

## **Supporting information**

### **Catalytic upgrading of fructose into 5-HMF over reusable-biphasic process**

Panya Maneechakr\* and Surachai Karnjanakom\*

<sup>a</sup> Department of Chemistry, Faculty of Science, Rangsit University, Pathumthani 12000,  
Thailand

\*Corresponding author.

E-mail addresses: [panya.m@rsu.ac.th](mailto:panya.m@rsu.ac.th) (P. Maneechakr) and [surachai.ka@rsu.ac.th](mailto:surachai.ka@rsu.ac.th) (S. Karnjanakom)

## 1. Experimental

### 1.1. 5-HMF production from fructose

The one-pot conversion of fructose into 5-HMF catalyzed by deep eutectic solvent-biphasic system was carried out using 50 mL of glass tube reactor equipped with a thermocouple thermometer. In a typical synthesis, 1 g of fructose and 3.6 g of ChCl were mixed with 30 mL of acetonitrile (ACN). Then, 0.3 mmol of acid catalyst was added to mixture solution. The glass tube reactor containing of as-prepared mixture solution was steeped in oil bath and heated at 120 °C for 60 min with a stirring speed of 650 rpm. After finishing process, the reaction was suddenly quenched by soaking in an ice bath. During this process, biphasic system with in-situ extraction of 5-HMF was created as follows: (I) ChCl in liquid phase was newly recrystallized and plummeted in bottom layer, and (II) the synthesized 5-HMF was in the organic layer of ACN. The schematic diagram for recycling process is shown in Fig. S2.

To obtain the crude 5-HMF, ACN was firstly separated from 5-HMF using rotary evaporator at water bath temperature of 50 °C. Thereafter, 30 mL of butanone was added into 5-HMF and stirred at ambient temperature for 5 min. During this process, the remaining ChCl interacting with 5-HMF was easily separated and recrystallized, resulting from the reduction of organic polarity (Fig. S3). The recrystallized ChCl obtained from two-step separation process could be directly reused in next time. Finally, butanone was separated from 5-HMF using rotary evaporator at water bath temperature of 50 °C. The obtained crude 5-HMF was stored in the refrigerator for further application or analysis.

### 1.2. Recycling procedure

The spent ChCl crystal after reaction was washed with ACN or THF for several times in order to remove some organic products adsorbed on ChCl surface. Then, fructose was added into the catalytic phase and the reaction was carried out again under optimum conditions.

### 1.3. Purification of crude 5-HMF

Crude 5-HMF without any solvent extracts was purified by column chromatography. Silica gel with a size of ~60-120 mesh weighted about three times of crude 5-HMF was poured in 5-HMF solution in the existence of 5 mL of  $\text{CH}_2\text{Cl}_2/\text{EtOAc} = 10:3$  V/V. Then, the silica gel slurry was dried at 55 °C in an oven. The 5-HMF-adsorbed dry silica was loaded on top of silica gel column with an internal diameter and a length of 10 mm and 300 mm, respectively. The column was eluted by 10:3  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  mixture. To obtain purified 5-HMF, the fractions containing 5-HMF were corrected, and the solvent was removed out using rotary at water bath temperature of 60 °C (Fig. S4).

#### *1.4. Product analysis*

The 5-HMF and LA products were determined by an Agilent 1200 high performance liquid chromatography (HPLC) system, operating with an ultraviolet (UV) detector at 284 nm, analytical column at 30 °C and a mobile phase of water/methanol (0.8/0.2 (v/v)). The fructose conversion was determined by an Aminex HPX-87H column, operating with a Refractive Index (RI) detector and analytical column at 65 °C using 0.05 M  $\text{H}_2\text{SO}_4$  as a mobile phase at a flow rate of 0.55 ml/min. The concentrations of each chemical product (%mol) were calculated based on an external standard method. To confirm their reproducibility tests, each experiment was repeated at least 3 times under the same conditions. Fourier transform infrared (FT-IR) spectroscopy using a Perkin Elmer Spectrum 100 FT-IR was applied to analyze the functional groups of ChCl structure before and after reactions.

#### *1.5. Kinetic study*

To determine the activation energies and pre-exponential factors for 5-HMF production under deep eutectic solvent-biphasic system, we investigated the effects of reaction temperatures (70, 80, 90 and 100 °C) and reaction times (10, 20, 30, 40 and 50 min) on fructose conversion in to 5-HMF while other factors were kept constant. Here, the reaction rate of

sucrose conversion into 5-HMF (r[fructose]) could be provided in the following equation as a first order reaction  $\ln(C_A/C_{A0}) = -k't$  (1) and since  $C_A = C_{A0}(1-X)$  (2); then [40,41]:

$$-\ln(1 - X) = k't \quad (3)$$

where  $C_{A0}$ ,  $X$  and  $t$  are the initial concentration of sucrose, sucrose conversion into 5-HMF and reaction time, respectively. A plot of  $-\ln(1-X)$  versus  $t$  will be a straight line with a slope of ( $k'$ ).

In the case that  $n \neq 1$  with  $k'' = k'/C_{A0}$ , it could be provided as follows:

$$(1 - X)^{(1-n)} = 1 + (n - 1)k''C_{A0}^nt \quad (4)$$

To determine the activation energy with pre-exponential factor in our catalytic system, the Arrhenius model was used based on a relationship between the reaction rate constant ( $k'$ ), absolute temperature ( $T$ ) and activation energy ( $Ea$ ), and provided as follows:

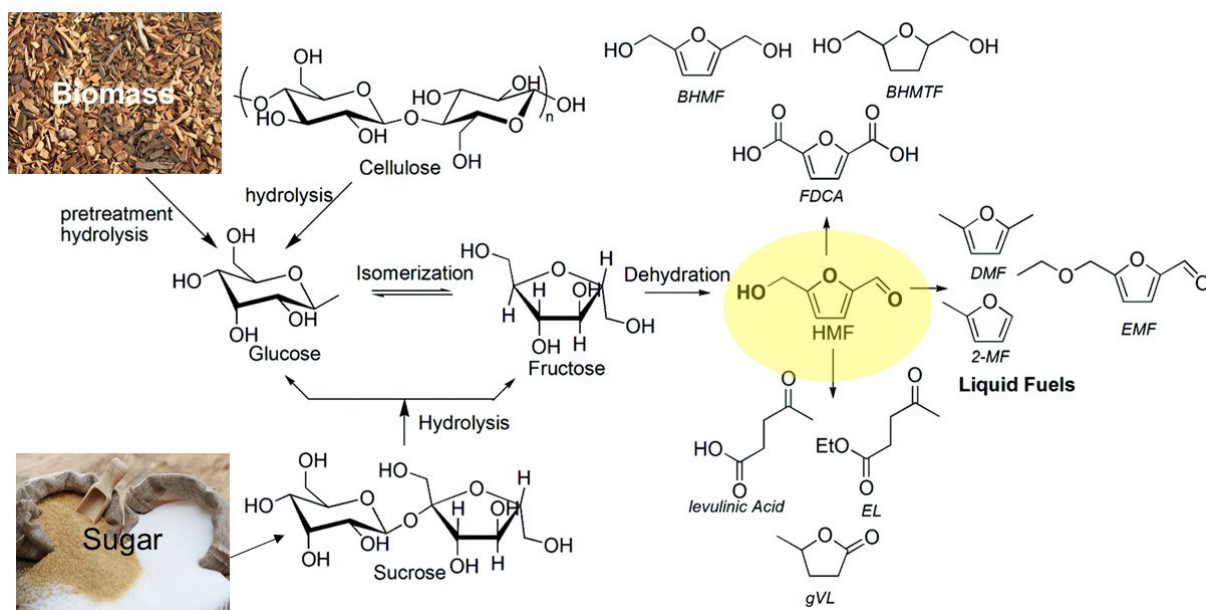
$$k' = A \exp \frac{-Ea}{RT} \quad (5)$$

Where  $Ea$  is the activation energy (kJ/mol),  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ),  $R$  is the universal gas constant (8.314 J/K.mol) and  $T$  is the reaction temperature (K).

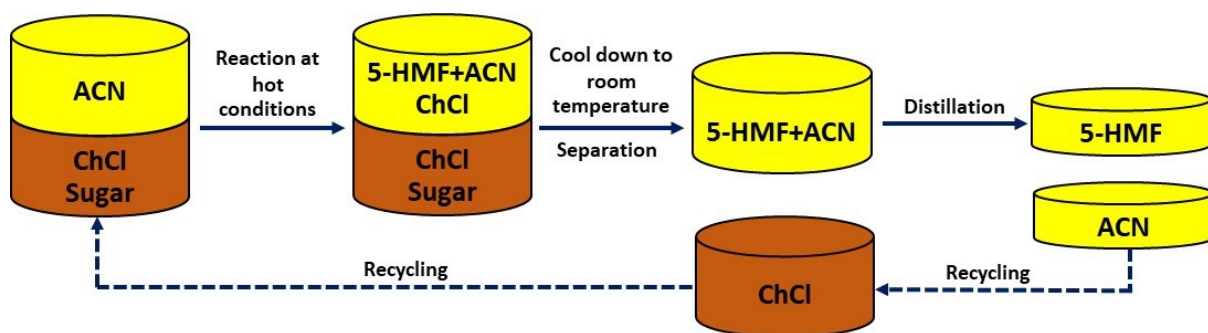
According to the Arrhenius equation, it could be rewritten in form of linear equation as:

$$\ln k' = -\frac{Ea}{RT} + \ln A \quad (6)$$

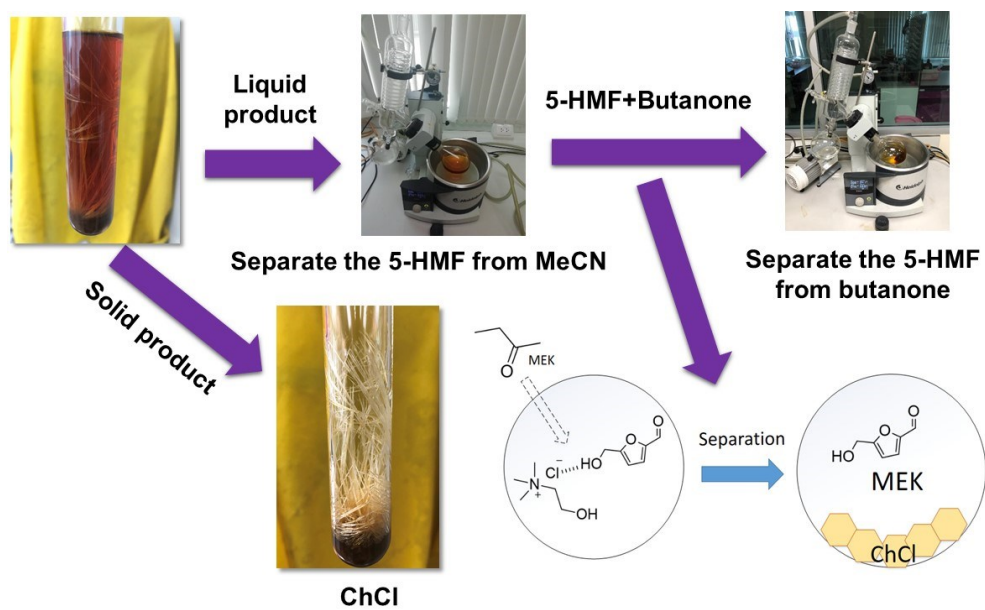
The activation energy and pre-exponential factor were determined from the slope and intercept of the Arrhenius plot, respectively.



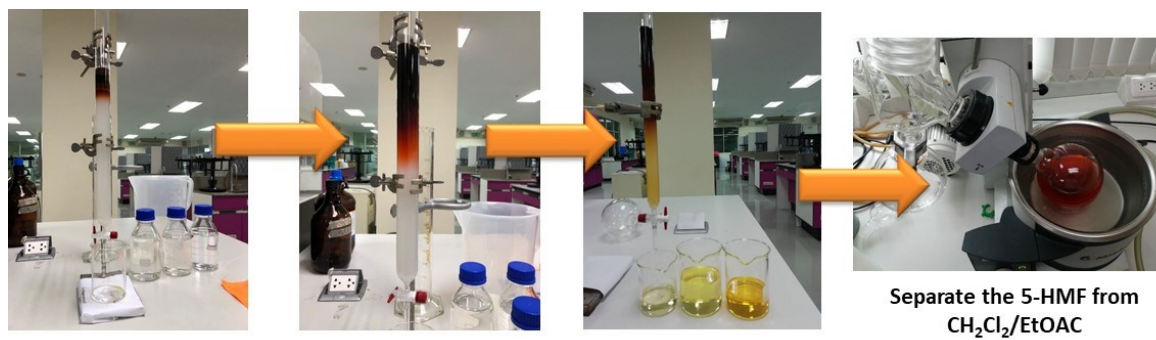
**Fig. S1.** Reaction pathways for transformations of biomass-based carbohydrates into high value platform chemicals.



**Fig. S2.** A schematic diagram for 5-HMF synthesis under deep eutectic solvent-biphasic system using recycling process.

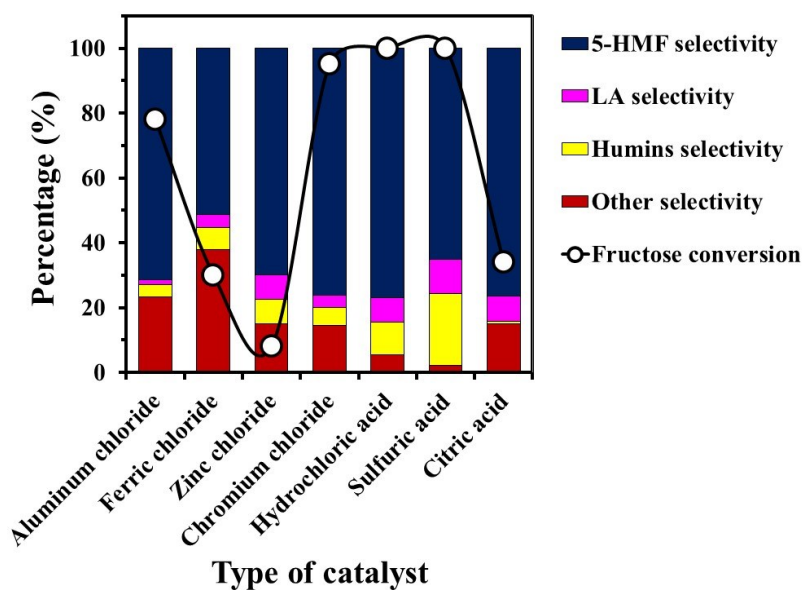


**Fig. S3.** Recrystallization and separation processes of ChCl during 5-HMF synthesis under deep eutectic solvent-biphasic system.

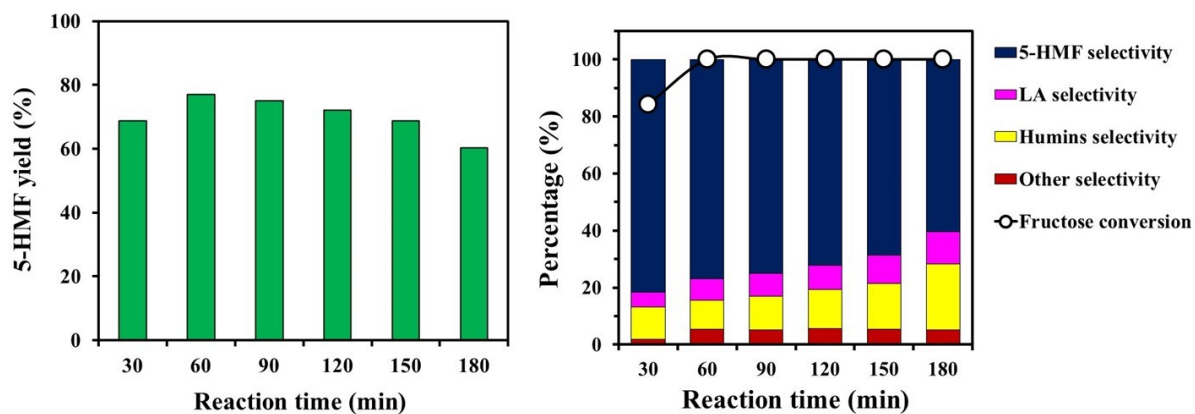


**Fig. S4.** Purification process of crude 5-HMF using column chromatography.

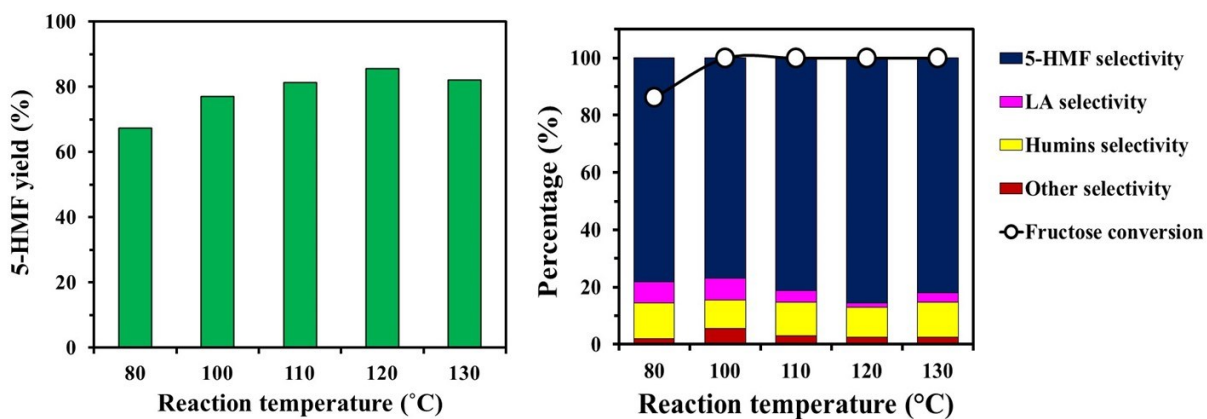




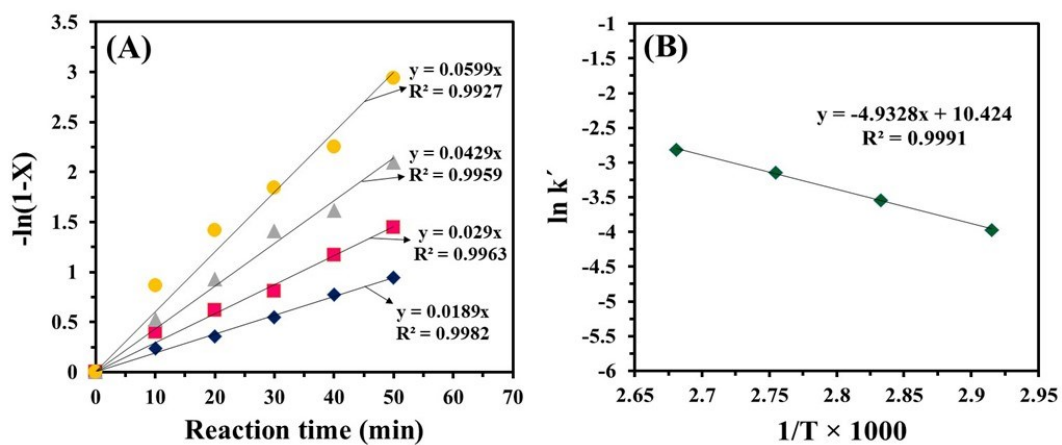
**Fig. S5.** Effect of various acid catalysts for product selectivity occurred from one-pot conversion of fructose into 5-HMF. Reaction conditions: fructose amount of 1 g, acid catalyst amount of 0.3 mmol, ChCl amount of 3.6 g, ACN amount of 30 mL, reaction time of 60 min and reaction temperature of 100 °C.



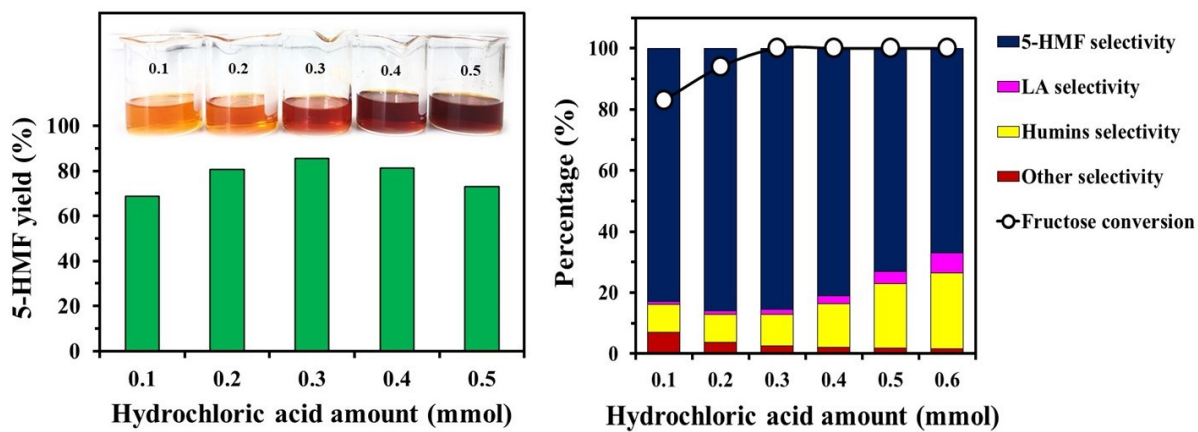
**Fig. S6.** Effect of reaction time for one-pot conversion of fructose into 5-HMF. Reaction conditions: fructose amount of 1 g, hydrochloric acid amount of 0.3 mmol, ChCl amount of 3.6 g, ACN amount of 30 mL and reaction temperature of 100 °C.



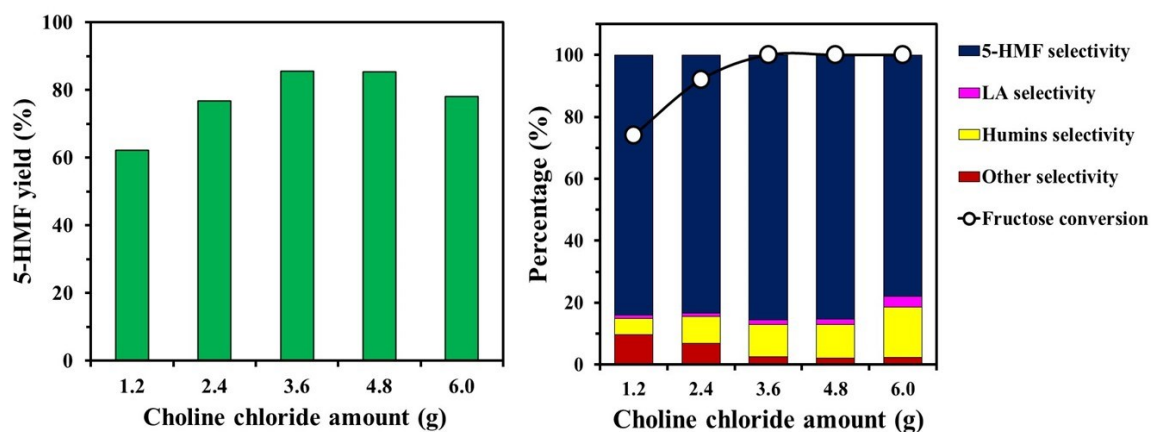
**Fig. S7.** Effect of reaction temperature for one-pot conversion of fructose into 5-HMF. Reaction conditions: fructose amount of 1 g, hydrochloric acid amount of 0.3 mmol, ChCl amount of 3.6 g, ACN amount of 30 mL and reaction time of 60 min.



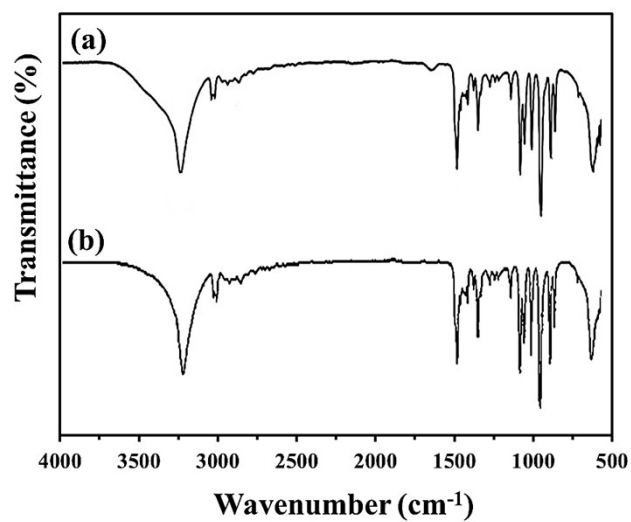
**Fig. S8** (A) Logarithms of fructose conversion into 5-HMF as a function of reaction time at 70-100 °C and (B) Arrhenius plots with reaction rate constants as a function of reaction temperature.



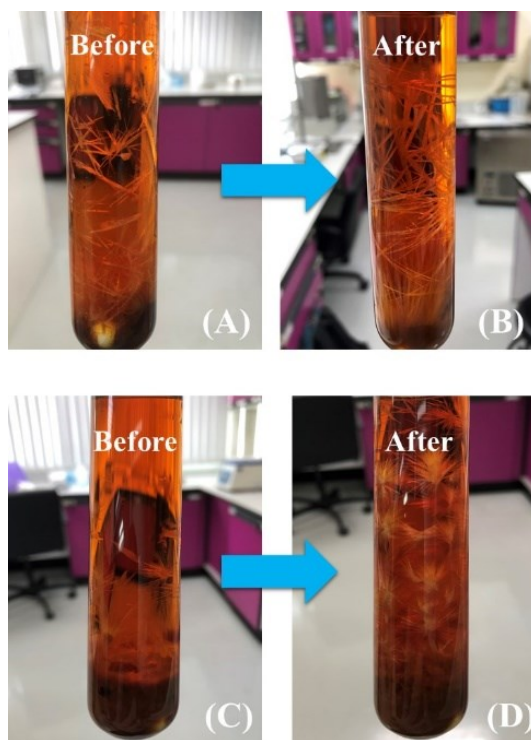
**Fig. S9.** Effect of hydrochloric acid amount for one-pot conversion of fructose into 5-HMF. Reaction conditions: fructose amount of 1 g, ChCl amount of 3.6 g, ACN amount of 30 mL, reaction time of 60 min and reaction temperature of 120 °C.



**Fig. S10.** Effect of ChCl amount for one-pot conversion of fructose into 5-HMF. Reaction conditions: fructose amount of 1 g, hydrochloric acid amount of 0.3 mmol, ACN amount of 30 mL, reaction time of 60 min and reaction temperature of 120 °C.

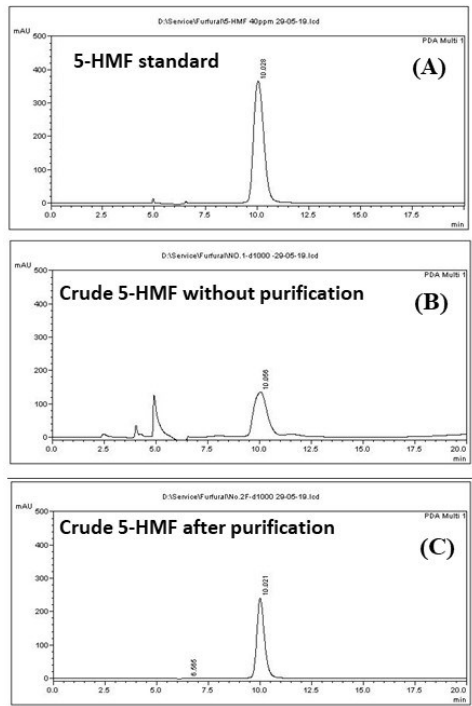


**Fig. S11.** FT-IR spectra of (a) fresh and (b) spent ChCl after reaction under deep eutectic solvent-biphasic system.



**Fig. S12.** Spent ChCl crystal in ACN (A) before and (B) after seeding process, with in THF (C) before and (D) after seeding process.





**Fig. S13.** HPLC chromatograms of 5-HMF chemicals.

**Table S1** Catalytic comparison of each acid catalyst for one-pot conversion of fructose into 5-HMF.

Entry	Catalyst	Solvent	Reaction conditions	5-HMF yield (%)	Ref.
1	CH <sub>3</sub> SO <sub>3</sub> H	[BMIM][Cl]	120 °C for 180 min	58.0	[55]
2	H <sub>2</sub> SO <sub>4</sub>	[BMIM][Cl]	120 °C for 120 min	33.2	[56]
3	H <sub>3</sub> PO <sub>4</sub>	Water	228 °C for 57 min	14.9	[57]
4	H <sub>3</sub> BO <sub>3</sub>	[EMIM][Cl]	120 °C for 180 min	41.0	[58]
5	HCl	Water-NaCl/1-Butanol	160 °C for 60 min	10.4	[59]
6	CrCl <sub>3</sub>	[BMIM][Cl]	100 °C for 120 min	75.3	[60]
7	Sm(Otf) <sub>3</sub>	DMSO	120 °C for 120 min	73.0	[61]
8	SnCl <sub>4</sub>	[EMIM][BF <sub>4</sub> ]	100 °C for 180 min	62.0	[62]
9	LiBr	Sulfolane	90 °C for 240 min	79.0	[63]
10	HCl/ChCl	ACN	120 °C for 60 min	85.6	This work