Electronic Supplementary Information

Effects of cations, anions and H⁺ concentration of acidic ionic liquids in the valorization of polysaccharides into furfural

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1. Materials, calculations and synthesis of ionic liquids (ILs)

1.1. Materials.

Hemicellulose substrates used in this study has following details: softwood derived hemicellulose [xylan from oat-spelt (Aldrich Chemicals, USA; \geq 70% xylose, 10% arabinose and 15% glucose], beechwood hemicellulose [TCI Chemicals, India; 90% C5 sugars], hardwood hemicellulose [xylan from birchwood (Sigma Chemicals, USA) \geq 90% xylose], and arabinogalactan from larch wood [TCI Chemicals, India. Xylooligosaccharide was purchased from Cascade Analytical Reagents and Biochemicals, USA.

1-methylimidazole (Sigma-Aldrich Chemicals, USA, 99%), 1-methylbenzimidazole (Alfa Aesar, India), pyridine (s. d. Fine-Chem Limited, India), 1,3-propanesultone (Alfa Aesar, India, 99%), p-toluenesulfonic acid monohydrate (Sigma-Aldrich Chemicals, USA, 98.5%), triethylamine (Alfa Aesar, India), and triphenylphosphine (Loba Chemie, India) were purchased for preparing ILs. The heterogeneous acid catalysts [HUSY (Si/Al=15) and HMOR (Si/Al=10)] were obtained from Zeolyst International, USA. Before use, solid acid catalysts were dried under vacuum (-760 Torr) at 150 °C for 2 h.

1.2. Calculation

For calculating the yields of C5 sugars (X+A) the molecular weight of hemicellulose was considered as 132. This is because hemicelluloses are made up of C5 sugar (xylose+arabinose) which has molecular weight 150. While forming hemicellulose loss of water (molecular weight 18) was obvious. Xylose and arabinose have molecular weight 150 and glucose have 160 but it is present in less amount in hemicellulose (10%) and therefore for simplicity of calculations molecular weight of hemicellulose was considered as 132.

Arabinogalactan used this reaction contains arabinose and galactose in the ratio of 1:6 *wt/wt*). Therefore for the calculation of arabinose and galactose yield, the molecular weight of arabinogalactan is considered as 1104. Arabinose weight obtained from 0.6 g arabinogalactan is calculated using formula 0.6x150/1104 = 0.08152 g. As the molecular weight of arabinose is 150 and molecular weight of arabinogalactan is 1104. Similarly, the galactose weight obtained from arabinogalactan is calculated using 0.6x180/1104 = 0.5869 g

1.3. 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([C₃SO₃HMIM][HSO₄]):

1-methyl imidazole, 7.625 mmol and 1,3–propane sultone, 7.625 mmol were dissolved in 10 mL toluene, and then it is refluxed in presence of inert atmosphere for 16 h in a round bottom flask under stirring. The product is precipitated out as zwitter ion as a white solid. The white precipitate formed was isolated by filtration, and dried at 80 °C for 4 h and used as such for the next step. Synthesis of BAIL was accomplished by mixing equimolar quantities of H_2SO_4 and zwitter ion. The resulting solution was stirred at 100 °C for 12 h. During this time the solids react, resulting in the formation of the [C₃SO₃HMIM][HSO₄] BAIL.

1.4. 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate ([C₃SO₃HMIM][PTS]):

For the synthesis of $[C_3SO_3HMIM][PTS]$ BAIL, 1-methylimidazole, (7.625 mmol) and 1,3– propane sultone, (7.625 mmol) were dissolved in 10 mL toluene and refluxed for 16 h in an inert atmosphere in a round bottom flask under constant stirring. The product; zwitter ion was precipitated out as a white solid in quantitative yield. The white precipitate formed was isolated by filtration, and washed with toluene and then dried at 80 °C for 4 h and then used as such in the next step. Synthesis of IL was accomplished by mixing equimolar quantities of *p*toluenesulfonic acid monohydrate (PTSA) and zwitter ion. The resulting mixture was stirred at 90 °C for 12 h. During this time the solids react, resulting in the formation of the $[C_3SO_3HMIM][PTS]$ BAIL. The color of the IL was pale yellow.

1.5. 1-methyl-3-(3-sulfobutyl)-imidazolium *p*-toluenesulfonate, [C₄SO₃HMIM][PTS]:

This BAIL was synthesized by refluxing mixture of equimolar ratio of 1-methyl imidazole and 1-4-butanesultone in toluene for 16 h giving white precipitate called zwitter ion. The white precipitate was isolated and dried at 80 °C for 4 h and then used as it is in the next step of reaction. Further the formed zwitter ion is then reacted with *p*-toluenesulfonic acid monohydrate for 12 h at 90 °C to give $[C_4SO_3HMIM][PTS]$ BAIL.

1.6. Synthesis of 1-methyl-3-(3-sulfopropyl)-imidazolium chloride ([C₃SO₃HMIM][Cl]):

For the synthesis of this IL also, similar procedure was used in the first step of reaction as explained in above section 1.2. In the second step of reaction, instead of *p*-toluenesulfonic acid monohydrate, HCl was used and it is reacted with zwitter ion which is obtained in the first step of reaction (reaction of 1-methylimidazole and 1,3-propane sultone). The equimolar mixture of zwitter ion and HCl is stirred at 90 °C for 12 h. This will result in the formation of desired BAIL ([C₃SO₃HMIM][Cl]).

1.7. N,N,N-triethyl-(3-sulfopropyl)-ammonium *p*-toluenesulfonate, [C₃SO₃HNEt₃][PTS]:

The synthesis of these $[C_3SO_3HNEt_3][PTS]$ BAIL was also carried out using a two-step reaction. In the first step, equimolar mixture of triethylamine (7.5 mmol) and 1,3-propane sultone (7.5 mmol) were mixed in 10 mL toluene. The mixture was refluxed for 16 h in an inert atmosphere to get zwitter ion. The zwitter ion obtained in the first step was isolated and washed with toluene and then dried at 80 °C for 4 h. In the second step, the formed zwitter ion was reacted with *p*-toluenesulfonic acid monohydrate (equimolar mixture), respectively and stirred at 90 °C for 12 to get [C₃SO₃HNEt₃][PTS] BAILs.

1.8.1-methyl-3-(3-sufopropyl)-benzimidazolium*p*-toluenesulfonate,[C3SO3HBenzMIM][PTS]:

1-methyl benzimdazole and 1,3-propane sultone were refluxed in toluene for 16 h in an inert atmoshpere to give zwitter ion. In next step zwitter ion is reacted with *p*-toluenesulfonic acid monohydrate without addition of any solvent at 90 °C for 12 h to get $[C_3SO_3HBenzMIM][PTS]$ BAIL.

1.9. Triphenyl-(3-sulfopropyl)-phosphonium *p*-toluenesulfonate ([C₃SO₃HPPh₃][PTS]) and 1-(3-sulfopropyl)-pyridinium *p*-toluenesulfonate ([C₃SO₃HPy][PTS]) BAIL:

For the synthesis of these BAILs, triphenylphosphine and pyridine were mixed individually in 1,3-propane sultone on the equimolar basis in the presence of toluene as a solvent and refluxed

for 16 h in an inert atmosphere to get respective zwitter ions. In the second step, these zwitter ions were mixed with *p*-toluenesulfonic acid monohydrate (equimolar mixture) and stirred at 90 °C for 12 h to get [C₃SO₃HPPh₃][PTS] and [C₃SO₃HPy][PTS] BAILs.

1.10. 1-butyl-3-methylimidazolium chloride [BMIM][Cl]:

[BMIM][Cl] IL was prepared according to literature procedure.¹ In a typical synthesis, a solution of 1-chlorobutane, (108 mmol) and 1-methylimidazole, (108 mmol) were taken in a round bottom flask fitted with a condenser. The mixture was refluxed in 60 mL acetonitrile for 48 h under vacuum. Then, the mixture was cooled to room temperature to observe two distinct layers. The upper layer containing unreacted starting material was decanted and the bottom layer was extracted with ethyl acetate. This procedure was repeated thrice to achieve efficient extraction of unreacted reactants still present in lower layer. The remaining solvent from ionic liquid was distilled off using rotary evaporator and the product was dried under high vacuum at 50 °C for 16 h. Dried [BMIM][Cl] IL showed slightly yellow appearance.

2. Characterization of BAILs

2.1. NMR analysis:

All the synthesized catalysts were characterized using ¹H NMR and ¹³C NMR spectroscopy and the results are presented in Fig. 2.4. to 2.24. All the ¹H NMR and ¹³C NMR characterization was carried out using D_2O solvent. The analysis of [BMIM][Cl] IL was performed using DMSO-d₆ solvent. The result showed that all the ILs synthesized are in pure form because in NMR there is no any extra peaks apart from IL.

2.1.1. ¹H NMR of ILs









S7



Fig. S6 ¹H NMR of [C₃SO₃HBenzMIM][PTS] BAIL



Fig. S8 ¹H NMR of [C₃SO₃HPy][PTS] BAIL.



Fig. S9 ¹H NMR of [BMIM][Cl] IL in DMSO-d₆.





Fig. S13 ¹³C NMR of [C₃SO₃HNEt₃][PTS] BAIL.



Fig. S15 ¹³C NMR of [C₃SO₃HPy][PTS] BAIL.



Fig. S16¹³C NMR of [BMIM][Cl] BAIL.

The ¹³C NMR characterization additionally support for the structure of BAIL. For ¹³C NMR also the D₂O solvent was used for all the IL except [BMIM][Cl]. DMSO-d₆ solvent was used for [BMIM][Cl] IL. The presence of primary, secondary and tertiary carbon atoms were understood from distortionless enhancement by polarization transfer (DEPT) NMR method and then these values are assigned in main ¹³C NMR spectra.

¹H NMR and ¹³C NMR characterization clearly showed that the synthesized ILs are pure in nature. After confirming the structure of all the ILs using this NMR spectroscopic method it is used in the hemicellulose conversion reactions.

2.2. Elemental analysis for the determination of C, H, N and S elements

The determined percentages of C, H, N, and S calculated using CHNS analysis. The microanalysis was performed using a Thermo Finnigan Flash EA 1112 series instrument (Table S1). The results of elemental analysis obtained for ILs showed that the synthesized ILs are pure in nature and also the molecular formula of ILs can be drawn with the help of values obtained from elemental analysis. Also, this analysis method helps for calculating the acid amount present in the catalyst, this can be calculated with the help of available percentage of sulfur.

No.	Catalyst	C (%)	H (%)	N (%)	S (%)
1	[C ₃ SO ₃ HMIM][HSO ₄]	27.5	4.8	9.0	21
2	[C ₃ SO ₃ HMIM][PTS]	44.2	7.1	7.7	16.6
3	[C ₄ SO ₃ HMIM][PTS]	46.2	5.7	7	16.4
4	[C ₃ SO ₃ HMIM][Cl]	34.7	5.2	11.5	12.6
5	[C ₃ SO ₃ HNEt ₃][PTS]	48.6	7.4	3.5	16.3
6	[C ₃ SO ₃ HBenzMIM][PTS]	50.7	5.3	6.6	15.0
7	[C ₃ SO ₃ HPPh ₃][PTS]	60.4	5.2	0	11.5
8	[C ₃ SO ₃ HPy][PTS]	48.3	5.1	3.7	17.2
9	[BMIM][Cl]	55	8.6	16	0

 Table S1 Elemental analysis of ILs.

All the above values obtained for element analysis are very much closer to theoretical values with $\pm 0.2\%$ difference. This implies that all the ILs synthesized are pure and does not contains any impurity.

3. TGA of BAILs

The TGA study of the synthesized ILs was studied for thermal stability of all the synthesized ILs by. The TGA was performed using Mettler Toledo Instrument TGA/SDTA851^e (Fig. S17). The result shows that there is no any mass loss because of IL up to 250 °C. This implies that ILs can be used up to 250 °C for the conversion of biomass. The TGA analysis was performed under the air atmosphere, and the heating rate used for the analysis was 10 °C min⁻¹. TGA of ILs is presented in Fig. 21. The initial loss in mass is observed because of loss of water from ILs. The hydrothermal stability of all BAILs was also checked at 170 °C for 5 h and it was found that these ILs are hydrothermally stable. For hydrothermal stability 0.24 g BAILs was taken in 60 mL water and stirred at 170 °C for 5 h, after 5 h the reactor was cooled to RT and the aqueous layer was analyzed using HPLC.



Fig. S17 TGA of ILs

All the TGA of ILs performed under air atmosphere and the TGA of [C₃SO₃HBenzMIM][PTS], and [C₃SO₃HPy][PTS] were performed in presence of N₂ atmosphere

4. Hammett acidity of catalysts

The Hammett acidity of all the catalysts calculated using Hammett acidity function (*Ho*), it is determined by means of UV-Vis spectrophotometer (Jasco V-570 Spectrophotometer, Jasco corporation, Japan) using 4-nitroaniline as a basic indicator. The Hammett function, H_O was calculated using Equation 1.

$$H_{O} = pk(I)_{aq} + log([I]/[IH^+])$$
 (1)

Here, $pk(I)_{aq}$ is the pka value of the indicator ($pk_a = 0.99$). The [IH⁺] & [I] are the molar concentrations of the protonated and un-protonated forms of the indicator solution after the addition of BAILs, respectively. The [I]/[IH⁺] ratio was determined from the difference in the measured absorbance before addition of a catalyst and after the addition of catalyst to the indicator solution. The maximum absorbance for un-protonated indicator in UV-Vis spectra was observed at 380 nm.

For acid strength the Hammett acidity (*Ho*) of catalysts were determined by using 4nitroaniline as a basic indicator. The Hammett acidity (*Ho*) was determined by UV-Vis spectrophotometer (Jasco V-570 spectrophotometer, Jasco Corporation, Japan)

The obtained acidity order of the catalysts with following *Ho* values (table 2): HUSY (Si/Al=15) (0.97) > HMORD (Si/Al=10) (1.31) > H₂SO₄ (1.67) > [C₃SO₄HMIM][HSO₄] (2.08) > [C₃SO₃HMIM][PTS] (2.33) > [C₄SO₃HMIM][PTS] (2.37) > [C₃SO₃HMIM][Cl] (2.47) > [C₃SO₃HEt₃N][PTS] (2.57).

Catalyst	λ Amax	[I]%	[IH]%	Но
Blank 1	0.94	100	0.0	-
HUSY (Si/Al=15)	0.46	48.9	51.1	0.97
HMORD (Si/Al=10)	0.64	68.0	32.	1.31
H_2SO_4	0.78	82.9	17.1	1.67
[C ₃ SO ₄ HMIM][HSO ₄]	0.87	92.5	7.5	2.08
[C ₃ SO ₃ HMIM][PTS]	0.90	95.7	4.3	2.33
[C ₄ SO ₃ HMIM][PTS]	0.90	96.	4.	2.37
[C ₃ SO ₃ HMIM][Cl]	0.91	96.8	3.2	2.47
[C ₃ SO ₃ HEt ₃ N][PTS]	0.91	97.5	2.5	2.57
[C ₃ SO ₃ HMBenzMIM][PTS]	0.917	97.6	2.4	2.61
[C ₃ SO ₃ HPPh ₃][PTS]	0.904	96.2	3.8	2.39
[C ₃ SO ₃ HPy][PTS]	0.903	96.1	3.9	2.38
[BMIM][Cl]	0.94	100	-	-

 Table S2 Hammett acidity for different types of BAIL's.

0.075 g of catalyst is mixed with 50 mL of water solution of p-nitroaniline (10 mg L⁻¹ p-nitroaniline, pKa of p-nitroaniline = 0.99)

5. Comparison study of BAILs with mineral acid and solid acid catalysts for the valorization of hemicellulose.

Catalyst	H ⁺ (mmol)	X+A yield (%)	Furfural yield (%)
H ₂ SO ₄	0.32	33	0
H_2SO_4	0.63	65	4
H_2SO_4	1.26	68	5
H_2SO_4	2.4	76	7
H_2SO_4	4.9	50	6
HCl	0.64	39	5
[C ₃ SO ₃ HMIM][PTS]	0.64	76	11
[C ₃ SO ₃ HMIM][HSO ₄]	1.58	87	10
HUSY (Si/Al = 15)	0.13	37	5
HMOR (Si/Al = 10)	0.28	22	3
HUSY (Si/Al = 15)	0.64	61	8
HMOR (Si/Al = 10)	0.64	48	6
PTSA	0.64	44	5

Table S3 Effect of H⁺ Concentration on the conversion of hemicellulos into C5 sugars.

All reactions were carried out using constant hemicellulose loading (0.6 g) at 160 °C for 1 h. The acidity of solid acid catalysts was calculated using NH_3 -TPD.

6. Structures of cations of BAILs

Table S4 3D-Structures of various cations of BAILs

[C₃SO₃HMIM]



[C₃SO₃HBenzMIM]



[C₃SO₃HNEt₃]

[C₃SO₃HPPh₃]







The structural difference in cations of BAILs were drawn using ChemBioDraw Ultra 14.0 software. After drawing all the structures in ball and stick model minimization of energy job was done. In the 3D structure (Fig. 3A.3.) grey ball denotes carbon atom, while the blue and pink ball denotes nitrogen and phosphorous atoms, respectively. The yellow and red balls denote sulphur and oxygen atoms, respectively. In all the structures it can be seen that the imidazolium and pyridinium based cations are planar while the quaternary ammonium and triphenylphosphonium based cations are not planar. This gives an idea that BAILs with imidazolium and pyridium cation can have significant interaction with polysaccharide because of their planar nature.

7. Effect of substrate concentration for valorization of hemicellulose into C5 sugars



S18. Conversion of different types of hemicellulose into sugar monomers using BAIL. Reaction condition: substrate 0.6 g, [C₃SO₃HMIM][PTS] 0.24 g, water 60 mL, 160 °C, 1 h.

8. Calculation of Partition Co-efficient of furfural in different organic solvents:

For the calculation of partition coefficient, 0.2010 g furfural was added in the water+organic biphasic solvent system 30 mL (1:5 v/v). The solution was stirred at RT for 2 h, after 2 h the water and organic phases were separated using a separating funnel and analyzed using HPLC and GC instrument. The aqueous layer was analyzed using HPLC and the organic phase was analyzed using GC. The furfural concentration present in aqueous and the organic phase was calculated with the help of slope of calibration curve obtained with furfural standard.

Table S5 Partition	Co-efficient	of furfural i	in water/organic	solvent system
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Solvent system	Distribution	Partition Co-	
Solvent system	Organic Phase (g)	Aqueous Phase (g)	efficient
Water/toluene	0.192	0.009	1.32
Water/p-xylene	0.185	0.016	1.06
Water/MIBK	0.193	0.008	1.38

*The error for distribution of furfural in organic phase was ± 2 mg.

Partition Co-efficient, (log P) organic/water = log₁₀ ([furfural] organic / [furfural] water)



Fig. S19 Partition coefficient of furfural in organic/water solvent system. Reaction condition: furfural 0.2 g, Water+Organic biphasic solvent 30 mL (1:5 v/v), RT, 2 h stirring

9. Effect of ratio of biphasic solvent system for the valorization of hemicellulose into furfural.



Fig. S20 Effect of the ratio of biphasic solvent for the valorization of hemicellulose into furfural. Reaction condition: substrate 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.125 g, Water+Toluene 60 mL, 170 °C, 4 h.

10. Effect of temperature on the valorization of hemicellulose into furfural using BAIL



Fig. S21 Effect of temperature on the valorization of hemicellulose into furfural. Reaction condition: substrate 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.12 g, water+toluene 60 mL (1:5 ν/ν), 4 h.

11. Effect of reaction time on the valorization of hemicellulose into furfural using BAIL



Fig. S22 Effect of time for the valorization of hemicellulose into furfural. Reaction condition: substrate 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.12 g, water+toluene 60 mL (1:5 ν/ν), 170 °C.

12. Effect of catalyst concentration for the valorization of hemicellulose into furfural



Fig. S23 Effect of catalyst concentration for the valorization of hemicellulose into furfural. Reaction condition: substrate 0.6 g, catalyst [C₃SO₃HMIM][HSO₄], water+toluene 60 mL (1:5 ν/ν), 170 °C.

13. Effect of substrate concentration on the valorization of hemicellulose into furfural



Fig. S24 Effect of hemicellulose concentration for its valorization into furfural. Reaction condition: $[C_3SO_3HMIM][HSO_4] 0.12$ g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

14. ¹H NMR of Fresh and recycled BAIL



Fig. S25 ¹HNMR of fresh and recovered [C₃SO₃HMIM][HSO₄] BAIL in hemicellulose to furfural reaction

15. Procedure for Recycling the catalyst

For the recycle study the separation of aqueous layer containing $[C_3SO_3HMIM][HSO_4]$ BAIL layer was carried out as follows; After the completion of the reaction, the aqueous and organic phases were separated using a separating funnel. The separated aqueous layer contains $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst because the $[C_3SO_3HMIM][HSO_4]$ BAIL is soluble in water and not in toluene solvent. Next, the aqueous layer was washed three times with fresh toluene solvent for the extraction of furfural which was soluble in the water layer. Then this aqueous layer obtained after furfural extraction by toluene was used for next reaction which contains $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst and small amount of sugars. In this aqueous layer, hemicellulose was added along with toluene and the reaction was performed. After the completion of reaction again the water and the toluene layers were separated using separating funnel and the reaction mixture was analyzed using HPLC and GC. The result showed 62% furfural yield along with 11% X+A yield.

For NMR analysis the catalyst recycled as follows; after completion of reaction the aqueous and toluene layer was separated using separating funnel. The aqueous layer contains BAIL catalyst, furfural and small amount of sugars, for removing furfural the aqueous layer was washed three times with toluene solvent. Next, after extraction of furfural the aqueous layer was subjected to rotavap for the removal of water and to obtain BAIL and sugars. After rotavap, the viscous liquid was obtained which contains BAIL and sugars, for removing sugars from BAIL the procedure used as follows; In this viscous liquid (BAIL+C5 sugars) 2 mL of water was added and then slowly acetone (30 mL) was added to give light white color solution. Up on excess addition of acetone, light white color disappears. The solution was kept under static condition for a while. Afterwards, the acetone layer is decanted (contains sugars) leaving viscous liquid at the bottom of a container. Net, the viscous liquid was dried at 80 °C for 4 h under vacuum. This dried viscous liquid (BAIL) was then dissolved in D₂O and used for ¹H NMR spectroscopy Fig. S24