

Supporting Information

Insights into the Kinetics and Reaction Network of Aluminum Chloride-Catalyzed Conversion of Glucose in NaCl-H₂O/THF Biphasic System

*Jinqiang Tang, Liangfang Zhu, * Xing Fu, Jinhang Dai, Xiawei Guo, and Changwei Hu**

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry,
Sichuan University, Chengdu, Sichuan 610064, P. R. China.

*Corresponding author, E-mail: changwei.hu@scu.edu.cn and zhul.f@scu.edu.cn. Tel / Fax: (+86)
028-85411105.

Experimental Section

ESI-MS.

ESI-MS were collected in continuum mode. A Micromass Quattro Micro mass (Waters) was used with the following operating parameters: capillary voltage, 2.8 kV; extractor voltage, 5 V; sample cone voltage, 20 V; source temperature, 363 K; desolvation temperature, 423 K; cone gas (N₂) flow, 40 L·h⁻¹. The data acquisition and analyses were performed using Masslynx v 4.1 software (Waters).

To study the promotion role of THF on generating FA directly from glucose, the mixture of glucose and H₂O-THF in the absence of AlCl₃ was heated at 413 K for 30 min, followed by being quenched with cold water and analyzed by ESI-MS. In contrast, the reaction mixture after reacting glucose in the presence of AlCl₃ in water or H₂O-THF at 413 K for 30 min was also analyzed by ESI-MS. Correspondingly, the promotion role of THF on generating FA directly from fructose was studied by analyzing the ESI-MS spectra of the reaction mixture after reacting fructose in the absence or presence of AlCl₃ in water or H₂O-THF.

ATR-IR Spectrometry.

The ReactIR iC10 system (Mettler Toledo) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector was used for the acquisition of mid-IR spectra with time. Measurements were taken optically using a DiComp TM immersion probe and ZnSe as an ATR crystal. The instrument was computer-controlled using software iC IR Version 4.1.882 (Mettler Toledo) for data acquisition. During the entire process, high purity nitrogen at a flow rate of 2.5 L·min⁻¹ was supplied continuously to ensure the light path clean, and each spectrum represented 256 co-added scans measured every minute at a resolution of 4 cm⁻¹ in the range of 1950~650 cm⁻¹ with the Happ-Genzel apodization method. Reaction profiles were generated from those data by taking peak heights and given as absorbance units relative to zero.

Reaction Rate Equations for the Estimation of k Value.

The conversion of HMF, fructose, and glucose in water, H₂O-THF, and NaCl-H₂O/THF could be considered as pseudo-first order reaction (Figure S1). According to the reaction network proposed in Scheme 1, the reaction rate equations in water and H₂O-THF solvents are established as eqs. (S1)~(S5).

$$\frac{d[\text{Glc}]}{dt} = k_{-1}[\text{Fru}] - (k_1 + k_2 + k_3)[\text{Glc}] \quad (\text{S1})$$

$$\frac{d[\text{Fru}]}{dt} = k_1[\text{Glc}] - (k_{-1} + k_4 + k_5 + k_6)[\text{Fru}] \quad (\text{S2})$$

$$\frac{d[\text{HMF}]}{dt} = k_4[\text{Fru}] - (k_7 + k_8 + k_9)[\text{HMF}] \quad (\text{S3})$$

$$\frac{d[\text{FA}]}{dt} = k_2[\text{Glc}] + k_5[\text{Fru}] + (k_7 + k_8)[\text{HMF}] \quad (\text{S4})$$

$$\frac{d[\text{LA}]}{dt} = k_9[\text{HMF}] \quad (\text{S5})$$

In NaCl-H₂O/THF biphasic solvent, the reaction rate equations are described as eqs. (S1), (S2), and eqs. (S6)~(S9).

$$\frac{d[\text{HMF}]_{aq}}{dt} = k_4[\text{Fru}] + k_{-10}[\text{HMF}]_{org} - (k_7 + k_8 + k_9 + k_{10})[\text{HMF}]_{aq} \quad (\text{S6})$$

$$\frac{d[\text{HMF}]_{org}}{dt} = k_{10}[\text{HMF}]_{aq} - k_{-10}[\text{HMF}]_{org} \quad (\text{S7})$$

$$\frac{d[\text{FA}]}{dt} = k_2[\text{Glc}] + k_5[\text{Fru}] + (k_7 + k_8)[\text{HMF}]_{aq} \quad (\text{S8})$$

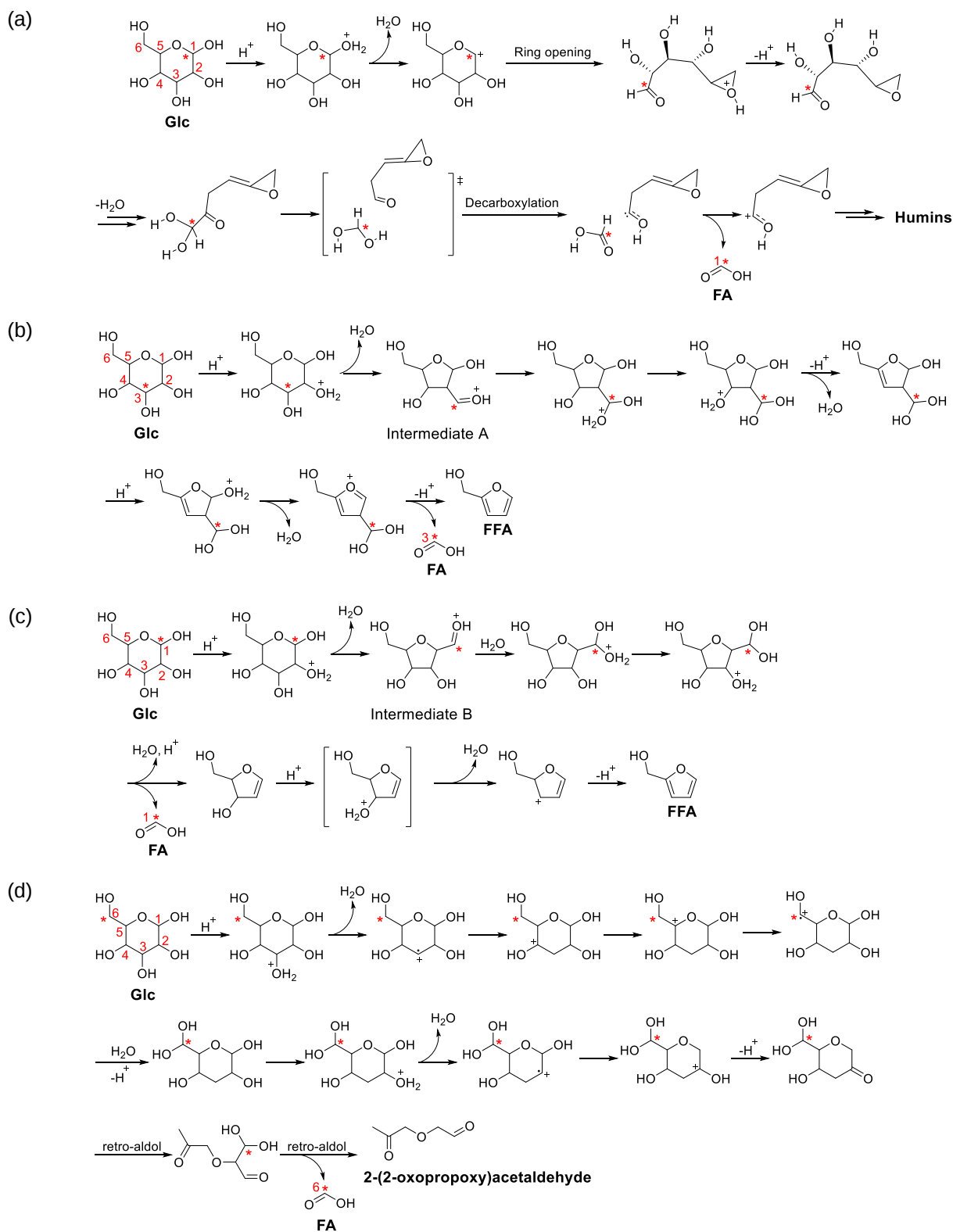
$$\frac{d[\text{LA}]}{dt} = k_9[\text{HMF}]_{aq} \quad (\text{S9})$$

The rates of mass transfer were assumed to be much higher than the rate of HMF formation as well as other reactions, that is, $k_{10}, k_{-10} \gg k_i$.

The kinetic models for the overall reaction pathways of the glucose conversion in NaCl-H₂O/THF, H₂O-THF, and water were a set of coupled nonlinear ordinary differential equations (ODEs). The kinetics parameters (reaction rate constant, k) of these reactions were determined by processing the experimental data (reactant/product concentrations) with the *lsqnonlin* nonlinear fitting function of MATLAB, which utilizes a trust-region-reflective algorithm to perform local minimization. An initial guess of k values was required to input into MATLAB to attain the best fitted curve. The sensitivity measurement for each k was carried out by recording the variations in the maximum of glucose

conversion and yields of HMF, FA, and LA as a result of changing these k values by $\pm 10\%$.¹ The standard error bar in these constants was determined by the sum of squares for error (SSE), which was computed by summing the squares of the prediction errors (*i.e.*, residues, the differences between the predicted and experimental concentrations) for each fitting. The normality of residues was tested at a significance level of 0.05. The statistical significance of kinetics constants was analyzed by Kolmogorov-Smirnov test between experimental data and predicted results.² The apparent activation energy (E_a) of each reaction was estimated by plotting $\ln k$ versus $1/T$ through Arrhenius equation (eq (S10)).

$$k = Ae^{-E_a/RT} \quad \text{S(10)}$$



Scheme S1. Possible mechanisms for the Brønsted acid-catalyzed glucose conversion *via* protonation of (a) O1H, (b, c) O2H, and (d) O3H in glucose to FA. (Reference to *J. Catal.* 2012, 295, 122–132 and *ChemSusChem* 2015, 8, 1334–1341)^{3,4}

Table S1. Product Distribution and Carbon Balance for the AlCl₃-catalyzed Conversion of Glucose in Different Solvents^a

Entry	Solvent	X_{Glc} (%)	Y_{Fru} (%)	Y_{HMF} (%)	Y_{FA} (%)	Y_{LA} (%)	Carbon balance (%)	TOF (h ⁻¹)
1	NaCl-H ₂ O/THF	79.1	16.0	27.9 ^b	33.8	11.0	79.5	2.6
2	H ₂ O-THF	82.1	26.0	14.5	28.5	3.6	67.5	2.7
3	H ₂ O	74.6	24.5	12.3	19.8	16.2	79.1	2.5

^aReaction conditions: 1.0 mL H₂O, 0.25 M Glc, 25.0 mM AlCl₃, 413 K, 3 h. In NaCl-H₂O/THF biphasic solvent, NaCl is saturated in aqueous solution. $V(\text{H}_2\text{O}): V(\text{THF}) = 1:3$. ^bTotal yield of HMF in aqueous phase (2.5%) and THF phase (25.4%). Small amounts of lactic acid (< 1%) and furfural (< 1%) were also detected.

Table S2. The ratios of measured rate constants for parallel reactions

Entry	Solvent	Ratios of rate constants		
		$k'_1 : k_2 : k_3$	$k_4 : k_5 : k_6$	$k_7 : k_8 : k_9$
1	H ₂ O	12:1.2:1	2.3:0.3:1	0.6:1.8:1
2	HO-THF	8:6.8:1	2.6:2.4:1	40:600:1
3	NaCl-H ₂ O/THF	966.7:966.7:1	4.0:1.6:1	70:600:1

Table S3. The ratios of given rate constants measured in different solvents^a

Ratios of rate constants								
k'_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9
0.6:0.8:	5.8:6.8:	0.008:1.3:	1.9:0.7:	6.5:6:	1.1:0.7:	0.08:0.04:	0.2:0.2:	0.0007:0.0007:
1	1	1	1	1	1	1	1	1

^a $k(\text{NaCl-H}_2\text{O/THF}) : k(\text{H}_2\text{O-THF}) : k(\text{H}_2\text{O})$.

The results show that the values of $(k'_1 : k_2 : k_3)$, $(k_4 : k_5 : k_6)$, and $(k_7 : k_8 : k_9)$, respectively, representing the reactivity of glucose, fructose, and HMF to corresponding desired and undesired products, vary significantly with changing solvent composition. Moreover, the ratios of given rate constants in different solvents are also various. That is, the ratios of these rate constants are very sensitive to solvent compositions.

Table S4. Conversion of glucose, fructose, and HMF in water or NaCl-H₂O/THF in the absence of AlCl₃^a

Entry	Solvent	Substrate	X_{Glc} (%)	Y_{Fru} (%)	Y_{HMF} (%)	Y_{FA} (%)	Y_{LA} (%)	Carbon balance (%)
1	NaCl-H ₂ O/THF	HMF	-	-	22.3 ^b	34.8	2.6	85.6
2	H ₂ O	HMF	-	-	33.0 ^b	32.9	14.1	84.2
3	NaCl-H ₂ O/THF	Fru	1.3 ^c	34.9 ^d	10.8 ^e	57.0	1.1	87.7
4	H ₂ O	Fru	0.4 ^c	35.8 ^d	12.2	17.0	1.8	81.0
5	NaCl-H ₂ O/THF	Glc	12.7	3.7	1.7 ^f	39.9	n.d. ^g	99.3
6	H ₂ O	Glc	9.0	2.3	0.2	7.5	0.5	95.2

^aReaction conditions: 1.0 mL H₂O, 0.25 M Glc/0.25 M Fru/0.2758 M HMF, 413 K, 4 h. In NaCl-H₂O/THF biphasic solvent, NaCl is saturated in aqueous solution, $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$.

^bConversion of HMF. ^cYield of glucose. ^dConversion of fructose. ^eTotal yield of HMF in aqueous phase (1.0%) and THF phase (9.8%). ^fTotal yield of HMF in aqueous phase (0.2%) and THF phase (1.5%). ^gNot detected.

Table S5. Statistical Significance Analysis and the Standard Error for Kinetics Parameters Determined

Entry	Solvent	T (K)	h^a					SSE^b (10^{-3})
			Glc	Fru	FA	LA	HMF	
1	H ₂ O	413	0	0	0	0	0	3.3
2	H ₂ O-THF	413	0	0	0	1	0	3.7
3	NaCl-H ₂ O/THF	413	0	0	0	0	0	4.6
4	NaCl-H ₂ O/THF	403	0	0	0	1	0	2.7
5	NaCl-H ₂ O/THF	423	0	0	0	0	0	3.8
6	NaCl-H ₂ O/THF	433	0	0	0	1	0	13.0

^a h is the value from Kolmogorov-Smirnov test, of which 0 represents no significance difference, whereas 1 represents the existence of significance difference. ^b SSE represents the sum of square for error, which is used to express the standard error.

Table S6. Sensitivity Measurements of the Rate Constants in H₂O or H₂O-THF co-solvent

Change in k	Change in $X(\text{Glc})$ (%)		Change in $Y(\text{Fru})$ (%)		Change in $Y(\text{HMF})$ (%)		Change in $Y(\text{FA})$ (%)		Change in $Y(\text{LA})$ (%)	
	H ₂ O	H ₂ O-THF	H ₂ O	H ₂ O-THF	H ₂ O	H ₂ O-THF	H ₂ O	H ₂ O-THF	H ₂ O	H ₂ O-THF
+10% k_1	+14.47	+11.83	+5.46	+6.78	+3.53	+4.88	+2.15	-0.87	+4.93	+6.05
-10% k_1	-17.71	-14.15	-6.07	-7.26	-4.16	-5.43	-2.40	+0.95	-5.48	-6.54
+10% k_{-1}	-4.92	-5.26	-1.06	-1.10	-1.03	-1.28	-0.43	+0.17	-0.94	-1.14
-10% k_{-1}	+5.01	+5.41	+1.07	+1.12	+1.05	+1.31	+0.44	-0.18	+0.96	+1.17
+10% k_2	+1.49	+9.24	-0.31	-1.54	-0.49	-2.80	+1.90	+3.01	-0.37	-2.05
-10% k_2	-1.51	-10.27	+0.32	+1.57	+0.49	+2.94	-1.92	-3.23	+0.38	+2.13
+10% k_3	+1.19	+1.42	-0.25	-0.23	-0.39	-0.42	-0.34	-0.43	-0.30	-0.31
-10% k_3	-1.21	-1.44	+0.25	+0.23	+0.40	+0.42	+0.34	+0.43	+0.30	+0.31
+10% k_4	+3.02	+2.78	-2.96	-1.71	+5.29	+6.72	+2.99	-0.78	+6.33	+7.56
-10% k_4	-3.30	-2.98	+3.09	+1.75	-5.87	-7.17	-3.23	+0.82	-6.81	-7.92
+10% k_5	+0.36	+2.57	-0.34	-1.58	-0.50	-2.76	+1.35	+2.15	-0.39	-2.05
-10% k_5	-0.36	-2.74	+0.34	+1.61	+0.50	+2.90	-1.36	-2.28	+0.39	+2.13
+10% k_6	+1.34	+1.09	-1.30	-0.66	-1.89	-1.17	-1.23	-0.51	-1.47	-0.86
-10% k_6	-1.40	-1.12	+1.32	+0.67	+1.95	+1.19	+1.26	+0.52	+1.51	+0.88
+10% k_7	-	-	-	-	-1.05	-0.33	+1.01	+0.11	+9.14	+9.78
-10% k_7	-	-	-	-	+1.07	+0.34	-1.03	-0.11	-9.29	-9.82
+10% k_8	-	-	-	-	-3.11	-1.18	+2.99	+0.38	-2.32	-0.69
-10% k_8	-	-	-	-	+3.26	+1.19	-3.15	-0.38	+2.41	+0.70
+10% k_9	-	-	-	-	-1.75	0	-0.78	0	-1.30	0
-10% k_9	-	-	-	-	+1.79	0	+0.80	0	+1.33	0

Table S7. Sensitivity Measurements of the Rate Constants in NaCl-H₂O/THF biphasic solvent^a

Change in k	Change in $X(\text{Glc})$ (%)				Change in $Y(\text{Fru})$ (%)				Change in $Y(\text{HMF})$ (%)				Change in $Y(\text{FA})$ (%)				Change in $Y(\text{LA})$ (%)			
	T_1	T_2	T_3	T_4	T_1	T_2	T_3	T_4	T_1	T_2	T_3	T_4	T_1	T_2	T_3	T_4	T_1	T_2	T_3	T_4
+10% k_1	+11.50	+13.98	+14.42	+14.16	+7.63	+7.24	+7.63	+7.30	+5.27	+5.32	+5.19	+5.09	-0.32	-0.74	-0.65	-0.61	+6.72	+6.31	+6.28	+6.22
-10% k_1	-13.18	-16.45	-17.02	-16.63	-8.00	-7.67	-8.00	-7.70	-5.84	-5.89	-5.77	-5.66	+0.32	+0.79	+0.69	+0.65	-7.17	-6.79	-6.77	-6.69
+10% k_{-1}	-2.63	-2.31	-2.03	-1.77	-1.02	-0.71	-0.57	-0.55	-1.04	-0.69	-0.58	-0.53	+0.03	+0.07	+0.06	+0.05	-0.99	-0.65	-0.56	-0.51
-10% k_{-1}	+2.69	+2.34	+2.05	+1.78	+1.03	+0.72	+0.57	+0.56	+1.06	+0.70	+0.59	+0.53	-0.03	-0.07	-0.06	-0.05	+1.01	+0.66	+0.56	+0.51
+10% k_2	+9.06	+9.47	+9.42	+8.74	-1.44	-1.50	-1.25	-1.31	-3.12	-2.67	-2.67	-2.54	+3.11	+3.18	+3.14	+3.23	-2.09	-2.08	-2.04	-1.92
-10% k_2	-9.98	-10.48	-10.41	-9.81	+1.47	+1.52	+1.27	+1.36	+3.28	+2.78	+2.79	+2.71	-3.36	-3.42	-3.37	-3.53	+2.17	+2.16	+2.11	+2.03
+10% k_3	+0.01	+0.01	+0.40	+0.30	0	0	-0.05	-0.04	0	0	-0.11	-0.09	0	0	-0.01	-0.09	0	0	-0.08	-0.07
-10% k_3	-0.01	-0.01	-0.40	-0.31	0	0	+0.05	+0.04	0	0	+0.11	+0.09	0	0	+0.01	+0.09	0	0	+0.08	+0.07
+10% k_4	+1.34	+1.57	+1.51	+1.44	-2.54	-3.69	-3.74	-4.68	+5.83	+4.54	+3.88	+3.27	-0.33	-0.33	-0.51	-0.26	+6.73	+5.35	+4.81	+4.31
-10% k_4	-1.45	-1.79	-1.73	-1.63	+2.64	+3.94	+3.95	+4.91	-6.33	-5.13	-4.41	-3.71	+0.36	+0.37	+0.57	+0.30	-7.17	-5.92	-5.32	-4.74
+10% k_5	+1.00	+0.64	+0.56	+0.36	-1.88	-1.46	-1.35	-1.12	-2.81	+1.37	-2.01	-1.52	+1.55	-1.65	+1.38	+1.10	-2.20	-1.96	-1.69	-1.28
-10% k_5	-1.06	-0.67	-0.59	-0.37	+1.93	+1.49	+1.38	+1.14	+2.97	-1.43	+2.09	+1.57	-1.64	+1.71	-1.44	-1.14	+2.30	+2.03	+1.75	+1.31
+10% k_6	+0.56	+0.41	+0.23	+0.18	-1.06	-0.94	-0.56	-0.57	-1.59	-1.26	-0.83	-0.78	-0.60	-0.49	-0.33	-0.30	-1.25	-1.07	-0.70	-0.66
-10% k_6	-0.58	-0.42	-0.24	-0.19	+1.08	+0.95	+0.56	+0.58	+1.64	+1.29	+0.84	+0.79	+0.62	+0.50	+0.33	+0.30	+1.27	+1.09	+0.71	+0.66
+10% k_7	-	-	-	-	-	-	-	-	-2.41	-1.69	-1.61	-2.05	+0.60	+0.85	+0.89	+1.25	+8.45	+8.56	+8.82	+8.45
-10% k_7	-	-	-	-	-	-	-	-	+2.48	+1.74	+1.64	+2.10	-0.62	-0.88	-0.91	-1.29	-8.70	-8.86	-9.03	-8.71
+10% k_8	-	-	-	-	-	-	-	-	-1.12	-0.92	-0.95	-0.80	+0.28	+0.47	+0.53	+0.49	-0.65	-0.67	-0.66	-0.56
-10% k_8	-	-	-	-	-	-	-	-	+1.14	+0.94	+0.96	+0.81	-0.29	-0.47	-0.54	-0.49	+0.66	+0.68	+0.67	+0.56
+10% k_9	-	-	-	-	-	-	-	-	0	0	0	-0.09	0	0	0	-0.01	0	0	-0.03	-0.07
-10% k_9	-	-	-	-	-	-	-	-	0	0	0	+0.09	0	0	0	+0.01	0	0	+0.03	+0.07

^a T_1 : 403 K; T_2 : 413 K; T_3 : 423 K; T_4 : 433 K.

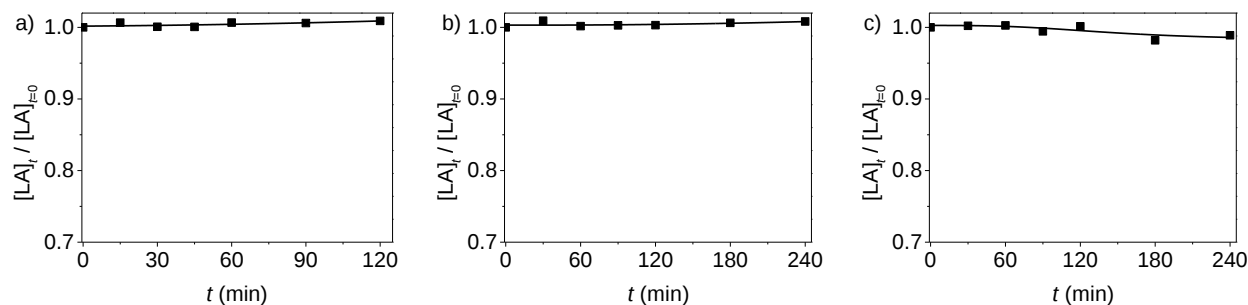


Figure S1. Variation of LA concentration remaining in solvents of (a) H₂O, (b) H₂O-THF, and (c) NaCl/H₂O-THF with time under the catalysis of AlCl₃. Reaction conditions: 1.0 mL H₂O, 0.125 M LA, 25.0 mM AlCl₃, 413 K. In NaCl-H₂O/THF biphasic system, NaCl is saturated in aqueous solution. $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$.

When LA was used as the reactant with AlCl₃ as the catalyst, no significant decrease of [LA] was observed in both H₂O and H₂O-THF solvents, indicating that LA itself was stable in the presence of AlCl₃. Therefore, the further transformation of LA in H₂O or H₂O-THF solvents could be ignored. However, slight decrease of [LA] was observed after 2 h's reaction in NaCl-H₂O/THF biphasic solvent, which might be ascribed to self-condensation of LA in the presence of high concentration of Cl⁻.⁵ In the meanwhile, the result also demonstrates that the self-condensation of LA occurs rather slowly under the experimental conditions. In contrast, we notice that the yield of LA was less than 2% while that of FA was 20% after 2 h's reaction when HMF was used solely as the reactant in NaCl-H₂O/THF biphasic solvent, thereby suggesting that the self-condensation of LA contributes little to the stoichiometric excess formation of FA relative to LA in NaCl-H₂O/THF biphasic solvent in the time range investigated.

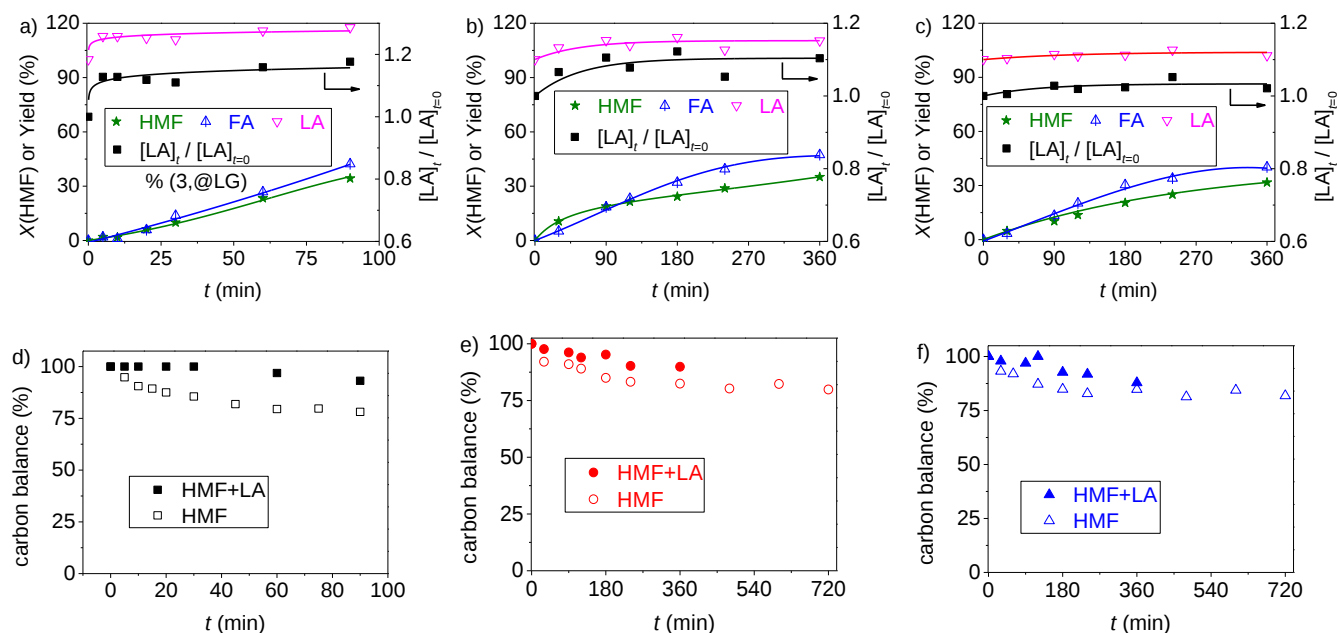


Figure S2. Variation of LA concentration remaining in solvents of (a) H₂O, (b) H₂O-THF, and (c) NaCl/H₂O-THF with time under the catalysis of AlCl₃ in the presence of HMF; Comparison of the carbon balance for HMF conversion in the presence and absence of LA in (d) H₂O, (e) H₂O-THF, and (f) NaCl/H₂O-THF. Reaction conditions: 1.0 mL H₂O, 0.125 M LA and HMF, 25.0 mM AlCl₃, 413 K. In NaCl-H₂O/THF biphasic system, NaCl is saturated in aqueous solution. $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$.

In water, the conversion of HMF in the presence of LA was comparable to that in the absence of LA, whereas the accompanied FA and LA yields were higher than those in the absence of LA. The results indicate that the presence of LA promotes the conversion of HMF to FA and LA, wherein LA acts as a catalyst because no esterified product from HMF and LA was detected. Besides, the observable better carbon balance reveals that the polycondensation between LA and HMF was ignorable. That is, the formed LA from HMF conversion was not consumed further, which indicates that the stoichiometric excess formation of FA relative to LA in water might be ascribed to the direct generation of FA from HMF. Similar explanation could be applied to that in H₂O-THF and NaCl-H₂O/THF solvents, revealing that the stoichiometric excess formation of FA relative to LA in the three solvent systems are ascribed to the direct generation of FA from HMF degradation. Therefore, the further consumption of LA was not included in our kinetic model.

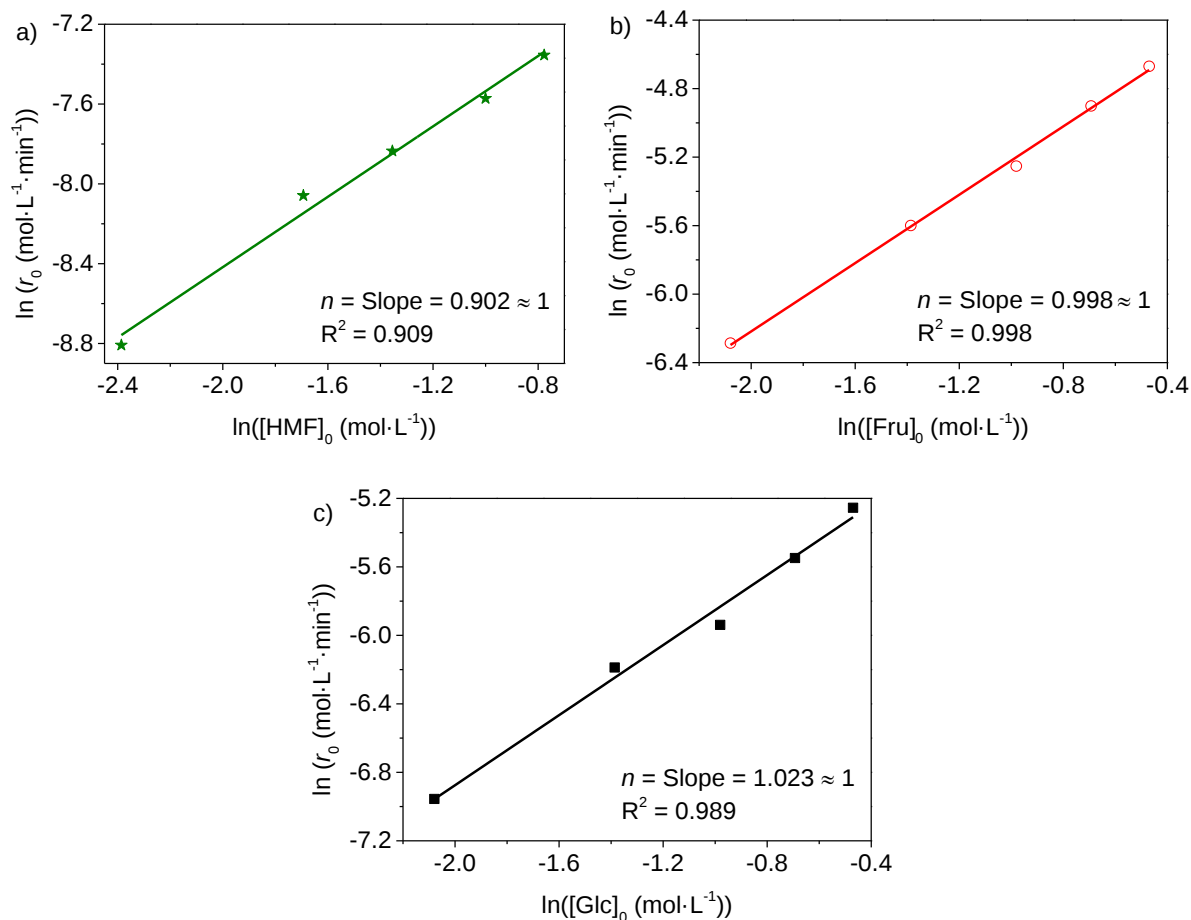


Figure S3. Reaction order of HMF, fructose, and glucose conversion in NaCl-H₂O/THF biphasic system determined by the initial concentration method. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl, 25.0 mM AlCl₃, $V(\text{H}_2\text{O}):V(\text{THF})=1:3$, 413 K. In NaCl-H₂O/THF biphasic system, the reaction order of HMF, fructose, and glucose conversion, determined by the initial concentration method, were considered as pseudo-first order.

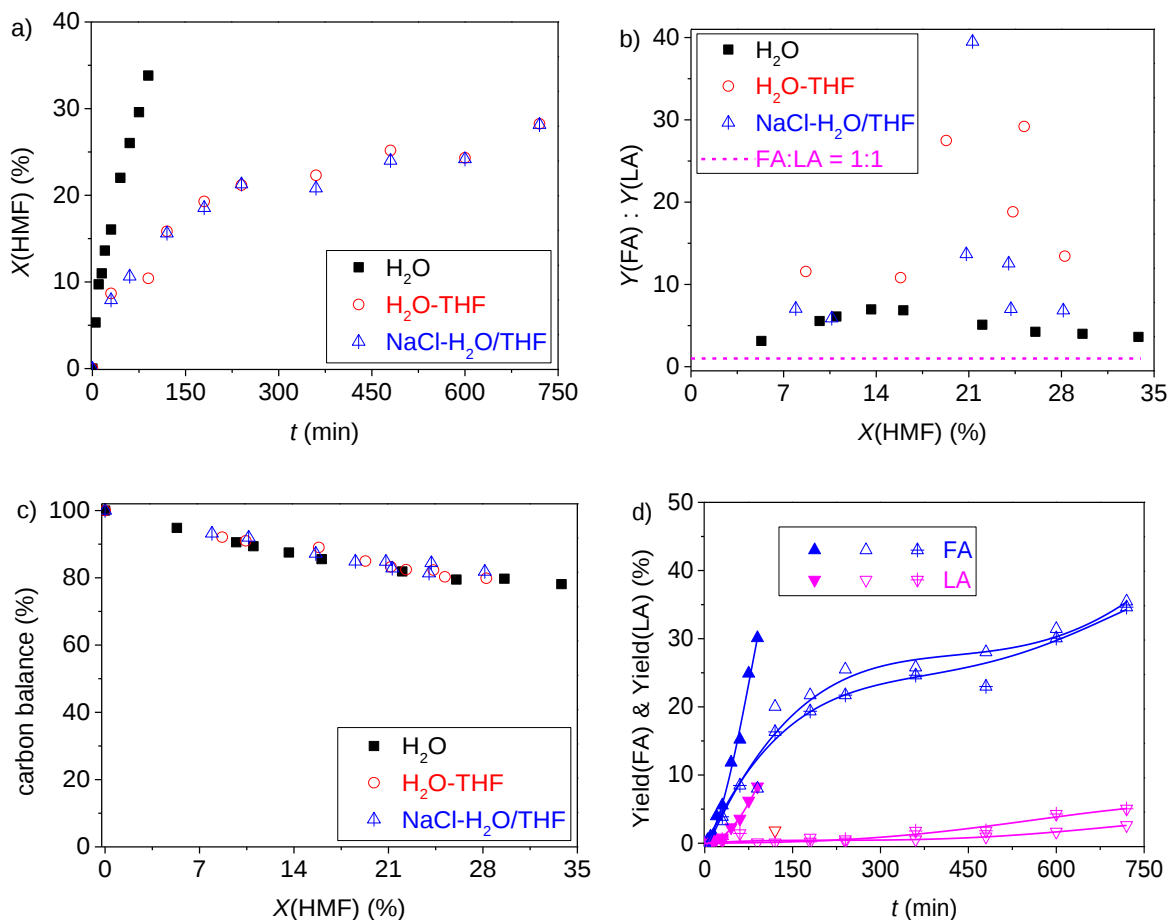


Figure S4. Comparison of AlCl_3 -catalyzed HMF conversion in the three solvent systems. (a) HMF conversion as a function of time, (b) mole ratio of FA/LA and (c) carbon balance as a function of HMF conversion. (d) FA and LA yields as a function of time, filled symbols, H_2O ; hollow symbols, H_2O -THF; partially filled symbols, NaCl - H_2O /THF. Reaction conditions: 1.0 mL H_2O , 0.2758 M HMF, 25.0 mM AlCl_3 , 413 K. In NaCl - H_2O /THF biphasic system, NaCl is saturated in aqueous solution. $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$.

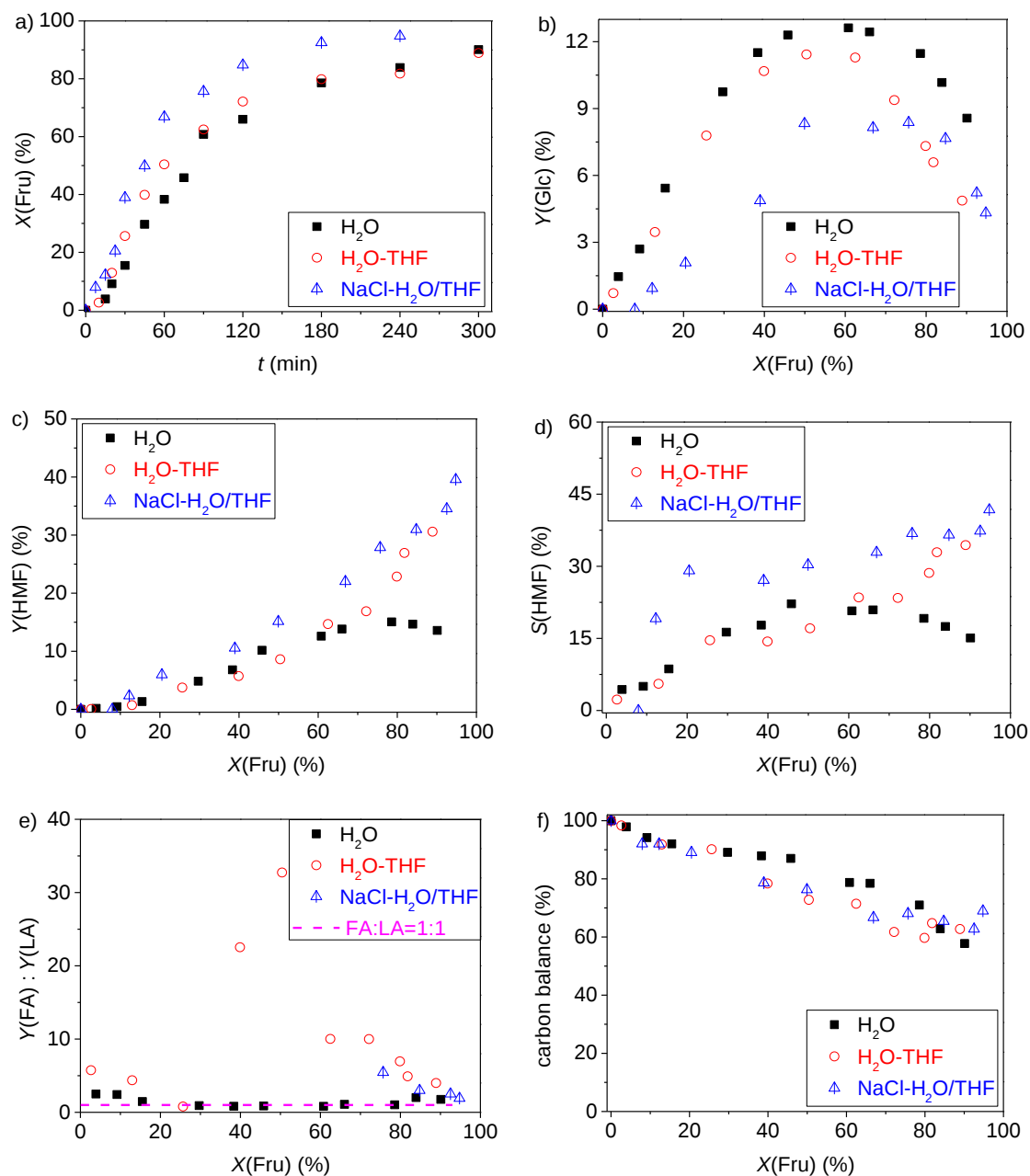


Figure S5. Comparison of AlCl_3 -catalyzed fructose conversion in the three solvent systems. (a) Fructose conversion as a function of time; (b) glucose yield, (c) HMF yield, (d) HMF selectivity, (e) mole ratio of FA/LA, and (f) carbon balance as a function of fructose conversion. Reaction conditions: 1.0 mL H_2O , 0.25 M Fru, 25.0 mM AlCl_3 , 413 K. In NaCl - H_2O /THF biphasic system, NaCl is saturated in aqueous solution. $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$.

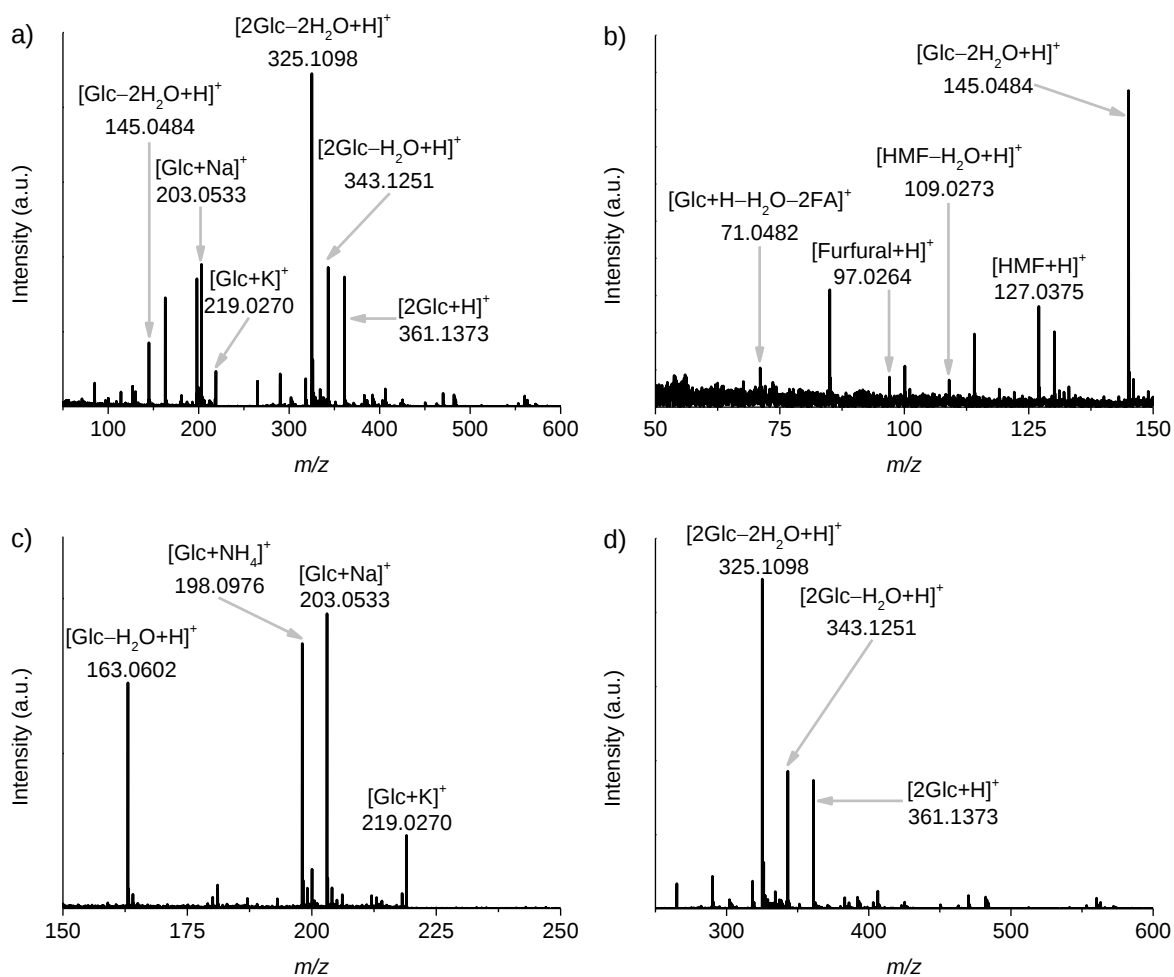


Figure S6. ESI-MS spectra of mixtures after reacting glucose in the absence of AlCl_3 in H_2O -THF co-solvent. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 150$, $150 \sim 250$, and $250 \sim 600$ regions, respectively. Reaction conditions: 1.0 mL H_2O , 3.0 mL THF, 0.25 M Glc, 413 K, 30 min.

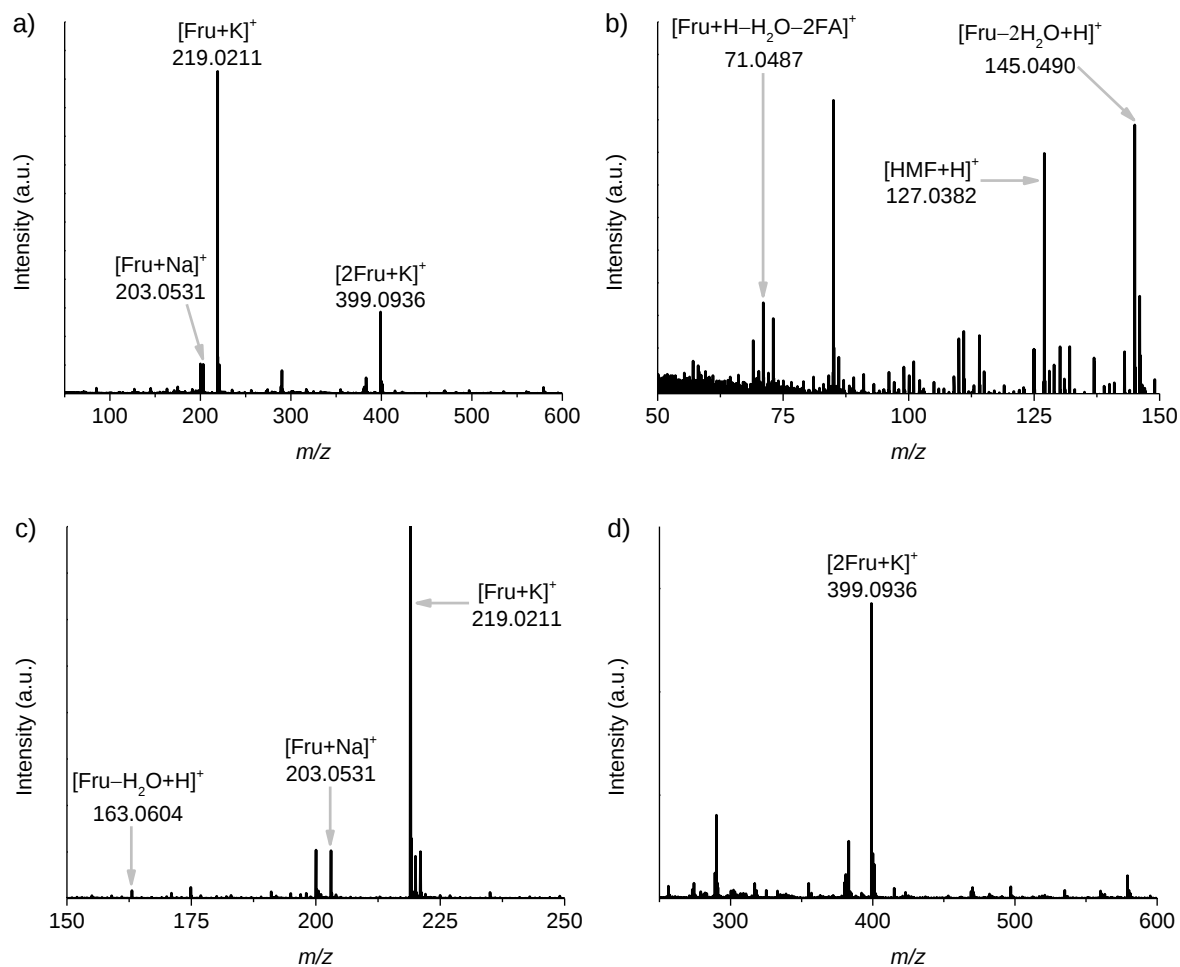


Figure S7. ESI-MS spectra of mixtures after reacting fructose in the absence of AlCl_3 in H_2O -THF co-solvent. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 150$, $150 \sim 250$, and $250 \sim 600$ regions, respectively. Reaction conditions: 1.0 mL H_2O , 3.0 mL THF, 0.25 M Fru, 413 K, 30 min.

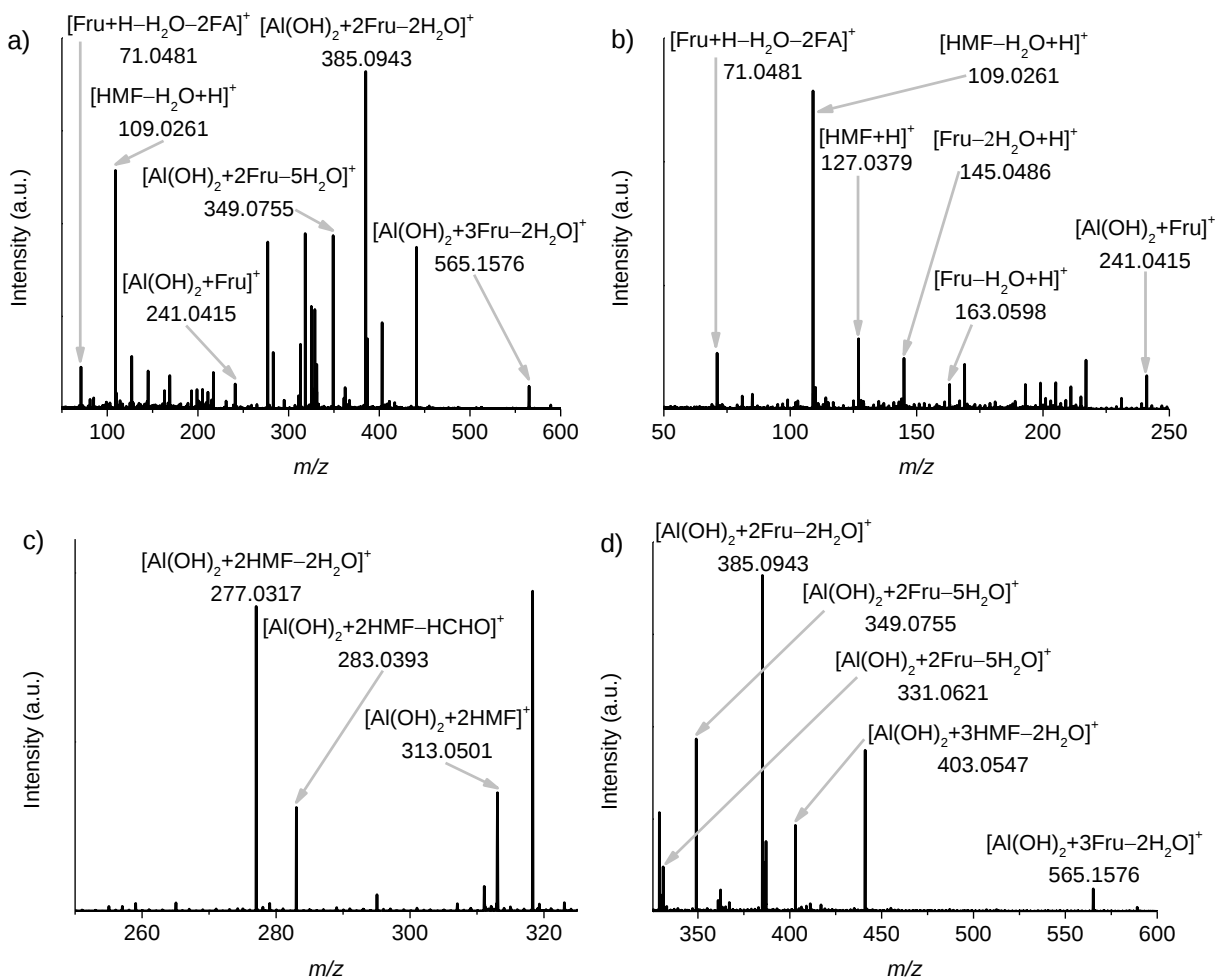


Figure S8. ESI-MS spectra of mixtures after reacting fructose in the presence of AlCl_3 in H_2O -THF co-solvent. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 250$, $250 \sim 325$, and $325 \sim 600$ regions, respectively. Reaction conditions: 1.0 mL H_2O , 3.0 mL THF, 0.25 M Fru, 25.0 mM AlCl_3 , 413 K, 30 min. As small amount of glucose already formed from the activity result, peaks assigning to fructose could also be assigned to glucose as well.

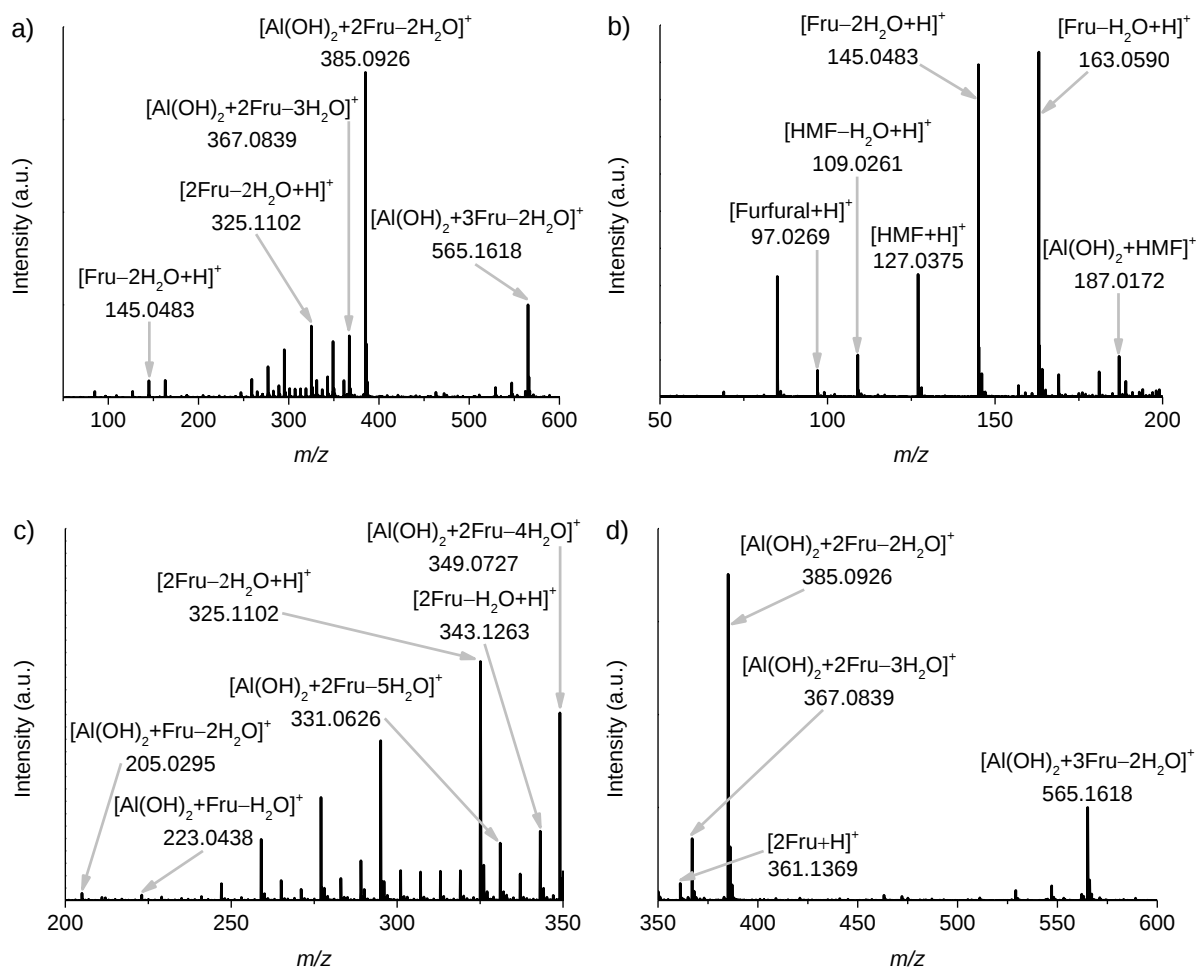


Figure S9. ESI-MS spectra of mixtures after reacting fructose in the presence of AlCl_3 in water. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 200$, $200 \sim 350$, and $350 \sim 600$ region, respectively. Reaction conditions: 1.0 mL H_2O , 0.25 M Fru, 25.0 mM AlCl_3 , 413 K, 30 min. As small amount of glucose already formed from the activity result, peaks assigning to fructose could also be assigned to glucose as well.

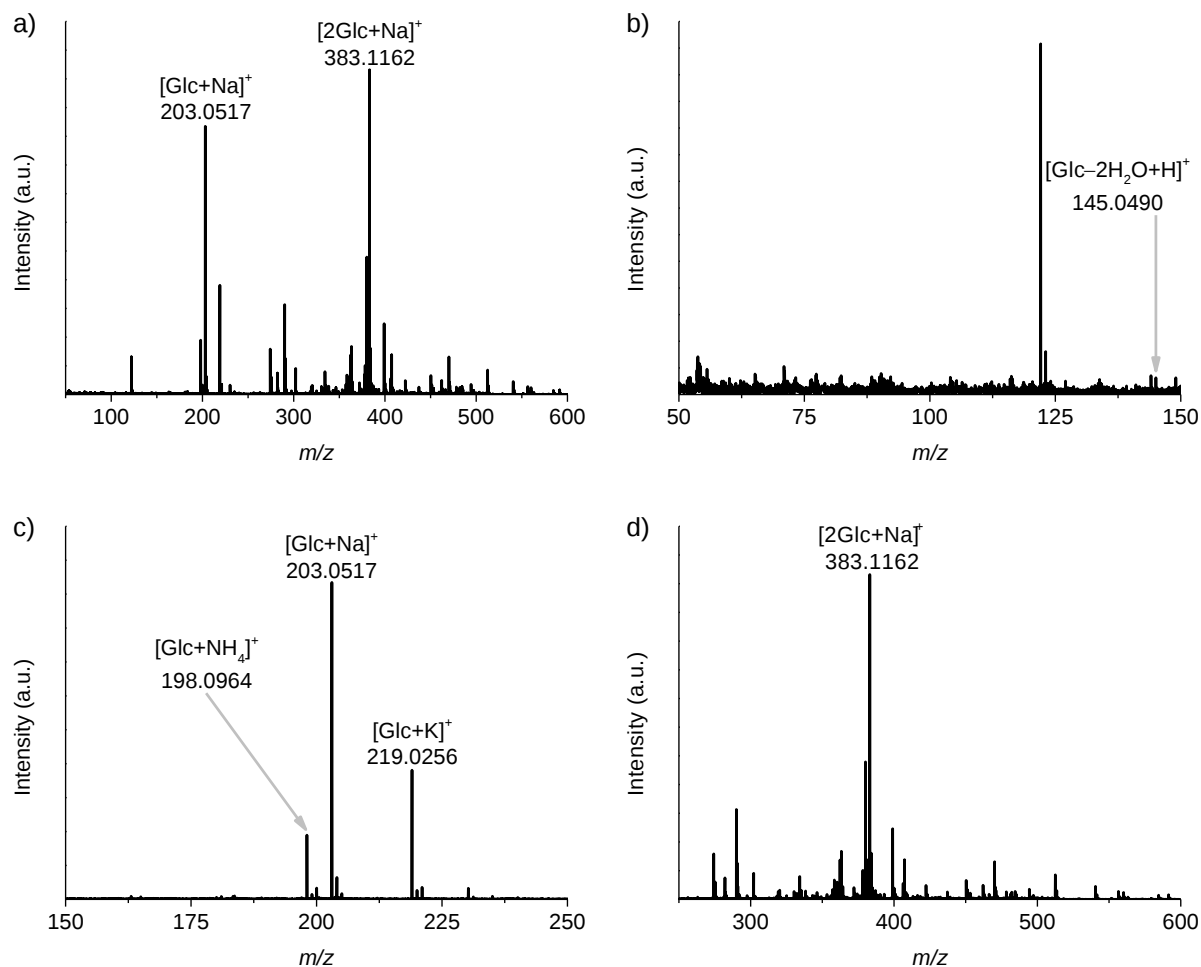


Figure S10. ESI-MS spectra of mixtures after reacting glucose in the absence of AlCl_3 in water. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 150$, $150 \sim 250$, and $250 \sim 600$ region, respectively. Reaction conditions: 1.0 mL H_2O , 0.25 M Glc, 25.0 mM AlCl_3 , 413 K, 30 min

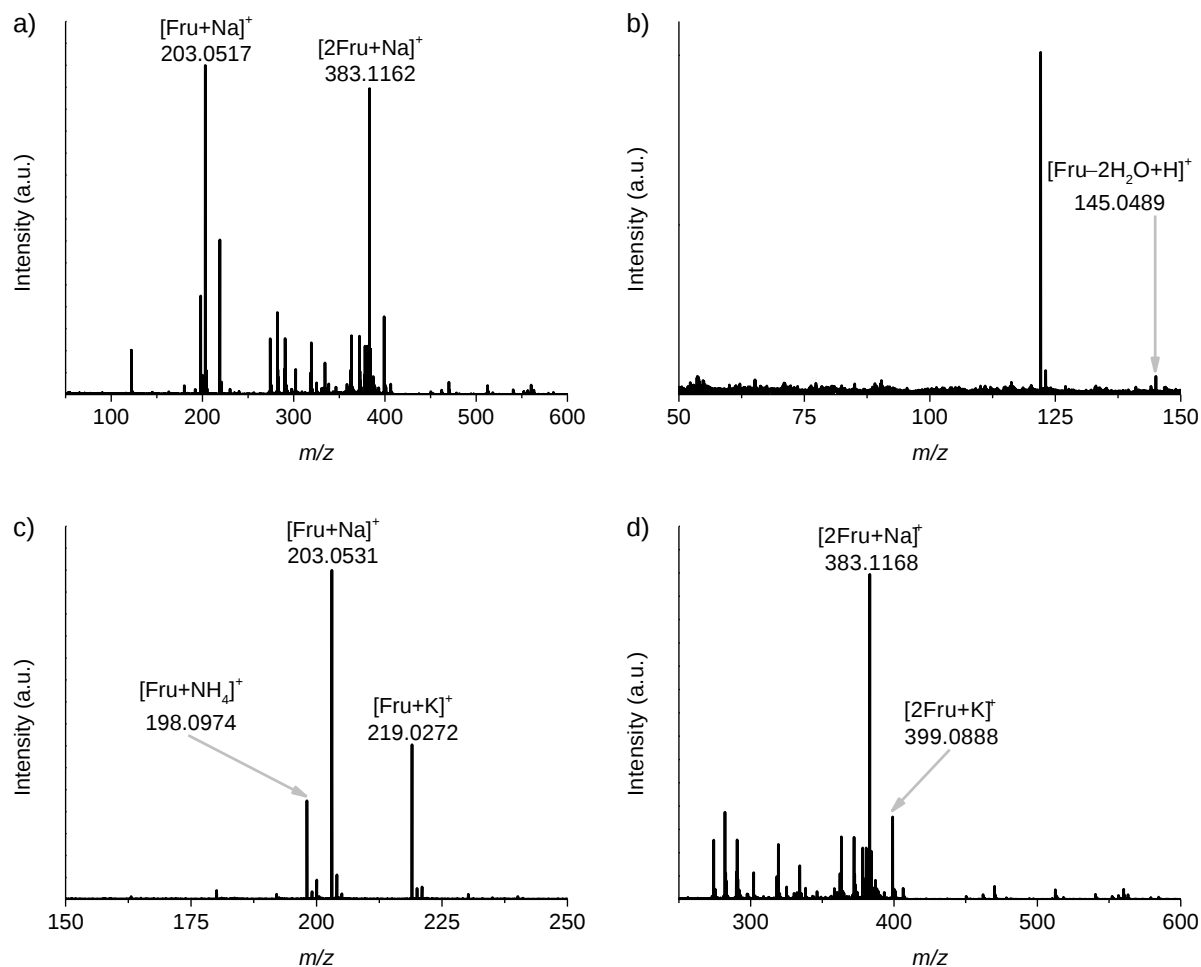


Figure S11. ESI-MS spectra of mixtures after reacting fructose in the absence of AlCl_3 in water. (a) Full spectrum; (b), (c), and (d) are the magnification of (a) in $m/z = 50 \sim 150$, $150 \sim 250$, and $250 \sim 600$ regions, respectively. Reaction conditions: 1.0 mL H_2O , 3.0 mL THF, 0.25 M Fru, 413 K, 30 min.

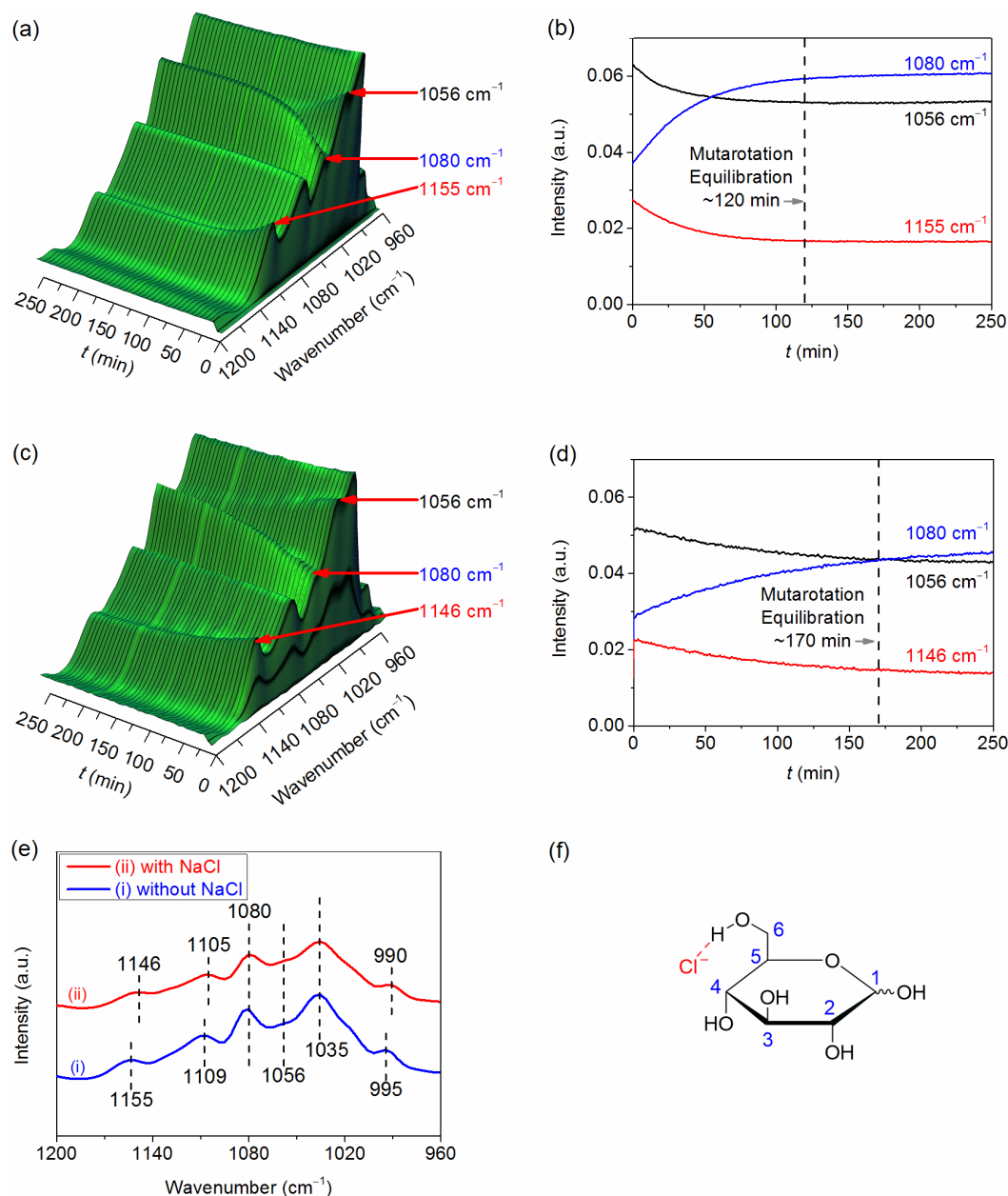


Figure S12. ATR-IR spectra of aqueous glucose solution with time at room temperature (a) in the absence or (c) presence of NaCl. (b) and (d) the intensity variation of corresponding IR bands in (a) and (c). (e) the ATR-IR spectra of the aqueous glucose solution at mutarotation equilibrium in the absence or presence of NaCl. (f) the schematic diagram for hydrogen bonding between glucose -OH and Cl^- . Reaction conditions: 10 mL H_2O , 0.25 M Glc, with or without 6.0 M NaCl, subtraction of reference water spectrum at 298 K. ($\nu = 995 \text{ cm}^{-1}$, $\delta((\text{C6})\text{O}-\text{H})$; $\nu = 1035 \text{ cm}^{-1}$, $\delta((\text{C4})\text{O}-\text{H})$; $\nu = 1055 \text{ cm}^{-1}$, α -D-Glc; $\nu = 1080 \text{ cm}^{-1}$, β -D-Glc; $\nu = 1109 \text{ cm}^{-1}$, $\nu(\text{C6}-\text{O})$; $\nu = 1155 \text{ cm}^{-1}$, deforming of pyranoid ring)^{6,7}

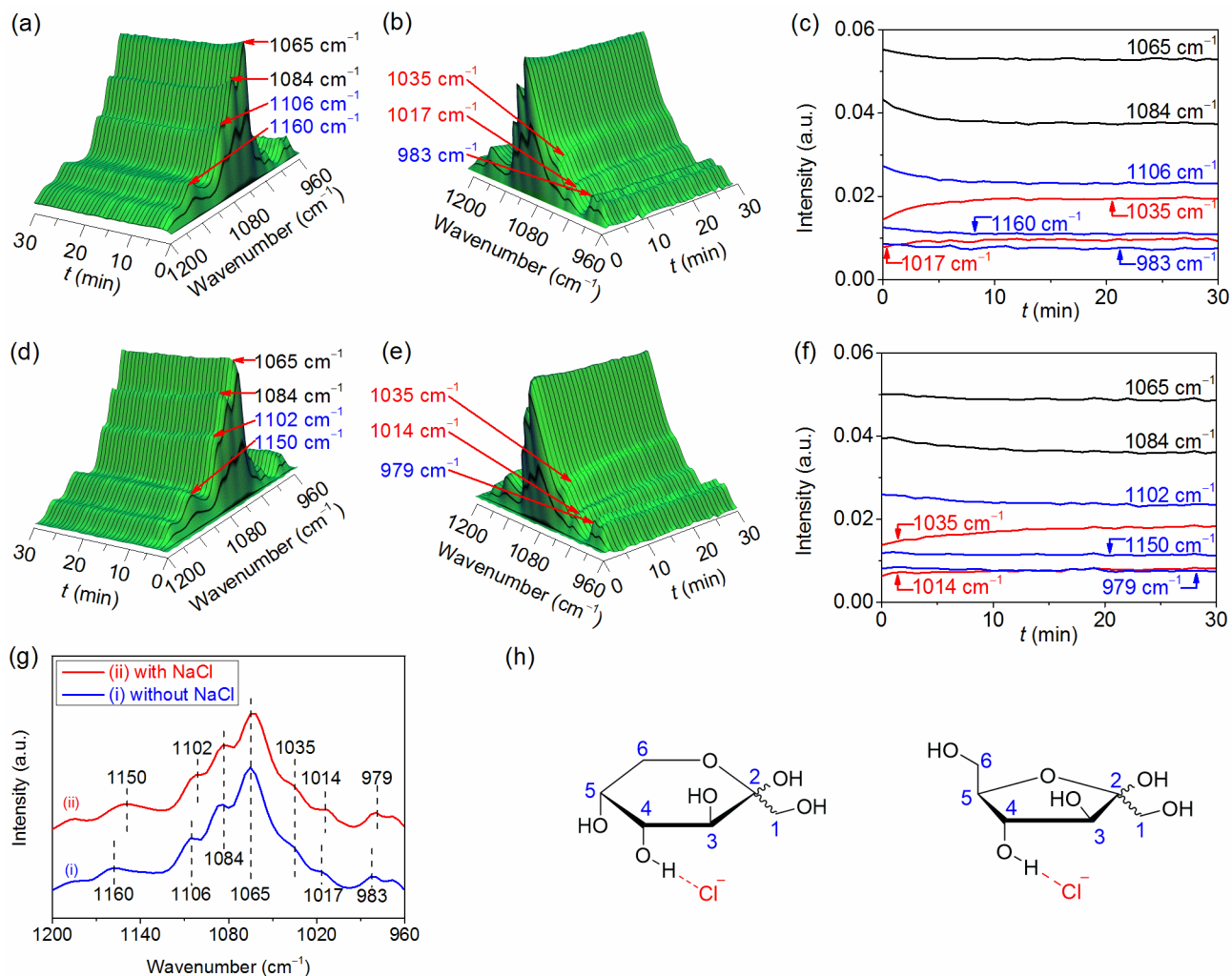


Figure S13. ATR-IR spectra of aqueous fructose solution with time at room temperature (a, b) in the absence or (d, e) presence of NaCl. (c) and (f) the intensity variation of corresponding IR bands in (a) and (c). (g) the ATR-IR spectra of the aqueous fructose solution at mutarotation equilibrium in the absence or presence of NaCl. (h) the schematic diagram for hydrogen bonding between fructose -OH and Cl^- . Reaction conditions: 10 mL H_2O , 0.25 M Fru, with or without 6.0 M NaCl, subtraction of reference water spectrum at 298 K. ($\nu = 983 \text{ cm}^{-1}$, $\delta(\text{CnO-H})$ and $\nu(\text{Cn-O})$; $\nu = 1017 \text{ cm}^{-1}$, $\delta(\text{C4-O, D-}f\text{-Fru})$; $\nu = 1035 \text{ cm}^{-1}$, D-*f*-Fru; $\nu = 1065 \text{ cm}^{-1}$, $\nu(\text{C1-O})$ and $\delta((\text{C1})\text{O-H})$; $\nu = 1084 \text{ cm}^{-1}$, $\delta(\text{C1-H})$; $\nu = 1106 \text{ cm}^{-1}$, $\nu(\text{C4-O, D-}p\text{-Fru})$; $\nu = 1160 \text{ cm}^{-1}$, deforming of pyranoid ring)^{7,8}

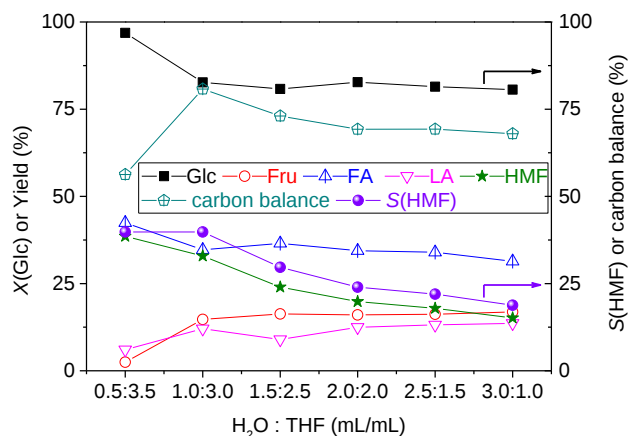


Figure S14. Influence of the volume ratio of H₂O/THF on the conversion of glucose to HMF in NaCl-H₂O/THF biphasic solvent. Reaction conditions: 0.25 mmol Glc, 0.025 mmol AlCl₃·6H₂O, 6 mmol NaCl, 4.0 mL solvent, 413 K, 4 h.

The conversion of glucose at 413 K for 4 h decreased from 97% to 83% with increasing $V_{(H_2O)}/V_{(THF)}$ from 0.5/3.5 to 1/3, then kept almost unchanged with further increasing $V_{(H_2O)}/V_{(THF)}$ to 3/1. Concomitantly, the yield of FA decreased firstly, reaching a minimum (35%) at $V_{(H_2O)}/V_{(THF)}$ of 1/3, then increased with the further increase of $V_{(H_2O)}/V_{(THF)}$. Whereas, the yield of HMF exhibited declining tendency with the increase of $V_{(H_2O)}/V_{(THF)}$. As a result, the maximum selectivity (40%) of HMF was obtained at $V_{(H_2O)}/V_{(THF)}$ of 1/3. Therefore, the ideal composition of the NaCl-H₂O/THF biphasic solvent for converting glucose to HMF is the one with $V_{(H_2O)}/V_{(THF)}$ of 1/3 wherein NaCl is saturated in aqueous solution.

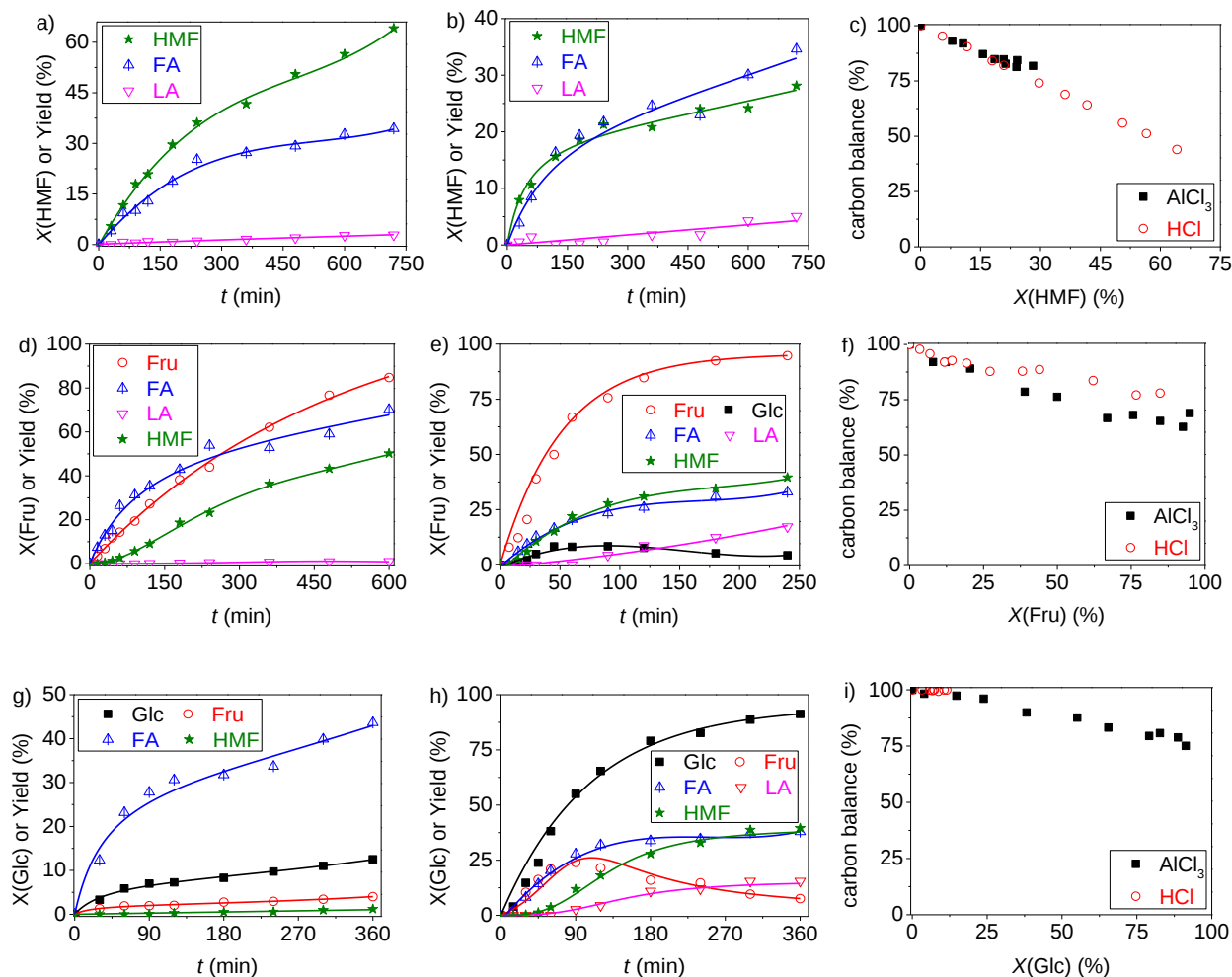


Figure S15. The conversion of (a, b) HMF by HCl and AlCl₃, respectively, (d, e) fructose by HCl and AlCl₃, respectively, and (g, h) glucose by HCl and AlCl₃, respectively, in NaCl-H₂O/THF biphasic system. Carbon balance for the conversion of (c) HMF, (f) fructose, and (i) glucose in NaCl-H₂O/THF biphasic system. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl, $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$, 0.2758 M HMF/0.25 M Fru/0.25 M Glc, HCl (pH 3.5) or 25.0 mM AlCl₃, 413 K.

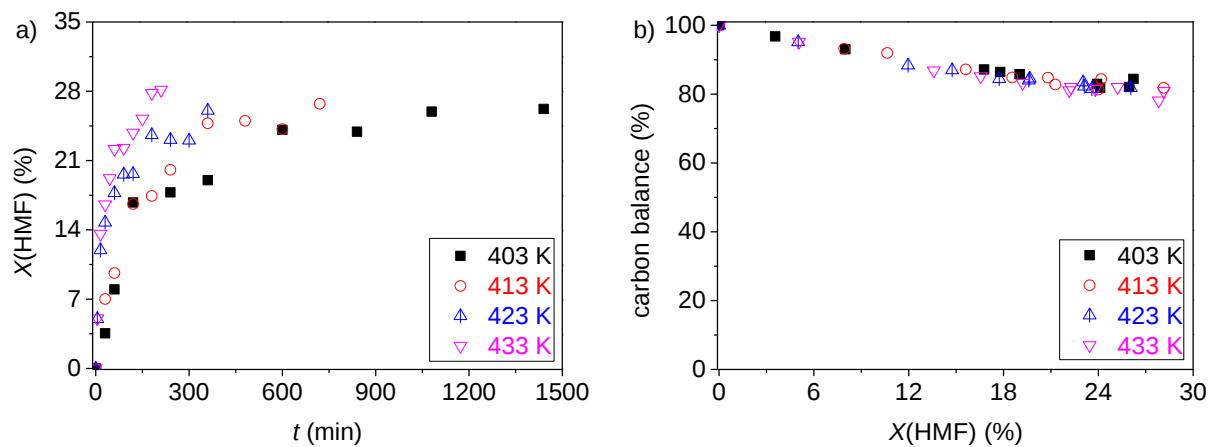


Figure S16. The conversion of HMF catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at different reaction temperatures. (a) HMF conversion as a function of time, (b) carbon balance as a function of HMF conversion. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.2758 M HMF, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$, 403~413 K.

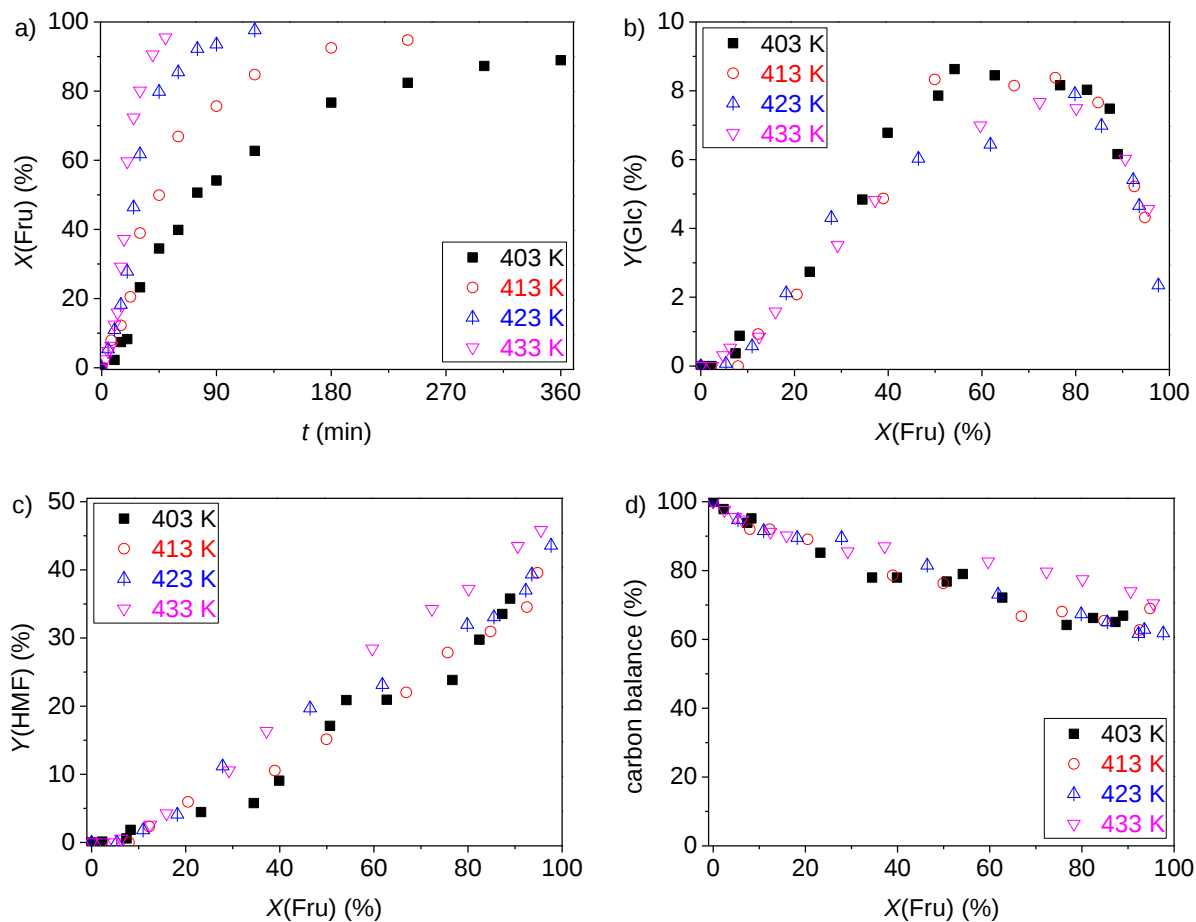


Figure S17. The conversion of fructose catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at different reaction temperatures. (a) Fructose conversion as a function of time; (b) glucose yield, (c) HMF yield, and (d) carbon balance as a function of fructose conversion. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.25 M Fru, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$, 403~413 K.

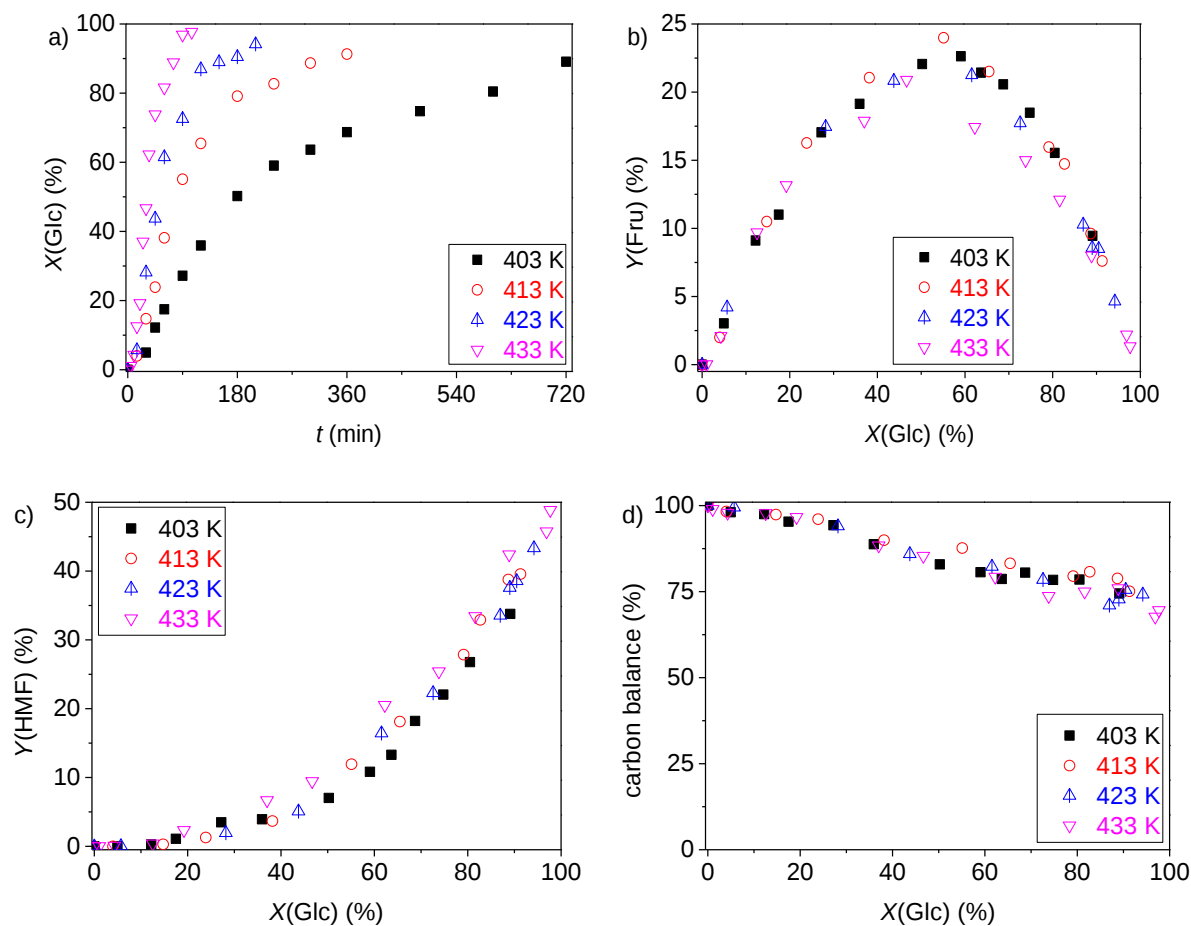


Figure S18. The conversion of glucose in NaCl-H₂O/THF biphasic system catalyzed by AlCl₃ at different reaction temperatures. (a) Glucose conversion as a function of time, (b) fructose yield, (c) HMF yield, and (d) carbon balance as a function of glucose conversion. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl, 0.25 M Glc, 25.0 mM AlCl₃, $V(\text{H}_2\text{O}):V(\text{THF}) = 1:3$, 403~413 K.

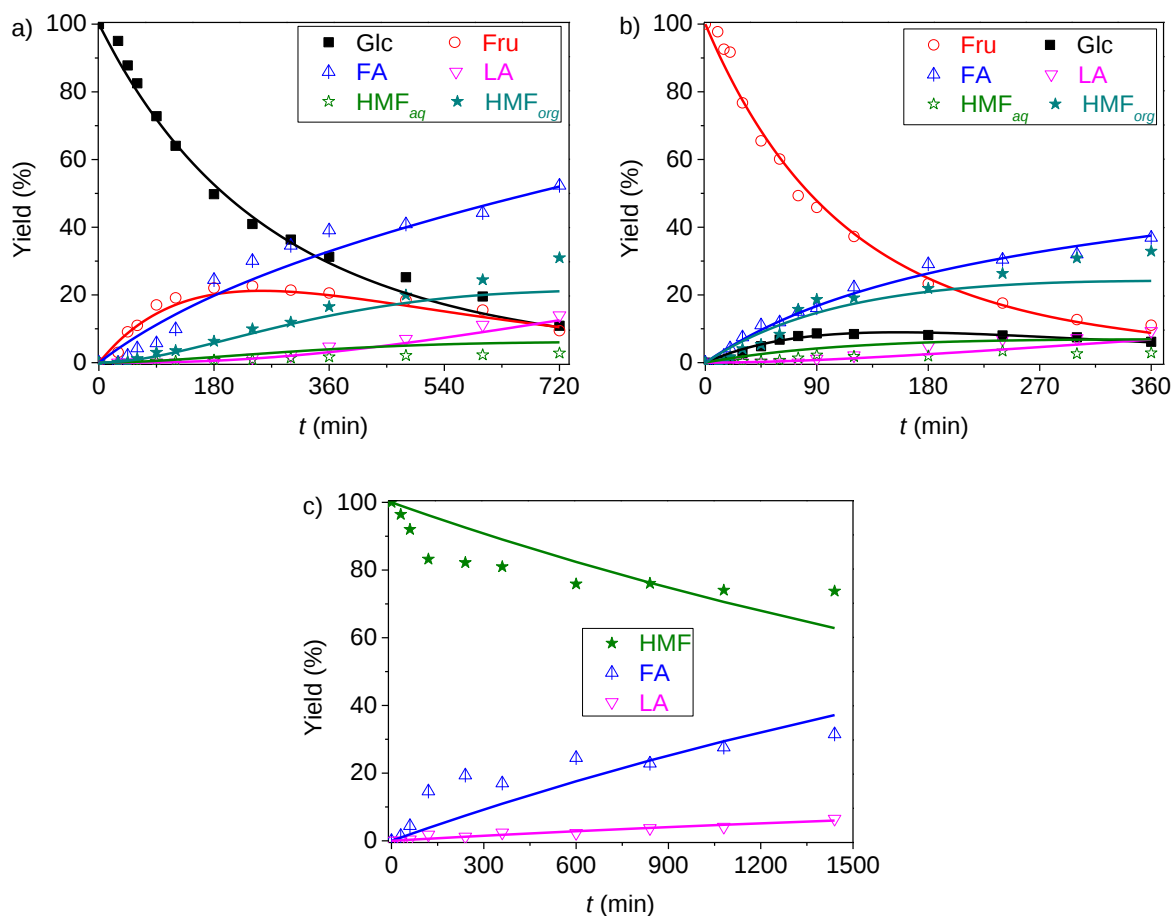


Figure S19. Comparison of experimental and model predicted results for the conversion of different substrates catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at 403 K. (a) Glucose, (b) fructose, and (c) HMF as the substrate. Symbols: experimentally obtained results. Lines: model predicted values. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.25 M Glc or Fru, or 0.2578 M HMF, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF})=1:3$, 403 K. The reactants and products profiles were simulated by MATLAB.

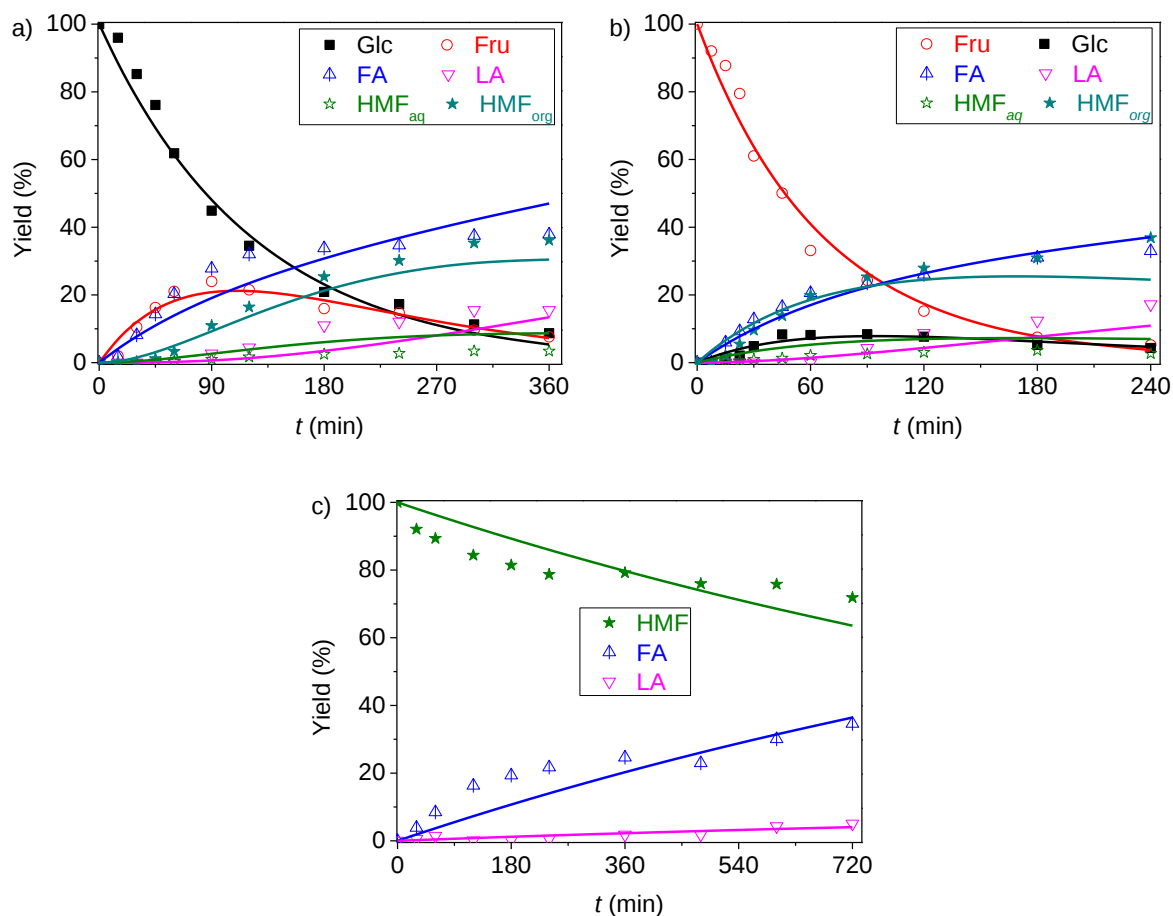


Figure S20. Comparison of experimental and model predicted results for the conversion of different substrates catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at 413 K. (a) Glucose, (b) fructose, and (c) HMF as the substrate. Symbols: experimentally obtained results. Lines: model predicted values. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.25 M Glc or Fru, or 0.2578 M HMF, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF})=1:3$, 413 K. The reactants and products profiles were simulated by MATLAB.

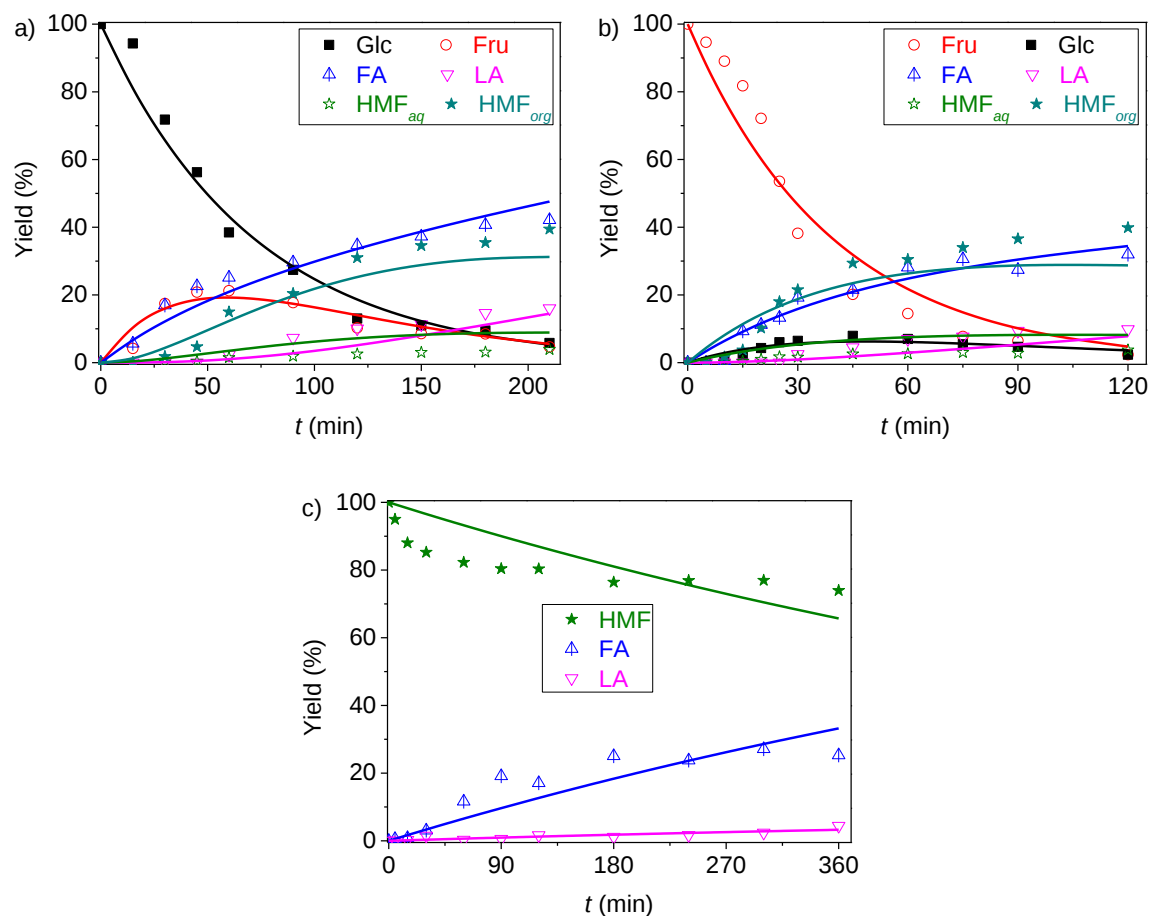


Figure S21. Comparison of experimental and model predicted results for the conversion of different substrates catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at 423 K. (a) Glucose, (b) fructose, and (c) HMF as the substrate. Symbols: experimentally obtained results. Lines: model predicted values. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.25 M Glc or Fru, or 0.2578 M HMF, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF})=1:3$, 423 K. The reactants and products profiles were simulated by MATLAB.

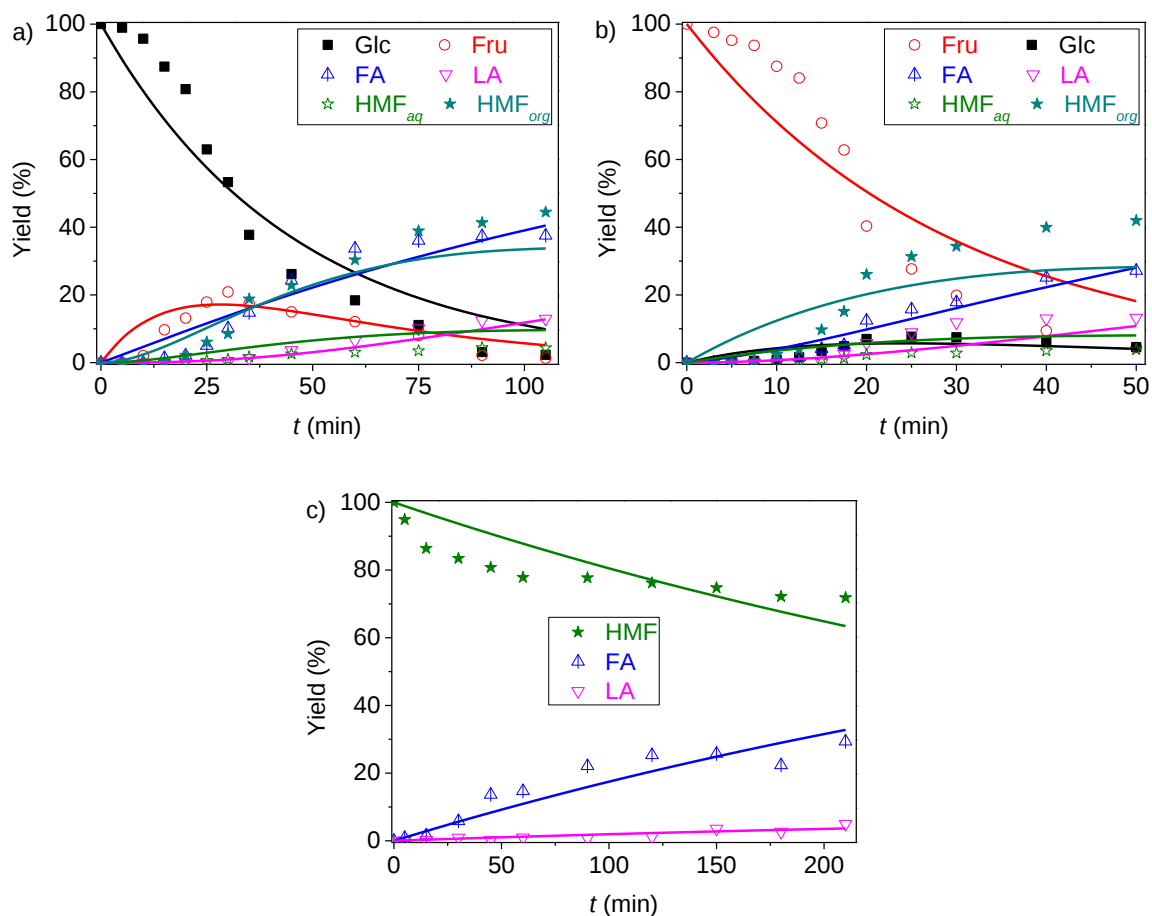


Figure S22. Comparison of experimental and model predicted results for the conversion of different substrates catalyzed by AlCl_3 in $\text{NaCl-H}_2\text{O/THF}$ biphasic system at 433 K. (a) Glucose, (b) fructose, and (c) HMF as the substrate. Symbols: experimentally obtained results. Lines: model predicted values. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl , 0.25 M Glc or Fru, or 0.2578 M HMF, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF})=1:3$, 433 K. The reactants and products profiles were simulated by MATLAB.

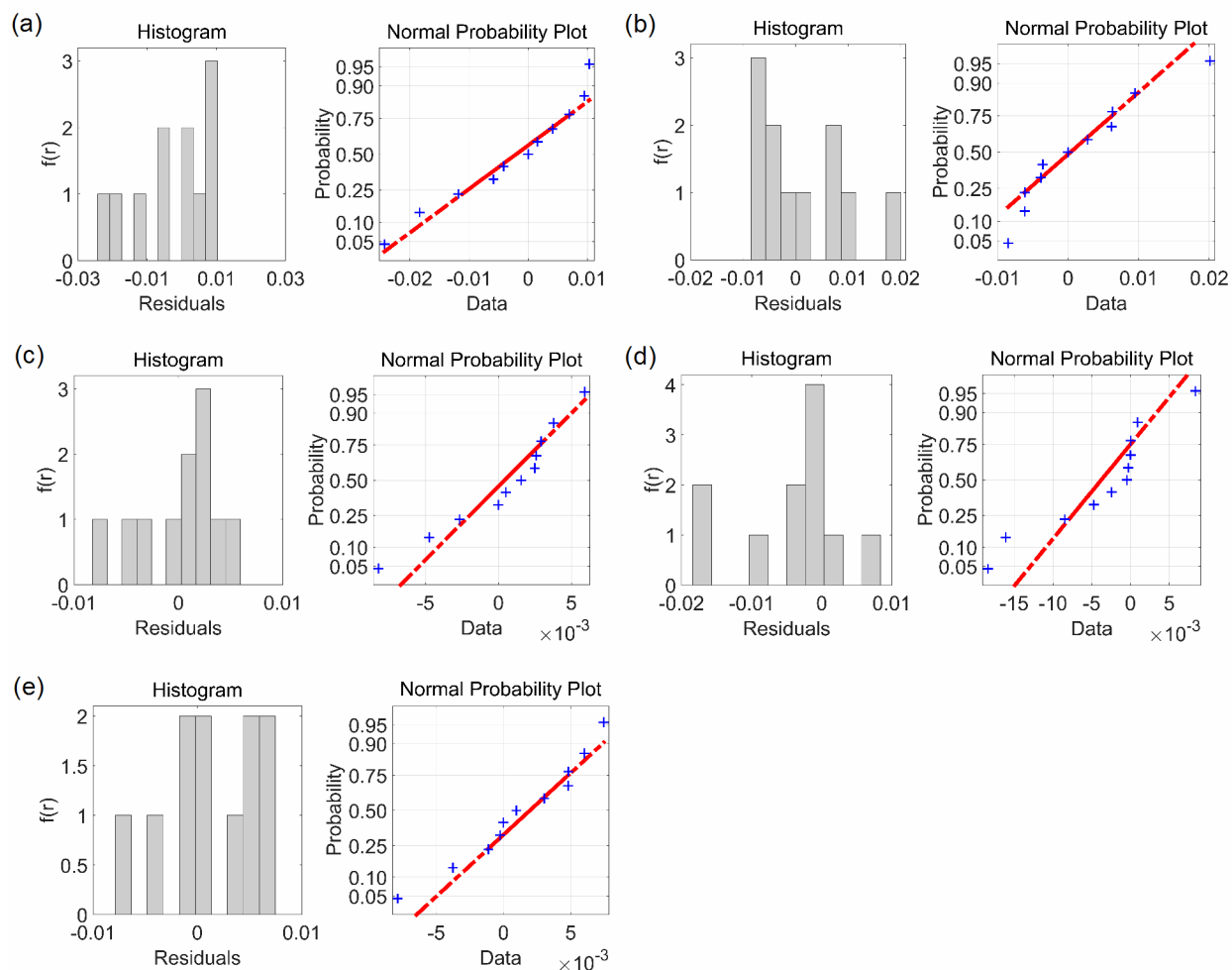


Figure S23. Histogram and normal probability plot of residuals for the estimation of each component concentration in H₂O at 413 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

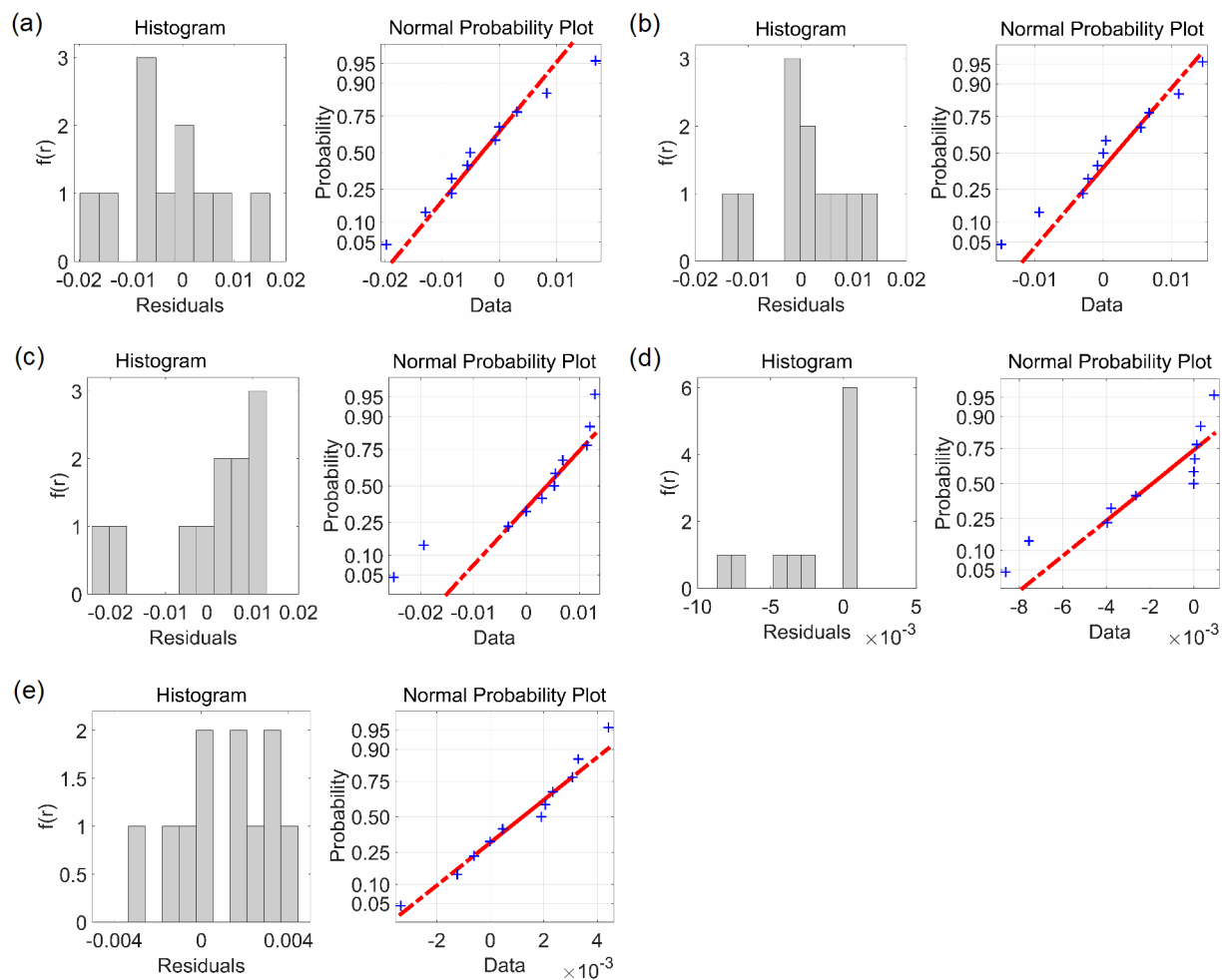


Figure S24. Histogram and normal probability plot of residuals for the estimation of each component concentration in H₂O-THF at 413 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

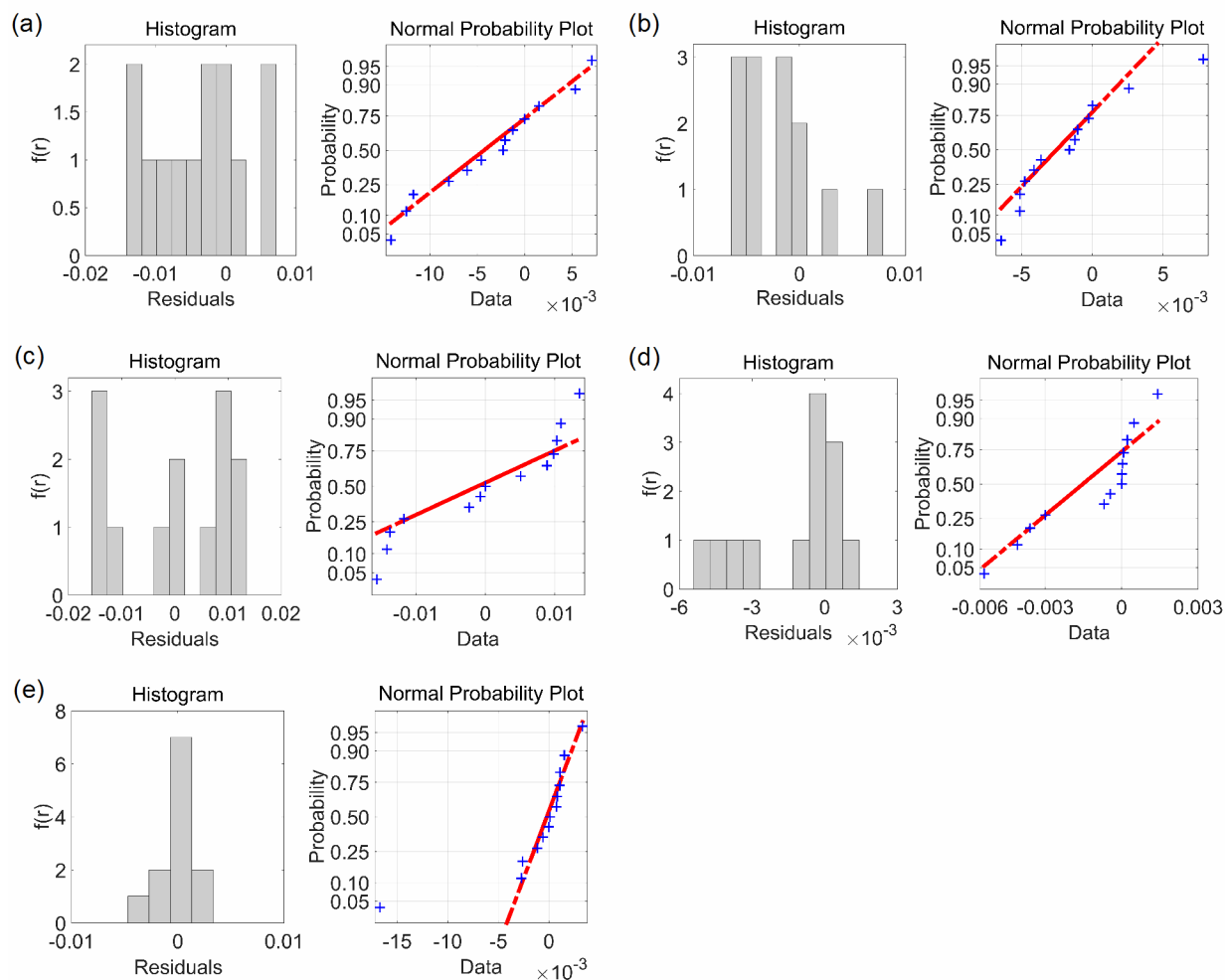


Figure S25. Histogram and normal probability plot of residuals for the estimation of each component concentration in NaCl-H₂O/THF at 403 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

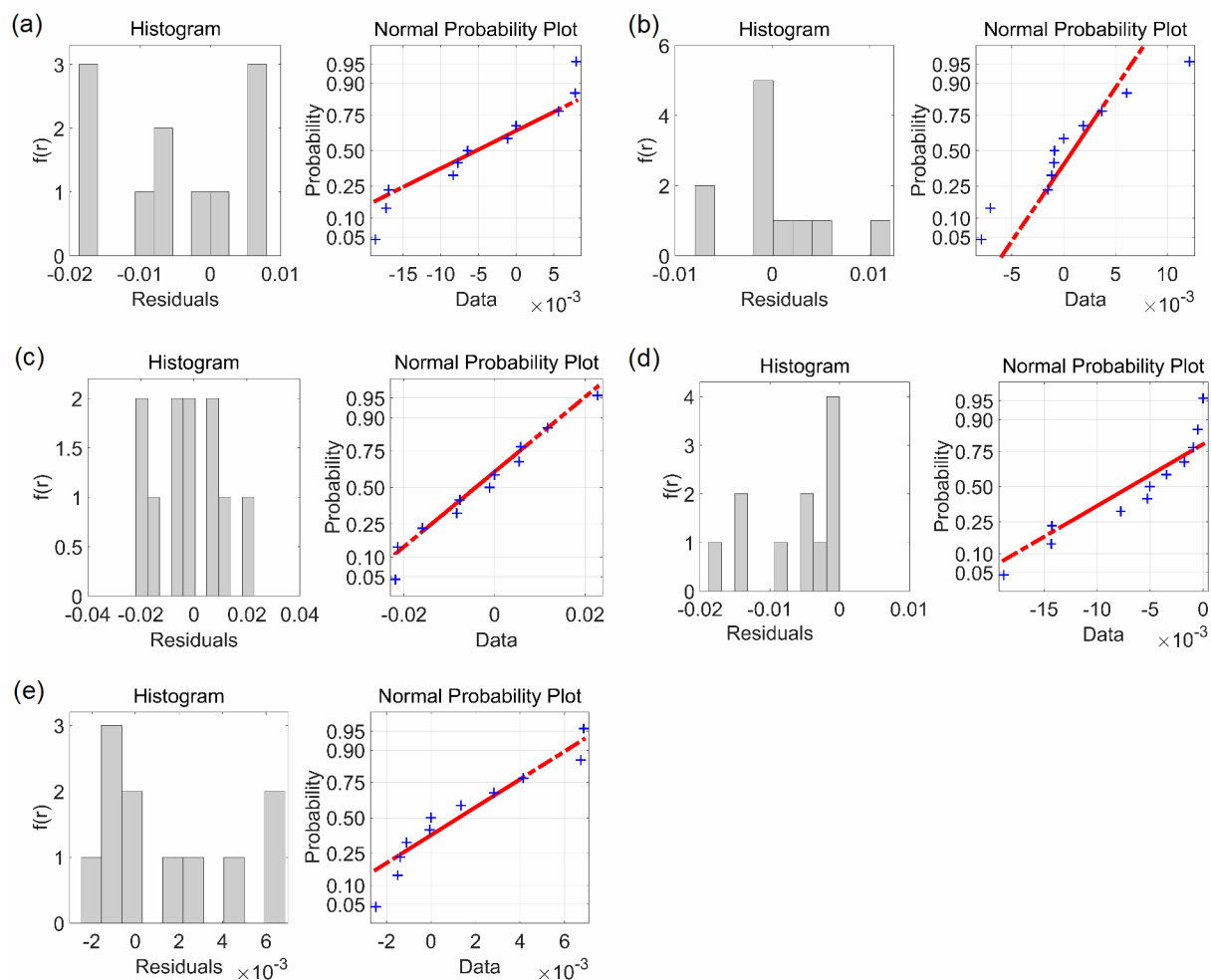


Figure S26. Histogram and normal probability plot of residuals for the estimation of each component concentration in NaCl-H₂O/THF at 413 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

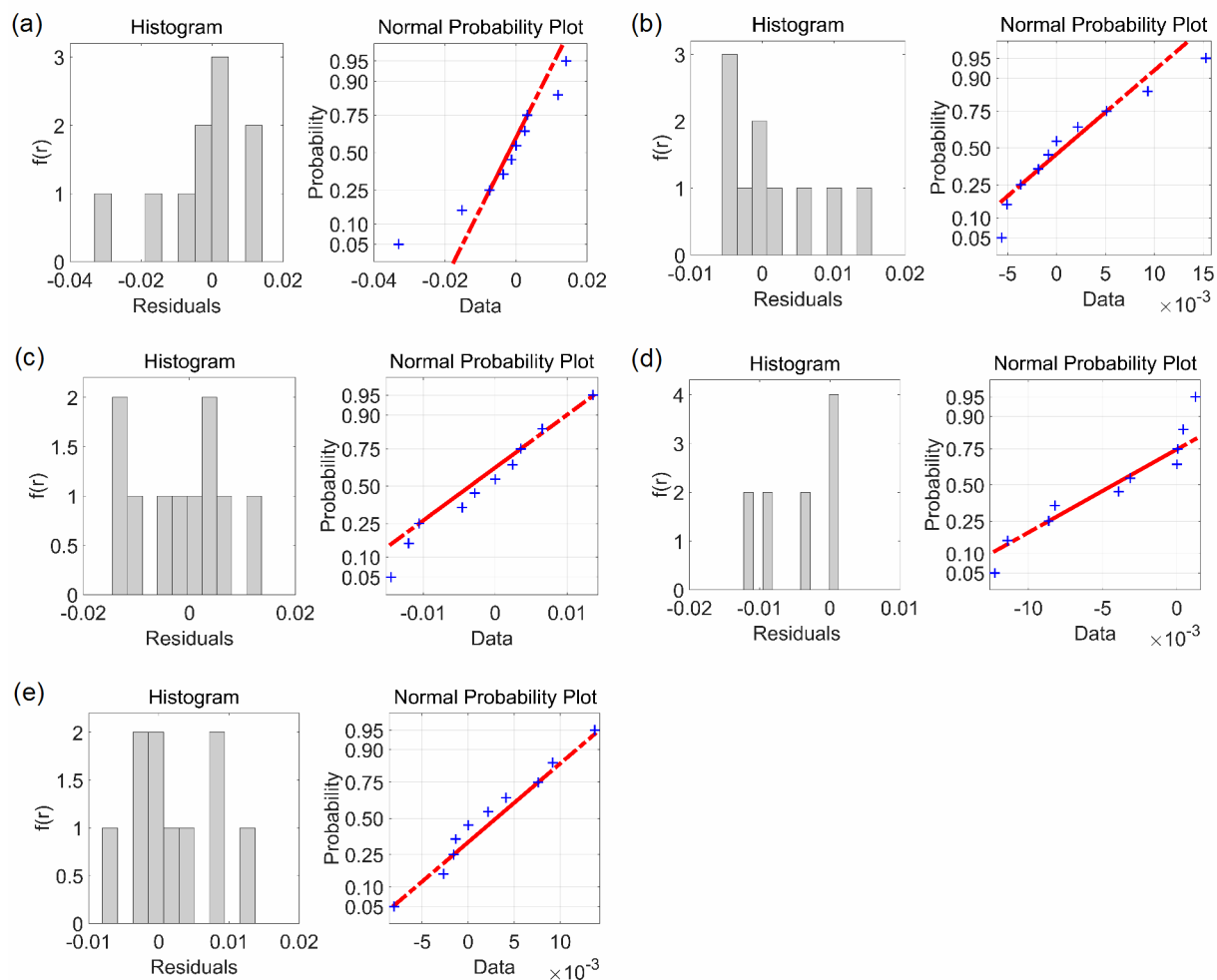


Figure S27. Histogram and normal probability plot of residuals for the estimation of each component concentration in NaCl-H₂O/THF at 423 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

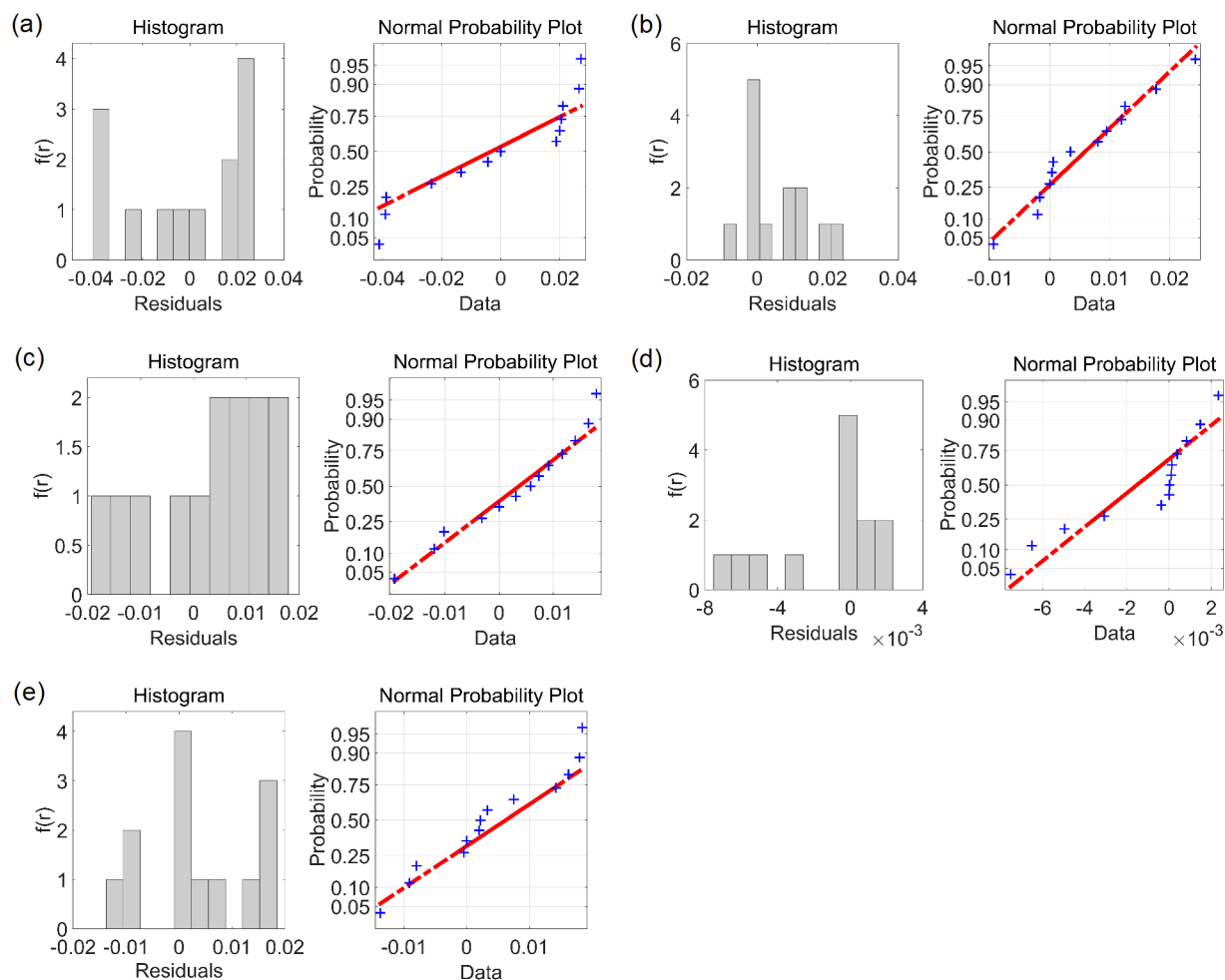


Figure S28. Histogram and normal probability plot of residuals for the estimation of each component concentration in NaCl-H₂O/THF at 433 K. (a) Glucose, (b) fructose, (c) FA, (d) LA, and (e) HMF.

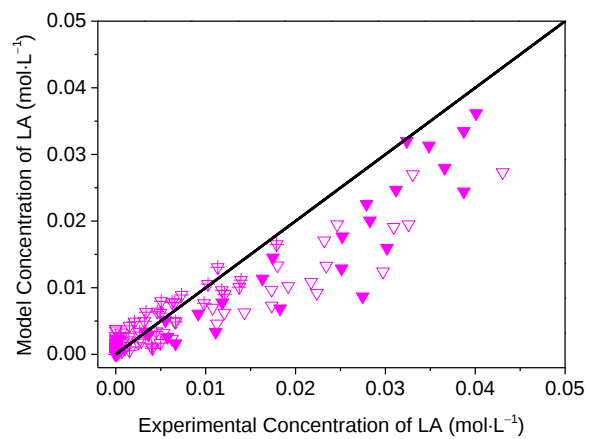


Figure S29. Parity plot of model predicted concentrations of LA in the NaCl-H₂O/THF biphasic system. Filled symbols, glucose as the substrate; hollow symbols, fructose as the substrate; partially filled symbols, HMF as the substrate.

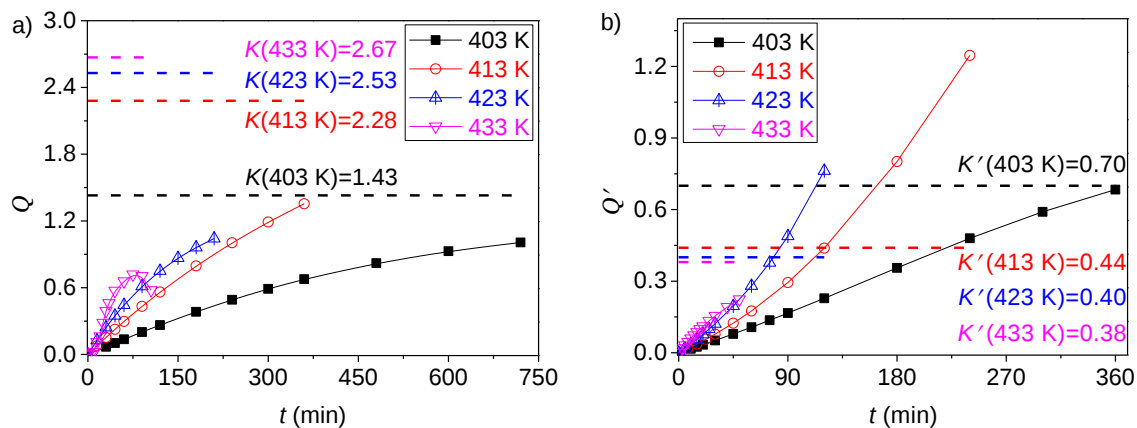


Figure S30. Comparison of activity product (Q) and equilibrium constant (K) at the temperature window of 403 ~ 433 K. (a) For $\text{Glc} \xrightleftharpoons[k_{-1}]{k_1} \text{Fru}$ (ideal system), $K = \frac{k_1}{k_{-1}}$, $Q = \frac{[\text{Fru}]/c^\theta}{[\text{Glc}]/c^\theta}$; (b) for $\text{Fru} \xrightleftharpoons[k_1]{k_{-1}} \text{Glc}$ (ideal system), $K' = \frac{k_{-1}}{k_1} = 1/K$, $Q' = \frac{[\text{Glc}]/c^\theta}{[\text{Fru}]/c^\theta}$. Where K and K' represents the equilibrium constant of reaction (a) and (b), respectively, at reaction temperature; Q and Q' represents the activity product of reaction (a) and (b), respectively, at reaction temperature; c^θ represents the standard concentration of certain component in reaction system which equals to $1 \text{ mol} \cdot \text{L}^{-1}$. Reaction conditions: 1.0 mL aqueous solution saturated with NaCl, 0.25 M Glc or Fru, 25.0 mM AlCl_3 , $V(\text{H}_2\text{O}):V(\text{THF})=1:3$.

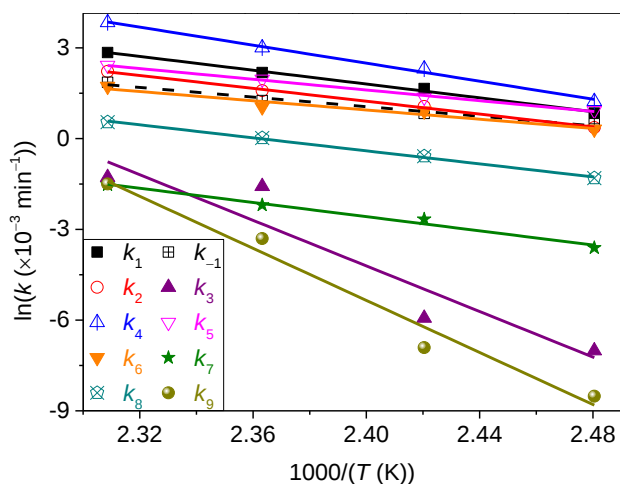


Figure S31. Plots of $\ln k \sim 1/T$. The apparent activation energy (E_a) of each reaction was estimated through the Arrhenius equation. $E_{a1} = 95 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a-1} = 66 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a2} = 89 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a3} = 310 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a4} = 124 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a5} = 74 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a6} = 60 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a7} = 98 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a8} = 90 \text{ kJ}\cdot\text{mol}^{-1}$, $E_{a9} = 354 \text{ kJ}\cdot\text{mol}^{-1}$.

Generally, the E_a of a chemical reaction ranges between 40 and 400 $\text{kJ}\cdot\text{mol}^{-1}$. The relatively higher value of E_{a3} (Glucose-to-humins, 310 $\text{kJ}\cdot\text{mol}^{-1}$) in NaCl-H₂O/THF biphasic solvent than that reported in water (136 $\text{kJ}\cdot\text{mol}^{-1}$ without catalyst; 76~165 $\text{kJ}\cdot\text{mol}^{-1}$ for Brønsted or Lewis acids) reveal the effective suppression of humins formation directly from glucose owing to the inhibition role of NaCl.

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