complex. The mixed sulfate/chromium chloride IL acid systems may form different species, which may change (in nature and amount) during the course of the reaction as the concentration of water varies.

4. Conclusions

It has been shown that the dehydration of xylose and fructose and, on the other hand, the one-pot hydrolysis and dehydration of di/polysaccharides containing fructose units, in [EMIM][HSO$_4$]/co-solvent gives fairly high yields of FUR or HMF (80–90%) at 100 °C. The reaction of xylose in [EMIM][HSO$_4$]/toluene at 100 °C gives better results (82% FUR yield at 4 h) than previously reported dimethylsulfoxide/(Keggin-type heteropolytungstates or sulfuric acid) systems at 140 °C [15]. Furthermore, better results were achieved with [EMIM][HSO$_4$] than with aqueous H$_2$SO$_4$, under similar conditions. Removal of FUR by evaporation under reduced pressure (instead of solvent extraction) gave poorer results, although it should be possible to improve on the 18% FUR yield obtained at 4 h by optimizing the control of the pressure in the system, the design and dimensions of the setup, the mixing efficiency of the reaction mixture, and the reaction temperature and residence time. For both methods of FUR removal, the IL can be recovered and reused without a significant drop in FUR yield in recycling runs. In considering the potential of acid ILs such as [EMIM][HSO$_4$] to replace sulfuric acid in processes for the transformation of saccharides into FUR and HMF, it must be recalled that H$_2$SO$_4$ is very hygroscopic and difficult to dry in vacuum, and when heated it emits highly toxic fumes, which include sulfur trioxide, leading to the accumulation of acidic waste. The use of [EMIM][HSO$_4$] instead of H$_2$SO$_4$ may allow process intensification with reuse of the acid IL.

Although [EMIM][HSO$_4$] is effective in converting fructose (88% yield at 30 min) and polymers containing these units into HMF, it is poorly selective in glucose dehydration. The [BMIM][Cl]/T/CrCl$_3$ system of Zhang and co-workers [12] is quite effective in converting glucose and related disaccharides into HMF, but not polysaccharides such as cellulose and starch. For the latter feedstocks, the addition of [EMIM][HSO$_4$] to cellulose/ [BMIM][Cl]/CrCl$_3$ enhances HMF yields, presumably by accelerating the hydrolysis step. However, the dehydration of glucose monomers to HMF is poorly selective (8–9% HMF yield), most likely due to the formation of different acid active species from those formed in the absence of the sulfate anions.

A drawback of the IL/CrCl$_3$ systems is that chromium (especially chromium(VI), which can be formed from chromium(III) in aqueous environments) poses risks to human health and the environment, which would mean that any process based on these systems would be subject to stringent environmental controls.

Nevertheless, the results show that hydrophilic ILs may be promising for FUR and HMF production from sugar feedstocks, allowing relatively easy work-up procedures for isolating the target product(s), reuse of the acidic medium and operation under relatively mild conditions. Attempts to find IL systems for selectively processing feeds composed of mixed fructose and glucose-based saccharides remains a challenge.

Acknowledgements

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