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Efficient microwave-assisted production of furfural from C$_5$ sugars in aqueous media catalysed by Brönsted acidic ionic liquids†

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Small amounts of SO$_3$H-functionalised room temperature synthesized ionic liquids efficiently dehydrate aqueous xylose to furfural under microwave heating at mild reaction conditions. The RT-ionic liquid catalysts were also found to be effective catalysts for the two step one-pot simultaneous hydrolysis and dehydration of a lignocellulosic waste biorefinery-derived syrup enriched in C$_5$ sugar oligomers.

A search for renewable sources of fuels and chemicals has been driven by global issues including the diminishing oil reserves and global warming as well as parallel demands on more efficient and sustainable processes. Biomass is increasingly being recognised as the most promising renewable source of organic carbon available today[1] and, consequently, it is the perfect equivalent of petroleum in the production of fuels and carbon-based materials.[2] An effective approach to process complex biomass resources into chemicals and fuels involves their initial conversion into simple building blocks or platform molecules, which can subsequently be easily converted into valuable products.[3] Furfural (furan-2-carbaldehyde) can be considered as a key biomass derivative that is currently obtained *via* acid-catalysed dehydration of xylose (a C$_5$ carbohydrate) which, as the main constituent of hemicellulose, can be found in significant quantities in lignocellulosic feedstocks such as corncobs, bagasse, wood chips and switchgrass. Furfural has attracted a great deal of attention in recent years due to its great platform potential for the simultaneous production of fuels including methyl-tetrahydrofuran (MTHF, a gasoline additive) and liquid alkanes[4,5] (for diesel and jet fuel applications) as well as important chemicals such as furfuryl alcohol or tetrahydrofuran (THF).[6]

Most of the annual production of furfural is currently manufactured by means of an old technology developed almost a century back.[7] This industrial process utilises corrosive, highly-toxic and difficult to recycle concentrated sulphuric acid as catalyst and requires large amounts of steam and long reaction times. Additionally, the harsh acidic conditions employed lead to extensive side reactions (*e.g.* the formation of humins), and typical furfural yields obtained by this technology are rarely above 50%. Furfural production consequently requires novel, more efficient and environmentally friendly processes to be developed. Intensive research endeavours have pursued the replacement of deleterious mineral acids with easily recyclable solid acids[8–10] as well as the utilisation of organic solvents to continuously extract furfural from the aqueous phase once produced (thus avoiding losses by overreaction).[11]

Recently, room temperature ionic liquids (RT-ILs, *e.g.* salts that are liquids below 100 °C) have proved to hold great potential for biomass conversion and pretreatment processes.[12,13] Their unique properties, including negligible vapour pressures, high thermal stabilities and most importantly their ability to interact and disrupt the recalcitrant lignocellulose structure, render ILs a very attractive medium to perform reactions involving solid biomass. Solid di/polysaccharides and simple hexoses including fructose and glucose have been dehydrated to hydroxymethyl-furfural (HMF) under IL environments.[14–17] Generally, ILs are employed as solvents in these processes combined with an external acid catalyst. This final mixture provides a unique reaction medium that facilitates biomass depolymerisation and enhances yields of dehydration products by stabilisation of the reactive intermediates and/or active catalytic species.[12] However, the elevated cost of ILs has to date discouraged their use as solvents, especially if large scale applications are envisaged.

An attractive approach that is currently being explored involves the use of functionalised acidic ILs as catalysts in various chemistries, which can in principle circumvent most economic and potential toxicity issues related to their use as solvents.[18,19] Most reports in this sense have nevertheless been limited to date to the processing of simple C$_5$ and C$_6$ sugars into HMF[20] or other chemistries including the production of biodiesel.[21] Among the functionalised ILs, those containing sulfonic acid (SO$_3$H–) groups have shown great potential as catalytic systems to perform acid-mediated transformations.

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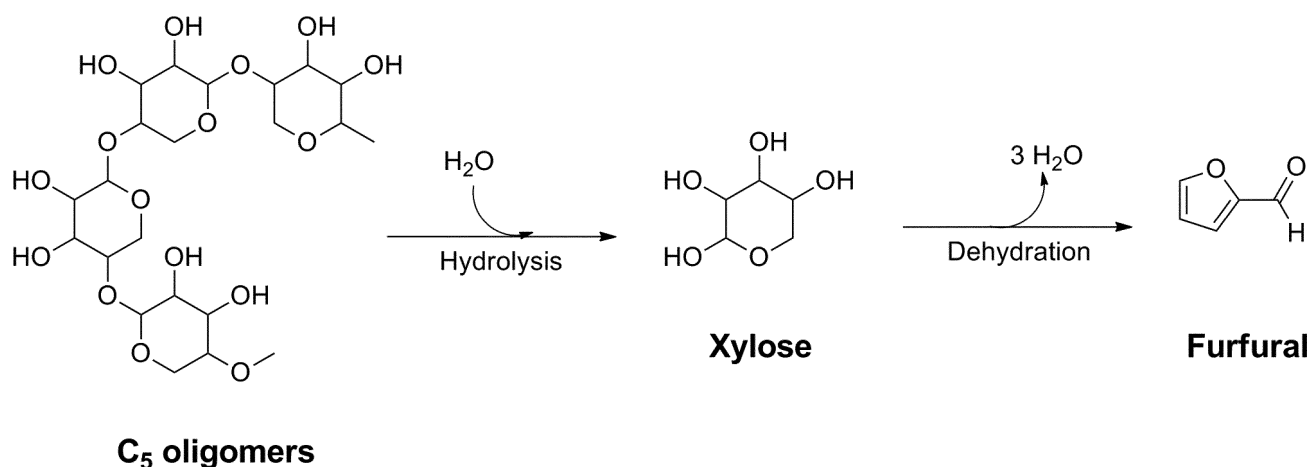
C₅ oligomers

Scheme 1 Reaction scheme for the conversion of C₅ oligomers into furfural.

In particular, sulfonic acid-functionalised ILs have been successfully utilised for oligomerisation of olefins[22] and for the synthesis of α-aminophosphonates.[23] Regarding biomass conversion reactions, these ILs have been found to be useful for cellulose dissolution[24] and for the conversion of biomass disaccharides into ethyl levulinate.[25]

In the present work, we report the utilisation of designed simple acid-functionalised ILs synthesised at room temperature in the catalytic dehydration of xylose to furfural. Interestingly, small amounts of Brönsted acidic RT-ILs were also found to effectively achieve moderate furfural production from a lignocellulosic waste-derived biorefinery syrup via two step one-pot depolymerisation of C₅ oligomers (by hydrolysis) followed by subsequent dehydration of sugars (Scheme 1).

Experimental

Preparation of ionic liquids

Methanesulfonic acid, 1,4-butanesultone, tetrafluoroboric acid (48 wt% in water), pyridine, triethylamine and D_2O were purchased from Sigma-Aldrich and used as received without any further purification. ^1H and $^{13}C\{^1H\}$ NMR were carried out on a Bruker 400 MHz spectrometer using D_2O as deuterated solvent and TMS as an internal standard. NMR data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentuplet, m = multiplet and n.r. = not resolved. Chemical shifts (δ) and coupling constant (J) values are given in ppm and Hertz (Hz) respectively. ^1H NMR spectra in D_2O of the four RT prepared ILs under study are shown in Fig. S1 (ESI†). In order to check the hydrothermal stability of the four ILs under study, the samples were dissolved in water (0.1 g of IL in 1 g of water) and then heated at 180 °C for 1 h under reflux. Subsequently, water was removed by distillation and the remaining ILs were dissolved in D_2O and ^1H NMR spectra obtained (Fig. S2, ESI†).

ILs were synthesised as follows:

1-(4-Sulfonylbutyl)pyridinium methanesulfonate: a mixture of 1-(4-sulfonylbutyl)pyridinium (0.077 mol) and methanesulfonic acid (0.077 mol) was stirred at room temperature overnight, resulting in the formation of 1-(4-sulfonylbutyl)pyridinium methanesulfonate as a slightly yellow sticky oil that was

dried under vacuum at 50 °C overnight. Yield 97.6%. ^1H NMR (D_2O, 400 MHz) δ ppm 1.62 (p, ^3J (HH) = 8 Hz, 2H, $-CH_2-CH_2-N^+$), 2.00 (p, ^3J (HH) = 8 Hz, 2H, $-CH_2-CH_2-SO_3H$), 2.61 (s, 3H, CH_3-SO_3H), 2.79 (t, ^3J (HH) = 8 Hz, 2H, $-CH_2-SO_3H$), 4.49 (t, ^3J (HH) = 8 Hz, 2H, $-CH_2-N^+$), 7.90 (t, ^3J (HH) = 8 Hz, 2H, $meta-H$ Py^+), 8.38 (t, ^3J (HH) = 8 Hz, 1H, $para-H$ Py^+), 8.69 (t, ^3J (HH) = 8 Hz, 2H, $ortho-H$ Py^+).
$^{13}C\{^1H\}$ NMR (D_2O, 100 MHz): δ (ppm) 20.79 ($-CH_2-CH_2-SO_3H$), 29.22 ($-CH_2-CH_2-N^+$), 38.39 ($CH_3-SO_3^-$), 49.88 ($-CH_2-SO_3H$), 61.08 ($-CH_2-CH_2-N^+$), 128.22 ($\beta-C$ Py^+), 144.13 ($\gamma-C$ Py^+), 145.61 ($\alpha-C$ Py^+).

1-(4-Sulfonylbutyl)triethylammonium methanesulfonate: a mixture of 1-(4-sulfonylbutyl)triethylammonium (0.077 mol) and methanesulfonic acid (0.077 mol) was stirred at room temperature overnight, resulting in the formation of 1-(4-sulfonylbutyl)-triethylammonium methanesulfonate as a slightly yellow sticky oil that was dried under vacuum at 50 °C overnight. Yield 92.7%. ^1H NMR (D_2O, 400 MHz): δ (ppm) 1.16 (t, ^3J (HH) = 8 Hz, 9H, CH_3), 1.72 (m, 4H, $CH_2-CH_2-CH_2-SO_3H$), 2.69 (s, 3H, $CH_3SO_3^-$), 2.86 (t, ^3J (HH) = 8 Hz, 2H, CH_2-SO_3H), 3.14 (n.r., 8H, $CH_3-CH_2- + -CH_2-CH_2-N^+$).
$^{13}C\{^1H\}$ NMR (D_2O, 100 MHz): δ (ppm) 6.57 (CH_3), 19.86 ($-CH_2-CH_2-N^+$), 21.15 ($-CH_2-CH_2-SO_3H$), 38.39 ($CH_3-SO_3^-$), 49.96 (CH_2-CH_3), 52.55 ($-CH_2-CH_2-N^+$), 55.90 (CH_2-SO_3H).

1-(4-Sulfonylbutyl)pyridinium tetrafluoroborate: a mixture of 1-(4-sulfonylbutyl)pyridinium (0.077 mol) and tetrafluoroboric acid (0.077 mol) was stirred at room temperature overnight, resulting in the formation of 1-(4-sulfonylbutyl)pyridinium tetrafluoroborate as a colourless sticky oil that was dried under vacuum at 50 °C overnight. Yield 91.3%. ^1H NMR (D_2O, 400 MHz) δ (ppm 1.72 (p, ^3J (HH) = 8 Hz, 2H, $-CH_2-CH_2-N^+$), 2.07 (p, ^3J (HH) = 8 Hz, 2H, $-CH_2-CH_2-SO_3H$), 2.86 (t, ^3J (HH) = 8 Hz, 2H, $-CH_2-SO_3H$), 4.56 (t, ^3J (HH) = 8 Hz, 2H, $-CH_2-N^+$), 7.98 (t, ^3J (HH) = 8 Hz, 2H, $meta-H$ Py^+), 8.45 (t, ^3J (HH) = 8 Hz, 1H, $para-H$ Py^+), 8.76 (t, ^3J (HH) = 8 Hz, 2H, $ortho-H$ Py^+).
$^{13}C\{^1H\}$ NMR (D_2O, 100 MHz): δ (ppm) 20.81 ($-CH_2-CH_2-SO_3H$), 29.25 ($-CH_2-CH_2-N^+$), 49.90 ($-CH_2-SO_3H$), 61.12 ($-CH_2-CH_2-N^+$), 128.24 ($\beta-C$ Py^+), 144.15 ($\gamma-C$ Py^+), 145.62 ($\alpha-C$ Py^+).

1-(4-Sulfonylbutyl)triethylammonium tetrafluoroborate: a mixture of 1-(4-sulfonylbutyl)triethylammonium (0.077 mol) and tetrafluroborate (0.077 mol) was stirred at room temperature overnight, resulting in the formation of 1-(4-sulfonylbutyl)triethyl-ammonium tetrafluoroborate as a colourless sticky oil that was dried under vacuum at 50 °C overnight. Yield 89.2%. ^{1}H NMR (D$_2$O, 400 MHz): δ ppm 1.13 (t, ^3J (HH) = 8 Hz, 9H, CH_3), 1.69 (m, 4H, CH_2–CH_2–CH_2–SO$_3$H), 2.83 (t, ^3J (HH) = 8 Hz, 2H, CH_2–SO$_3$H), 3.09 (n.r., 8H, CH$_3$–CH_2 + –CH_2–CH$_2$–N$^+$).

^{13}C{^{1}H} NMR (D$_2$O, 100 MHz): δ (ppm) 6.52 (CH_3), 19.85 (–CH_2–CH$_2$–N$^+$), 21.15 (–CH_2–CH$_2$–SO$_3$H), 49.97 (CH_2–CH$_3$), 52.52 (–CH$_2$–CH_2–N$^+$), 55.89 (CH_2–SO$_3$H).

Thermogravimetric (TG) and IR analysis of the ILs

TG analysis of the ILs was carried out using a Setaram thermobalance Setsys 12 under flowing Argon (50 mL min^{-1}) at a heating rate of 20 °C min^{-1} from RT to 1000 °C.

IR experiments with IL-1 were carried out using an ABB IR-ATR instrument equipped with an environmental chamber. Before performing the measurements IL-1 was subjected to a thermal treatment at two different temperatures (120 °C and 180 °C) for 1 h.

C$_5$ dehydration experiments

Dehydration experiments were carried out under microwave irradiation using a CEM-DISCOVER microwave reactor model with PC control. In a typical reaction, 0.1 g xylose (or syrup) and 0.1 g RT-IL were dissolved in 1 g of water. Several organic liquids (2 g) including THF (Panreac, 99.5%), toluene (Sigma-Aldrich, 99%), methyl isobutyl ketone (MIBK, Sigma-Aldrich, 99.5%), and ethyl acetate (Panreac, 99%) were used as extracting solvents. The final mixture was then microwaved at varying power and temperatures. Experiments were conducted in a closed vessel (pressure controlled) under continuous stirring, and the temperature of the reactions was measured using an IR probe. The temperature was carefully monitored during MW experiments and variations not larger than ±5 °C were observed for all the tests detailed in the present study.

Aqueous and organic fractions were collected and analysed by using a HPLC Model Series 200 (Perkin Elmer) provided with a UV-Vis detector (SPD-20AV) and an Ascentis Express C$_{18}$ column (10 cm × 4.6 mm, 2.7 μm), operating with a mobile phase of 5% acetonitrile/95% water at a flow of 1.2 mL min^{-1}.

A lignocellulosic waste-derived C$_5$ syrup was also utilised as starting material to produce furfural. This syrup, kindly provided by CIMV (Toulouse, France, http://www.cimv.fr/), was produced from cereal straws (*e.g.* wheat or barley straw) through organic refining *via* treatment with acetic and formic acids. It is composed of 60% dry matter, 25% water and 5% formic acid in which the dry matter fraction contains C$_5$ sugar monomers (12%, mainly xylose and arabinose), oligomers (30–35%), minerals (18–20%) and other compounds including tannins, proteins, waxes, *etc.* The viscosity of the syrup is 1.25 Pa s, with a density of 1.35 g mL^{-1} at 20 °C.

Results and discussion

The combination of microwave irradiation and ILs has been demonstrated to greatly enhance reaction rates and selectivity of desired products in a variety of processes.[12] In our experiments, we employed an extracting organic solvent to increase furfural yields and to avoid overreaction of furfural in the aqueous phase. Several solvents were screened including THF, toluene, MIBK, ethyl acetate and others. Ethyl acetate showed poor stability under the investigated reaction conditions (it was hydrolysed to water soluble ethanol and acetic acid under the acidic conditions originated by the IL). Reactions performed with less polar solvents including toluene or MIBK produced large amounts of black deposits (most probably humins) under identical conditions of power and temperature to those employed with the other solvents. THF was comparatively proved to be the optimum solvent under the investigated conditions. Its selection as extracting solvent was further motivated by its good affinity for furfural, low boiling-point and low vaporization heat,[4] which are advantageous properties for subsequent furfural separation from the organic solvent. We note that monophasic experiments carried out in the absence of organic solvent led to considerably lower furfural yields (∼20% for IL-1) and resulted in massive formation of black deposits (*e.g.* humins) as a consequence of overreaction of furfural in the aqueous phase. The presence of an extractive organic solvent seems thus to be crucial to increase furfural yields, in good agreement with previous works dealing with HMF production.[11,20]

Results of the dehydration of xylose to furfural have been summarised in Table 1. Four different Brönsted acidic RT-ILs (Fig. 1) have been tested in the present study. The ionic liquids were composed of pyridinium/tetraethylamonium cations functionalised with butyl sulfonic acid groups which provide Brönsted acidity to the ILs. Two different anions, tetrafluoro-borate (BF$_4$$^-$) and methylsulfonate (MeSO$_3$$^-$), were also investigated as counterions. BF$_4$$^-$ is a low coordinating ion

Table 1 Results obtained in the dehydration of xylose to furfural utilising acid-functionalised RT ionic liquids under microwave heating[a]

Entry	Ionic liquid	Power (W)	Temperature (°C)	Reaction time (h)	Xylose conversion (%)	Furfural yield[b] (%)
1	IL-1	100	150	1	90	75
2	IL-2	100	150	1	50	40
3	IL-3	100	150	1	45	36
4	IL-4	100	150	1	32	28
5	IL-1	300	150	0.5	75	62
6	IL-1	100	150	0.5	65	55
7	IL-1	100	120	1	<5	<5
8	IL-1	100	180	1	>95	85

[a] Reaction conditions: 0.1 g xylose, 0.1 g IL, 1 g H$_2$O, 2 g THF. [b] Other products found include humins and related compounds that were not quantified in the analysis.
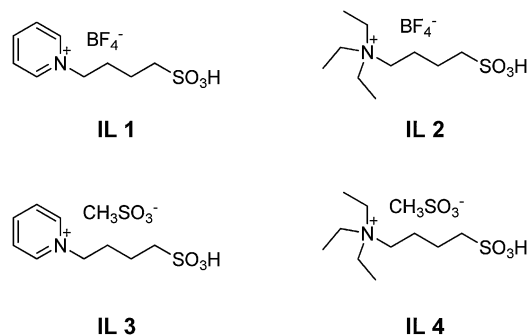
IL 1

IL 2

IL 3

IL 4

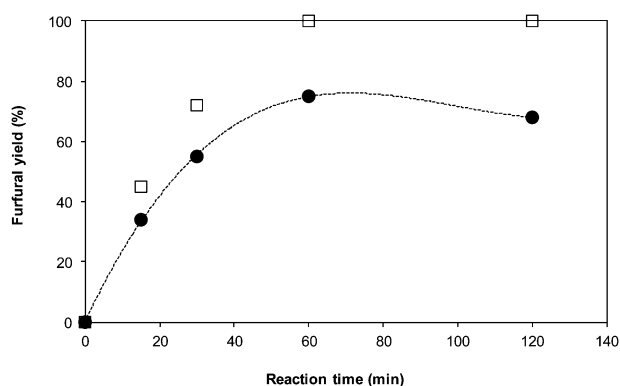**Fig. 1** Brönsted acidic RT-ILs investigated in C_5 dehydration to furfural.

Fig. 2 Furfural yield (black dots) and xylose conversion (white blocks) as a function of reaction time for xylose dehydration under microwave heating (100 W, 150 °C) using acid-functionalised IL-1 as catalyst.

with reported base properties, similar to $MeSO_3^-$. All investigated RT-ILs exhibited a significant xylose dehydration activity at 150 °C and 100 W. As shown in Fig. 2, IL-1 showed a rapid increase in furfural yield with reaction time reaching a maximum value of 75% at 1 hour under microwave heating and 150 °C. This value could be increased to a maximum of 85% by operating at 180 °C (Table 1, entry 8), while a minimum at 150 °C seems to be necessary to achieve significant dehydration activities (see Table 1, entry 7). The obtained values are in the range of the maximum 82–90% furfural yields reported for xylose dehydration using ionic liquids, typically after several hours of reaction (4–10 h) under conventional heating.[13,20]

Longer reaction times generally decreased furfural yields probably due to overreaction and the formation of undesired solid products (Fig. 2). In contrast to the effect of temperature, the microwave power did not show a significant effect on xylose dehydration activity (Table 1, entries 5 and 6). Consequently, 100 W was selected as optimum power for all subsequent experiments.

As shown in Table 1, IL-1, combining the pyridinium-stabilised sulfonic acid group as a cation and BF_4^- as an anion, exhibited the highest activity among the tested ILs. This may be correlated with two main effects of the ILs in the selected reaction: the cationic structure and its stabilisation effect on the SO_3H group as well as the anionic structure. It is clearly obvious that the effect of the anion is critical in the activity of the systems, with BF_4^- providing improved yields of furfural compared to $MeSO_3^-$. ILs with BF_4^- and PF_6^- have been reported as less important in carbohydrate

(*e.g.* cellulose) interaction phenomena due to their poor solubilising effects on polysaccharides.[13,20,26] However, BF_4^- can undergo hydrolysis in aqueous solutions to give HF.[27] The presence of a strong acid such as HF in solution (even at trace quantities) can significantly improve dehydration yields but such plausible hydrolysis will partially decompose the RT-ILs. While this decomposition has not been observed, at least to a certain extent, a minimum BF_4^- hydrolysis cannot be completely ruled out taking into account the highly acidic pH of the final solution. Comparatively, the anion $MeSO_3^-$ has been proved to be more stable, with a negligible aqueous hydrolysis to H_2SO_4, which correlates well with the reduced yields of furfural obtained with $MeSO_3^-$ as compared to BF_4^--RT-ILs.

Apart from the counteranion effect, the structure of the cation has also a significant influence on furfural production. Thus, the pyridinium-derived cation is likely to enhance the acidity of the SO_3H group *via* stabilisation of the deprotonated sulfonic group. As a result, the ILs containing a pyridinium cation in their structure (IL-1 and IL-3) showed improved dehydration yields as compared to their counterparts containing more basic and less stabilising triethylammonium cations (IL-2 and IL-4).[13,20]

Thermal and hydrothermal stabilities of the ILs under the reaction conditions of the present study were checked by performing additional ^{1}H-NMR (Fig. S2, ESI†) as well as TG (Fig. S3, ESI†) and IR (Fig. S4, ESI†) experiments. As indicated in TG profiles, ILs were thermally stable up to a temperature of *ca.* 300 °C which is well above the maximum reaction temperature employed herein (180 °C). We note that the slight weight loss observed at *ca.* 150 °C is produced by the release of absorbed ambient water, as corroborated by online MS measurements. Thermal stability was further studied for IL-1 by means of IR analysis after a thermal treatment in air at 120 and 280 °C for 1 h (Fig. S4, ESI†). IR profiles of both samples indicated that the structure of IL-1 was preserved after a thermal treatment at 280 °C which is in good agreement with previous TG results. We note that a hydrothermal treatment at 180 °C did not significantly affect the structure of the ILs as corroborated by ^{1}H-NMR measurements (see Fig. S1 and S2, ESI†).

Upon successful demonstration of the proof of concept of RT-ILs as catalysts in xylose dehydration, a complex biorefinery-derived mixture was selected as a feedstock for the process using the optimum catalyst IL-1. The chosen starting material was an agricultural lignocellulosic waste-derived syrup containing a mixture of sugar monomers (12%, mainly xylose and arabinose) and oligomers (30–35%, with a number of monomers ranging from 2 to 7) as well as other impurities (*e.g.* up to 20 wt% minerals and traces of tannins, proteins, waxes, *etc.*). Small amounts of the Brönsted acid IL showed an interesting activity for the processing of such a syrup (Table 2).

A 30% furfural yield was obtained at 150 °C and 2 hour reaction under microwave irradiation (Table 2, entry 2). A longer reaction time (4 h) keeping the temperature constant at 150 °C produced an increase in the furfural yield to 45% (Table 2, entry 3). An increase in temperature (180 °C) maintaining irradiation time constant (2 h) only caused a modest increase in furfural yield (35%, Table 2, entry 4). The high degree of oligomerisation of the sugars composing the syrup could explain the moderate yields

Table 2 Results obtained in the dehydration of a biorefinery-derived syrup to furfural using IL-1 under microwave heating[a]

Entry	Temperature (°C)	Reaction time (h)	Furfural yield[b] (%)
1[c]	150	2	2
2	150	2	29
3	150	4	45
4	180	2	35
5[d]	150	2	14
6[e]	150	2	16

[a] Reaction conditions: 0.1 g of syrup, 0.1 g IL-1, 1 g H_2O, 2 g THF, 100 W. [b] Considering a 45 wt% sugar content in syrup. [c] Blank experiment. [d] 0.05 g IL-1. [e] 0.2 g IL-1.

obtained as well as the presence of some of the minerals in solution which may interact and/or partially degrade the IL-1. We note that an increase in the amount of ILs used did not improve the results (Table 2, entry 6).

A recycling experiment was also performed with the optimum IL-1 in the particular case of the C_5 sugar syrup. The organic layer was removed and the reactor was fed with a new dose of syrup. The first use gave a 31% yield of furfural (total sugar content of syrup around 45 wt%). Unfortunately, the second reaction with the same IL showed a noticeable decrease in the furfural yield (14%), and the third use showed a further decrease to 8%. This could be due to partial removal of the IL to the organic layer as a consequence of the high salt content of the syrup. This generates a salting out effect which in turn drives the transfer of the IL to the organic phase[11] and/or the aforementioned partial decomposition of the IL (e.g. via hydrolysis of BF_4^-, exchange with anions in solution, interaction with the mineral of the syrup under microwave irradiation, etc.).

Since this is a crucial point, further experiments are currently ongoing in our group to improve the reusability of ILs in the conversion of a bio-derived syrup to furfural. Several strategies involving different extracting solvents (with different polarities to avoid extraction of ILs during the process) and the possibility to utilise easily-separable ionic liquids supported on porous materials (e.g. carbons, mesoporous silicas, etc.) are currently being explored. Results in this regard will be reported in due course.

Acknowledgements

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