- Supporting Information-

Suppression of Oligomer formation in Glucose Dehydration by CO_2 and Tetrahydrofuran

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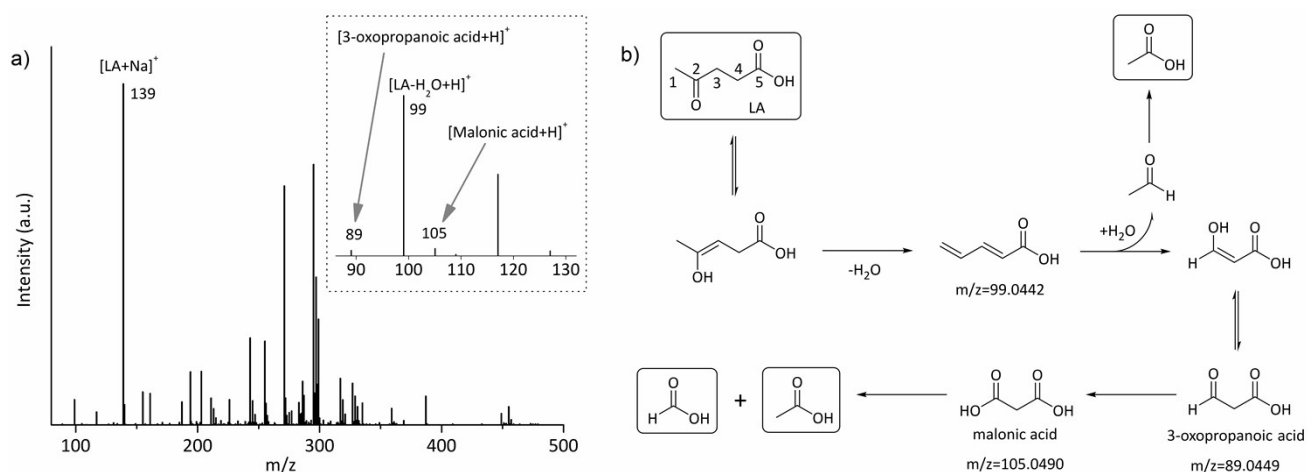
Fig. S1. Profile of product evolution with time during glucose conversion in H_2O. Reaction conditions: 4.4 mmol glucose, 64 mL H_2O, 190 °C, no extra initial pressure.

Fig. S2. Formation of AA and FA from LA. (**a**) ESI-MS spectrum of reaction mixture from reaction of LA in H_2O without extra initial pressure of gas. Inserted spectrum shows the ions of 3-oxopropanoic acid, dehydrated LA and malonic acid in the range of m/z of 86 ~ 132. (**b**) Possible reaction pathway for the LA conversion to AA and FA. Reaction conditions: 2.2 mmol LA, 2.2 mmol HMF, 32 mL H_2O, no extra initial pressure. Liquid products were obtained by being quenched with air when reaction temperature reached 190 °C.

When LA was used as the reactant without extra initial pressure in water, three characteristic peaks were observed at m/z of 89.0449, 99.0442 and 109.0267 in ESI-MS spectra (Fig. S2a). Combined the possible reaction pathway for the LA conversion to AA and FA (Fig. S2b), these peaks were corresponding to 3-oxopropanoic acid, dehydrated LA and malonic acid, respectively. Meanwhile, FA (5.1%) and AA (2.5%) was observed while the conversion of LA was 5.4% (see Table S1). The results and possible mechanism indicated that the 3-oxopropanoic acid formed after C(1)-C(2) breaking of dehydrated LA, while a molecule of acetaldehyde generated, then oxidized to AA. By oxidizing of 3-oxopropanoic acid to malonic acid and following C-C breaking, FA and s AA are obtained. However, imbalanced carbon (96.6%) and excess FA relative to AA indicated the extra reaction pathway for the oligomer formation derived from the condensation of LA with intermediates (acetaldehyde and/or 3-oxopropanoic acid) in which the α-H beside aldehyde groups had higher reactivity. Ions (m/z > 136) in ESI-MS spectrum confirmed the polymerization of intermediates.
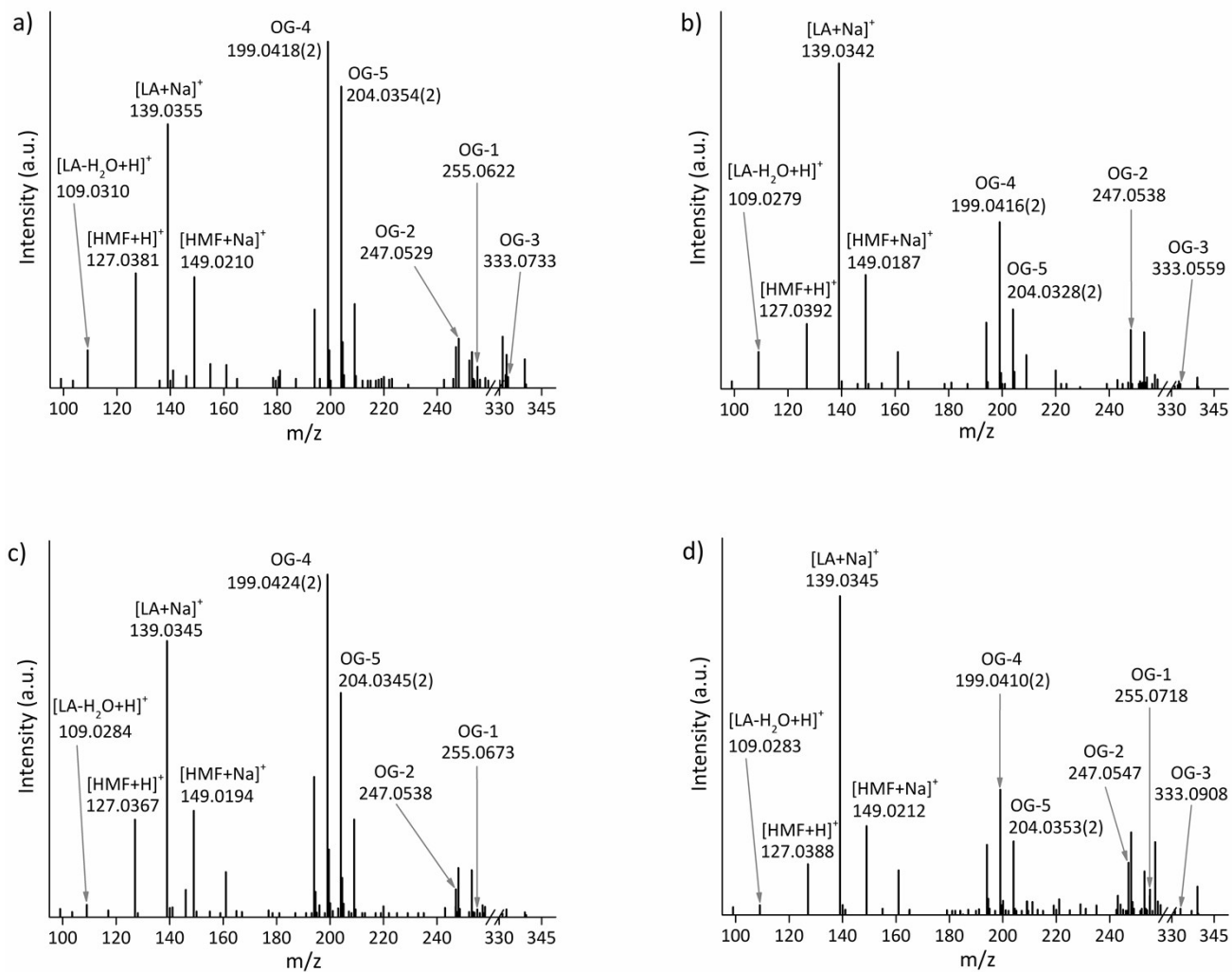
Fig. S3. ESI-MS spectra (*m/z* = 100 ~350) of the reaction mixture from reaction of LA (2.2mmol) and HMF (2.2 mmol) at 180 °C for 1 h in H_2O (32 mL). (**a**) no extra initial pressure, (**b**) 1.0 MPa initial pressure of N_2, (**c**) 1.0 MPa initial pressure of CO_2, and (**d**) in H_2O-THF (32 mL , V_{H2O}/V_{THF} = 1:1), no extra initial pressure.
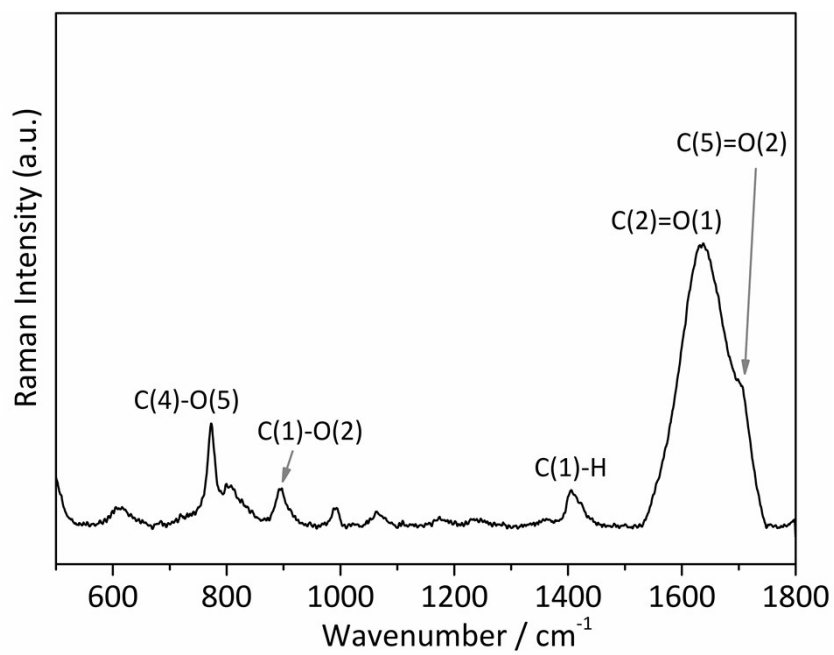
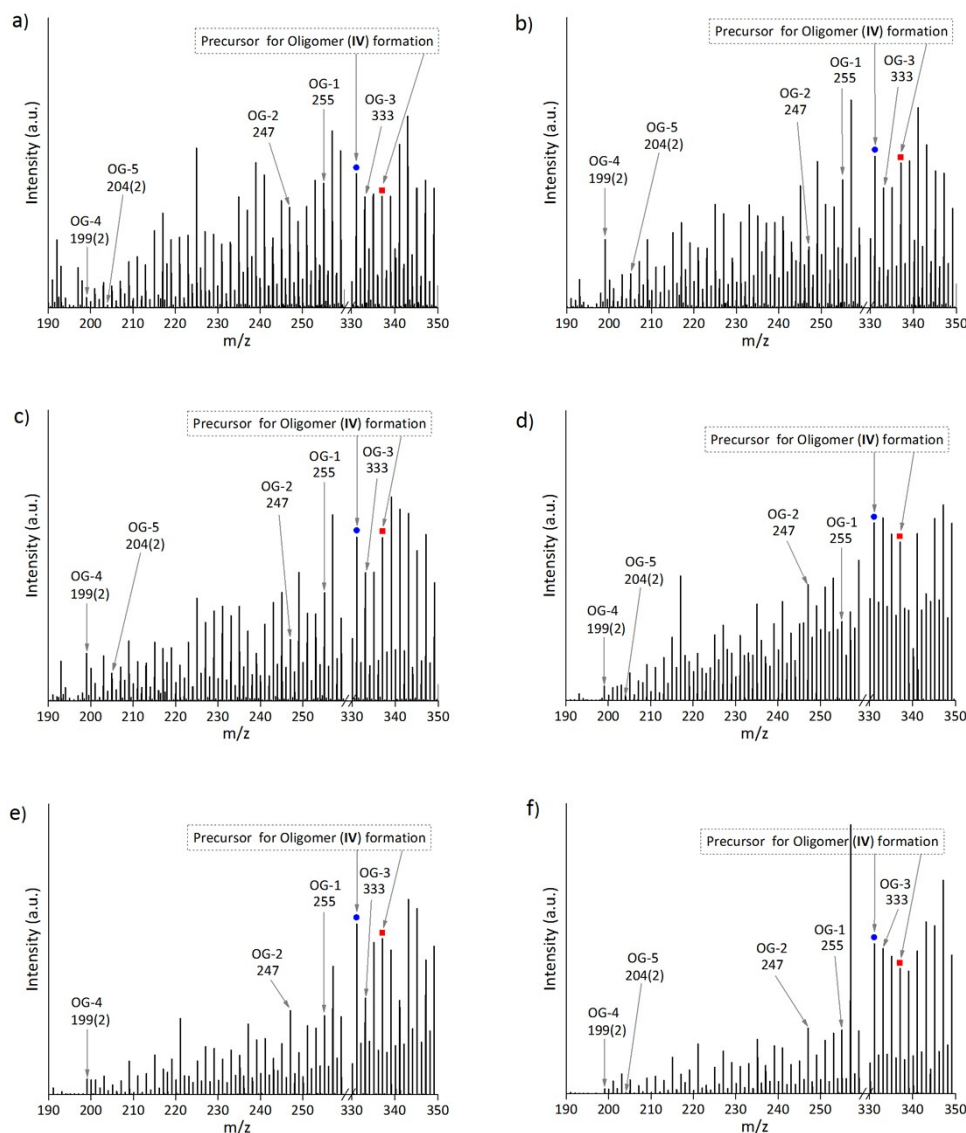**Fig. S4.** Raman spectrum of LA in H_2O at room temperature.

Fig. S5. ESI-MS spectra of the reaction mixture from reaction of glucose (2.2mmol) at 190 °C for 4 h [in H_2O (32 mL) for **a-c**, in H_2O-THF (32 mL, V_{H2O}/V_{THF} = 1:1) for **d-f**], (**a**) no extra initial pressure, (**b**) 1.0 MPa of initial pressure of N_2, (**c**) 1.0 MPa of initial pressure of CO_2, (**d**) no extra initial pressure, (**e**) 1.0 MPa of initial pressure of CO_2, (**f**) 2.4 MPa of initial pressure of CO_2. Legend: blue solid circle (●), [2(glucose/fructose) - HCHO+H]$^+$; red solid square (■), [2(glucose/fructose)–HCOOH + Na]$^+$.

The peaks at *m/z* of 331.0995 and 337.1039 (marked as blue solid cycle and red solid square), assigned to [2(glucose/fructose)-HCHO+H]$^+$ and [2(glucose/fructose)–HCOOH+Na]$^+$ species, respectively, were observed in all reaction conditions. The results revealed that [2(glucose/fructose)-HCHO] and [2(glucose/fructose)-HCOOH] intermediates formed during glucose dehydration. That is, the condensation of two hexose molecules and following decarbonylation/decarboxylation generated HCHO/FA, accompanying with the formation of dimerized dehydrated intermediate. These species might be also precursors for the formation of Oligomer (**IV**).
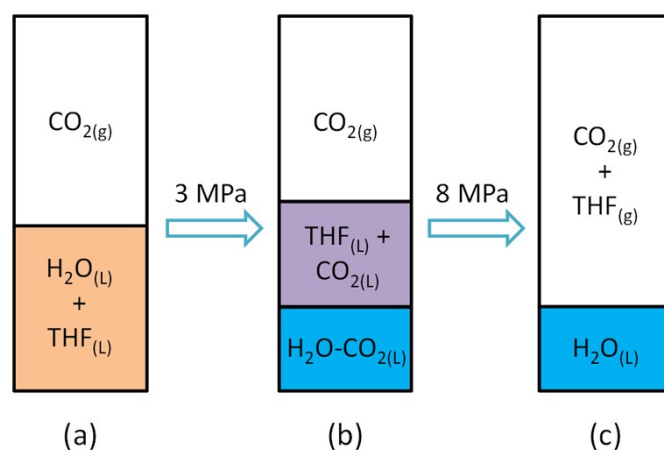
Fig. S6. Phase splitting of H_2O-THF-CO_2 ternary solvent system under different pressure.[2-7] (**a**) biphasic H_2O-THF(l)/CO_2(g), (**b**) triphasic H_2O-CO_2(l)/THF-CO_2(l)/CO_2(g), and (**c**) biphasic H_2O(l)/CO_2-THF(g).

In the H_2O-THF-CO_2 ternary solvent system, biphasic H_2O-THF(l)/CO_2(g) formed with liquid H_2O-THF phase and gaseous CO_2 phase when the pressure of CO_2 was less than 3 MPa (Fig. S6a).[2-5] Increased CO_2 pressure (more than 3 MPa and less than 8 MPa) caused liquid phase splitting and CO_2 dissolving, a triphasic H_2O-CO_2(l)/THF-CO_2(l)/CO_2(g) solvent system including liquid H_2O-CO_2 phase, liquid THF-CO_2 phase (CO_2 expanded THF liquid), and gaseous CO_2 phase was generated (Fig. S6b).[2-5] A CO_2 pressure more than 8 MPa resulted the formation of a biphasic H_2O/CO_2-THF(g) reaction system containing liquid H_2O phase and gaseous CO_2-THF phase (Fig. S6c).[6,7]

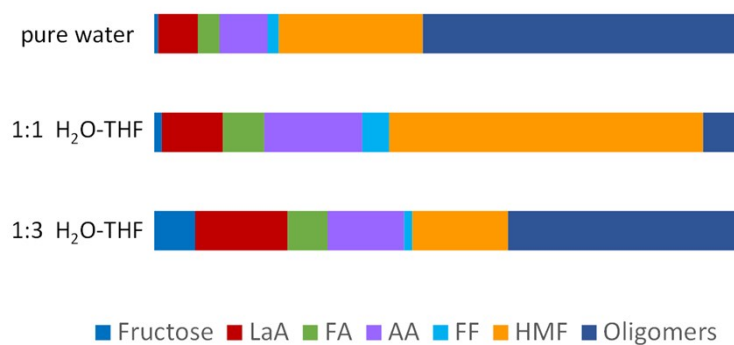**Fig. S7.** The percentage of each product from the glucose conversion in H_2O-THF with different V_{H2O}/V_{THF}. Reaction conditions: 2.2 mmol glucose, 32 mL of solvent, 190 °C, 4 h, 1.0 MPa initial pressure of CO_2.

Table S1. Conversion of LA to AA and FA.[a]

Entry	Solvent	X_{LA}/%	Y_{FA}/%	Y_{AA}/%	Carbon balance/%
1	H_2O	5.4	5.1	2.5	96.6

[a]Reaction conditions: 2.2 mmol LA, 2.2 mmol HMF, 32 mL solvent, no extra initial pressure of gas. Liquid products were obtained by quenching with air when reaction temperature reached 190 °C.

In water, FA (5.1%) and AA (2.5%) were detected in the final products with LA conversion of 5.4%. The imbalanced carbon illustrated the formation of oligomers from the self-condensation of LA or aldol-condensation of LA with its decomposed intermediates. Because the peaks assigned to [3-oxopropanoic acid + H]$^+$ (m/z = 89.0449), [LA - H_2O + H]$^+$ (m/z = 99.0442) and [malonic acid + H]$^+$ (m/z = 109.0267) were observed in the ESI-MS spectrum (as shown in Fig. S2a), the oligomer formation was most possibly derived from the condensation of LA with acetaldehyde and/or 3-oxopropanoic acid. This process also contributed to the stoichiometric excess of FA relative to AA.

Table S2. Weight-average (M_w) and number-average (M_n) molecular weight of oligomers in the liquid products.[a]

Entry	Solvent ($V_{H2O}:V_{THF}$)	Initial atmosphere (MPa)	HMF%	Peak 1[b]		Peak 2[c]	
				M_n (Da)	M_w (Da)	M_n (Da)	M_w (Da)
1	H_2O	-	20.1	90	103	363	447
2	H_2O	N_2/1.0	24.3	92	102	410	534
3	H_2O	CO_2/1.0	24.5	117	121	431	543
4	H_2O-THF (1:1)	-	21.8	104	121	483	582
5	H_2O-THF (1:3)	-	14.4	94	111	396	440
6	H_2O-THF (1:1)	N_2/1.0	29.8	89	102	372	467
7	H_2O-THF (1:1)	CO_2/1.0	51.5	109	121	390	431
8	H_2O-THF (1:3)	CO_2/1.0	16.3	108	117	346	382
9	H_2O-THF (1:1)	CO_2/0.6	32.2	111	119	367	406
10	H_2O-THF (1:1)	CO_2/2.4	31.0	108	117	346	382

[a]Reaction conditions: 2.2 mmol glucose, 32 mL solvent, 190 °C, 4 h, with initial pressure of gas. The average molecule weight of products, [b]<180 Da, and [c]≥ 180 Da.

Peak 1 was defined as small molecules with average molecule weight below 180 Da (such as HMF, FA, AA, LaA, LA and partial intermediates), and peak 2 was defined as oligomers with average molecule weight more than 180 Da.

Table S3. Conversion of LA and HMF into oligomers.[a]

Entry	Solvent ($V_{H2O} : V_{THF}$)	Atmosphere	X_{HMF}/%	X_{LA}/%	Y_{FA}/%	Carbon Balance/%	Oligomers[b]		
							M_w (Da)	M_n (Da)	M_w/M_n
1	H_2O	-	26.8	12.6	16.3	81.1	12628	11586	1.09
2	H_2O	N_2	23.9	-4.1[c]	35.5	92.1	9092	7729	1.08
3	H_2O	CO_2	23.4	0.8	35.2	90.1	5854	4365	1.34
4	H_2O-THF (1:1)	-	38.2	-28.0[c]	64.2	97.7	1819	1078	1.68

[a]Reaction conditions: 2.2 mmol LA, 2.2 mmol HMF, 32 mL solvent, 180 °C, 1 h, 1.0 MPa initial pressure of gas. [b]The products with average molecule weight above 180 Da. [c]The negative LA conversion indicates the occurrence of HMF-to-LA/FA rehydration.

To reduce the formation of solid humins from oligomers, the reaction temperature was decreased to 180 °C instead of 190 °C (the reaction temperature used in glucose conversion). Comparable HMF conversions were obtained in H_2O under different reaction pressure and atmosphere (entry 1-3), while the different LA conversion and carbon balance indicated the difference in the reaction pathways between HMF and LA. In H_2O without extra initial pressure, the higher LA conversion (12.6%) and lower carbon balance (81.1%) indicated that significant cross-condensation between HMF and LA occurred. In pressured N_2 atmosphere, the negative LA conversion (-4.1%) with better carbon balance (92.1%) revealed the primary occurrence of HMF-to-LA/FA rehydration. While in pressured CO_2 atmosphere, the lower conversion of LA (0.8%) with carbon balance of 90.1% suggested an approximately equal HMF rehydration and condensation. In H_2O-THF without extra initial pressure, a higher HMF conversion of 38.2% and negative LA conversion with highest carbon balance (97.7%) illustrated the predominant occurrence of HMF-to-LA/FA rehydration. From the GPC analysis, when LA and HMF were used as substrates, the average molecule weights were significantly higher (above 1000 Da) than that in glucose conversion (below 600 Da) because of the use of high concentration LA. Notably, insoluble humins were observed in H_2O, especially in the atmosphere without extra initial pressure.

Table S4. Characteristic Raman scattering peaks of LA and HMF (500-2000 cm^{-1}).[7, 8]

Entry	Peak/cm^{-1}	Raman Vibration
HMF	966	C(2)-O(1) stretching vibration
	986	C(5)-O(1) stretching vibration
	1025	C(1)-O(2) stretching vibration, C(3)/C(4)-H scissoring vibration
	1200	C(3)-H/C(5)-H rocking vibration
	1368	C(1)-H wagging vibration
	1400	H-C(6)-C(5)/O(3) bending vibration
	1457	C(1)-H scissoring vibration
	1524	C(2)=C(3)/C(4)=C(5) symmetric stretching vibration
	1580	C(2)-C(3)/C(4)-C(5) asymmetric stretching vibration
	1659	C(6)=O(3) stretching vibration
LA	770	C(4)-C(5) stretching vibration
	896	C(1)-C(2) stretching vibration
	1410	C(1)-H twisting vibration
	1662	C(2)=O(1) stretching vibration
	1714/1743	C(5)=O(2) stretching vibration

Table S5. Time-resolved conversion of LA and HMF.^{a}

Entry	Solvent	X_{HMF}/%	X_{LA}/%	Y_{FA}/%	Y_{AA}/%	Carbon Balance/%
1	100 °C (0 min)	-	-	-	-	100
2	150 °C (0 min)	0.9	1.0	0.4	0.3	98.7
3	180 °C (0 min)	1.8	1.6	0.7	0.4	98.8
4	180 °C (15 min)	6.2	1.7	1.0	0.5	96.2
5	180 °C (30min)	15.3	14.2	4.3	1.0	85.7

^{a}Reaction conditions: 2.2 mmol LA, 2.2 mmol HMF, 32 mL solvent, 160 °C, 1 h, without extra initial pressure.

Table S6. Production of different product in glucose conversion.

Entry	Solvent	Catalyst	Time (h)	Temperature (°C)	Initial pressure (MPa)	Conversion (%)	Main Product (%)	Selectivity (%)	Carbon Balance (%)	Ref.
1	H_2O	Sn-beta	0.5	110	-	55	Fructose (32)	58.2	86	*Proc. Natl. Acad. Sci.*, 2010, **107**, 6164-6168.
2	H_2O	Ba(OH)$_2$	48	25	-	99.5	LaA (95.4)	95.9	95.9	*Green Chem.*, 2017, **19**,76-81.
3	H_2O	Amberlyst-15	3	120	-	89	FA (37.4)	42.3	84.6	*J. Am. Chem. Soc.*, 2011, **133**, 4224-4227.
4	water/(THF+NMP)[a]	P-TiO$_2$	1.75	175	2.0 (Ar)	98.2	HMF (90.5)	92.2	92.3	*ChemSusChem*, 2015, **8**, 2907-2916.
5	THF	sulfuric acid	3	190	-	~97	LGO (40)[b]	~41	~60	*Energy Environ. Sci.*, 2015, **8**, 1808-1815.

[a]$V_{water}/V_{(THF-NMP)}$ = 1:4, 4 g of NaCl. [b]Levoglucosenone

Table S7. Conversion of typical carbohydrates into HMF in triphasic CO_2-H_2O-THF with 1.0 MPa initial pressure of CO_2.[a]

Entry	Substrate	$Y_{glucose}$/%	Y_{HMF}/%	$Y_{fructose}$/%	Y_{LaA}/%	Y_{FA}/%	Y_{AA}/%	Y_{LA}/%	Carbon balance/%
1	maltose	25.0	39.9	3.4	3.0	13.7	9.7	-	75.3
2	cellobiose	24.9	40.9	2.0	-	14.2	10.9	-	73.8
3	starch	31.4	36.9	2.4	-	10.3	10.8	-	76.0
4	glycogen	34.0	41.4	2.4	-	10.7	12.7	-	83.8
5	sucrose	10.6	35.9	0.6	6.0	16.3	8.7	2.3	57.6

[a]Reaction conditions: 2.2 mmol substrate (based on the C_6 unit), 32 mL solvent (V_{H2O}/V_{THF} = 1:1), 190 ºC, 4 h.

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