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Ionic liquid binary mixtures: Promising reaction media for carbohydrate conversion into 5-hydroxymethylfurfural

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ABSTRACT

The conversion of carbohydrates into 5-hydroxymethylfurfural (5-HMF) has been studied in binary mixtures of ionic liquids (ILs), using strongly acidic resin Amberlyst 15 as the catalyst. In particular, both mono- and disaccharides, such as fructose, glucose and sucrose have been investigated. Considering the favorable effect exerted by chloride-based ionic liquids in the dissolution of carbohydrates, we used binary mixtures of 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) with [bmim$^+$] based ionic liquids differing in size, shape and coordination ability of the anion ([bmim][BF_4], [bmim][$N(CF_3SO_2)_2$], [bmim][$N(CN)_2$], [bmim][SbF_6] and [bmim][CF_3SO_3]). Carbohydrate conversion in [bmim][BF_4]/[bmim][Cl] binary mixtures, has been studied under both magnetic stirring and ultrasound (US) activation. The catalytic system used led to the formation of 5-hydroxymethylfurfural in good yield under mild conditions. A significant influence of IL binary mixture composition on the outcome of the target processes was evidenced. Improvements in both reaction time and temperature have been observed, under US activation.

1. Introduction

Energy demand in modern society and the negative consequences of global warming during the last decade have raised a growing interest in the scientific community toward renewable energy sources. In this scenario, the production of energy by means of solar cells or from bio-resources is an issue of paramount importance. In particular, as far as vegetable biomass is concerned, much attention has been paid to the production of industrially relevant intermediates from carbohydrates. These are a major component of biomass derived from wood processing by-products, agricultural surplus and so on. The dehydration of carbohydrates can give rise to important chemicals, such as furfural (FUR) and 5-hydroxymethylfurfural (5-HMF), which are currently obtained from petroleum manufacturing, and are used as starting materials for many industrial processes [1–7]. Thus, the implementation of carbohydrate conversion processes might have significant outcomes from both an economical and, most importantly, an environmental point of view.

The conversion of mono- and disaccharides into FUR and its derivatives has been widely investigated in both water [8–14] and conventional organic solvents [15–22]. Very recently, with the introduction of ionic liquids (ILs) as alternative reaction media, many studies have been directed toward the possibility to study these processes changing the nature of both the solvent media and the catalyst, or even varying other important operational parameters such as the reaction time and temperature dependence of different heating methods used [23–33]. Regarding this topic, different reports have analyzed the effect of microwaves on carbohydrate conversion [34–38]. On the other hand, US activation has been little investigated and it has been mostly applied only to improve carbohydrate dissolution in the solvent media used [39–42].

The use of ILs is advantageous because of their low flammability and possible reuse of the reaction media. Reports have highlighted that conversion of mono- and polysaccharides is favored in particular by chloride based ILs. Indeed, the high coordination ability of the chloride anion allows the formation of hydrogen bonds with the hydroxyl groups of the sugar units, favoring the dissolution of the substrate and, on the whole, its dehydration [43–45]. However, from a practical point of view the use of halide based ILs poses some limitations. As a matter of fact, these ILs are usually solid at room temperature and the liquid phases obtained on their melting show

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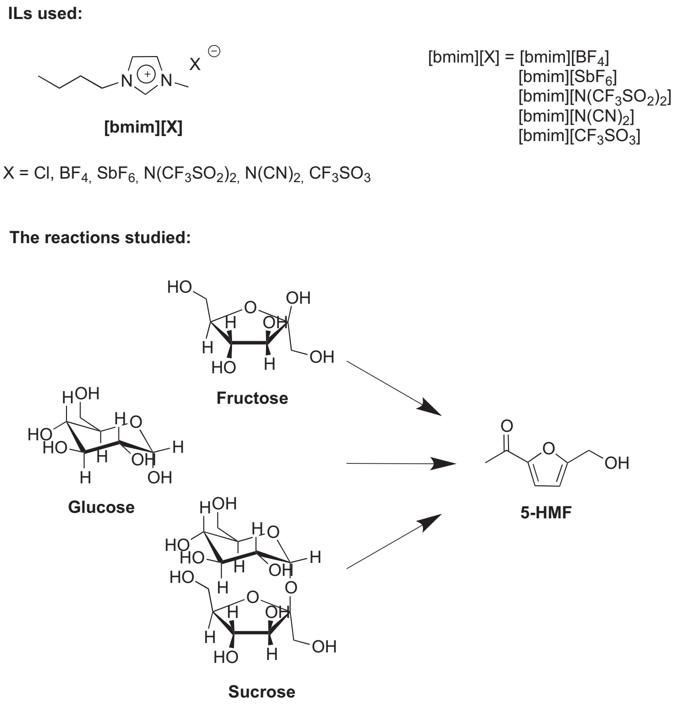
high viscosities. Consequently, high reaction temperatures have to be used in order to overcome these problems. This frequently causes the reaction mixture to turn brown, with the concomitant degradation of FUR and its derivatives into by-products of low industrial value. Furthermore, as the degradation processes of FUR are favored by water, an additional problem stems from the significant hygroscopicity of halide based ILs, making it difficult to carry out the target process in perfectly anhydrous media. From an environmental point of view, also the good water solubility and high thermal stability of halide based ILs pose some problems. Indeed, as a consequence of their possible release, the aqueous solubility might induce unwanted effects in aquatic ecosystems. On the other hand, the high thermal stability might favor their bioaccumulation [46–49].

Several attempts have been made to lower the viscosity of halide based ILs, and the use of conventional solvents/IL binary mixtures has been suggested [50]. However, this option could increase the environmental impact of the process. Therefore, to overcome the aforementioned problems, and bearing in mind the role played by chloride based ILs, we reasoned that the use of IL binary mixtures could be a valid alternative. Recent reports have highlighted some peculiar features of IL binary mixtures, which frequently show a strikingly different behavior with respect to the pure components, in particular as far as mixtures of anions are concerned [51–54]. Indeed, in the latter case, differences in size and coordination abilities of anions may give rise to either an ideal behavior or to a solvent system characterized by the presence of different micro-domains [55]. In this area, using the mononuclear rearrangement of heterocycles as a probe reaction, we have recently demonstrated that mixing of cations having significantly different electronic properties, induced a gradual change in the properties of the binary mixtures which perfectly reside between those corresponding to pure components. On the other hand, mixing anions differing in size, shape and coordination ability produced a discontinuous behavior, so that the properties of the binary mixtures obtained could not be related to the pure ILs [56].

In view of this, we studied on the conversion of carbohydrates into 5-HMF using IL binary mixtures such as [bmim][X]/[bmim][Cl], i.e. ILs all sharing the imidazolium cation, but differing in size, shape and coordination ability of the anion. This study was mainly aimed at identifying the most suitable co-solvent able to decrease the [bmim][Cl] viscosity, thus allowing the target process to be carried out close to room temperature. Fructose, glucose and sucrose were used as substrates (Scheme 1).



Scheme 1. Schematic representation of ILs used and reactions studied.

Carbohydrate conversion was carried out under acidic catalysis; in particular, we tested both species derived from renewable sources such as citric and tartaric acid, as well as strongly acidic resins differing in particles size, such as Amberlyst 15 and Dowex 50W X8 (hereafter indicated as Dowex). Reactions were initially carried out under magnetic stirring. However, taking into account that the sustainability of a process heavily depends on the amount of energy used, we also investigated the effect of US activation on the target processes, with the aim to decrease the reaction temperature and time.

2. Experimental

2.1. Materials

Fructose (≥99.0), glucose (≥99.5), sucrose (≥99.5), citric and tartaric acids (≥99.5) were purchased from Sigma–Aldrich and used without further purification. Amberlyst 15 (hydrogen form) and Dowex 50W X8 resins were purchased and kept before use overnight in a desiccator at 373 K, under vacuum and over phosphorus pentoxide.

[bmim][Cl], [bmim][BF$_4$] and [bmim][CF$_3$SO$_3$] were purchased from Iolitec. [bmim][N(CF$_3$SO$_2$)$_2$], [bmim][SbF$_6$] and [bmim][N(CN)$_2$] were prepared according to previously reported procedures [57–59]. Before use, all ILs were dried on a vacuum line at 343 K for 2 h, lyophilized for 48 h at 0.06 mbar, and stored in a desiccator under argon and over calcium chloride.

Each IL binary mixture was prepared by weighing the required amount of IL into a round bottom flask. To favor mixing, each mixture was vigorously stirred, sonicated for 1 min (45 kHz, 200 W) and then left to equilibrate overnight. In all cases the mixtures appeared to be homogeneous after this treatment.

2.2. General procedure for carbohydrate conversion under magnetic stirring

A suitable amount of carbohydrate (0.025 g) was weighed in a round bottom flask containing the pure IL or IL binary mixture (0.5 g). To favor carbohydrate dissolution, the mixture was stirred at 353 K for 30 min under argon. In all cases, the mixtures appeared to be homogeneous after this treatment. After equilibration at the reaction temperature, the suitable amount of acidic catalyst (0.025 g for fructose and glucose and 0.05 g for sucrose) was added. After reaction time, each sample was diluted with 0.250 g of ultra pure water, stirred at room temperature and diluted with methanol in such a way to have a 5-HMF concentration ranging from 7×10^{-6} M up to 7×10^{-5} M. The concentration of 5-HMF was determined from UV absorbance recorded at 277 nm. The presence of 5-HMF in the reaction mixture, as single UV absorbing product, was further verified by means of TLC on silica gel by comparison with a standard sample (eluent: ethyl acetate/methanol 5:1, v/v).

2.3. General procedure for carbohydrate conversion under US activation

Sonochemical reactions were carried out in a thermostated ultrasonic bath operating at a frequency of 45 kHz, with an output power of 200 W. The bath was filled with a 1% (w:w) aqueous solution of the surfactant Contrad 2000. Prior to each reaction we identified the portions of the bath experiencing the maximum ultrasonic intensity by aluminum foil mapping [60]. For this purpose, a sheet of aluminum foil (15 cm × 7 cm) was immersed vertically in the bath and subjected to sonication for 30 s. The distance at which the sheet underwent the maximum damage was chosen as the horizontal position of the reaction vessel. As for the vertical position, the bottom of the reaction vessel was placed 5 cm beneath the water surface. Samples were prepared in a tube having a 10 cm length, and subjected to the same analysis reported above for the reactions carried out under magnetic stirring.

2.4. *General procedure for the determination of acid exchange between the resin and ILs*

The determination was carried out using a previously reported procedure [61]. In a typical experiment, 0.025 g of Amberlyst 15 were added to the suitable [bmim][Cl]/[bmim][BF_4] solvent mixture and subjected to sonication or stirring under the best reaction conditions found for each substrate. Then 5 mL of ultrapure water were added to the mixture and the resin was filtered off. The amount of acid dissolved in the resulting aqueous solution was determined by potentiometric titration with standard NaOH (0.02 M). No appreciable change in pH was observed in a blank test after stirring or sonicating the same amount of resin in 5 mL of ultrapure water, in the absence of ILs.

3. Results and discussion

3.1. *The effect of co-solvent nature*

Initially, we screened for the IL to be able to behave as the most suitable co-solvent for the conversion of fructose into 5-HMF. To pursue this goal, we used [bmim][BF_4], [bmim][$N(CN)_2$], [bmim][$N(CF_3SO_2)_2$], [bmim][SbF_6] and [bmim][CF_3SO_3]. The ILs used also have very different viscosities (η = 40,890, 154, 90, 52 and 39 cP at 293 K for [bmim][Cl], [bmim][BF_4], [bmim][CF_3SO_3], [bmim][$N(CF_3SO_2)_2$] and [bmim][$N(CN)_2$] respectively; η = 108 cP for [bmim][SbF_6] at 298 K) [62–65]. The viscosity of IL binary mixtures could be significantly different than those of pure ILs. However, in all cases, the addition of IL co-solvent should significantly decrease the viscosity of solvent mixtures.

Then, we performed the reaction without the acid catalyst. In all cases we did not observe the formation of 5-HMF. In the presence of catalyst we carried out the reaction at 298 K, using various binary mixtures of ILs having a 1:1 [Cl^-]/anion molar ratio (hereafter expressed as [bmim][Cl] mole fraction, X_{Cl} ~0.5). The results collected are illustrated in Fig. 1, which reports 5-HMF yields as a function of the different nature of ILs used (the data are summarized in Table S1 of the Supplementary Material).

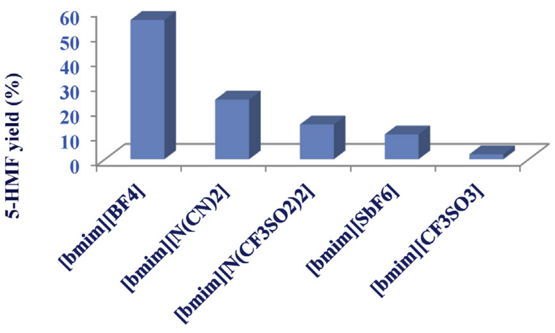


Fig. 1. 5-HMF yields as a function of different IL nature at 298 K, in 0.5 g of [bmim][X]/[bmim][Cl] binary mixture (X_{Cl} = 0.5, $m_{\text{Amberlyst 15}}$ = 0.025 g, m_{fructose} = 0.025 g, t = 3 h).

The data show that the course of the target reaction is significantly affected by the different nature of the IL used as co-solvent. Indeed, yields significantly decreased on going from [bmim][BF_4] to [bmim][CF_3SO_3] according to the following trend: [bmim][BF_4] > [bmim][$N(CN)_2$] > [bmim][$N(CF_3SO_2)_2$] > [bmim][SbF_6] > [bmim][CF_3SO_3]. Considering that a higher anion coordination ability favors the dissolution of carbohydrates in ILs [43–45], it can easily be noticed that experimental data cannot be correlated with the anion ability of the co-solvent IL to accept a hydrogen bond, as accounted for by β parameter values. Indeed, for the ILs used, β decreases along the series: [bmim][$N(CN)_2$] > [bmim][CF_3SO_3] > [bmim][BF_4] > [bmim][$N(CF_3SO_2)_2$] > [bmim][SbF_6] (β = 0.71, 0.46, 0.38, 0.24 and 0.15, respectively) [66]. This suggests that carbohydrate dissolution is not the only factor determining the outcome of the target reaction. Furthermore, according to previous reports [55], this result indicates that the behavior of IL binary mixtures cannot be simply related to the properties of the pure components.

3.2. *Experimental conditions*

Having identified the most suitable co-solvent, we studied the conversion of fructose in the presence of different acidic catalysts. We reasoned that it could be interesting to investigate the use of either carboxylic acids derived from renewable sources, such as citric and tartaric acids or, on the other hand, solid recyclable catalysts such as acidic resins. Focusing in particular on solid catalysts, we considered that differences in size of resin particles could be an important factor in determining the outcome of the process studied. In this light, the target reaction was performed using the strongly acidic resins Dowex and Amberlyst 15. The data collected at 298 K by using a [bmim][BF_4]/[bmim][Cl] binary mixture, at X_{Cl} ~0.5, are reported in Table S2 of the Supplementary Material.

It was found that Amberlyst 15 was the most effective catalyst under our experimental conditions. To explain these results, we have to consider the nature of the resins, the amount of acidic sites and particle size. Amberlyst 15 is a macroporous resin, whereas Dowex is a gel resin. Our results account for a stronger activity of the macroporous resin with respect to the gel one and this agrees with recent reports [26]. Differently from previous observations in literature [67,68], in our case HMF yields increased on increasing the particle size of resin (Amberlyst 15: 18–23 mesh; Dowex: 20–50 mesh). However, the catalysts used have a different amount of acidic sites (higher for Amberlyst 15 than for Dowex). To ascertain if the results obtained could be rationalized as a function of the latter parameter, we also performed fructose conversion using equivalent amounts of the catalysts (i.e. 25 mg of Amberlyst 15 or 75 mg of Dowex). 5-HMF yields were very different (56% and 6% in the presence of Amberlyst 15 or Dowex respectively), probably indicating that the trend obtained was significantly affected by the nature of the resin.

Previous studies report that in many cases the use of Brønsted solid acids in ILs gives rise to homogeneous catalysis [61]. In order to get deeper insights, we carried out investigations to verify the presence of homogeneous acidic species using a method previously reported [61]. Under both magnetic stirring and US activation, we detected the presence of 0.07 mmol of acid dissolved in the solvent mixture, evidencing homogeneous as well as heterogeneous catalysis.

Of course, before studying the effect of IL binary mixtures on the efficiency of glucose and fructose conversion, we tried to evaluate in both cases the relevance of all other experimental parameters in optimizing the target processes. So, we carried out the carbohydrate conversion varying the reaction times and temperatures, as well as the catalyst/substrate ratio and the solvent/substrate weight ratio. Also in these cases, we used a [bmim][BF_4]/[bmim][Cl] binary mixture at X_{Cl} ~0.5 as the solvent system. Relevant data

Table 1
5-HMF yields obtained from fructose and glucose conversion in [bmim][Cl]/[bmim][BF$_4$], as a function of reaction time and temperature.[a]

Fructose			Glucose		
Time (h)	Temperature (K)	Yield (%)[b]	Time (h)	Temperature (K)	Yield (%)[b]
1	298	7	0.5	298	0
2	298	34	1	298	0
3	298	56	1.5	298	5
3	313	52	2	298	32
4	298	38	3	313	0
5	298	35	3	298	15
			3	363	14
			4	298	5

[a] Reaction conditions: $X_{Cl} = 0.5$, $m_{carbohydrate} = 0.025$ g, $m_{Amberlyst\ 15} = 0.025$ g.
[b] Yields were reproducible within 2%.

are presented in Table 1, whereas results about the effect of substrate/catalyst and substrate/solvent ratios are reported in Tables S3 and S4 of the Supplementary Material.

It is noteworthy that, unlike fructose, few effective systems are reported for glucose conversion to 5-HMF. In the case of fructose, conversion to 5-HMF has been already studied in [bmim][Cl] and in the presence of Amberlyst 15, at 353 K (reaction time: 10 min, 5-HMF yield: 82%).[69] As far as glucose is concerned, it has been frequently reported that best experimental conditions for its dehydration require the use of a basic catalyst. This favors the isomerization of glucose to fructose, which in turn more easily undergoes the dehydration process. Generally, strong mineral or Lewis acids have been used at temperatures higher than 363 K (reaction times: 1–4 h, 5-HMF yields: 17–81%) [36,70–73]. Under our experimental conditions, the dehydration of glucose occurred under much milder conditions. Furthermore, to the best of our knowledge [74], this is one of the few examples in which glucose conversion has been performed using an acidic resin.

The data show that, at equivalent reaction times ($t = 3$ h), a higher temperature did not improve 5-HMF yields. Furthermore, in both cases, an increase in temperature caused the browning of the reaction system. According to previous reports [75–77], we ascribed the observed browning to the presence of by-products such as polymers and humins.

As far as the reaction time is concerned, our data indicate that also under relatively mild conditions ($T = 298$ and 333 K for fructose and glucose respectively), prolonged contact between catalysts and 5-HMF exerts a negative effect on the process efficiency. Indeed, the 5-HMF yield gradually decreased after three hours for fructose, whereas in the case of glucose the best 5-HMF yield (32%) was obtained after two hours.

Finally, for both fructose and glucose the best 5-HMF yields were obtained using 25 mg of sugar, 25 mg of catalyst and a 20/1 solvent/substrate weight ratio (Tables S3 and S4 of the Supplementary Material). Indeed, both increasing the amount of catalyst and diluting the reaction mixture resulted in a lower yield. A larger amount of catalyst may negatively affect the reaction favoring the hydration and poly-condensation of 5-HMF. According to previous reports [26] this may result in a more difficult mass transfer. On the other hand, an increase in the initial carbohydrate loading may cause concomitant secondary reactions between sugar and FUR, giving rise to the formation of mixed polymers such as humans [78] humins.

3.3. *The effect of IL binary mixture composition*

The last factor to be analyzed was the effect of composition of the IL binary mixture. As we pointed out above, IL binary mixtures can give rise to different behaviors according to whether different cations or anions are mixed. Literature reports underline that mixtures of anions generally show the most distinct behavior. In these cases, the largest deviations from the ideal behavior have been observed when the anions possess large differences in size [55].

On the grounds of this information, and using the optimized experimental conditions identified above (see Section 3.2), we studied both fructose and glucose conversion into 5-HMF across the whole [Cl$^-$]/anion mole fraction range. For the sake of clarity, the data collected are presented in Fig. 2 (5-HMF yields as a function of [bmim][Cl] mole fraction, for both fructose and glucose conversion are reported in Table S5 of the Supplementary Material).

In both cases 5-HMF yields show a bell-shaped trend centered at X_{Cl} ~0.5. Low yields detected in pure [bmim][BF$_4$] or in binary mixtures richer in this component could be due to the lower ability of [BF$_4^-$] in favoring the dissolution of the sugar. On the other hand, low yields detected in pure [bmim][Cl], or in IL binary mixtures richer in this component, could be ascribed to the large viscosity of the solvent media, which probably hampers the approach between the reagents.

Therefore, our results suggest that the outcome of the reaction is a consequence of a balance between the favorable effect resulting from a higher concentration of chloride ion, able to form hydrogen bonds with sugar units, and the unfavorable one due to the higher viscosity of the solvent medium.

3.4. *Sucrose conversion*

It is well known that the demanding energy of sucrose conversion into 5-HMF is larger than the one of fructose or glucose. Indeed, this reaction generally requires high reaction temperatures and strong acidic catalysts. According to literature, the above process has been studied both in conventional organic solvents and in IL solution, in the temperature range 363–413 K and using acidic catalysts such as HCl or Lewis acids [79–83]. In order to test the efficiency of our reaction system in this process, we analyzed the

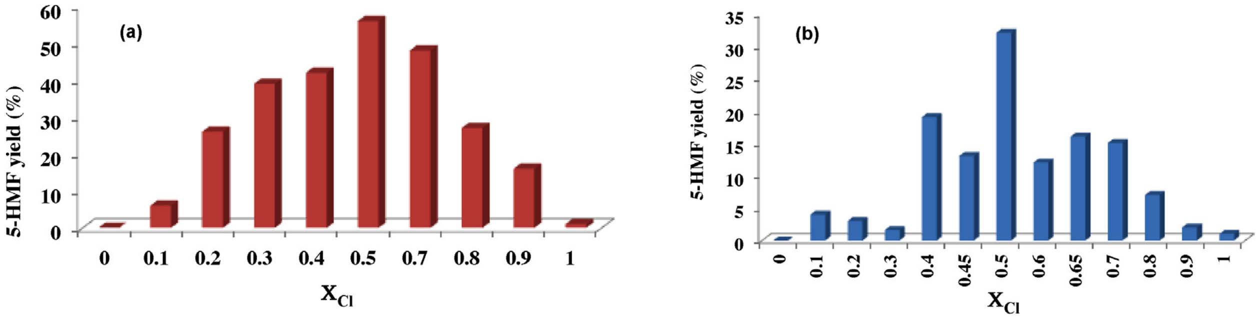


Fig. 2. 5-HMF yields as a function of IL binary mixtures composition: (a) from fructose at 298 K; (b) from glucose at 333 K ($m_{carbohydrate} = 0.025$ g, $m_{Amberlyst\ 15} = 0.025$ g, $t_{fructose} = 2$ h, $t_{glucose} = 3$ h).

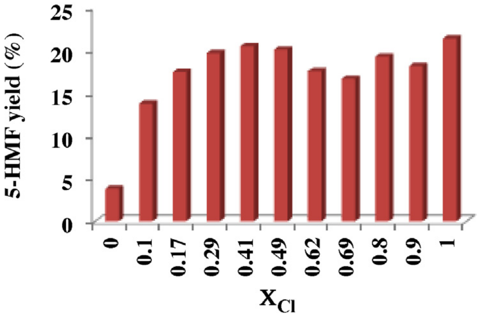


Fig. 3. 5-HMF yields as a function of IL binary mixtures composition from sucrose at 363 K ($m_{sucrose}$ = 0.025 g, $m_{Amberlyst\ 15}$ = 0.05 g, t = 2 h).

effect of temperature, reaction time, catalyst/substrate weight ratio and solvent mixture composition. The data collected are reported in Tables S6 and S7 of the Supplementary Material.

In agreement with the large energy demand of this process, the investigation carried out using a solvent/substrate weight ratio equal to 20/1 and a catalyst/substrate weight ratio equal to 2/1 showed that the largest 5-HMF yield (17%) can be obtained only at 363 K. Such a reaction temperature is higher than the one used in the case of fructose or glucose conversion, and affords a lower yield.

Data previously reported in literature cannot be directly compared. Indeed, to the best of our knowledge, Amberlyst 15 has only been used in DMF solution at 393 K [84]. Furthermore, in the latter case 5-HMF yield was larger than the one obtained under our experimental conditions (58 and 17% in DMF and IL binary mixture respectively). On the other hand, in one of the few examples of sucrose conversion without catalyst, the target reaction was performed in [hmim][Cl] at 363 K and gave rise to a modest 5-HMF yield (37%) [85]. Notwithstanding the yield obtained, also in this case we analyzed the effect of different operational parameters, such as reaction time, solvent/substrate and catalyst/substrate ratios. Analysis of the data reported in Table S6 of the Supplementary Material shows that the best yield was obtained in 2 h using a catalyst/substrate weight ratio as large as 2/1. Indeed, an increase in both reaction time and amount of catalyst led to a lower 5-HMF yield. On the other hand, increasing the reaction temperature induced a browning of the reaction mixture and a decrease in 5-HMF yield.

Furthermore, 5-HMF yield from sucrose conversion increased up to X_{Cl} ~0.3 and, unlike fructose or glucose conversion, the subsequent increase in X_{Cl} did not affect the yield (Fig. 3).

This result probably stems from the balance of the different and contrasting effects that solvent composition can exert on the different steps of the sucrose conversion, namely the hydrolysis of glycosidic bond, the glucose–fructose isomerization and finally the fructose conversion to 5-HMF.

3.5. The effect of US activation

As we stated previously (see Section 1), we were also interested in the possibility of using US activation to promote the target processes. Indeed, this alternative methodology has seldom been used in studying the conversion of carbohydrates. On the other hand, different reports have highlighted the suitability of ILs to carry out ultrasound assisted reactions [86–92]. In particular, we have recently studied the formation of aryl azides under US activation. We have demonstrated that ILs are able to induce highly efficient cavitation processes, generating favorable physical conditions for the occurrence of the reaction. This is a consequence of their low vapor pressure and network of cation–cation and cation–anion interactions [93].

Initially, we investigated the possible 5-HMF formation under US activation in the absence of the acidic catalyst. However, in all the cases examined, we did not observe the presence of the desired product. Furthermore, we analyzed the possible dispersion of the catalyst particles as a consequence of US application, but we did not observe particles dispersion or loss in weight. The images of the resin before and after US action are reported in Fig. S1 of the Supplementary Material.

We tried to convert all the carbohydrates used in this work under US activation. However, under our experimental conditions (ultrasonic bath operating at 45 kHz and 200 W), we did not detect the formation of 5-HMF from glucose. In this case, after US action in the temperature range 298–343 K, only a faint browning of the reaction mixture was observed. HPLC analysis of the reaction mixture evidenced only a slight decrease in glucose concentration; minor amounts of possible by-products such as 5-HMF, levulinic acid, lactic acid were not detected even in trace amount. Consequently, the results discussed hereafter are exclusively referred to fructose and sucrose.

We searched for the best experimental conditions to obtain 5-HMF from fructose and sucrose under US activation. The first experimental parameter we optimized was the reaction time, using the best experimental conditions found for the reaction under magnetic stirring and with a IL binary mixture at X_{Cl} ~0.5 as solvent (the data collected are reported in Table S8 of the Supplementary Material). The data (reported in the Table) evidence that US activation is able to favor the outcome of the target reactions. Furthermore, in the case of fructose, at equivalent temperature (298 K), the best 5-HMF yield was obtained in shorter reaction time (3 h and 1 h under magnetic stirring and US activation respectively). On the other hand, changes in the optimal reaction time were not observed for sucrose (2 h under both magnetic stirring and US activation). Nevertheless, a good increase in 5-HMF yield was obtained (20 and 34% under magnetic stirring and US activation respectively) at a significantly lower reaction temperature (363 and 298 K under magnetic stirring and US activation respectively). Moreover, the data collected demonstrate also the negative outcome of a prolonged contact between the acidic catalyst and the reaction mixture.

We also tried to evaluate possible changes in yields as a function of different catalyst/substrate weight ratios (the data collected are reported in Table S8 of the Supplementary Material). In this case, different trends were obtained for fructose and sucrose. While in the case of sucrose the best catalyst/substrate weight ratio was the same as the one employed under magnetic stirring, for fructose the US promoted reaction required a lower amount of resin than the one used under magnetic stirring.

In the latter case, comparable yields were obtained by using weight ratios as large as 0.5 and 1. Probably, as far as the catalyst concentration is concerned, differences in the behavior of the substrates could be once again ascribed to the occurrence of different reaction pathways giving rise to 5-HMF from either fructose or sucrose, and to different effects that US activation can exert on each step.

Data discussed hitherto allow us to underline some important advantages deriving from use of US activation. Indeed, according to our previous report [93], a high efficiency of the cavitation process in IL solution can be proposed. In some cases (namely fructose), this results in a reduction of the amount of catalyst needed as well as of the reaction time. In other cases (namely sucrose), the high efficiency of the cavitation process induces a significant decrease in the reaction temperature. The use of ultrasound reduces the waste of materials and energy, which represents a benefit from both an environmental and economic point of view.

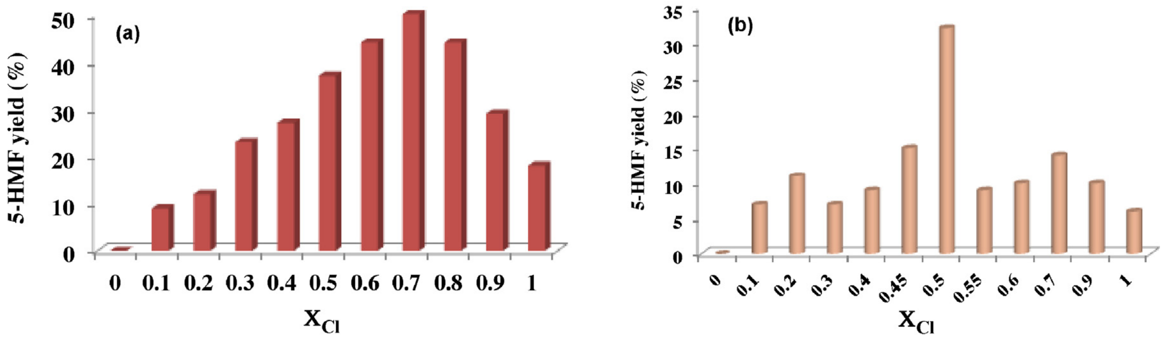


Fig. 4. 5-HMF yields, obtained under US activation, as a function of IL binary mixtures composition at 298 K from: (a) fructose ($m_{\text{fructose}} = 0.025$ g, $m_{\text{Amberlyst 15}} = 0.0125$ g, $t = 1$ h); (b) sucrose ($m_{\text{sucrose}} = 0.025$ g, $m_{\text{Amberlyst 15}} = 0.05$ g, $t = 2$ h).

In view of these results, we analyzed the effect of IL binary mixtures composition also under US activation. The data collected as a function of X_{Cl} are illustrated in Fig. 4, and are reported in Table S9 of the Supplementary Material.

Comparison between data collected for fructose and sucrose highlights the different relevance of the solvent mixture composition even under US activation. Indeed, in the case of fructose, 5-HMF yields regularly change with X_{Cl}, whereas for sucrose this parameter barely affects the outcome of the reaction. However, in this latter case it is noteworthy that US activation allows us to obtain, under mild conditions (298 K), 5-HMF yields slightly lower than those observed at 363 K. Differently from magnetic stirring, the best 5-HMF yields require the use of IL binary mixtures that are richer in chloride anion (X_{Cl} ~0.5). Furthermore, bearing in mind the absence of US activation effect on the conversion of glucose, it can be proposed that 5-HMF originated from the fructose moiety.

By analogy with data collected under magnetic stirring, in the case of fructose, the trend of 5-HMF yields as a function of X_{Cl} is represented by a bell-shaped curve. Comparison with the data collected under magnetic stirring accounts also in this case for significant catalytic efficiency in IL binary mixtures rich in chloride anions. Indeed, the highest 5-HMF yield was obtained at X_{Cl} ~0.7 and yields collected at larger X_{Cl} values were larger than those collected under magnetic stirring. The above finding can be ascribed to the synergistic action of different factors, such as the effect of chloride anion concentration on the outcome of the reaction and the effect of the solvent viscosity on the ultrasound efficiency.

As stated previously (see Section 3.3), a solvent mixture richer in the chloride anion should improve the dissolution of carbohydrates in ILs and, consequently, their conversion to 5-HMF. However, the presence of a larger chloride concentration also boosts the viscosity of the solvent, slowing the reaction rate under magnetic stirring as a consequence of more difficult mass transfer. By contrast, bearing in mind that a higher solvent viscosity positively acts on the cavitation efficiency [60], the increase in the chloride mole fraction enhances the efficacy of ultrasounds, allowing us to explain the trend observed.

4. Conclusions

All of the data collected sheds light on the suitability of IL binary mixtures as reaction media for the conversion of carbohydrates to 5-HMF. According to previous reports, our data show that the properties and catalytic activity of IL binary mixtures cannot be related to the behavior of pure ILs [56].

Among the binary mixtures investigated, the [bmim][BF_4]/[bmim][Cl] mixture has been proven able to give the best 5-HMF yields under mild conditions. The use of [bmim][BF_4] as co-solvent allows [bmim][Cl] to be utilized at room temperature, taking advantage from the ability of the latter IL to improve the dissolution of carbohydrates.

Investigations carried out by using this solvent system evidence how the results obtained are affected by the catalyst/substrate and the solvent/substrate weight ratios. In all cases the IL binary mixture composition plays a significant role in determining the outcome of the reaction.

To the best of our knowledge, this is one of the few reports analyzing the effect of US activation in the formation of 5-HMF from both mono- and disaccharides. Our results shed light also on the advantages deriving from US activation of reaction mixtures. Indeed, the US assisted reactions proceed with lower reaction times and temperatures than the ones needed under magnetic stirring. Furthermore, in the case of fructose, the US action induces a change in the composition of the solvent mixture giving rise to the best 5-HMF yield (X_{Cl} ~0.5 and 0.7 under magnetic stirring and US activation respectively). Probably, because this binary mixture is richer in [bmim][Cl], this result could be a consequence of the higher efficiency of cavitation process in more viscous solvent systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.05.039.

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