Efficient process for direct transformation of cellulose and carbohydrates to 5-(hydroxymenthyl)furfural with dual-core sulfonic acid ionic liquids and co-catalyst

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Electronic Supplementary Information

Contents

1. Synthesis Procedure of various ILs

Preparation of [bi-C_3SO_3Hmim][HSO_4] (IL-1)

Preparation of bisimidazolemethane was according to literatures[1, 2], reacting one equivalent of imidazole and 1, 2-dibromoethane with two equivalents of potassium hydroxide in the presence of anhydrous ethanol. Reaction was performed at 70℃ for 6 h and bisimidazolemethane was isolated by extraction followed by column chromatography. According to the route in Scheme 1, bisimidazolemethane and 1, 3-propane sultone were mixed in a molar ratio of 1 : 1.2 at 70℃ in anhydrous ethanol for 24 h. The resulting white powder was pulverized, washed with ethanol and ethyl acetate, and dried in vacuo for 24 h. The white powder and H_2SO_4 were mixed in a molar ratio of 1 : 1 in the solvent, and heated at 85℃ for 5 h, followed by washing with ethyl acetate and ether and drying in vacuo to obtain the final IL-1.

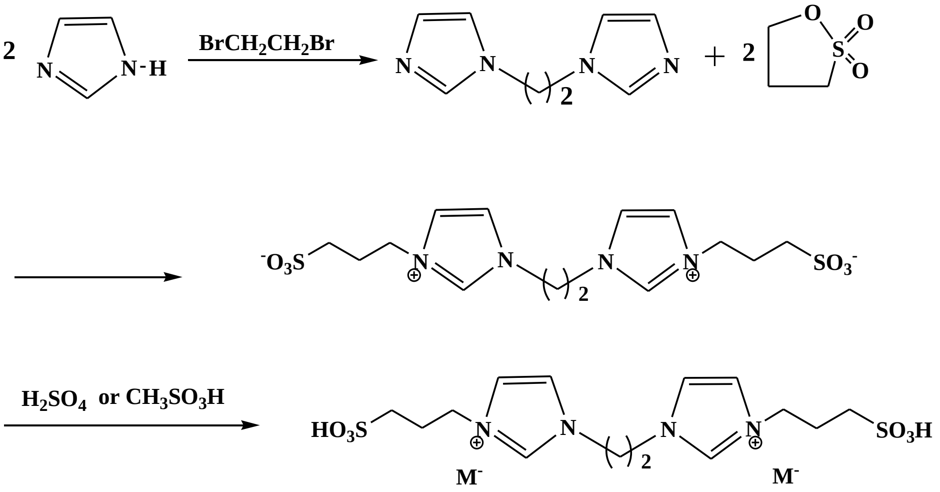
^{1}H-NMR (400 MHz, D_2O): δ_H (ppm) = 8.67 (2H, s), 7.43 (2H, s), 7.35 (2H, s), 4.21-4.26 (4H, t), 3.99 (4H, s), 2.76-2.83 (4H, t), 1.91-2.02 (4H, m).

Preparation of [bi-C_3SO_3Hmim][CH_3SO_3] (IL-2)

The synthesis procedure of IL-2 was similar to IL-1, but the acid reagent is CH_3SO_3H.

^{1}H-NMR (400 MHz, D_2O): δ_H (ppm) = 8.80 (2H, s), 7.61 (2H, s), 7.53 (2H, s), 4.39-4.44 (4H, t), 3.92 (4H, s), 2.94-2.99 (4H, t), 1.91-2.03 (4H, m).

Scheme 1



$M=HSO_4^-$, $CH_3SO_3^-$

Scheme 1. Synthesis of the dual-core sulfonic acid ionic liquids.

Preparation of $[C_3SO_3Hmim][HSO_4]$[3](IL-3)

Methylimidazole (0.11 mol) and 1, 3- propane sulfone (0.10 mol) were dissolved in anhydrous ethanol (20 mL) and stirred for 3 h at 80℃ under a nitrogen atmosphere. A white precipitate formed which was filtered, washed with diethyl ether three times, and then dried in avacuum. The resulting white precipitate (0.06 mol) was added to an aqueous solution of H_2SO4 (0.06 mol), and then the mixture was stirred at room temperature for 2 h. Water was removed in vacuum to give the product.

^1H NMR (400 MHz, D_2O): δ_H (ppm) = 8.75 (1H, s), 7.53 (1H, s), 7.46 (1H, s), 4.35-4.39 (2H, t), 3.91 (3H, s), 2.91-2.95 (2H, t), 2.29-2.36 (2H, m).

Preparation of $[C_3SO_3Hmim][CH_3SO_3]$[3](IL-4)

The synthesis procedure of IL-2 was similar to IL-1, but the acid reagent is CH_3SO_3H.

^1H NMR (400 MHz, D_2O): δ_H (ppm) = 8.50 (1H, s), 7.29 (1H, s), 7.22 (1H, s), 4.11-4.14 (2H, t), 3.66 (3H, s), 2.67-2.71 (2H, t), 2.04-2.11 (2H, m).

Preparation of solvent

The solvent [BMIM]Cl used for the study was prepared according to the method described in the literature reported by Rogers et al[4].

2. Experimental Procedures of HMF synthesis from sugars and lignocellulosic material

Sugars

The catalytic conversion of sugars to HMF was carried out in a stainless steel autoclave with glass liner tube that was heated in the oil-bath. Typically, 0.925 mmol sugar was added into 3 mL [BMIM]Cl solvent that was preheated under vigorous stirring (about 0.5 h), followed by the addition of the desired catalyst and H_2O at the reaction temperature. After the appointed reaction time, 0.2 mL samples were pipetted, quenched immediately with 0.3M NaOH solution and diluted with deionized water (×50). The solution was centrifuged at 10,000 rpm for 10 min and the upper clear liquid was pipetted off and diluted with deionized water (×6). The samples were analyzed using high performance liquid chromatography (HPLC).

Lignocellulosic materials

The as-received lignocellulosic materials were dried for 24 h at 80℃ prior to hydrolysis. Then the catalytic conversion of lignocellulosic materials to HMF was carried out in a stainless steel autoclave with glass liner tube that was heated in the oil-bath. Typically, 0.925 mmol lignocellulosic material was added into 3 mL [BMIM]Cl solvent that was preheated under vigorous stirring until a transparent solution was obtained (about 0.5 h), followed by the addition of the desired catalyst and H_2O at the reaction temperature. After the appointed reaction time, 0.2 mL samples were pipetted, quenched immediately with 0.3M NaOH solution and diluted with deionized water (×50). The solution was centrifuged at 10,000 rpm for 10 min and the upper clear liquid was pipetted off and diluted with deionized water (×6). The samples were analyzed using HPLC for HMF yield and UV detector for TRS analysis.

3. HMF Quantification Procedure[5]

The received reaction mixture (0.2 mL) was diluted with 10 mL of deionized water and the solution was centrifuged at 10,000 rpm for 10 min. Then 1.0 mL of the upper clear liquid was pipetted off and diluted with deionized water to 6.0 mL for analysis. HMF concentration was measured on a HPLC (Waters Alliance 2695 series chromatograph equipped with UV detector) at 283 nm using standard curve method (Fig. S2).

M_{HMF} was calculated as follows

M_{HMF} (mg) = HMF concentration (mg/mL) × V_{RM} × DF × 10^{-3}

In which,

V_{RM} is the volume of reaction mixture = 3.3 mL

DF is the dilution factor in dilution = (10 mL ÷ 0.2 mL) × 6 = 300

The yield of HMF was calculated from the equation

HMF Yield (%) = [M_{HMF} (mg) ÷ MW_{HMF}] ÷ [M_{CL} (mg) ÷ [MW_{GL} - MW_{WT}]] × 100%

In which,

M_{HMF} is the mass of HMF

M_{CL} is the mass of cellulose

MW_{HMF} is the molecular weight of HMF = 126.11

MW_{GL} is the molecular weight of glucose (monomer of cellulose) = 180.16

MW_{WT} is the molecular weight of water = 18.02

4. Total Reducing Sugar (TRS) analysis

100 mL deionized water were added into potassium sodium tartrate (91 g), 3, 5-dinitrosalicylic acid (DNS, 3.15 g) and 20 g NaOH. After dissolved at 45℃, phenol (2.5 g) and sodium sulfite (2.5 g) were added in the solution and stirred until homogeneous solution. Then the solution was cooled to room temperature and diluted with deionized water to 500 mL to give the DNS reagent.

A mixture of DNS regent (1.5 mL) and diluted reaction sample (1.0 mL) then diluted with deionized water (2.5 mL) was stayed at 100°C for 5 min and then cooled to room temperature. The resulting mixture was diluted to 15 mL with deionized water and absorbance of the mixture was measured by UV spectrophotomer (UV-1100) at 522 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose (Fig. 6).

The mass of TRS (M_{TRS}) and the yield of TRS were calculated as follows:

M_{TRS} (mg) = TRS concentration (mg/mL) × V_{RM} (mL) × DF × 10^{-3}

TRS Yield = [M_{TRS} ÷ MW_{GL}] ÷ [M_{CL} (mg) ÷ [MW_{GL} - MW_{WT}]] × 100%

In which,

V_{RM} =3.3 mL

DF is the dilution factor = 300

M_{CL} is the mass of cellulose

$MW_{GL} = 180.16$

$MW_{WT} = 18.02$

5. Definitions of Conversion and Selectivity[6]

Substrate Conversion = [1- (Amount of substrate) ÷ (Starting amount of substrate)] ×100%

Selectivity of HMF = (Yield of HMF / Substrate conversion) × 100%

6. References

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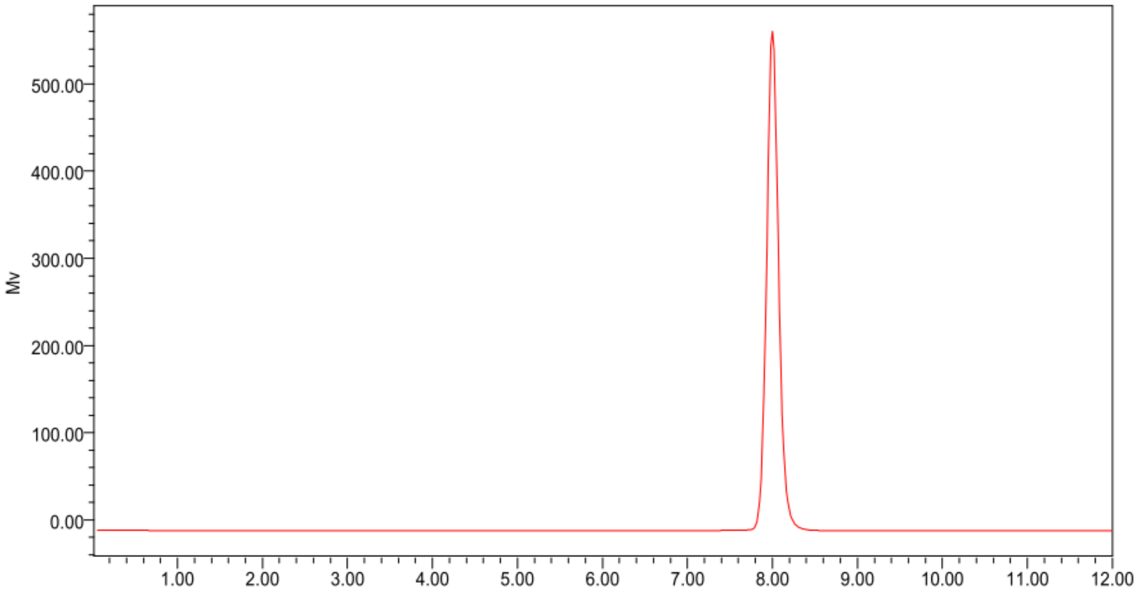
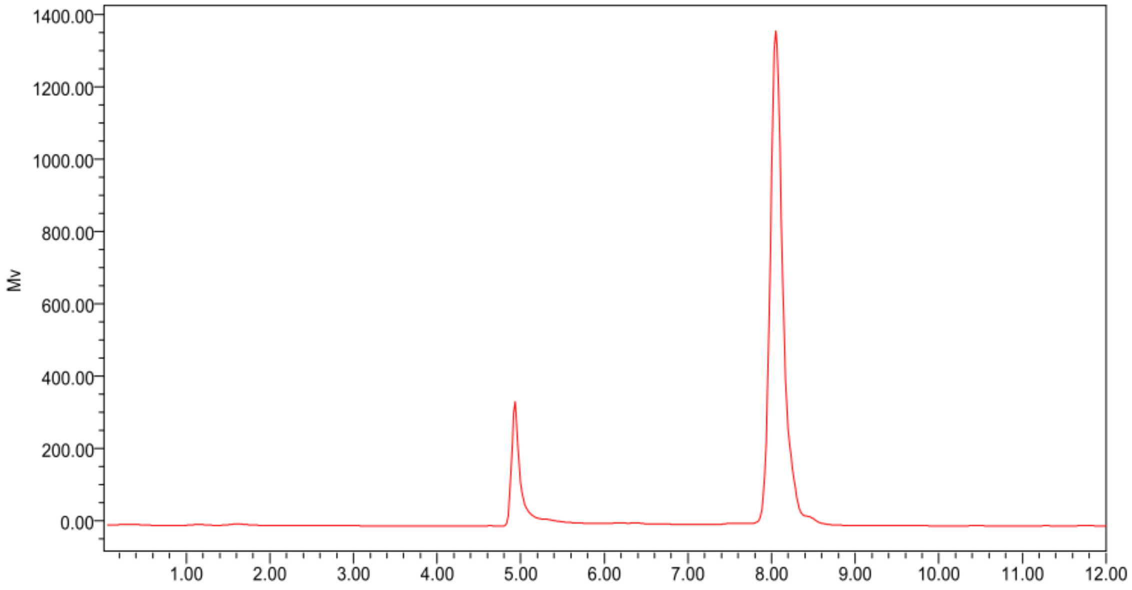
7. Figs for key Products

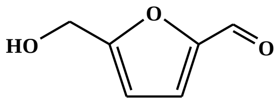


(a)



(b)

Fig. S1. HPCL chromatograms of (a) authentic sample of HMF and (b) representative reaction mixture of HMF synthesis from cellulose at 283 nm (C18 5 μm 250 × 4.6 mm, water/methanol (70 : 30, v/v), o.6 mL/min).



HMF

Chemical Formula: $C_6H_6O_3$ Molecular Weight: 126.11

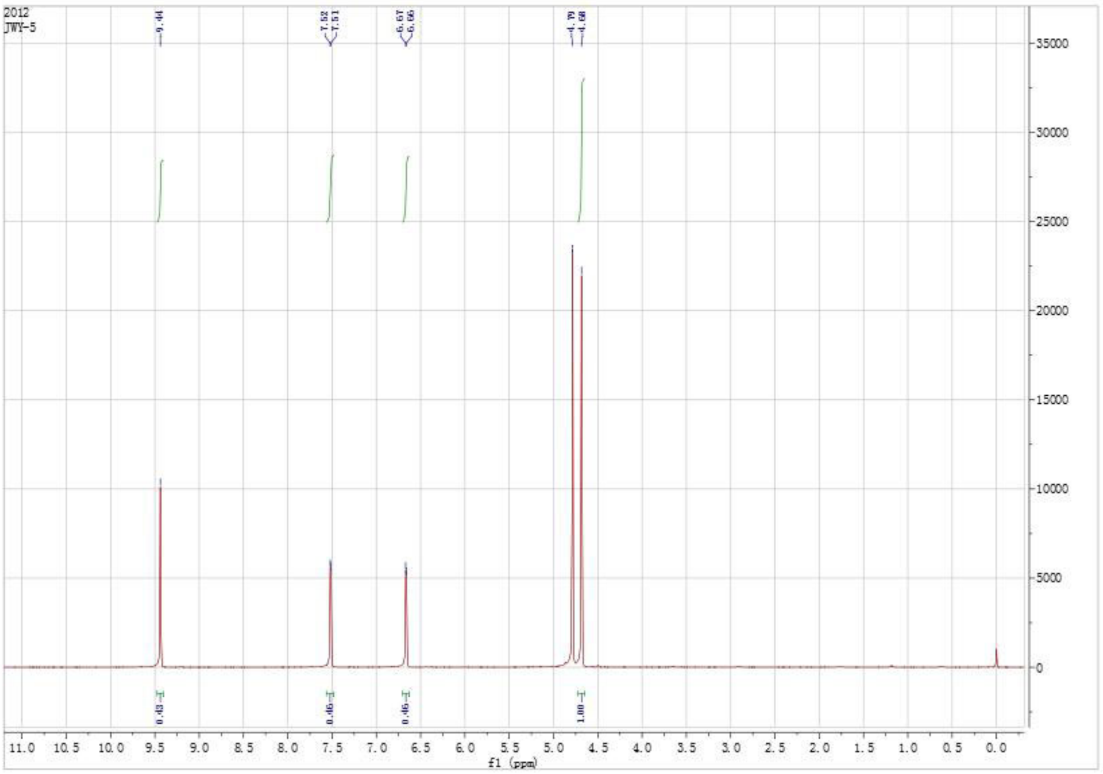


Fig. S2. ^{1}H NMR spectra of synthetic HMF.

^{1}H NMR (400 MHz, D_2O) δ 9.44 (1H, s, -C**H**O), 7.52 (1H, s, =CH-C**H**=), 6.66 (1H, d, =C**H**-CH=), 4.68 (2H, s, -C**H**$_2$-).

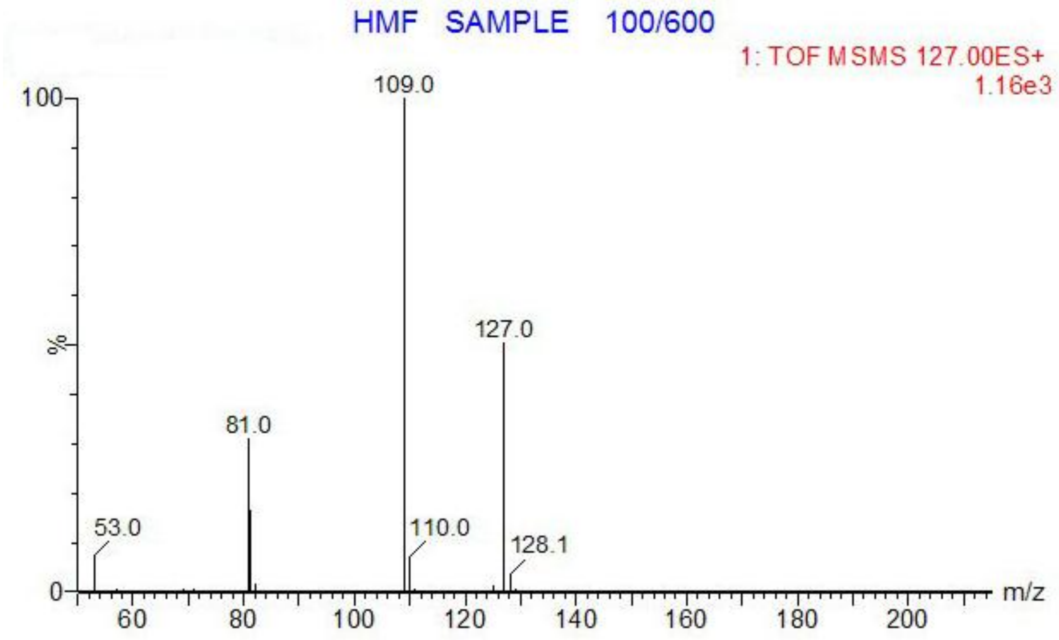


Fig. S3. LC-MS spectra of synthetic HMF.

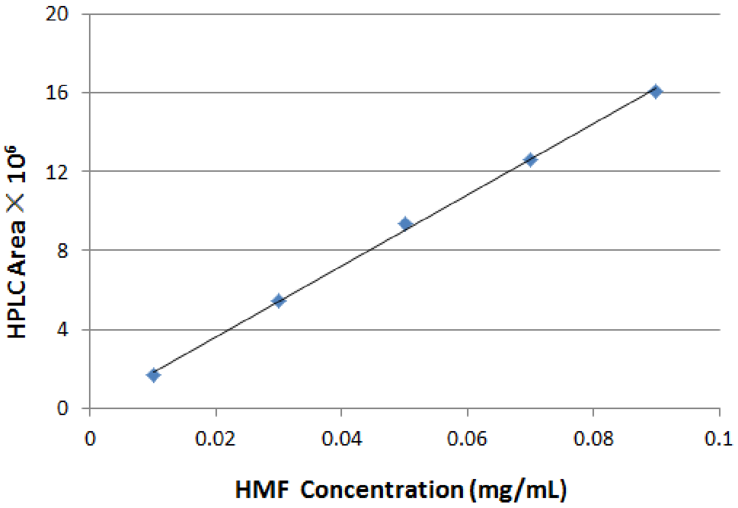


Fig. S4. Standard curve of authentic HMF in H_2O (HPLC area = 1.81 × 10^6 × HMF concentration (mg/mL), $R^2 = 0.9987$).

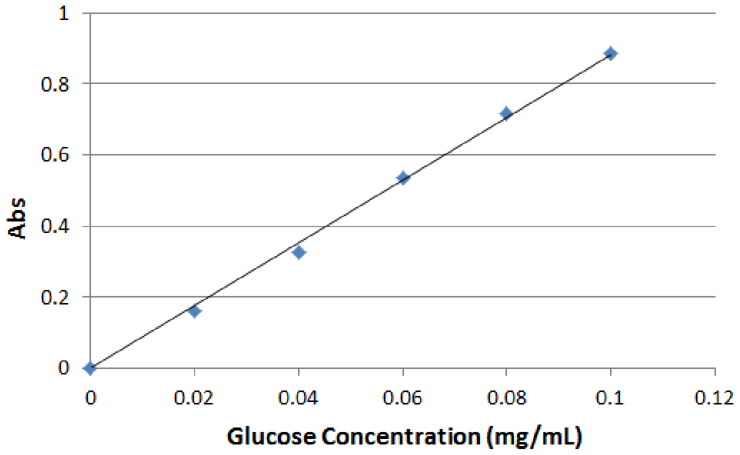


Fig. S5. Standard curve of Glucose in H_2O (UV absorbance = 8.823 × Glucose concentration (mg/mL), $R^2 = 0.9979$).