

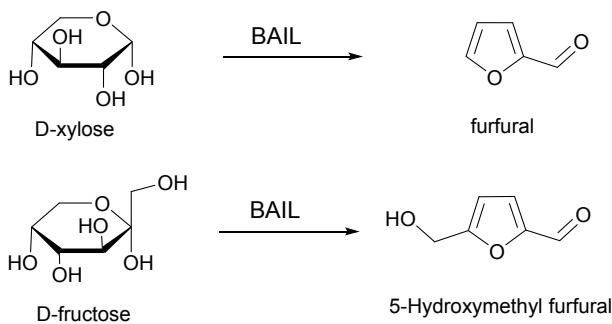
Supporting information

Conversion of concentrated sugar solutions in to 5-hydroxymethyl furfural and furfural using Brönsted acidic ionic liquids

Babasaheb M. Matsagar,^[a] Mudassir K. Munshi,^[b] Ashutosh A. Kelkar*^[b] and Paresh Laxmikant Dhepe*^[a]

[a] Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India. Tel. No. 91-20-25902024. E-mail:
pl.dhepe@ncl.res.in

[b] Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India. Tel. No. 91-20-25902544. E-mail:
aa.kelkar@ncl.res.in



Scheme S1 Dehydration of D-xylose to furfural and D-fructose to HMF

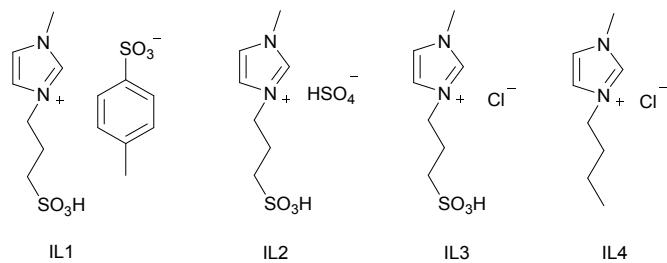


Fig. S1 Structure of ionic liquids used for fructose and xylose dehydration reaction

1. Synthesis and characterization of ionic liquids

1.1 Synthesis of ionic liquids

a) 1-methyl-3-(3-sulfopropyl)-imidazolium 4-methylbenzenesulfonate (IL1)

1-methyl imidazole, 7.625 mmol and 1,3–propane sultone, 7.625 mmol were dissolved in 10 mL toluene and refluxed at 110 °C for 16 h in a round bottom flask under stirring. The product; the zwitter ion was formed in quantitative yield and was precipitated out as a white solid. The white precipitate formed was isolated by filtration, dried and then used as such in the next step. Synthesis of IL was accomplished by mixing equimolar quantities of para-toluene sulfonic acid monohydrate (PTSA) and zwitter ion. The resulting solution was stirred

at 90 °C for 12 h. During this time the solid reacts, resulting in the formation of the IL1. The color of the IL was pale yellow.

b) 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate (IL2)

The synthesis procedure is same as mentioned above. However, in second step of reaction instead of PTSA equimolar quantities of sulphuric acid and zwitter ions were mixed together.

c) 1-methyl-3-(3-sulfopropyl)-imidazolium chloride (IL3)

1-Methyl imidazole, 7.625 mmol and 1,3-propanesultone, 7.625 mmol were dissolved in 10 mL toluene and refluxed in a RB flask for 16 h, under constant stirring. The product; zwitter ion was precipitated out as a solid. The precipitate formed was isolated by filtration, dried and then used as such in the next step. Equimolar quantity of HCl was added to this precipitate and heated at 90 °C for 12 h. This results in the formation of the ionic liquid, IL3.

d) 1-butyl-3-methylimidazolium chloride (IL4)

1-butyl-3-methylimidazolium chloride was prepared according to literature procedure.^[1] In a typical synthesis a solution of 1-chlorobutane, 108 mmol and N-methyl imidazole, 108 mmol was taken in round bottom flask fitted with a reflux condenser, and refluxed in acetonitrile for 48 h at 70-80 °C under inert atmosphere. Then the reaction mixture was cooled to room temperature to observe two distinct layers. The upper layer containing unreacted starting material was decanted and bottom layer was extracted with ethyl acetate. This procedure was repeated thrice to achieve efficient extraction. Washing with ethyl acetate should suffice to remove any untreated starting material from bottom layer. The remaining solvent from crude ionic liquid was distilled off on rotavac and the product was dried under high vacuum. Dried IL4 showed slightly yellow appearance.

1.2 Catalyst characterization

1.2.1 NMR

NMR measurements were carried out on a Bruker AV 200 MHz NMR spectrometer equipped with a 4.7 Tesla superconducting magnet. The samples were dissolved in D₂O. The resonance frequency for ¹H and ¹³C NMR was 200 MHz. The proton NMR spectra were taken with a standard one pulse experiment using a 30 degree flip angle and 1 sec relaxation delay. 32 to 64 scans and 32K data points were used for data collection. The raw data obtained were Fourier Transformed to get the frequency domain spectrum without the application of any window function. ¹³C spectra were obtained with a standard pulse sequence with continuous proton decoupling. A flip angle of ~ 30 degrees, the relaxation delay of 2 sec and 32K data points were used for data collection. The proton decoupling was achieved by a standard ZGPG30 pulse technique. A standard DEPT pulse sequence with a sorting pulse of 135 degrees (DEPT135) was employed for the ¹³C spectral editing so that the CH₂ peaks appear as negative and CH and CH₃ as positive. The number of scans for the ¹³C spectral data collection varied from a few hundred to a couple of thousand depending on the concentration. Prior to Fourier Transformation, the raw ¹³C data (FIDs) were multiplied by an exponential window function with a line broadening (LB) of 2Hz for sensitivity enhancement. The chemical shifts for the solvent peak (HDO) is found at 4.72 ppm.

1.2.2 Elemental analysis

Elemental micro analysis was done on a Thermo Finnigan Flash EA 1112 series instrument.

1.2.3 Hammett acidity

Hammett acidity functions (H_O) of various catalysts were determined by means of UV-Vis spectrophotometer (V-570 Spectrophotometer, Jasco corporation, Japan) using 4-nitroaniline as a basic indicator. The Hammett function, H_O was calculated using Equation 1.

$$H_O = p k(I)_{aq} + \log([I]/[IH^+]) \quad \dots \quad (1)$$

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

1.3 1-methyl-3-(3-sulfopropyl)-imidazolium 4-methylbenzenesulfonate (IL1)

1.3.1 NMR

^{13}C NMR

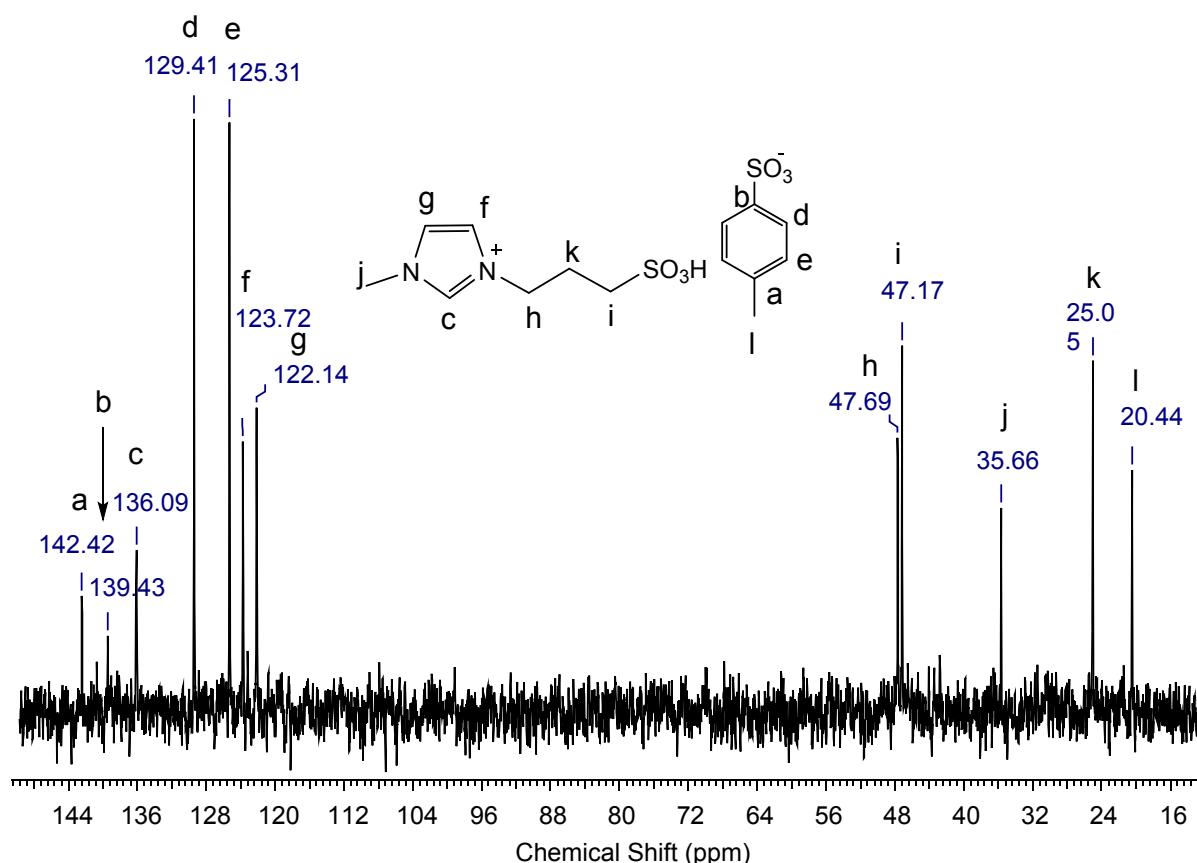


Figure S2. ^{13}C spectrum of IL1

¹³C DEPT spectra

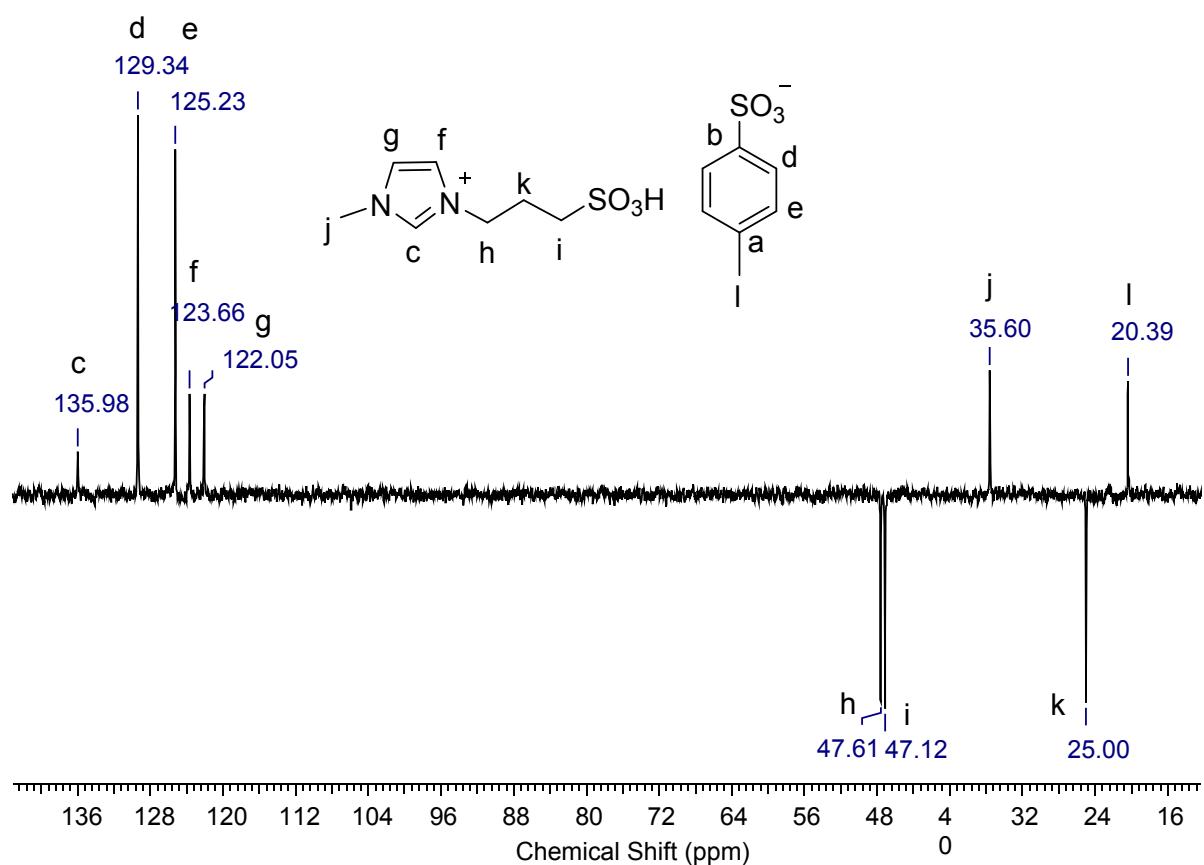


Figure S3. DEPT ¹³C spectrum of IL1

¹H NMR

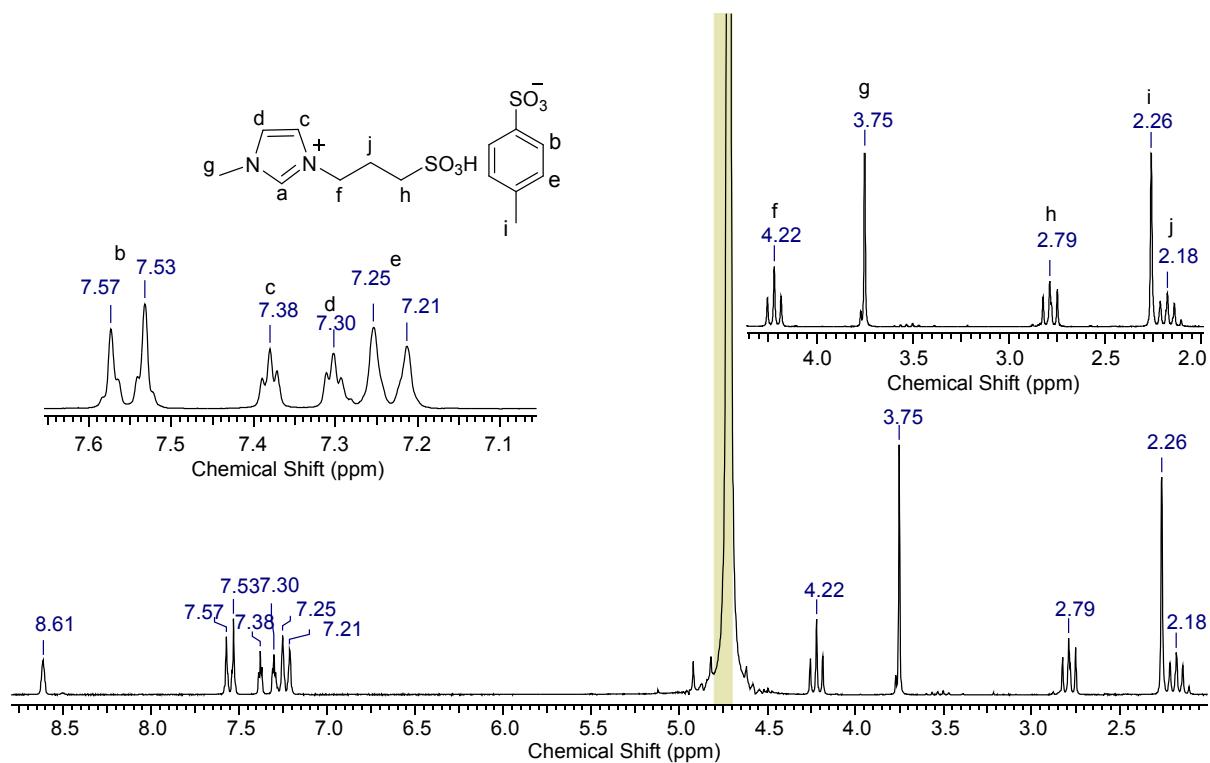


Figure S4. ¹H NMR spectrum of IL1

1.3.2 Elemental analysis

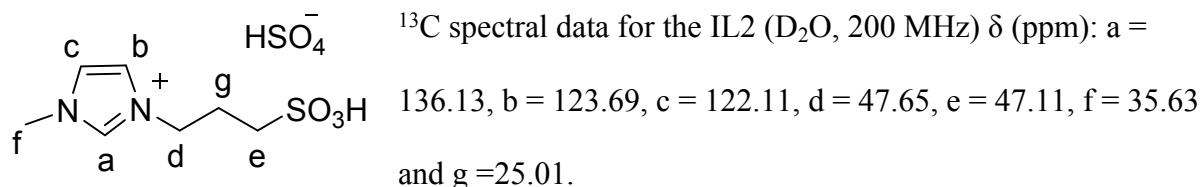
Observed (%): C, 42.4; H, 6.1; N, 7.7; S, 14.6

Theoretical (%): C, 42.6; H, 6.3; N 7.4; S, 15

1.4. 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate (IL2)

1.4.1 NMR

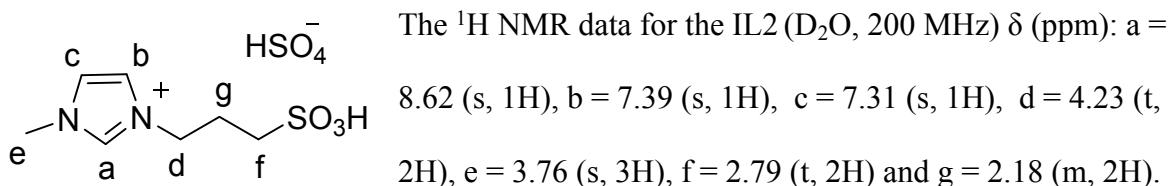
^{13}C NMR



DEPT ^{13}C spectra

^{13}C DEPT spectra data of the IL2 (D_2O , 200 MHz, TMS) δ (ppm): a = 136.13, b = 123.66, c = 122.09, d = 47.61, e = 47.08, f = 35.59 and g = 24.98.

^1H NMR



1.4.2 Elemental analysis

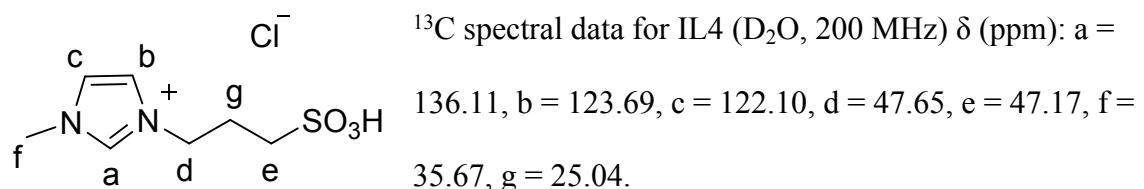
Observed (%): C, 27.5; H, 4.8; N, 9.0; S, 20.1

Theoretical (%): C, 27.8; H, 4.6; N, 9.2; S, 20.5

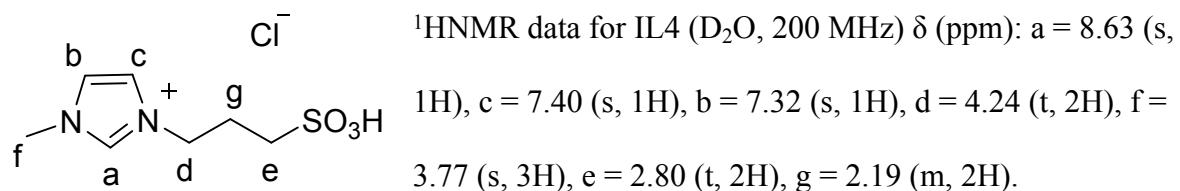
1.5 1-methyl-3-(3-sulfopropyl)-imidazolium chloride (IL3)

1.5.1 NMR of IL3

^{13}C NMR of IL3



^1H NMR of IL3



1.5.2 Microanalysis of IL3

Observed (%): C, 31.7; H, 6.2; N, 11.5; S, 12.6

Theoretical (%): C, 31.9; H, 6.44; N, 11.6; S, 12.3

1.6 Hammett acidity function (H_O)

Table S1. Hammett acidity function (H_O) data for different catalysts

Sample	A _{max}	[I] %	[H ⁺] %	H_O
Blank	0.94	100	0.0	-
HUSY	0.46	48.9	51.1	0.97
Amberlyst-15	0.52	55.5	44.5	1.09
H-MOR	0.64	68.0	32.	1.31
H ₂ SO ₄	0.78	83.0	17.1	1.68
IL3	0.91	96.8	3.2	2.47
IL2	0.87	92.5	7.5	2.08
IL1	0.91	96.8	4.3	2.33
IL4	0.94	100	-	-

0.075 g of catalyst is mixed with 50 ml aqueous solution of 4-nitroaniline (10 mg L⁻¹, pKa = 0.99).

The UV-Vis spectra measured for aqueous solution of only BAIL did not show any peak at 380 nm which confirms that peak observed at 380 nm is only due to indicator.

2 Experimental

2.1 Materials

The chemicals required for the synthesis of ILs such as, N-methyl imidazole, 1,3-propane sultone were purchased from Aldrich Chemicals (USA) and *p*-toluene sulfonic acid and sulfuric acid (98%) were procured from Loba Chemicals (India). While toluene was purchased from Spectrochem (India), D-fructose (AR grade), D-glucose (AR grade), D-xylose (AR grade), furfural (AR grade) and 4-nitroaniline were purchased from Loba Chemicals (India). 5-hydroxymethyl furfural (HMF) (>99% purity) was purchased from Aldrich Chemicals (USA). All the chemicals were used as received. All the solvents were purchased from Loba Chemicals (India) and Merck Chemicals (India). Zeolites, H β (Si/Al=19), HUSY (Si/Al=15), HMOR (Si/Al=10) were procured from Zeolyst International (USA). Prior to use, zeolites were calcined at 550 °C for 16 h in an air flow. Amberlyst-15 was purchased from Aldrich Chemicals (USA) and before use was dried at 80 °C for 2 h.

2.2 Catalytic runs

Fructose (0.5 g), solvent (water+MIBK=30 mL 1:5 v/v) and IL were charged in the Parr reactor and reaction mixture was heated to desired temperature under stirring (100 rpm). After attaining the reaction temperature, stirring was increased to 800 ppm.

Xylose (0.6 g) solvent (water+toluene=60 mL 1:5 v/v) and IL were charged in the Parr reactor and the reaction mixture was heated to desired temperature under stirring (100 rpm). After attaining the reaction temperature, stirring was increased to 800 rpm.

2.3 Catalyst recycle study

Catalyst recycle studies were performed with IL2 as a catalyst.

2.3.1 Fructose to HMF reaction

After 1st reaction, methyl isobutyl ketone (MIBK) and water layer were separated using separating funnel. While HMF is soluble in MIBK, ionic liquid was not. From aqueous layer HMF is extracted 3 times using fresh MIBK solvent and after that the water layer was passed through activated charcoal to adsorb any degraded products. This water (containing IL) was then used for the next reaction. Three times extraction of HMF from aqueous layer and after passing this aqueous layer through activated charcoal showed 50% decrease of volume. Subsequent reactions were carried out by decreasing the quantity of substrate and solvent (by keeping S/C ratio and S/solvent ratio constant).

2.3.2 Xylose to furfural

The similar procedures were used as explained in fructose dehydration reaction.

2.4 Analysis and calculations

The aqueous phase of the reaction was analyzed using HPLC (Agilent Technology 1260 infinity) equipped with Pb²⁺ column (Rezex RPM-Monosachharide, 300 x 7.8 mm) and RID (40 °C). The Millipore water was used as an eluent. Organic layer was analysed using Agilent 7890B GC system, equipped with HP-5 column (50 m × 0.22 μm ID) and FID. All samples were filtered through 0.22 μm syringe filter.

For the calculation of conversion and product yield, calibration curves were drawn using commercially procured compounds.

% Conversion of substrate = [Initial substrate, mol] – [Final substrate, mol] / [initial substrate, mol] × 100

% Yield of product = [product formed, mol]_(GC[org] + HPLC[water]) / [product expected, mol(theoretical: based on substrate consumed, mol)] × 100

2.5 Isolation of furfural

Isolation of furfural was done from the reaction carried out with following details,

Xylose 0.6 g, IL2, 0.08 g; water+toluene = 60 mL, 1:5 (v/v); 170 °C, 4 h.

In this reaction we obtained total furfural yield of 74% (65% from toluene layer and 09% from water layer).

After the reaction toluene layer was separated from the water layer using separating funnel. Again, toluene was added to water layer and furfural was extracted from the water layer. This toluene layer after separation from water layer was added to earlier toluene layer. This extraction procedure was repeated for total 4 times to make sure that all the furfural is extracted in toluene layer from the water layer. This was also checked by color change of the water and toluene layers. Afterwards, toluene was evaporated using rotary evaporator and remaining mass was considered as furfural. From the weight of furfural we calculated the isolated yield to be 65%. To confirm the obtained mass is pure furfural it was injected after dilution (toluene) in the GC and GC-MS.

3. Results

3.1 Solvent effect on dehydration of fructose

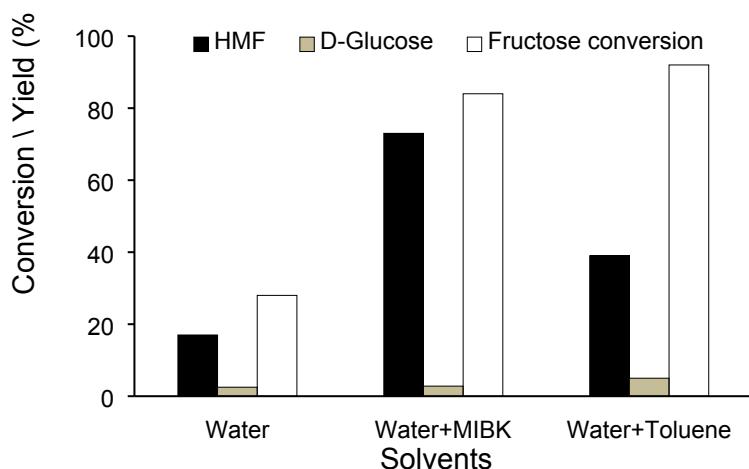


Figure S5. Effect of solvent on the dehydration of fructose to HMF.

Fructose, 0.5 g; IL2, 0.025 g; water+organic solvent, 30 mL (1:5 v/v); 150 °C; 30 min.

3.2 Effect of catalyst concentration for fructose dehydration in to HMF

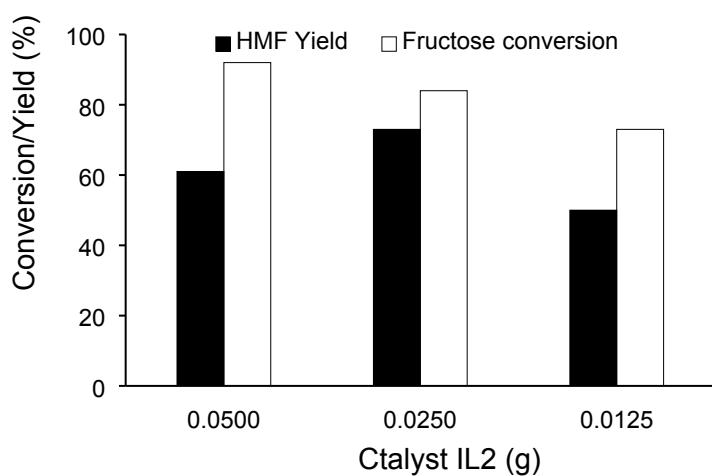


Figure S6. Effect of catalyst concentration (IL2) on fructose to HMF reaction.

Fructose, 0.5 g; water+MIBK, 30 mL (1:5 v/v); 150 °C; 30 min.

Table S2 Dehydration of fructose to HMF and xylose to furfural using various catalyst.

Catalyst	Acid amount [mmol/g] ^[a]	HMF yield [%] ^[b]	Furfural yield [%] ^[c]
H β (Si/Al= 19)	0.94	0	-
HUSY (Si/Al=15)	0.55	0	60
H-MOR Si/Al=10)	1.2	0	57
H-MOR Si/Al=10)	1.2	6 ^[d]	-
H-MOR Si/Al=10)	1.2	13 ^[e]	-
Amberlyst-15	4.65 ^[f]	68	64
H ₂ SO ₄	20.0 ^[g]	59 ^[h]	60
H ₂ SO ₄	20.0 ^[g]	33	-
H ₂ SO ₄	20.0 ^[g]	47 ^[i]	-
IL2	6.61 ^[g]	73 ^[h]	73
IL1	2.65 ^[g]	72	70

[a] Acid amount measured by TPD-NH₃.

[b] Fructose 0.5 g, catalyst 0.05 g, 150 °C, 30 min.

[c] xylose 0.6 g, catalyst 0.08 g, 170 °C, 4 h.

[d] Fructose 0.5 g, catalyst 0.140 g, 150 °C, 30 min.

[e] Fructose 0.5 g, catalyst 0.140 g, 160 °C, 30 min.

[f] Acid amount was determined by back titration with 0.01 M NaOH.

[g] Acid amount calculated by considering molecular Weight.

[h] Reaction condition; fructose 0.5 g, catalyst 0.025 g, 150 °C, 30 min.

[i] Reaction condition; fructose 0.5 g, catalyst 0.0082 g, 150 °C, 30 min.

- [1] S. A. Dharaskar, M. N. Varma, D. Z. Shende, C. K. Yoo, K. L. Wasewar, *The Scientific World Journal* **2013**, 2013, 395274.