

Ionic liquids binary mixtures and zeolites: a combination to promote carbohydrates conversion into 5-hydroxymethylfurfural

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Abstract

The efficient conversion of biomass into value-added compounds under mild and safer conditions is a cornerstone of present research efforts to meet the needs of chemical industry with sustainable development.

In this work, we studied the dehydration of fructose, glucose and sucrose into 5-hydroxymethylfurfural (5-HMF), catalyzed by HY zeolite, in three ionic liquid mixtures differing for the cation, aromatic or aliphatic. We investigated the effect of several operational parameters such as temperature, catalyst loading, zeolite counterion, solvent mixture and added chloride. In the optimal experimental conditions, we obtained good to very good yields especially for fructose and sucrose, using the relatively low temperatures of 80 °C and 120 °C, respectively. We also investigated the dehydration of fructose under sonochemical activation, obtaining a yield of 71 % in 30 minutes, at the remarkably low temperature of 40 °C.

KEYWORDS: Carbohydrate conversion, zeolites, ionic liquids, 5-HMF, sonichemistry

Introduction

The increasing energy consumption and demand associated with industrial development is at the root of important environmental issues, from depletion of energy sources, pollution of the environment to global warming. For this reason, it is mandatory to consider the sustainability of chemical processes, and researchers are presently putting extensive effort and interest on this topic. In particular, an effective strategy to tackle the depletion of fossil energy sources lies in the use of renewable feedstocks. In this context, processing vegetable biomass is attracting considerable interest. Produced at an estimated rate of 10^{11} ton per year, it is the most abundant renewable feedstock.¹ Furthermore, it poses no environmental risks and is also remarkably cheap, since can be obtained in considerable amounts from waste of crops and food industries. A significant fraction of vegetable biomass is rich in carbohydrates, being composed by a variety of polysaccharides. Hence, conversion of sugars obtained by its hydrolysis can open the door to the obtainment of several chemical platforms,²⁻⁴ *i.e.* compounds enabling synthetic access to industrially relevant products. One the most important chemical platforms is 5-hydroxymethylfurfural (5-HMF).⁵⁻⁷ Indeed, a diverse range of furanic derivatives can be obtained from 5-HMF, through transformations like oxidations, reductions, olefination and etherification. These products find application in fields like biofuel and pharmaceutical chemistry. Furthermore, some of them are useful monomers for the synthesis of bioplastics.⁶

More specifically, the synthesis of 5-HMF occurs by acid-catalyzed dehydration of hexoses, and requires the formal elimination of three water molecules.⁸ Although the process is simple in principle, recent mechanistic studies have recently uncovered the complexity of the actual pathway.

In particular for fructose, the most reactive carbohydrate, several reports show that the reaction requires several steps and proceeds through the formation of different cyclic intermediates, whose distribution ultimately determine selectivity in 5-HMF.^{9,10} Conversely, the most abundant monosaccharide, glucose, is much less reactive, and its dehydration to 5-HMF requires a first isomerization step to fructose.⁸ Accordingly, obtaining 5-HMF from di- and polysaccharides requires

a further step of hydrolysis into the relevant monosaccharides. This mechanistic picture is further complicated because, under the same experimental conditions that favor its formation, 5-HMF also undergoes degradation to levulinic and formic acids or polymeric species known as humins. Conventional methods for the synthesis of 5-HMF, employ strong mineral acids or metal-based Lewis acid like CrCl_3 together with high temperatures.¹¹ These conditions raise concerns for the likely occurrence of side reactions and also from an environmental point of view, given the corrosiveness and the toxicity of the catalysts used. For this reason, in agreement with the Green Chemistry approach,¹² the interest of researchers has shifted to safer, milder and less environment impacting protocols for this valuable process. In particular, this can be achieved by substituting strong acids or metal salts with heterogeneous catalysts¹³ such as ion exchange resins,¹⁴ or zeolites,¹⁵ which provide catalytic efficiency together with ease of recovery and, in principle, recyclability.

In particular, zeolites are aluminosilicates with orderly distributed microporous networks in molecular dimensions.¹⁶ Pertaining to catalysis, these materials are highly acidic and possess different combinations of both Lewis and Brønsted acid sites. Furthermore, their ordered porous structure often shows shape selectivity, being able to accommodate within its pore only substrates with a given size.¹⁵ An important advantage of zeolites is the large number of structures available, and the relatively easy possibility of introducing modifications such as incorporation of metal ions, with the aim of fine-tuning their properties.

All these characteristics make them useful catalysts in the field of sustainable chemistry.^{16,17} Applying similar consideration to solvents, has pushed research to explore more environmentally friendly solvent media¹⁸ such as deep eutectic solvents¹⁹ and ionic liquids (ILs).²⁰ ILs are organic salts with a low melting point ($< 100\text{ }^\circ\text{C}$) and often liquid at room temperature.^{21,22} They provide unique fully ionic reaction media with a distinct nanostructure.^{23,24}

Concerning biomass conversion, some ILs stand out for their remarkable ability of solubilizing cellulose, the fraction of biomass richest in carbohydrates, by disrupting intra- and intermolecular hydrogen bonds.²⁵ In this context, we found that imidazolium-based IL mixtures proved suitable

solvent media for converting mono- and disaccharides into 5-HMF under heterogeneous conditions, in the presence of the ion exchange resin Amberlyst 15.²⁶ However, the use of aromatic ILs has recently come under scrutiny, as ILs based on aliphatic cations exhibited higher biodegradability and lower toxicity.²⁷ Bearing all this in mind, we herein report a study of the dehydration of fructose, glucose and sucrose in three different IL mixtures, bearing aliphatic and aromatic cations, in the presence of the natural zeolites HY and NH₄Y as heterogeneous catalysts (Chart 1). We chose these two zeolites to study the effect of a different counterion on the reaction outcome.

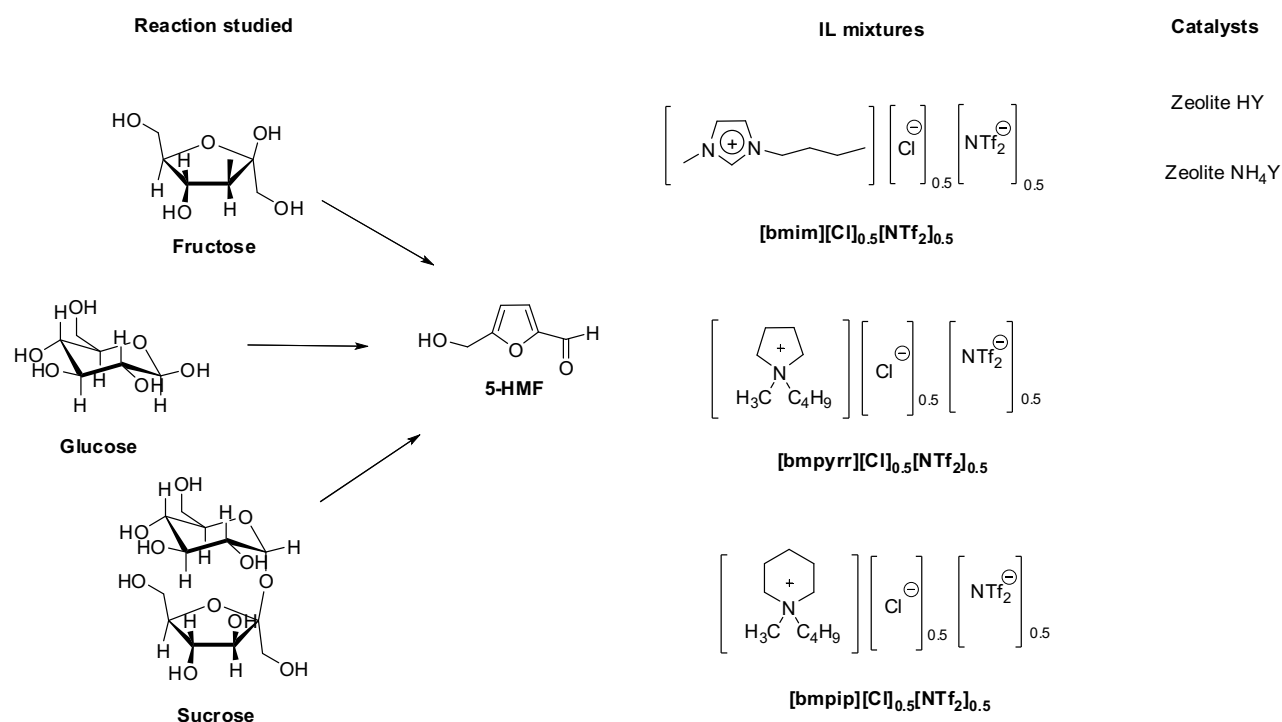


Chart 1. Reaction studied, ionic liquid mixtures and catalysts used.

We chose equimolar IL mixtures on the grounds of the good results we obtained at this composition when studying the dehydration of carbohydrates in aromatic IL mixtures.²⁶

We carried out a full investigation of the effect of operational parameters like temperature, catalyst loading, nature of the solvent and added chloride to find the optimal experimental conditions.

Employing non-conventional means of activation can also be useful to improve the sustainability of a given process. Among these innovative methodologies, ultrasound (US) irradiation has been successfully applied in biomass processing,²⁸⁻³⁰ and appears especially convenient in the presence of highly viscous and low vapor pressure solvents like ILs. This stems from enhanced efficiency of the cavitation process as a result of these physical properties^{31,32} and often entails drastic reductions in reaction times and temperature and, in turn, in significant energy saving. Accordingly, we observed such favorable effect for heterocyclic reactions in neat ILs^{33,34} and also for the dehydration of fructose and sucrose in solution of a mixture of aromatic ILs, catalyzed by Amberlist 15.²⁶ Bearing this in mind, we also performed the conversion of carbohydrates into 5-HMF under sonochemical activation, observing a remarkable reduction in the reaction times and temperature, without compromising yields in 5-HMF. We obtained high yields in 5-HMF, which are competitive with those recently reported using modified zeolites.³⁵ Our results show an interesting potential considering that the use of materials containing toxic metals like tin or iron is avoided.

Experimental section

Materials

Commercially available fructose, glucose, sucrose, HPLC grade acetonitrile and water were used without further purification. ILs such as 1-butyl-3-methyl-imidazolium chloride [bmim][Cl], N-butyl-N-methyl-pyrrolidinium chloride [bmpyrr][Cl] and N-butyl-N-methyl-piperidinium chloride [bmpip][Cl] were obtained from commercial sources and lyophilized at 0.01076 atm before use. Commercially available 1-butyl-3-methyl-imidazolium bis-(trifluoromethanesulfonyl)imide [bmim][NTf₂], N-butyl-N-methyl-pyrrolidinium bis-(trifluoromethanesulfonyl)imide [bmpyrr][NTf₂] and N-butyl-N-methyl-piperidinium bis-(trifluoromethanesulfonyl)imide [bmpip][NTf₂] were dried at 60 °C for 2 h under reduced pressure and kept in a desiccator over calcium chloride and under argon. IL mixtures were prepared weighing the suitable amounts of ILs in a screw-capped vial. To ensure full mixing, each mixture was vigorously stirred, sonicated in a

bath for 1 minute (200 W, 45 kHz), then left to equilibrate overnight at room temperature. All mixtures appeared homogeneous after this treatment. Commercially available zeolite HY (surface area 730 m²/g, SiO₂:Al₂O₃ 5.1:1) and zeolite NH₄Y (surface area 925 m²/g, SiO₂:Al₂O₃ 5.1:1) were kept at 250 °C for 6 h and for further 8 h at 100 °C in a drying oven under vacuum before use.

General procedure for the carbohydrate dehydration in IL mixtures under silent conditions

For a typical reaction, 50 mg of carbohydrate were added in a screw-capped vial to 1 g of the relevant IL mixture and stirred at 80 °C for 30 minutes to achieve complete dissolution. The mixture was then allowed to cool down at room temperature and the suitable amount of zeolite was added. The resulting mixture was heated at the suitable temperature and kept under stirring. To analyze the reaction mixture composition, aliquots (~10 mg) were withdrawn at suitable times, weighed and diluted with methanol to reach a formal concentration of 5-HMF ranging from $7 \cdot 10^{-6}$ M up to $7 \cdot 10^{-5}$ M. The resulting suspension was centrifuged and the supernatant was transferred in a quartz cuvette to record its UV-vis spectrum to determine the amount of 5-HMF formed. The concentration of 5-HMF was determined by recording the absorbance at 277 nm in the basis of a calibration curve previously determined. At selected times, another aliquot of the supernatant was diluted in 10 mL of acetonitrile:water 80:20 (v:v) and injected in a HPLC chromatographic system to determine the amounts of unreacted carbohydrates. The sample for HPLC determination was analyzed using a LC-NH₂ capillary column and eluted with acetonitrile:water 80:20 (v:v) mixture at a flow 0.8 mL/min. The amounts of each carbohydrate were determined by integration of the peaks in the chromatograms at the respective retention times, on the basis of a previously determined calibration curve.

Yield in 5-HMF, carbohydrate conversion and selectivity for 5-HMF were defined as follows:

$$\text{Conversion (\%)} = \frac{\text{Initial moles of carbohydrate} - \text{residual moles of carbohydrate}}{\text{Initial moles of carbohydrate}} \cdot 100$$

$$\text{Yield in 5-HMF (\%)} = \frac{\text{Moles of 5-HMF produced}}{n \cdot \text{Initial moles of carbohydrate}} \cdot 100$$

$$\text{Selectivity for 5-HMF (\%)} = \frac{\text{Moles of 5-HMF produced}}{n \cdot \text{Moles of carbohydrate reacted}} \cdot 100$$

where n is the stoichiometric coefficient, which amounts to 1 for fructose and glucose and to 2 for sucrose.

General procedure for carbohydrate dehydration in IL mixtures under ultrasonic activation

Ultrasound promoted reactions were carried out by placing the reaction vessel under an ultrasonic probe equipped with a microtip (diameter 0.5 cm). The nominal output power was 80 W and the operating frequency 25 kHz. For a typical reaction, 100 mg of carbohydrate were placed in a vial and 2 g of IL mixture were added. The resulting mixture was stirred at 80 °C for 30 minutes to ensure complete dissolution, then the solution was allowed to cool down to room temperature and 200 mg of HY zeolite were added. Then, the reaction vessel was placed in a thermostated bath and sonication was applied for the suitable time. Monitoring and work-up of reaction were carried out as described for the silent conditions.

Determination of proton release in IL mixtures

The extent of proton exchange between HY zeolite and ionic liquid was determined by using a reported procedure.³⁶ To this aim, 1 g of ionic liquid mixture were placed in a screw-capped vial and

100 mg of zeolite were added. The suspension was stirred at the suitable temperature for 7 h. Subsequently, 5 mL of ultrapure water were added and the resulting mixture was centrifuged at 5000 rpm for 5 minutes. The supernatant was removed and its *pH* value was measured with a *pH*-meter. The amount of protons released in the IL mixture (n_H) was calculated as: $n_H = 10^{-pH} \cdot V$, where *V* is the volume in L of the solution.

Results and Discussion

Optimization of reaction conditions for the dehydration of carbohydrates

Firstly, we set out to find the best experimental conditions to carry out our reactions. To this aim, parameters such as temperature, reaction time and catalyst loading were considered. To choose the suitable temperature for the dehydration of fructose, we first carried out the reaction in the presence of HY zeolite, in [bmpip][Cl]_{0.5}[NTf₂]_{0.5} at different temperatures ranging from 60 °C to 100 °C. At temperatures lower than 60 °C, only negligible yields in 5-HMF could be observed. Results obtained are reported in Figure 1a and Table S1 in Supporting Information.

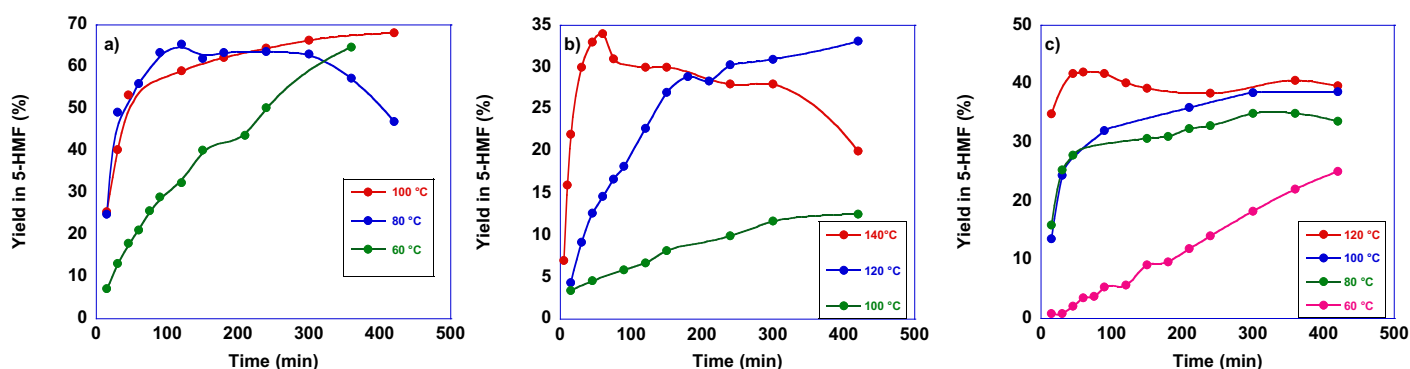


Figure 1. Yields in 5-HMF obtained in [bmpip][Cl]_{0.5}[NTf₂]_{0.5} in the presence of HY (100 mg) at different temperatures from a) fructose, b) glucose, c) sucrose. Lines are drawn purely as a visual aid. Yields are reproducible within 3%.

Looking at the plot reported in Figure 1a reveals that fructose affords good yields in 5-HMF in all cases. However, an apparent change occurs depending on the temperature. In particular, the rate of

dehydration steeply increases on raising the temperature from 60 °C to 80 °C, while a modest gain in rate occurs when the temperature is further raised to 100 °C. Furthermore, at 80 °C the highest yield of 65% is achieved after 2 h and stays constant until 5 h, after which it drops rapidly due to degradation of 5-HMF. Notably, at 100 °C we observed no obvious gain in yield and, after 4 h, the yield is practically identical to the one obtained at 80 °C. Accordingly, we chose to conduct all reaction from fructose at this latter temperature.

We carried out similar experiments using glucose and sucrose, the results of which are reported in Figures 1b-c and Tables S2-3. In particular, in the case of glucose, while at 100 °C only modest yields are observed, at 140 °C a remarkable increase in rate is accompanied by degradation of the product after only 70 minutes. On the other hand, at 120 °C we detected no obvious evidence of degradation after 7 h, obtaining a yield of 32 %. Finally, in the case of sucrose, setting the reaction temperature at 120 °C allowed us to achieve a maximum yield of 40 %, within 1 h, with limited degradation.

Subsequently, we investigated the effect of catalyst loading by performing the dehydration of carbohydrates in $[\text{bmpip}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5}$, in the presence of increasing amounts of zeolite HY.

The results obtained are shown in Figure 2 and Tables S4-6.

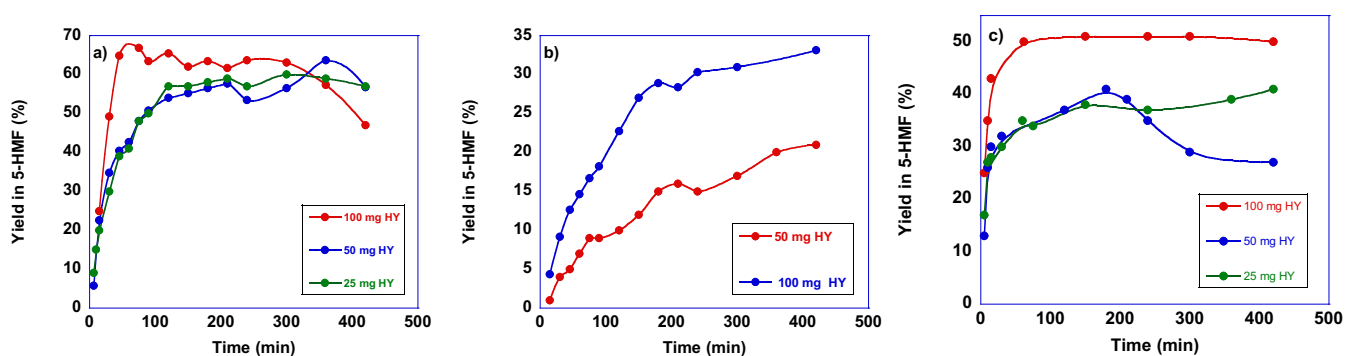


Figure 2. Yields in 5-HMF obtained in $[\text{bmpip}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5}$ in the presence of different amounts of HY from a) fructose, T= 80 °C, b) glucose, T=120 °C and sucrose, T= 120 °C. Lines are drawn purely as a visual aid. Yields are reproducible within 3%.

Plots reported in Figure 2 show that using 100 mg of zeolite consistently affords the highest dehydration rate and yields in 5-HMF. Consequently, this amount of catalyst was used for all the other reactions. Notably, in the case of sucrose, moving from 25 mg to 50 mg of zeolite lead to a modest increase in the dehydration rate with a concomitant degradation of 5-HMF. Conversely, in the presence of 100 mg of catalyst, a sizably faster dehydration occurs with no appreciable degradation of 5-HMF over 7 h. In other words, increasing the catalyst loading to 100 mg, in this case, appears to favor the dehydration step more than the degradation of 5-HMF.

Another operational parameter we considered is the counterion of the zeolites. To this aim, we carried out the reaction, under the same optimal experimental conditions, also in the presence of the NH₄Y zeolite. Yields obtained as a function of time from all substrates are reported in Figure 3, and Tables S7-9.

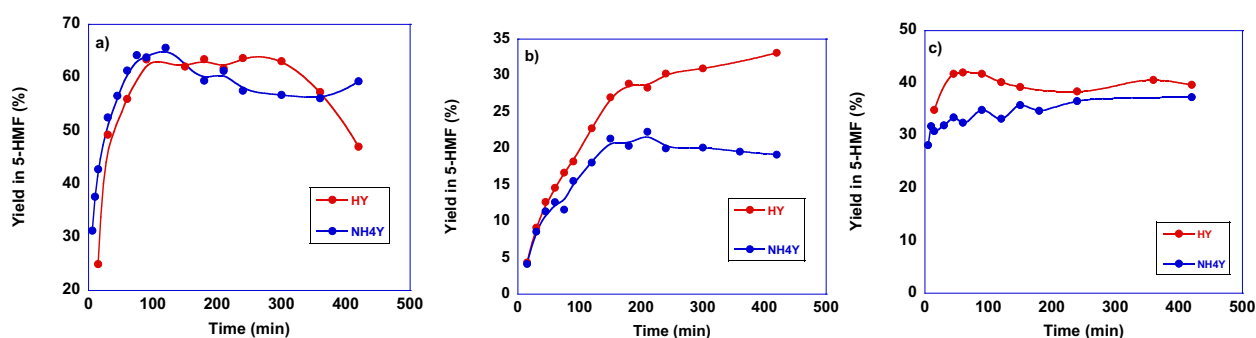


Figure 3. Yields in 5-HMF obtained in [bmpip][Cl]_{0.5}[NTf₂]_{0.5} in the presence of 100 mg of different zeolites from a) fructose, T= 80 °C, b) glucose, T=120 °C and c) sucrose, T= 120°C. Lines are drawn purely as a visual aid. Yields are reproducible within 3%.

Plots reported in Figure 3 consistently point out that HY zeolite provides better catalysis, particularly when sucrose and glucose are used as starting materials, while we found less marked differences with fructose. Since fructose is the most reactive substrate, this finding can be easily explained on the grounds of the reactivity-selectivity principle. Based on these results, we employed HY as catalyst for all the other reactions.

The last operating parameter we investigated, was the effect of adding LiCl in the reacting mixture, given the beneficial effects observed in 5-HMF production from carbohydrates upon adding alkali metal chlorides like NaCl or LiCl in conventional solvents^{37,38} as well as in the presence of ILs.³⁹ To this aim, we carried out the dehydration of fructose and glucose, under the same experimental conditions described above and in the presence of 10 mol % of LiCl with respect to the substrate. Results obtained are reported in Figure 4 and Tables S9-10.

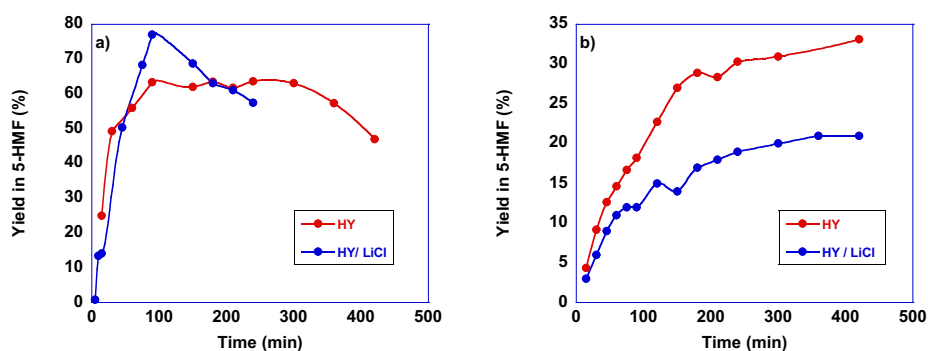


Figure 4. Yields in 5-HMF obtained in [bmpip][Cl]_{0.5}[NTf₂]_{0.5} as a function of time in the presence of HY zeolite and 10 mol % LiCl from a) fructose at 80 °C and b) glucose at 120 °C. Lines are drawn purely as a visual aid. Yields are reproducible within 3%.

Adding LiCl to the reacting mixture appears to have a slightly beneficial effect for the fructose conversion although the increase in yield detected at 80 °C (yields= 63% and 77 % in the absence and in the presence of LiCl, respectively) is counteracted by a faster degradation of the product.

Conversely, in the case of glucose, adding LiCl has a detrimental effect and the yields are almost halved. In particular, in the presence of LiCl the selectivity in 5-HMF drops from 79 % to 21 %, suggesting that adding external chloride favours the occurrence of side reactions. Based on these findings, we did not add LiCl for the rest of the study.

Effect of the IL mixture

After setting up the optimal experimental conditions for the dehydration of carbohydrates into 5-HMF, we carried out the reactions in two other IL mixtures to investigate the solvent effect. The results obtained are reported in Figure 5 and Tables S11-13. From now on, in the plots we will identify each IL mixture by its cation, for the sake of simplicity.

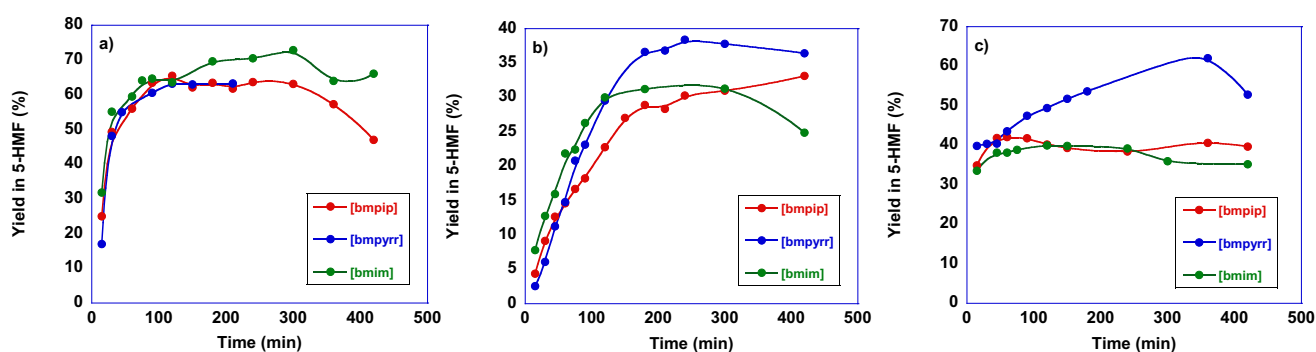


Figure 5. Yields in 5-HMF obtained in the three IL mixtures considered in the presence of HY (100 mg) from a) fructose, T= 80 °C, b) glucose, T=120 °C and c) sucrose, T= 120°C. Lines are drawn purely as a visual aid. Yields are reproducible within 3%.

A first glance at results reported in Figure 5, points out that changing the IL mixtures has a more pronounced effect on glucose and sucrose dehydration compared with that of fructose. In this latter case, the highest yield is obtained in the aromatic IL mixture [bmim][Cl]_{0.5}[NTf₂]_{0.5}, while the amounts of 5-HMF formed in the aliphatic IL mixtures [bmpip][Cl]_{0.5}[NTf₂]_{0.5} and [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5} are practically superimposable. Since fructose is the most reactive substrate, this result recalls once again the reactivity-selectivity principle. Furthermore, in the aromatic IL mixture [bmim][Cl]_{0.5}[NTf₂]_{0.5} we obtained a maximum yield of 73% after 5 h, whereas in the two other mixtures yields never exceed 65%.

A different picture arises for the dehydration of glucose (Figure 5b). In particular, the highest yield, 38 %, is observed in the IL mixture [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5} after 4 h, while in the other aliphatic IL mixture, [bmpip][Cl]_{0.5}[NTf₂]_{0.5}, the yield is slightly lower, 33 %, and requires a longer reaction time,

5 h. Using the mixture [bmim][Cl]_{0.5}[NTf₂]_{0.5} leads to the worst performance, as the yield barely exceeds 30%. Lastly, in the case of sucrose, the maximum yield obtained in the [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5}, 62%, is much higher than those detected in the two other mixtures which amount to 44% and 40% in solution of [bmpip][Cl]_{0.5}[NTf₂]_{0.5} and [bmim][Cl]_{0.5}[NTf₂]_{0.5}, respectively (Figure 5c).

To summarize, for the reaction of fructose, the highest yield in 5-HMF was obtained in the aromatic mixture [bmim][Cl]_{0.5}[NTf₂]_{0.5}, whereas for sucrose and glucose the aliphatic [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5} was the best reaction medium, although with less pronounced differences in the latter case. Comparing the selectivities for 5-HMF sheds further light on the influence of the reaction media on the dehydration of carbohydrates. In Figure 6, we report a plot of highest selectivities in 5-HMF obtained, as a function of the IL mixture used.

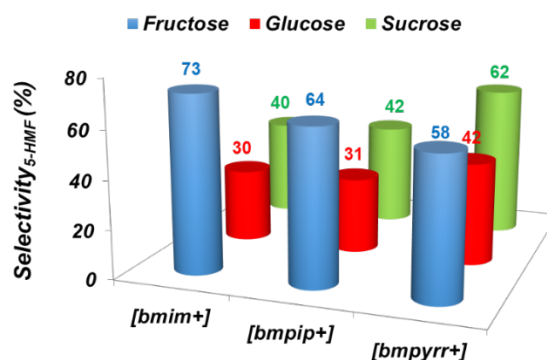


Figure 6. Plot of selectivities in 5-HMF as a function of the IL mixtures used.

Examination of Figure 6 points out that in general, within a given IL mixture, selectivity in 5-HMF is the highest for fructose and the lowest for glucose. This can be easily explained on the grounds of the higher temperature required for the more recalcitrant substrates glucose and sucrose, which can favor the occurrence of side-reactions. Moreover, selectivity follows a different trend for each substrate as a function of the IL mixture used. In particular, in the case of fructose it increases on going from going from [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5} to [bmim][Cl]_{0.5}[NTf₂]_{0.5}. In this latter mixture, the reaction is so fast that no fructose could be detected by HPLC, meaning that conversion reached 100

%. Interestingly, this trend parallels the one of the hydrogen bonding ability of the IL cations as estimated by the Kamlet-Taft parameter α which amount to 0.43, 0.50 and 0.62 for [bmpyrr][NTf₂]⁴⁰ [bmpip][NTf₂],⁴¹ and [bmim][NTf₂],⁴⁰ respectively. Since this parameter is mainly governed by the cation, we are reasonably confident that they can be suitably applied also in the equimolar mixture. Our findings suggest that hydrogen bonding by IL cations is beneficial in reducing the occurrence of side reactions. For glucose and sucrose similar results were obtained. In particular, selectivity is practically comparable in [bmim][Cl]_{0.5}[NTf₂]_{0.5} and [bmpip][Cl]_{0.5}[NTf₂]_{0.5} while is highest in [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5}. In these cases however, the mechanism is more complex and the observed trend of selectivities can result from the concomitant action of different factors.

To further explain the reaction outcomes observed as a function of the reaction media, we determined the entity of proton exchange from the zeolite into the IL mixtures. It is indeed well known that zeolites in contact with ILs can exchange protons with IL cations which can enter the inner channels of the catalyst.³⁶ This impacts on the yields and reaction rates of the conversion of carbohydrates into 5-HMF since the dehydration steps are acid-catalyzed. To this aim, we put in contact the same amount of HY zeolite used in the reactions, with the relevant amount of each IL mixture under the same reaction conditions used for each dehydration process. The amounts of protons released in solution (n_H) are reported in Table 1.

Table 1. Amounts of protons released from 100 mg of HY zeolite in contact with 1g of IL binary mixture for 7h.

IL mixture	n_H (μmol) at 80 °C	n_H (μmol) at 120 °C
[bmim][Cl] _{0.5} [NTf ₂] _{0.5}	1.7	2.8
[bmpyrr][Cl] _{0.5} [NTf ₂] _{0.5}	4.1	10.9
[bmpip][Cl] _{0.5} [NTf ₂] _{0.5}	1.3	1.3

Looking at the results reported in Table 1, reveals that the extent of proton release in the solvent medium, irrespective of the temperature, increases along the order:

$[\text{bmpip}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5} \leq [\text{bmim}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5} < [\text{bmpyrr}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5}$. At higher temperature, with the exception of $[\text{bmpip}][\text{Cl}]_{0.5}[\text{NTf}_2]_{0.5}$, we observe an enhancement in release, and differences are more pronounced. Notably, this trend holds close resemblance to the one observed for the reactivity of glucose and sucrose, as a function of the solvent. Indeed, these substrates exhibited a marked solvent effect on the rate of dehydration. On the other hand, we found no obvious correlation between reactivity and extent of proton release in the case of fructose, which in turn appeared less affected by the nature of the solvent. Furthermore, in all cases there is no clear correlation between proton release and selectivity. This is in agreement with a recent mechanistic study elucidating that the acidity of the reaction medium does not affect selectivity in 5-HMF for the homogeneous dehydration of fructose.⁹

To better assess the performance of our system, it is useful to compare our results with those described for the same process in other works reported in the literature. Since a complete review of the existing literature is not appropriate and falls outside the scope of the work, we chose recent or significant representative reports featuring zeolites as heterogeneous catalysts. These are reported in Table 2.

Table 2. Comparison of 5-HMF yield with other zeolite employing systems reported in literature.

Entry	Substrate	Catalyst	T (°C)	Reaction time (h)	Yield in 5 HMF (%)
1	Fructose ^a	HY zeolite	80	5	73
2	Fructose ⁴²	MWW zeolite	120	3	68
3	Fructose ⁴³	H-USY zeolite	120	5	65
4	Fructose ⁴⁴	L zeolite	120	0.5	99
5	Fructose ⁴⁵	Metal - SAPO	170	2.5	65
6	Fructose ⁴⁶	β -zeolite	150	1	80
7	Fructose ⁴⁷	H-mordenite	165	5	53
8	Fructose ⁴⁸	β -HBL zeolite mixture	180	0.5	82
9	Glucose ^a	HY zeolite	120	4	38
10	Glucose ⁴⁹	IL encapsulated zeolite	170	3	38
11	Glucose ³⁸	H-ZSM zeolite	195	0.5	42
12	Glucose ⁴⁸	β (OL)-Cal500 zeolite mixture	180	3	66
13	Glucose ⁵⁰	Fe- β zeolite	120	1.5	61
14	Glucose ³⁵	H β -zeolite	150	0.83	50
15	Glucose ⁵¹	Modified mordenite	100	6	64
16	Glucose ⁵²	Dealuminated β -zeolite	180	3	43
17	Glucose ⁵³	H-ZSM-5 zeolite	110	8	45
19	Sucrose ^a	HY zeolite	120	3	62
20	Sucrose ³⁵	H β -zeolite	150	0.8	68
21	Sucrose ⁵⁴	Amberlite IR 120	100	15	50

[a] This work.

Examining the results reported in Table 2, shows that for the dehydration of fructose, the performance of our system is superior to that of other ones employing modified zeolites^{42,43} (entries 1,2,3), natural zeolites⁴⁷ (entries 1 and 7) or metal containing silicoaluminophosphates (entries 1 and 5).⁴⁵ Notably, we attained this performance using a much lower reaction temperature. Furthermore, compared with systems employing β -zeolite⁴⁶ or β -zeolite mixture⁴⁸ (entries 1,6 and 8) we attained a slightly lower yield although, once again at a considerably lower temperature. Only comparing our results with the system using L-zeolite, at a much higher temperature, (entries 1 and 4), we observe less convenient yields and reaction times.⁴⁴

Moving to the dehydration of glucose, the highest yield in 5-HMF obtained by us is comparable with those obtained employing an IL-encapsulated zeolite at higher temperature,⁴⁹ (entries 9 and 10), and only slightly lower compared with other systems employing modified zeolites^{38,52,53} (entries 9,11,16 and 17). However, our system does not outperform for glucose other systems reported in the literature using modified zeolites^{48,50,51} (entries 9,12,13, 14 and 15).

Finally, in the case of sucrose our highest yield is sizably superior to that obtained using the acidic ion exchange resin Amberlite IR 120⁵⁴ (entries 19 and 21), and only slightly lower than that obtained by employing H β -zeolite,³⁵ (entries 19 and 20), in which cases a much higher temperature was used.

Dehydration of carbohydrates under US activation

All US-promoted reactions were carried out using a sonication probe. We employed the same substrate/catalyst ratio chosen for the reactions carried out under silent conditions. Comparing the outcomes observed in the two cases sheds light on whether US irradiation can be beneficial for the HY zeolite promoted dehydration of carbohydrates into 5-HMF in IL mixtures.

Firstly, we carried out preliminary tests to find the best operating conditions for all the substrates. In the case of glucose we did not observe any evidence of 5-HMF formation even upon raising the

temperature to 80 °C. Differently, when sucrose was the substrate, only modest yields were obtained (< 15%) even applying sonication at 80 °C.

We observed much better results with fructose by carrying out the reactions at 40 °C. Yields obtained in the solution of each IL binary mixture are reported in Figure 7 and Table S14.

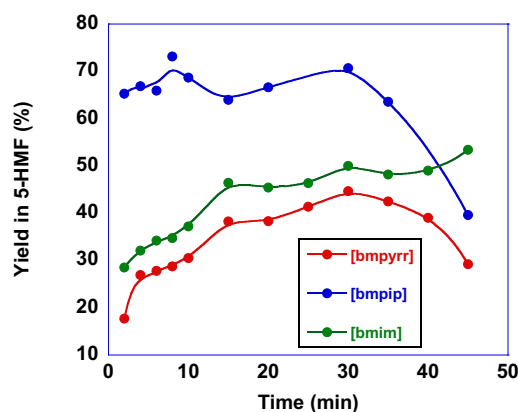


Figure 7. Plot of yields in 5-HMF from fructose obtained under US activation, at 40 °C in the presence of HY zeolite (100 mg) as a function of time. Lines are drawn purely as a visual aid.

Looking at results reported in Figure 7, reveals that in all cases a time span as short as 45 minutes is sufficient to obtain the highest yields in 5-HMF, thus achieving a drastic reduction in time compared with what happens under silent conditions where at least 100 minutes are required. Notably, in the IL mixture [bmpip][Cl]_{0.5}[NTf₂]_{0.5}, the reaction proceeds much faster and the yield exceeds 60 % after only 2 minutes. Furthermore the highest value, 71 % is detected after 30 minutes, after which it rapidly declines due to degradation of 5-HMF. The reaction proceeds so rapidly that even after 2 minutes no appreciable amount of residual fructose could be detected by HPLC. Moreover, the highest yield is comparable with the maximum value observed under silent condition, in the best performing mixture, [bmim][Cl]_{0.5}[NTf₂]_{0.5} (71 % and 73 % under sonochemical and silent conditions, respectively) requiring a much shorter time (30 minutes and 5 h) and at a much lower temperature (40° C compared with 80 °C under silent conditions). This favorable effect of ultrasonic activation is less pronounced

for the two other mixtures, in which cases the maximum yields obtained amount to 53 % after 45 minutes in [bmim][Cl]_{0.5}[NTf₂]_{0.5} and 45% after 30 minutes in [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5}.

In both cases selectivity in 5-HMF was 50% and conversion reached 80%. Overall, yields were slightly lower than those obtained under silent conditions in the same mixtures, although the rate of the process is still significantly increased, considering the shorter times and much lower temperature. To the best of our knowledge, this is the first work describing the obtainment of 5-HMF from fructose by probe sonication. Indeed, the only published report on the application of probe sonication on carbohydrate dehydration employs glucose and cellulose as substrates.⁵⁵

To further quantify the advantage of using ultrasonic activation for the dehydration of fructose from the standpoint of sustainable chemistry, we estimated the energy consumption per mass of material processed in the best performing systems, namely [bmpip][Cl]_{0.5}[NTf₂]_{0.5} at 40 °C for sonochemical activation and [bmim][Cl]_{0.5}[NTf₂]_{0.5} for silent conditions. Full details of the calculation procedure are reported in Supplementary Material. The results obtained shows that performing the reaction under sonochemical activation enables a 99% reduction in energy consumption.

Conclusions

We investigated the dehydration of fructose, glucose and sucrose into 5-HMF catalyzed by HY zeolite in the IL mixtures [bmim][Cl]_{0.5}[NTf₂]_{0.5}, [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5}, and [bmpip][Cl]_{0.5}[NTf₂]_{0.5}.

Our study shows that these reacting systems are suitable for this transformation, providing good to very good yields in 5-HMF, particularly in the cases of fructose and sucrose, with yields of 73 % and 62 % achieved in 5 h and 3 h, in the mixtures [bmim][Cl]_{0.5}[NTf₂]_{0.5} and [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5}, respectively. Notably, these values are comparable or superior to most of the zeolite employing systems reported in the literature for this reaction and were achieved using relatively low temperatures.

From the standpoint of sustainability, it is also worth noting that our system employs a natural zeolite, avoiding the use of metal ions. Furthermore, our investigation pointed out that the most pronounced

solvent effects on the reaction occurs for the less reactive substrates, glucose and sucrose, recalling the reactivity-selectivity principle. Changing the IL mixtures also affects the amount of protons exchanged by the zeolite, and hence the acidity of the medium.

Notably, in the cases of glucose and sucrose the best yields were observed using the mixture of aliphatic ILs [bmpyrr][Cl]_{0.5}[NTf₂]_{0.5} which is considerably less toxic than the aromatic one [bmim][Cl]_{0.5}[NTf₂]_{0.5}. This enhances the sustainability of the process, opening the door to safer conversion of biomass. Finally, we carried out the dehydration of fructose also by probe sonication, obtaining a yield of 71 %, which is comparable to that observed under silent conditions, but with a 10-fold reduction in reaction time (30 min compared with 5 h) and at a much lower temperature, 40 °C, as opposed to 80 °C under silent conditions. Overall, this entails a net reduction in energy consumption per mass of materials processed of 99 %.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge. Tables of conversions, yields and selectivities in 5-HMF for the studied reactions. Calculation details of net energy consumption.

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Declaration of interest

The authors declare no competing financial interest

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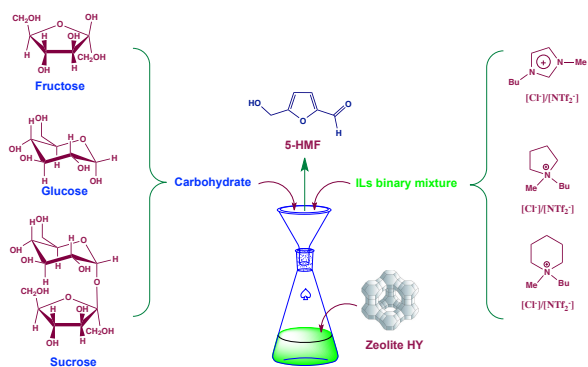
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TOC



Synopsis

Natural zeolite HY and low toxicity ionic liquids afford mild, fast and efficient conversion of carbohydrates into 5-HMF also under sonication.