Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Glucose isomerization catalyzed by bone char and the selective production of 5-hydroxymethylfurfural in aqueous media

Babasaheb M. Matsagar,[a] Chi Van Nguyen[a] Md. Shahriar A. Hossain,[bc] Md. Tofazzal Islam,[d] Yusuke Yamauchi,[befg] Paresh L. Dhepe,[h] and Kevin C.-W. Wu[a]

[a] *Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan*

[b] *College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*

[c] *School of Mechanical & Mining Engineering, The University of Queensland, Brisbane, QLD 4072, Australia*

[d] *Department of Biotechnology, Bangabandhu Sheikh Mujibur Rahman Agricultural University, Gazipur 1706, Bangladesh*

[e] *School of Chemical Engineering and Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, QLD 4072, Australia*

[f] *International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

[g] *Department of Plant & Environmental New Resources, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, South Korea*

[h] *Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr Homi Bhabha Road, Pune 411 008, India*

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1. Materials

Glucose (95.5%) and fructose (99%) used in the present study were procured from Sigma-Aldrich while levulinic acid (98%) and formic acid (99%) were obtained from Alfa Aesar and Sigma-Aldrich. The chemicals required for the synthesis of acidic IL such as 1,3-propane sultone (98%; Across Organics), 1-methylimidazole (99%; Alfa Aesar), sulfuric acid (96%; Honeywell Fluka), and toluene (99.5%; J.T.Baker) were procured and used without any treatment and further purification. The methyl isobutyl ketone (MIBK; 98.5%) solvent and hydroxyapatite ($Ca_5(OH)(PO_4)_3$; 99.8) were procured from Sigma-Aldrich while 5-hydroxymethylfurfural (HMF 99%) received from Across Organics.

2. Catalyst characterization and reaction analysis

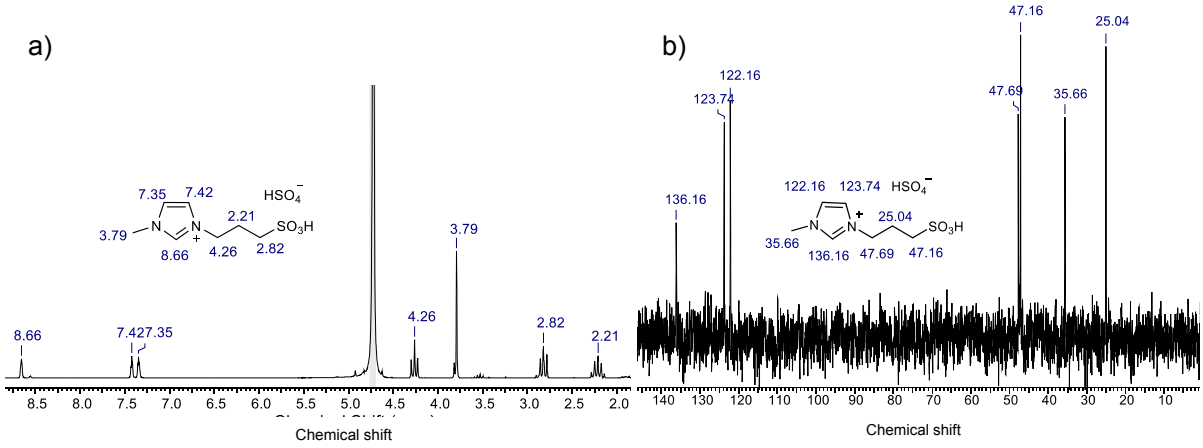

Fig. S1 NMR spectum of acidic IL. a) ^{1}H NMR, b) ^{13}C NMR.

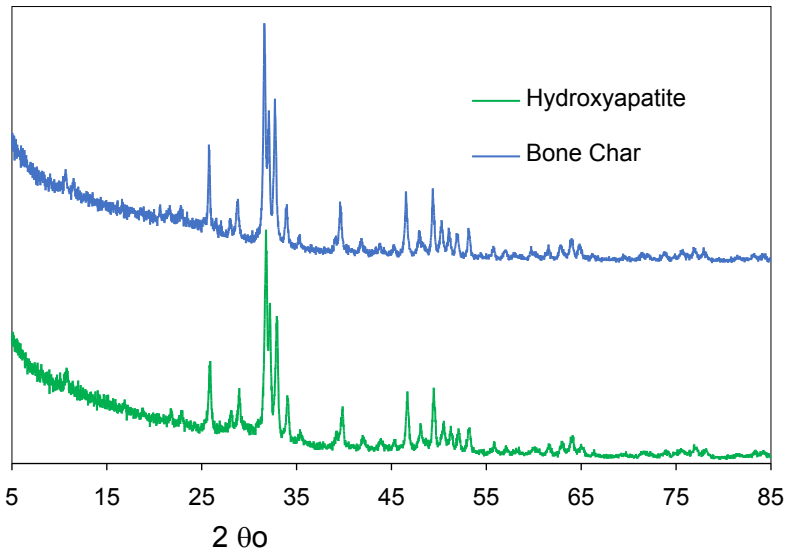

Fig. S2 XRD pattern of hydroxyapatite and bone char.

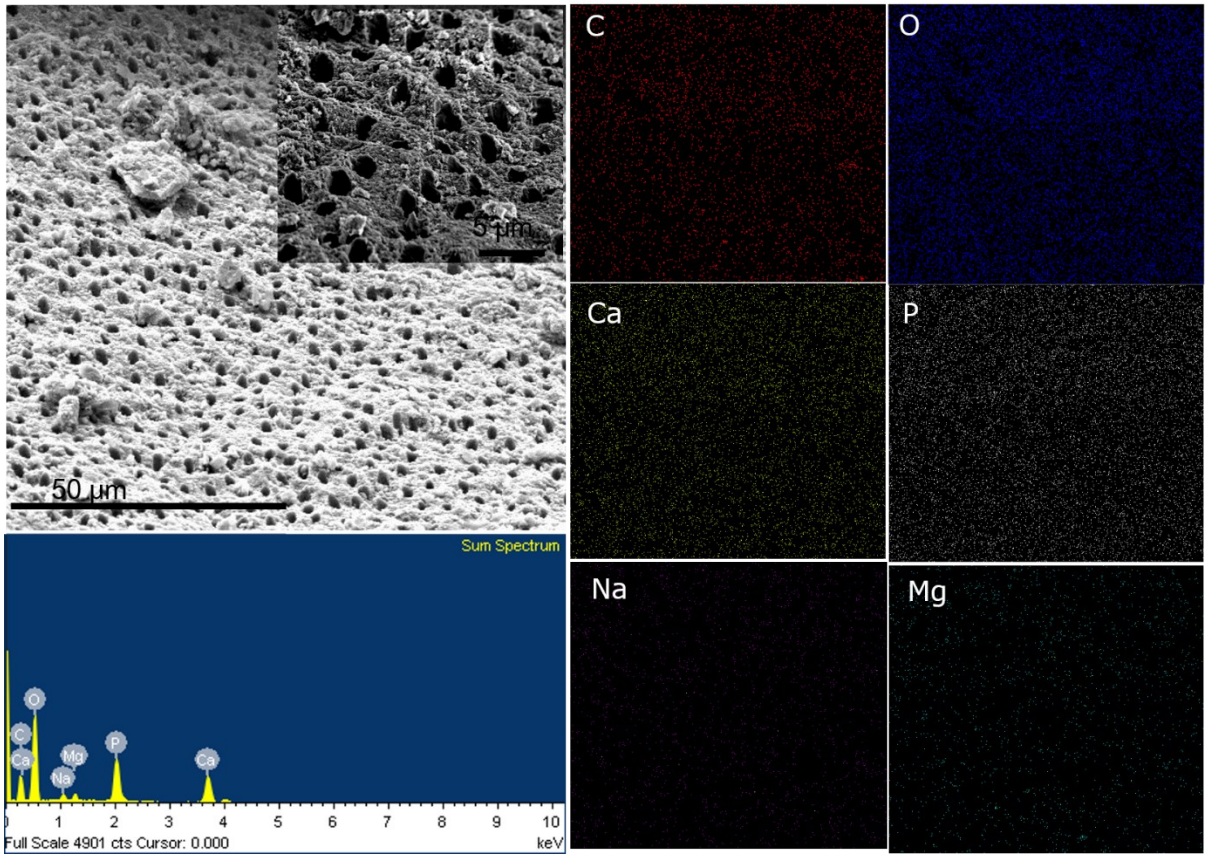

Fig. S3 SEM-EDX analysis of bone char.

Table S1 EDX-Elemental mapping.

Element	Weight (%)	Atomic (%)
C K	14.16	22.62
O K	46.44	55.68
Na K	1.45	1.21
Mg K	1.27	1.00
P K	13.68	8.48
Ca K	23.00	11.01
Totals	100.00	

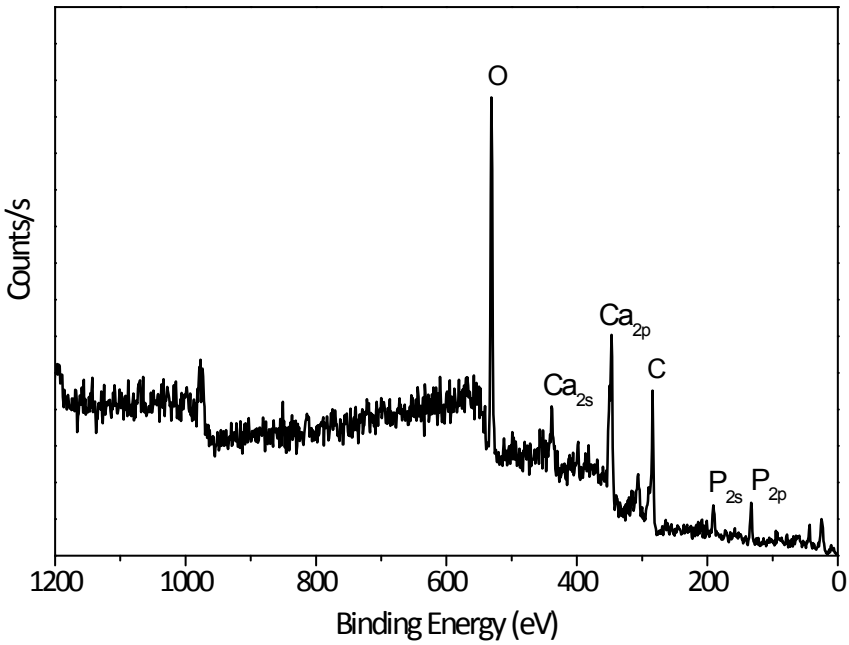

Fig. S4 XPS spectra of bone char catalyst.

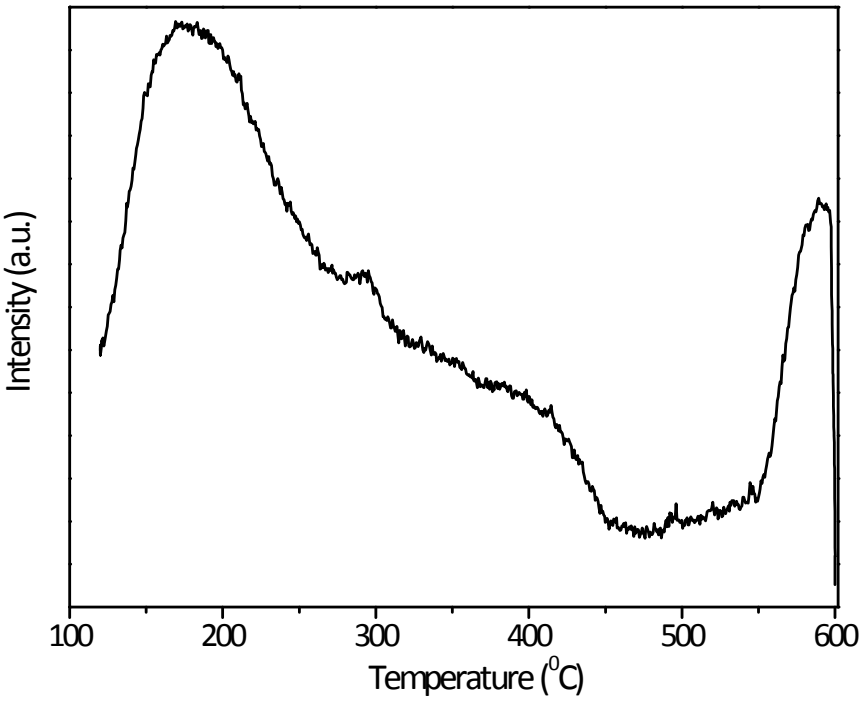

Fig. S5 CO_2-TPD analysis of bone char catalyst.

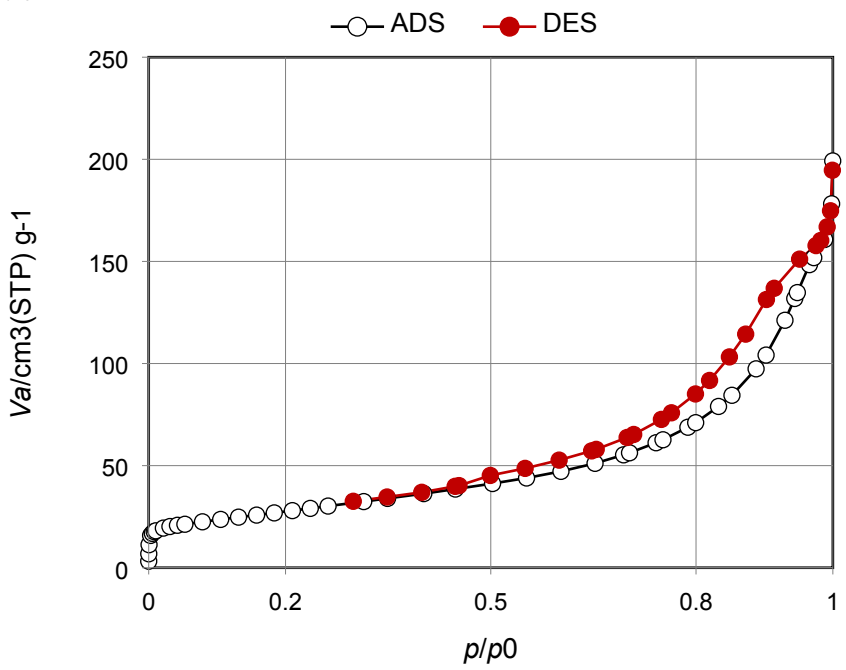

Fig. S6 N_2-adsorption/desorption isotherm of bone char.

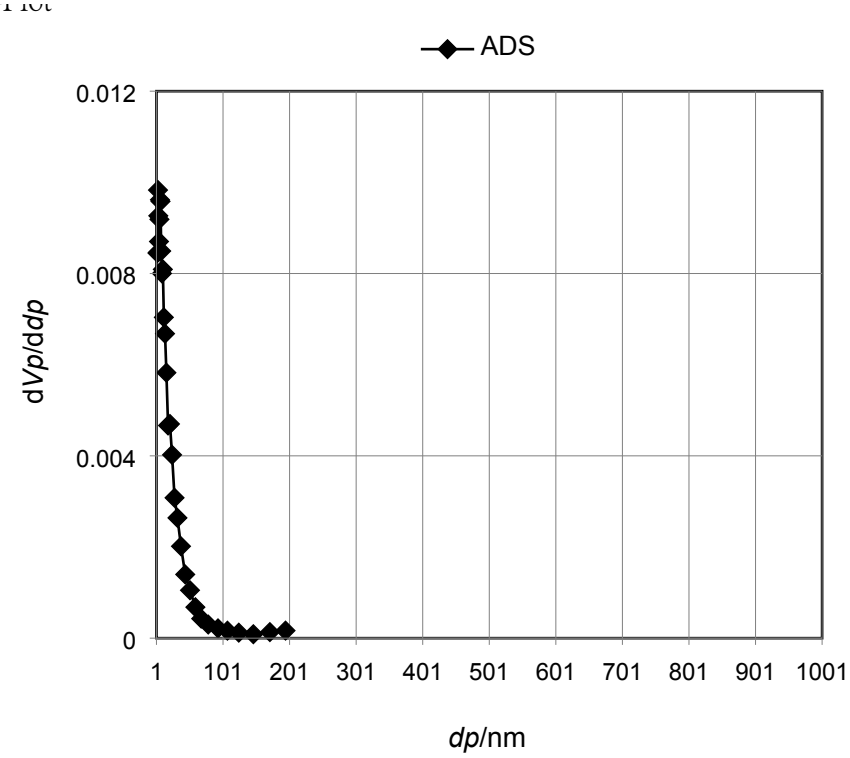

Fig. S7 Pore size distribution of bone char.

Table S2 Pore characteristic of bone char.

BET Surface Area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
98.3	0.25	10.32

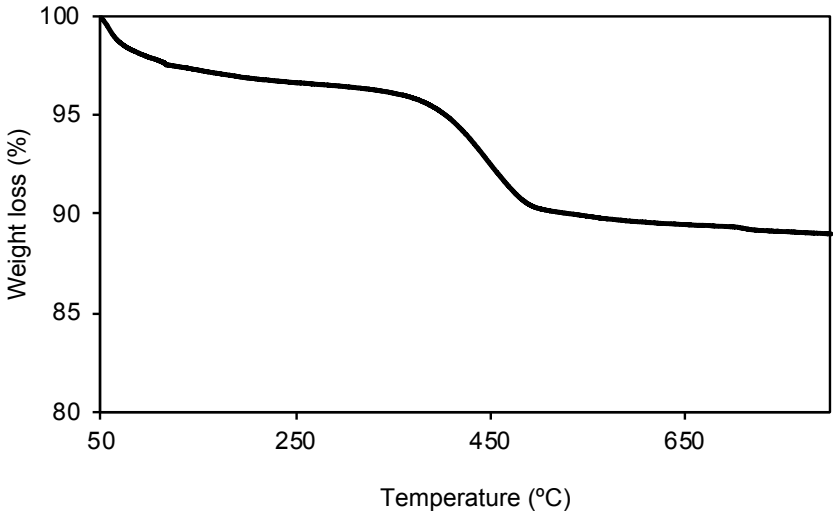

Fig. S8 TGA of fresh bone char (performed under air)

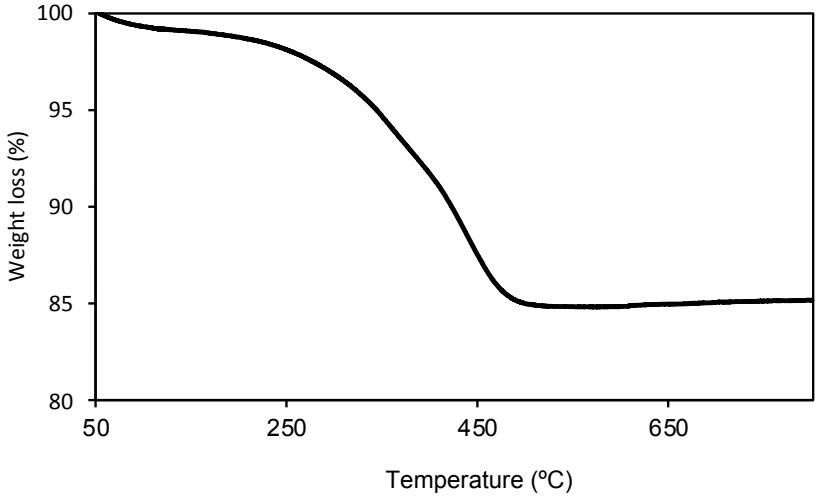

Fig. S9 TGA of bone char (performed under air) recovered from reaction mixture. This TGA sample was dried before analysis at 120 ºC for 20 h. Therefore, more loss of water cannot be seen in the TGA plot.

Reaction analysis

The analysis glucose reaction mixture and the calibration of standards (glucose, fructose, HMF, formic acid levulinic acid, etc.) were performed using HPLC. HPLC equipped with a refractive index detector and Shodex Asahipark NH_2P-50 4E column was employed for the analysis of glucose and fructose. The acetonitrile+water (7:3 *v/v*) solution was used as the mobile phase with a flow rate of 1 mL min^{-1}. The concentration of HMF in the reaction mixture was quantified using an ICE-Coregel 87H3 column (operated at 35 ºC). In this case, sulfuric acid (8 mM) was used as the mobile phase with a flow rate of 0.6 mL min^{-1}. The calculations for glucose conversion, HMF yield and selectivity were mentioned in the ESI (Section 5).

3. Results for the reactions of glucose isomerization and fructose dehydration

Table S3 Glucose isomerization to fructose using bone char catalyst.

Entry	Bone-Char catalyst (g)	Temperature (ºC)	Time (h)	Conversion (%)	Fructose yield (%)	Selectivity (%)
1	Non	90	3	0	0	0
2	0.03	90	3	19	12	63
3	0.05	90	3	27.2	15	55
4	0.1	90	3	32	15	47
5	0.15	90	3	34	15	44
6	0.05	50	3	2	0	0
7	0.05	70	3	17	9	53
8	0.05	110	3	35	13	37
9	0.05	130	3	36	12	33
10	0.05	90	1	21	12	57
11	0.05	90	2	21	13	61
12	0.05	90	4	27	13	48

Reaction Condition: Glucose 0.1 g, H_2O 10 mL.

Table S4 Dehydration of fructose.

Entry	C6 Sugar	Catalyst	Solvent	Time (h)	Temp (ºC)	Glucose Conv. (%)	Fructose Conv. (%)	HMF Yield (%)
1	Fructose	–	H_2O+MIBK (1:5 v/v)	0.5	150	–	9	0.7
2	Fructose	H_2SO_4	H_2O+MIBK (1:5 v/v)	0.5	150	–	85	32
3	Fructose	BAIL	H_2O+MIBK (1:5 v/v)	0.5	150	-	84	73

Reaction condition: Fructose 0.5, Catalyst 0.025 g, H_2O 5 mL, MIBK 25 mL.

Table S5 Some recent work of glucose dehydration using water as a solvent.

Entry	Glucose	Catalyst	Solvent	Time (h)	Temp (ºC)	Glucose Conv. (%)	HMF Selectivity (%)	HMF Yield (%)	Ref.
1	0.4 g	PTSA_PMO 0.2 g, $AlCl_3 6H_2O$ 0.15 g	H_2O 16.5 mL	1	140	14.3	8.4	1.2	1
2	10 %	$FeCl_3 6H_2O$ 1%	H_2O	6	130	-	-	1.7	2
3	10 %	$AlCl_3$ 1%	H_2O	5	130	-	-	11	2
4	10 %	$CrCl_3 6H_2O$ 1%	H_2O	2	130	-	-	13	2
5	0.1 g	NaCl 0.37 g, [MimAM] H_2PW 30 μmol	H_2O 12 mL	7.5	160	69.3	10	6.9	3
6	0.01 g	$Nb_{0.2}$-WO_3 0.1 g	H_2O 1 mL	12	120	93	33	31	4
7	0.2 g	Bone char 0.05 g, BAIL 0.05 g	H_2O 20 mL	12	170	72	54	39	This work

4. Separation of BAIL from reaction mixture

After completion of the reaction, the collected reaction mixture contains BAIL and bone char catalysts. It also contains HMF and some unconverted sugars (fructose and glucose). HMF was extracted using MIBK solvent (the BAIL catalyst is not soluble in MIBK), and bone char were separated using filtration method. Then from remaining reaction mixture (aqueous layer), water was removed using rotavap to get viscous liquid which contains BAIL and some unconverted sugars. Then 2 mL of water was added to the viscous liquid which makes IL and sugars soluble and decreases viscosity. Afterword 25 mL acetone was added slowly to this solution which results in a light white colored solution. The solution is then kept for 20 min in static condition results in separation of BAIL from the solution (Fig. S8). The acetone layer was decanted leaving BAIL at the bottom of the vial. Next, the BAIL was dried under vacuum for 4 h at 80 ºC. Finally, the dried BAIL characterized using ^{1}H NMR spectroscopy (Fig. S9).

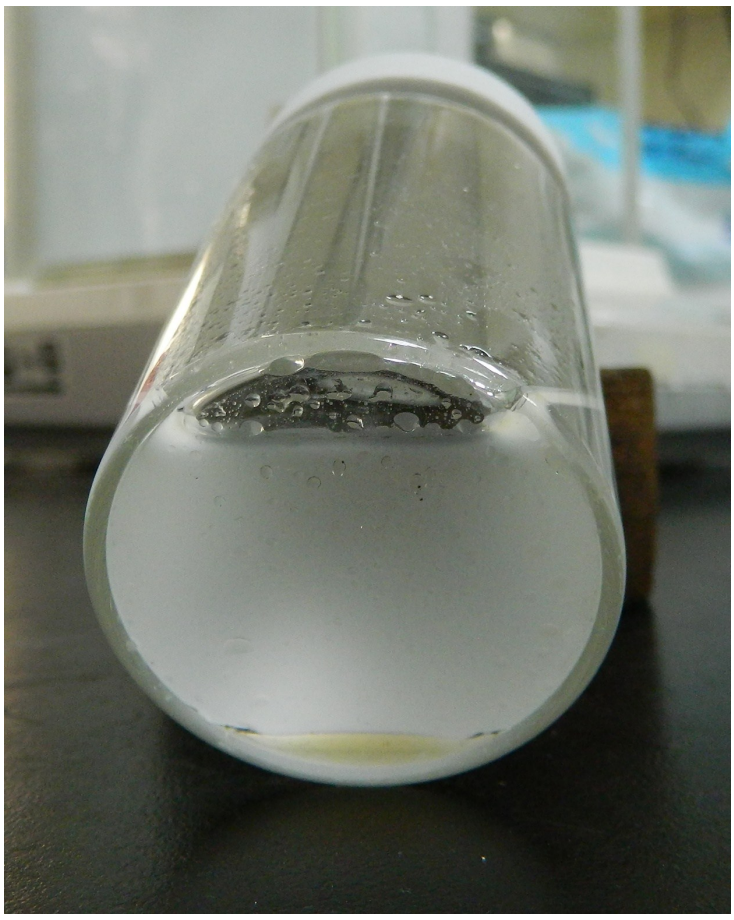

Fig. S10 BAIL separated from the reaction solution after 20 min of acetone addition.

In single experiment around 68% BAIL was recovered for complete extraction of BAIL repetition of IL separation experiments are required. As it can be seen from Hammet acidity analysis data and NMR data that the recycled BAIL has similar Hammet acidity and NMR spectrum like fresh BAIL. This shows that it is stable under reaction condition.

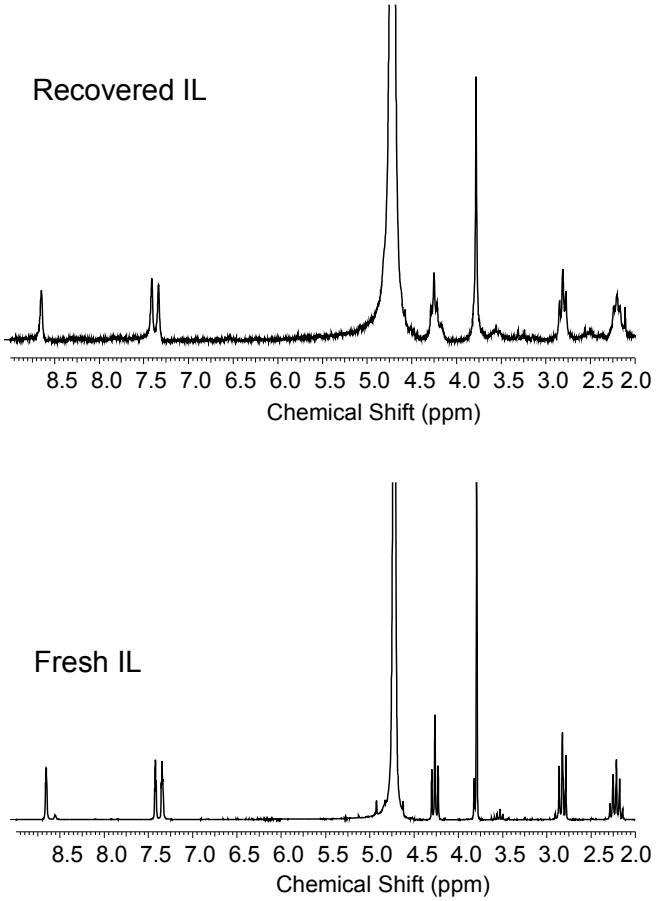

Fig. S11 ^{1}H-NMR of fresh and recovered 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate (acidic IL) from the reaction mixture. Reaction condition: Glucose 0.2 g, bone char 0.1 g, $[C_3SO_3HMIM][HSO_4]$ 0.1 g, H_2O 20 mL, 170 ºC, 3 h.

5. Calculations

The glucose conversion, HMF yield and selectivity were calculated using following equations:

$$Glucose\ conversion\ (\%) = \frac{(wt.\ of\ starting\ glucose - wt.\ of\ remaining\ glucose)}{wt.\ of\ starting\ glucose} x100$$

$$HMF\ yield\ (\%) = \frac{wt.\ HMF\ (HPLC)}{wt.\ of\ HMF\ (theortical)} x100$$

$$HMF\ selectivity\ (\%) = \frac{HMF\ yield}{Glucose\ conversion} x100$$

Reference:

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