Supporting information for

Organic acid catalyzed production of platform chemical 5-hydroxymethylfurfural from fructose: process comparison and evaluation based on kinetic modeling

Muhammad Sajid [1,2,3], Yuchen Bai [1, 2], Dehua Liu [1, 2], Xuebing Zhao [1, 2, *]

[1] *Key Laboratory of Industrial Biocatalysis, Ministry of Education, Tsinghua University, Beijing 100084, China;*[2] *Institute of Applied Chemistry, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China;*[3] *Department of Chemical Engineering, University of Gujrat, Gujrat 50700, Pakistan,*

* Corresponding authors: Xuebing Zhao, Email: zhaoxb@mail.tsinghua.edu.cn

Figure S1. Possible reaction mechanisms of acid catalyzed dehydration of fructose to HMF and HMF rehydration to levulinic and formic acids (van Dam et al., 1986),(Pawar and Lali, 2014)

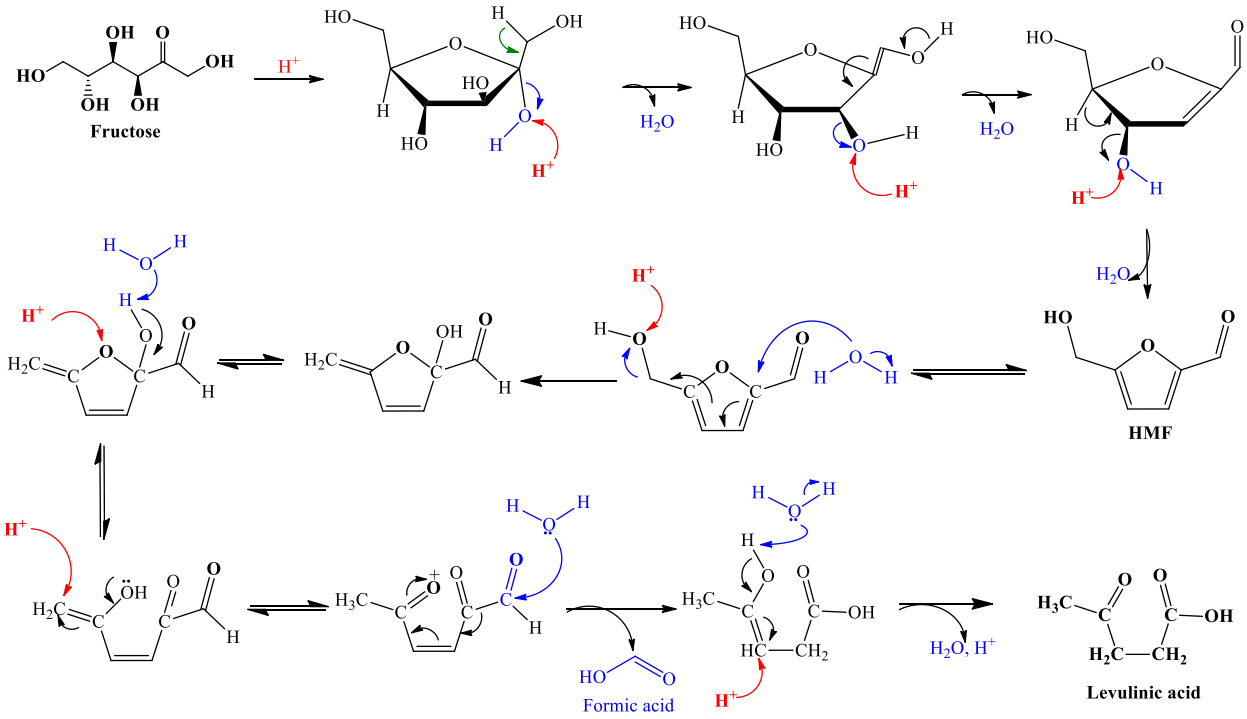

Figure S2. Dehydration of fructose to produce HMF under the catalysis of several organic acids in water medium. A: fructose conversion; B: HMF yield; C: levulinic acid yield. Reaction conditions: 1 M fructose and 1M catalysts in 50 ml of ultrapure water system heated in an oil bath at 100 ºC and stirred at 200 rpm for 12 hours.

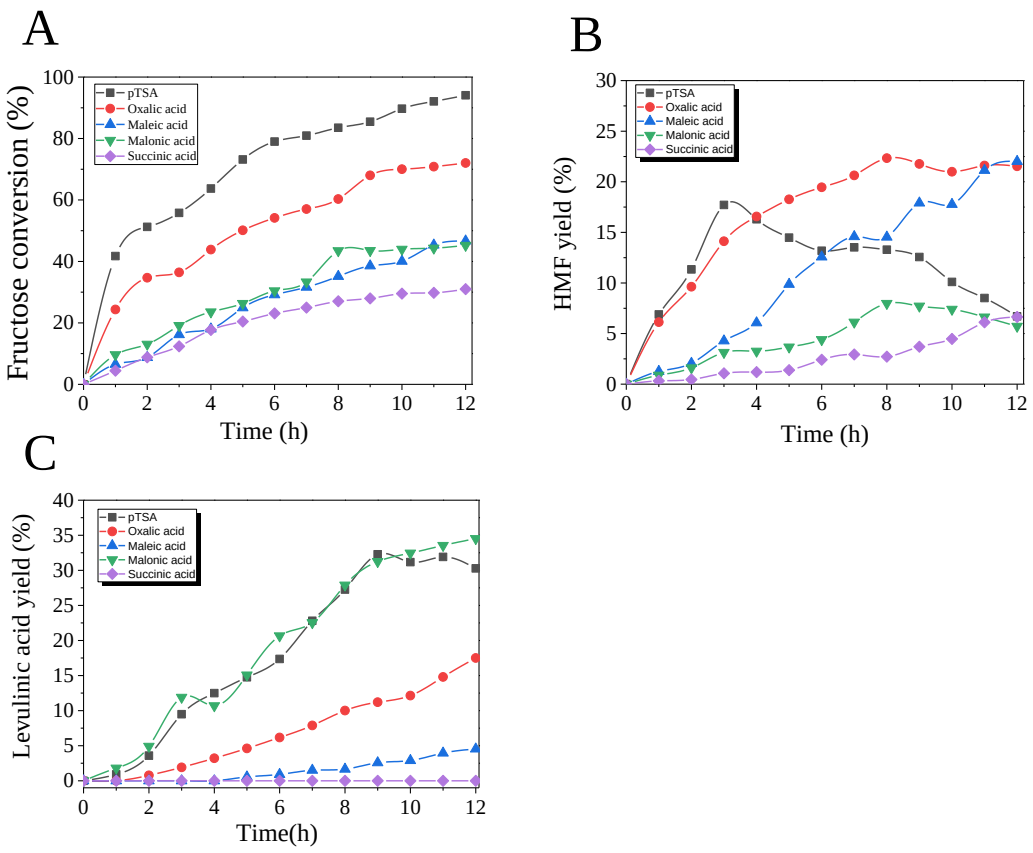

Figure S3. Effect of initial fructose concentration on fructose dehydration to HMF in the DMSO medium. Reaction conditions: 0.5- 2 M fructose with 1 M acid catalyst heated at 120 ºC at a stirring speed of 200 rpm. (A): 1 M *p*TSA as the catalyst for half-hour; (B): 1 M oxalic acid as the catalyst for 2 hours.

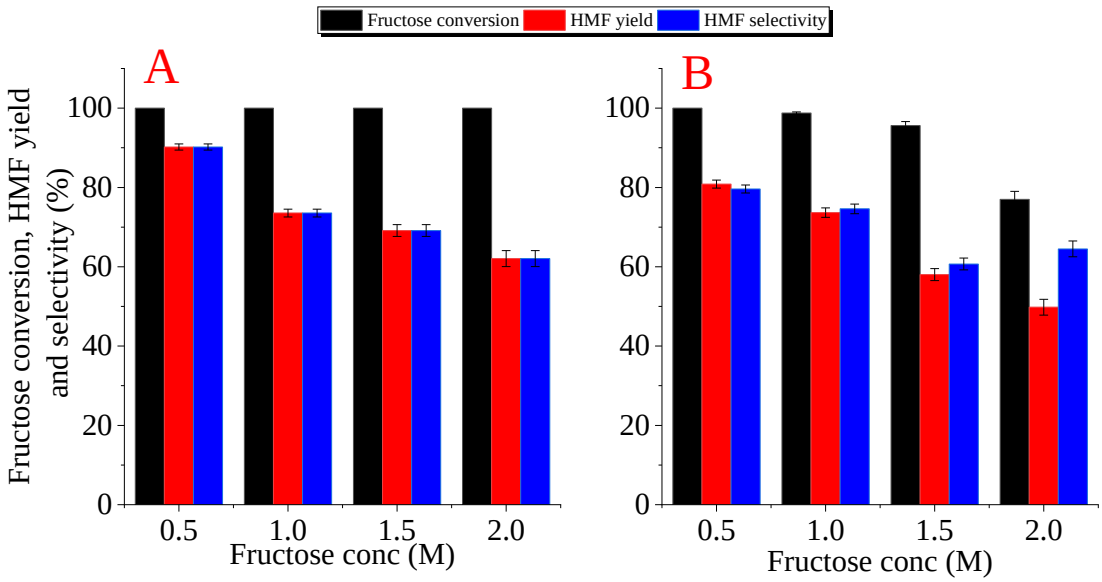

Table S1. Comparison of oxalic acid and pTSA-catalyzed conversion of fructose to HMF in different solvent medium. Reaction conditions: 1 M acid catalyst and with 1 M fructose in 50 ml solvent heated in oil bath for certain time with a stirring speed of 200 rpm; the flask was heated in oil bath at 100 ^{o}C for water medium, at 110 ^{o}C for DMSO, DMF and IPA medium, and at 120 ^{o}C for PEG-400, PEG-1000 and PEG-2000 medium.

Solvent	Catalyst	Time (hour)	Fructose conversion (X_F %)	HMF yield (Y_{HMF} %)	Levulinic acid yield (Y_{LA} %)	Formic acid yield (Y_{FA} %)	HMF Selectivity (S_{HMF} %)
Water	Oxalic acid	8	60.3±2	23.3±1.0	10.01	9.04	37.04
DMF	Oxalic acid	4	49.93±1.5	16.3±1.0	1.25	0.881	32.65
DMSO	Oxalic acid	7	99.37±0.5	79.8±0.5	3	2.6	80.28
IPA	Oxalic acid	6	39.31±2.5	9.05±0.8	0	0	23.04
PEG-400	Oxalic acid	2	46.61±2	45.8±1.1	0	0	98.15
PEG-1000	Oxalic acid	7	98.59±1	40.7±1.2	0	0	41.3
PEG-2000	Oxalic acid	6	100	42.9±0.9	0	0	42.93
Water	pTSA	3	50.77±2	17.7±2.0	9.49	7.79	34.89
DMSO	pTSA	1	100	79.03±1.0	0	0	79.03
IPA	pTSA	2	94.96±1.8	36.1±0.8	0	0	38.05

Table S2. Comparison of the activation energy for acid-catalyzed conversion of fructose to HMF in different solvent systems

Catalyst	Solvent	Temperature °C	Activation Energy (kJ/mol)				Ref.,
			E_{a1}	E_{a2}	E_{a3}	E_{a4}	
Oxalic acid	DMSO	100 - 140	96.51	78.39	-	-	This work
pTSA	DMSO	100 - 140	33.75	24.94	-	-	This work
HCl-KCl pH = 1.1	water	74 - 147	126	135	97	62	(Swift et al., 2014)
	water	75	115	-	-	-	
	water	150	136	-	-	-	
HCl pH = 1.8	Sub critical water	210 - 270, 40 Bar	160.6	101.9	97.2	108	(Asghari and Yoshida, 2007)
Bronsted Acid* pH = 1.8	Water	210 - 270	159.1	24.65	23.26	31.51	(Nikbin et al., 2012)
Formic acid	Water	180 - 220, 100 bar	112	-	-	-	(Li et al., 2009)
Acetic acid	Water	180 - 220, 100 bar	125	-	-	-	
H_2SO_4	Water	140 – 180	123	148	92	119	(Fachri et al., 2015)
H_2SO_4	[HMIM]Cl	90 - 120	143	-	69	-	(Moreau et al., 2006)
H_2SO_4	Water-acetone	180 - 300, 200 bar	99	-	-	-	(Bicker et al., 2003)
$NbOPO_4$	Water	90 - 110	65.8	-	-	-	(Carniti et al., 2006)
$IrCl_3$	[BMIM]Cl	80 - 100	165	124			(Wei et al., 2011)
Dowex50wx8-100	Water-acetone	100 - 180	103.4				(Qi et al., 2008a)
Dowex50wx8-100	DMSO-acetone	100 - 180	60.4				(Qi et al., 2008b)
Activated carbon	Water	160 – 220 50 bar	135				(Sairanen et al., 2014)

*Simulation study

Table S3 Comparison of reported results on HMF production from fructose.

Fructose conc. (mol/L)	Solvent	Catalyst	Temp (°C)	Reaction time (h)	Conversion (%)	HMF Yield (M %)	Ref.
0.5	Water–PEG 4000 (50:50 v/v)	pTSA 1 M	88	5	97	45.6	(van Dam et al., 1986)
0.05	Subcritical water	Oxalic acid pH = 1.5	240	2 min	94.12	18.20	(Yoshida, 2006)
0.05	Subcritical water	pTSA pH = 2	240	2 min	99.72	37.01	(Yoshida, 2006)
0.28	THF–DMSO (70:30 v/v) 10 ml	Glucose-TsOH 2.5 Wt. %	160	1	99	98	(Wang et al., 2013)
0.46	DMSO 6 ml	Glucose-TsOH 5.6 wt. %	130	1.5	99.9	91.2	(Wang et al., 2011)
0.14	Water-DMSO (1:3 g/g) 40 g	MeSAPO-11 0.1 g	170	2.5	ND	65.1	(Sun et al., 2018)
0.5	DMSO 50 ml	pTSA 1 M	120	0.5	100	90.2 ±0.6	This work
1.0	DMSO 50 ml	pTSA 1.5 M	110	1.5	100	85.8 ±0.8	This work
0.5	DMSO 50 ml	Oxalic acid 1 M	120	2	100	80.9 ±0.7	This work
1.0	DMSO 50 ml	Oxalic acid 0.5 M	130	2	100	84.1 ±0.8	This work

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