Electronic Supplementary Material (ESI) for Green Chemistry.

– Supporting information –

Sequential extraction separation of soluble humins from fructose conversion for structural and evolutional understandings

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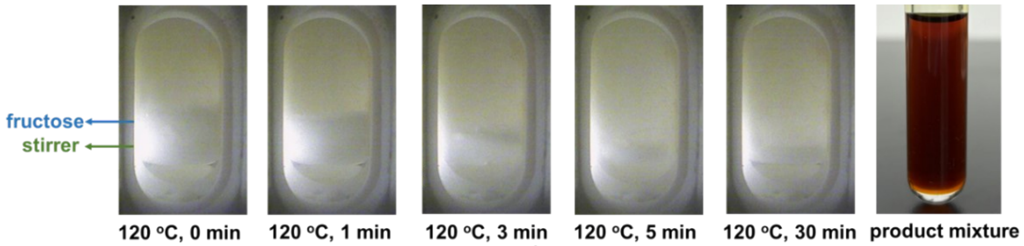
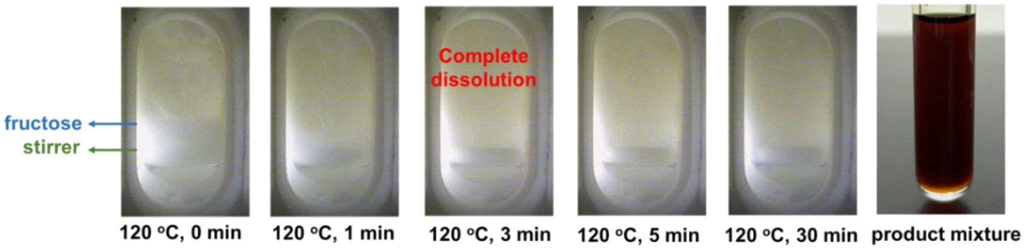
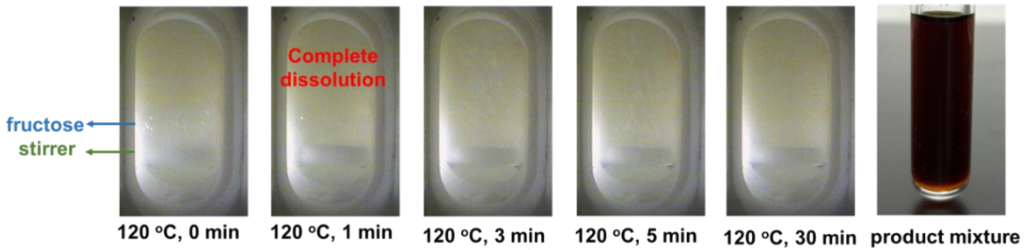
Table S9. Weight-average and number-average molecular weights of the liquid products after reaction under different conditions.



(a) DIO



(b) EtOH-DIO



(c) EtOH

Fig. S1. *In-situ* observation of fructose dissolution in various solvents at 120 ^{o}C under microwave heating. (a) DIO, (b) EtOH-DIO (V_{EtOH}/V_{DIO} = 1:4), (c) EtOH.

The installation of a visible window allowed our direct observation of the dissolution process of fructose in experimental amount (i.e. 20 *wt.*%) at 120 ^{o}C under microwave heating. A fast and complete dissolution of fructose was observed within 1 min in EtOH and within 3 min in EtOH-DIO without adding any acid catalyst, whereas a slow and incomplete dissolution was observed in DIO within 30 min. This variation in fructose dissolution was deemed to be resulted from the difference in polarity and hydrogen-bond acceptor/donor ability of various solvents, wherein the higher α value (0.86) and dielectric constant (ε, 24.5) of EtOH were indicative of its better affinity with fructose and better ability for dissolution, whereas the medium β value (0.37) and ε (2.22) of DIO suggested its worse affinity with fructose and worse ability for dissolution. The adoption of a mixed solvent EtOH-DIO (V_{EtOH}/V_{DIO} = 1:4) enabled similarly fast dissolution of fructose as that in EtOH with a time difference below 2 min, which was indicative of the less influence of solvent composition on dissolution rate of fructose in polar EtOH-DIO and EtOH. However, the rather slow dissolution of fructose in DIO was thought to slow down the reaction kinetics of fructose conversion. Nevertheless, the deliberate observation of the liquid products after fructose conversion in DIO for 30 min revealed the formation of a homogeneous liquid mixture with fructose conversion approaching to 100%, accompanied with no solid residues (undissolved fructose and solid humins) obtained after centrifuging. This result indicated the complete dissolution and conversion of fructose in medium-polar DIO under experimental conditions. As such, it was inferred that the formation of intermediates and products accelerated the dissolution of fructose.

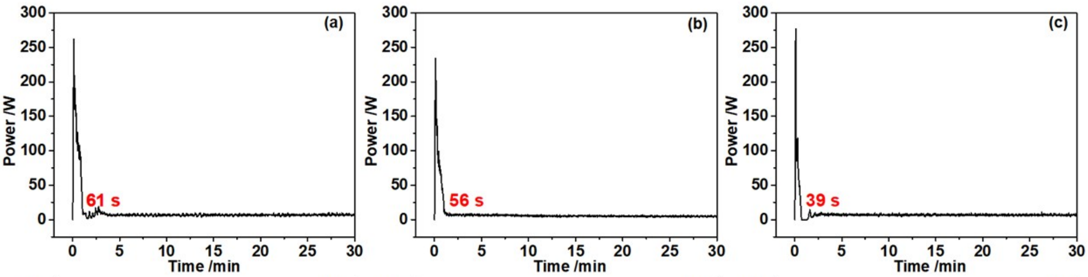


Fig. S2. The variation in output power of microwave with time during the conversion of fructose in a glass tube containing different solvents. (a) DIO, (b) EtOH-DIO ($V_{\mathrm{EtOH}}/V_{\mathrm{DIO}}$ = 1/4), (c) EtOH.

Considering the potential microwave absorption of polar and non-polar solvents and their influence on fructose conversion, we adopted **a rapid heating mode** in experiments for fructose-to-EMF/HMF conversion, wherein the output power of microwave could be adjusted automatically. Time profiles of output power could be used to reflect the heating pattern. In addition, it should be noted that the fructose-to-EMF/HMF conversion was experimentally carried out in **a glass tube**, which was thought to be unable to absorb the microwave and thereby provided possibility for microwave absorption by the solvents. Therefore, the variation of the output power of microwave with time in a glass tube was expected to reflect the microwave absorption capacity of solvents and its influence on the heating rate. As shown in Fig. S2a ~ c, the time required for reaching 120 $^{\circ}$C was different (61 s in DIO, 56 s in EtOH-DIO, and 39 s in EtOH). The fast temperature-rising in EtOH was deemed to be caused by the better absorption of microwave by EtOH with higher polarity (*Angew. Chem. Int. Ed. 2004, 43,6250 – 6284*). Nevertheless, the difference of heating rate in these three solvents was not significant (< 22 s).

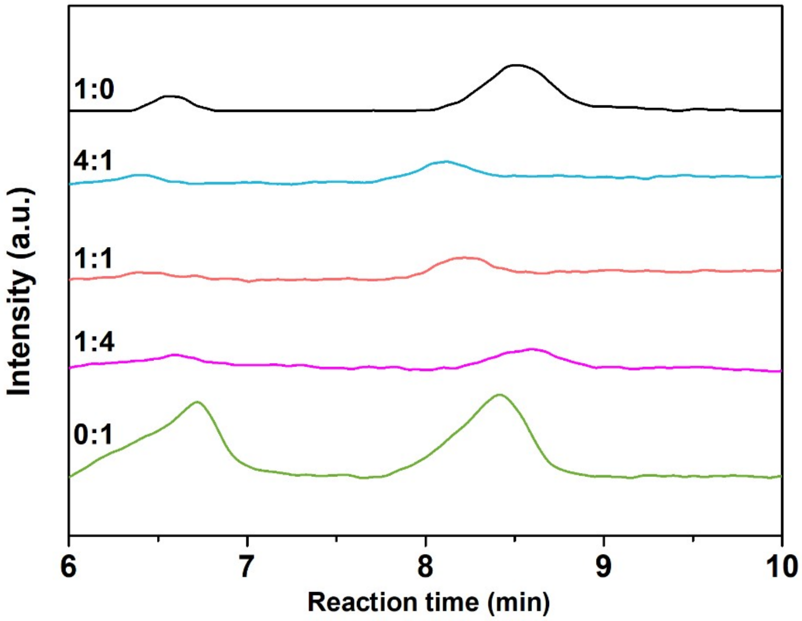


Fig. S3. GPC profiles of the product mixture after fructose conversion in the mixed solvent of EtOH-DIO with various $V_{\mathrm{EtOH}}/V_{\mathrm{DIO}}$.

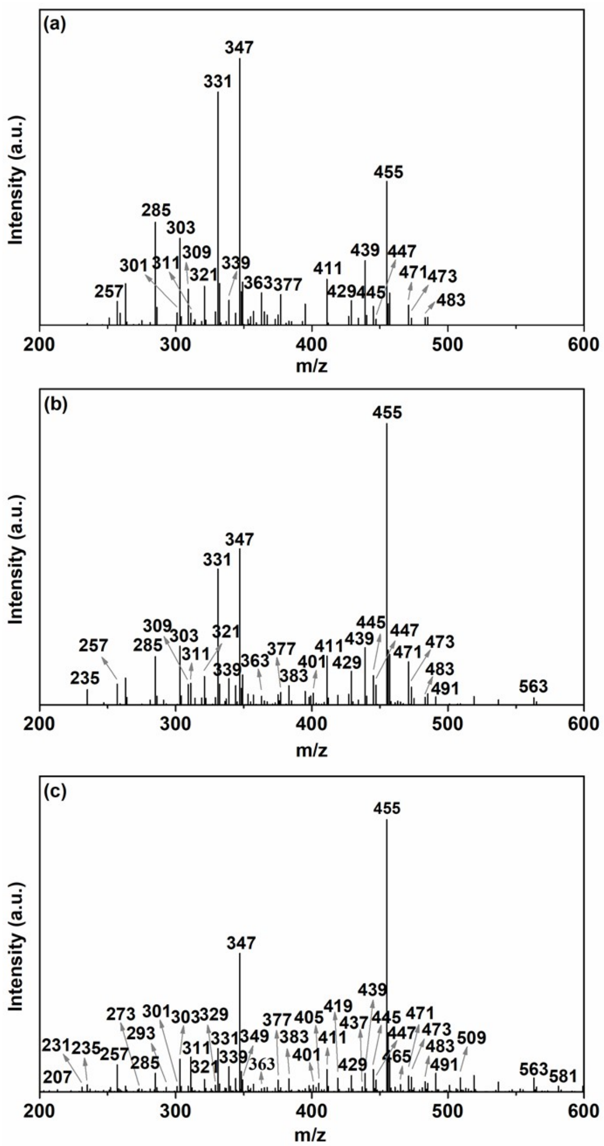


Fig. S4. ESI-MS spectra of the reaction mixture after the acid-catalyzed conversion of fructose with various initial concentrations at 120 °C for 0.5 h in the mixed solvent of EtOH-DIO (V_{EtOH}/V_{DIO} = 1:4). (a) 5 *wt*.%, (b) 10.0 *wt*.%, (c) 20.0 *wt*.%.

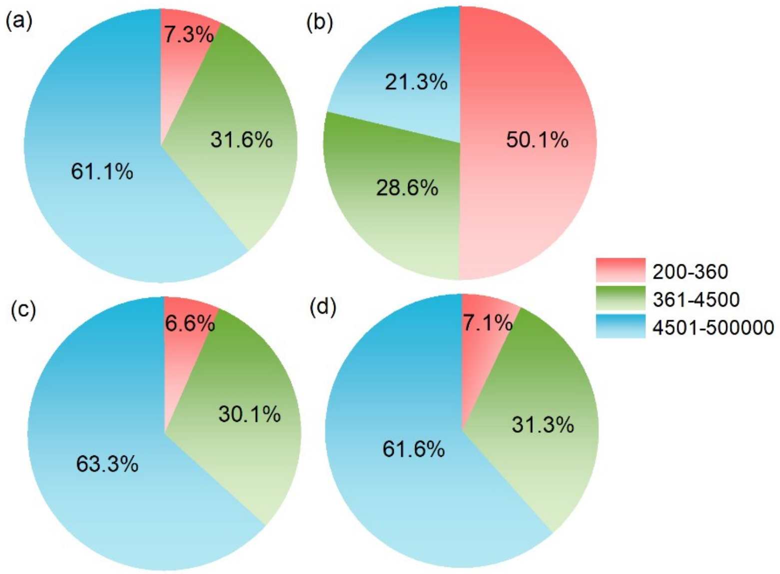


Fig. S5. Proportional distribution of the humin species with various molecular ranges in the four types of humin samples. (a) humins **I,** (b) humins **II**, (c) humins **III**, (d) humins **IV**.

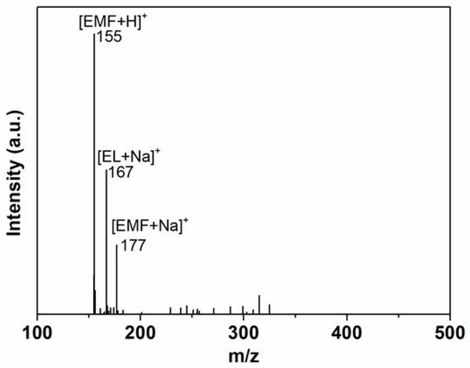
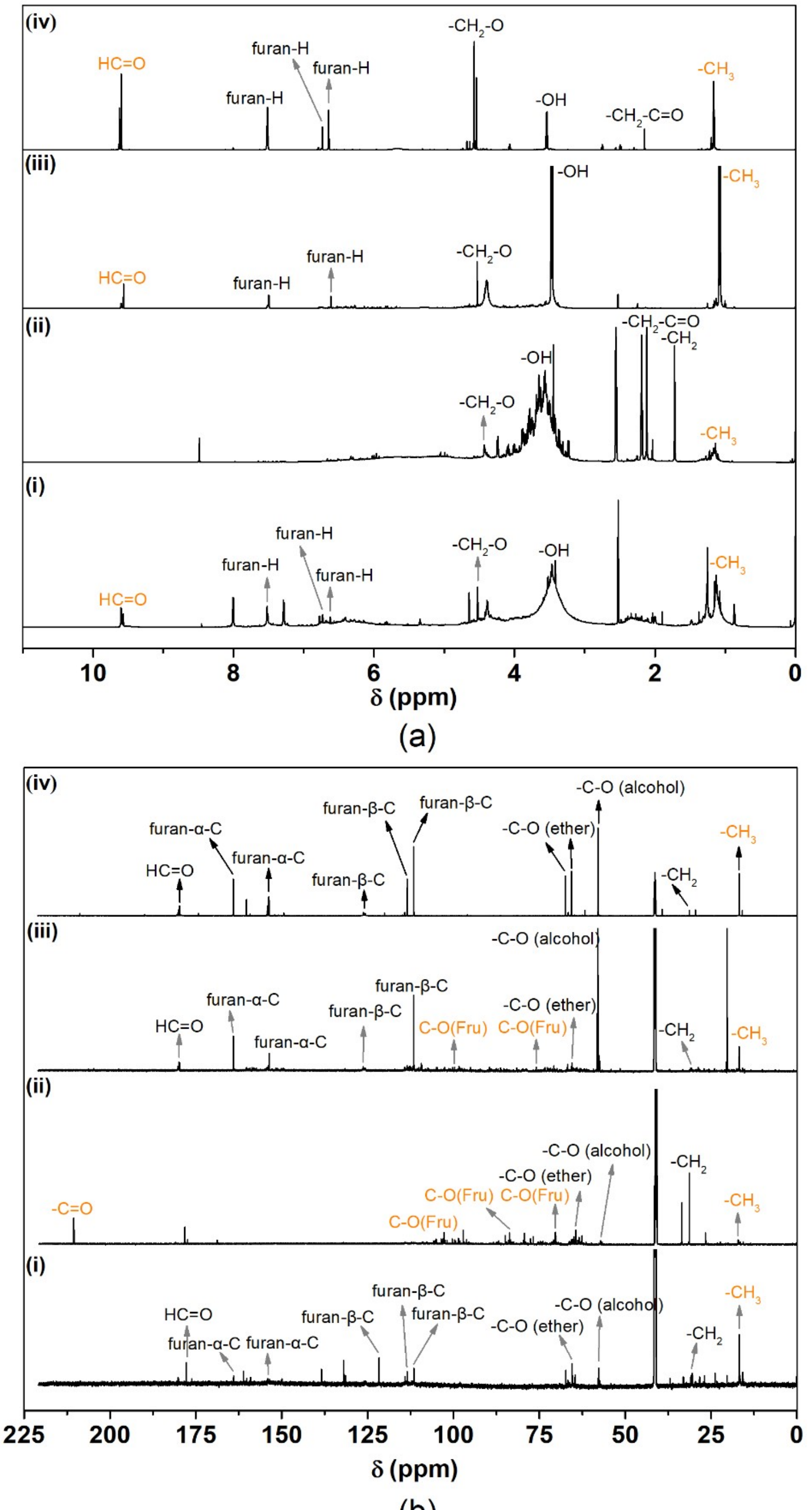


Fig. S6. ESI-MS spectrum of the liquid products after the acid-catalyzed conversion of HMF and LA at 120 ^{o}C for 0.5 h in V_{DIO}/V_{EtOH} = 4:1. Reaction conditions: 0.5 mmol HMF, 0.5 mmol LA, 0.1 g HND-580, 5 mL solvent.

The peaks with m/z of 155 and 177 were assigned to $[EMF+H]^+$ and $[EMF+Na]^+$, respectively. The peak with m/z of 167 was assigned to $[EL+Na]^+$. Therefore, the reaction HMF and LA at 120 ^{o}C for 0.5 h in V_{DIO}/V_{EtOH} = 4:1 produced EMF and EL as the products, thereby excluding the possibility of esterification between HMF and LA under experimental conditions.



(a)

(b)

Fig. S7. (a) ^{13}C-NMR and (b) ^{1}H-NMR spectra of the four types of humin samples. (i) humins **I**, (ii) humins **II**, (iii) humins **III**, (iv) humins **IV**.

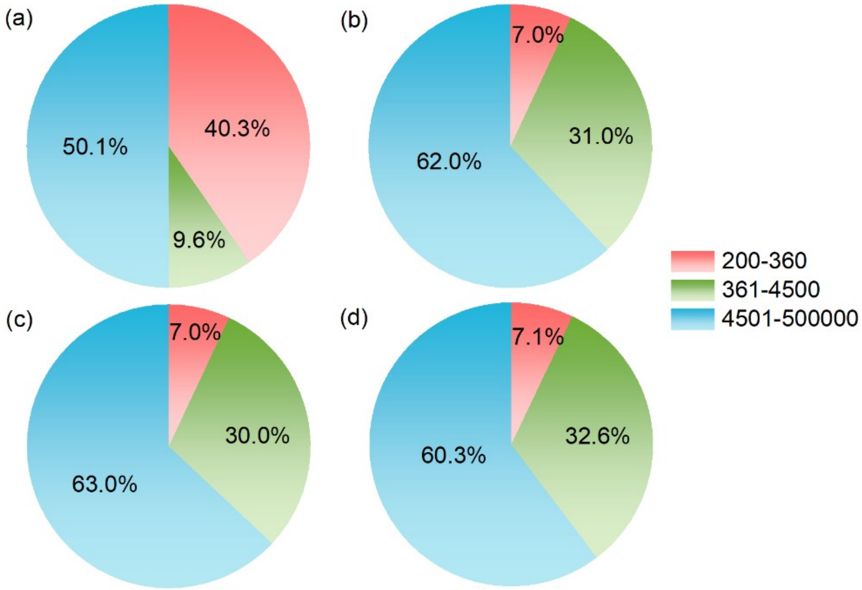


Fig. S8. Molecular weight distributions of liquid products after fructose conversion under different reaction conditions. (a) 0.5 h, 120 ^{o}C, 0.1 g HND-580; (b) 1.5 h, 120 ^{o}C, 0.1 g HND-580; (c) 0.5 h, 140 ^{o}C, 0.1 g HND-580; (d) 0.5 h, 120 ^{o}C, 0.3 g HND-580.

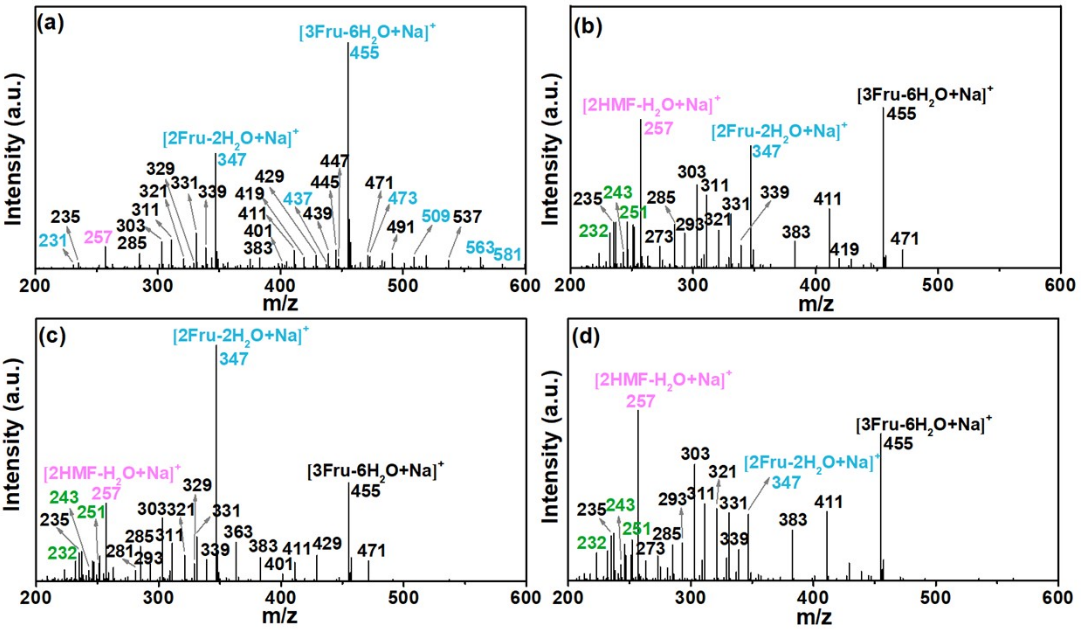


Fig. S9. The ESI-MS spectra of the reaction mixture from the dehydration and etherification of fructose under different reaction conditions. (a) 0.5 h, 120 °C, 0.1 g HND-580, (b) 1.5 h, 120 °C, 0.1 g HND-580, (c) 0.5 h, 140 °C, 0.1 g HND-580, (d) 0.5 h, 120 °C, 0.3 g HND-580.

Table S1. Product distributions for the acid-catalyzed conversion of high-concentration fructose in various mixed solvents.

Entry	Solvent	Conv. of fruc. /%	Yield /%								Carbon balance /%
			MMF	i-PMF	HMF	FA	MF	LA	ML	FF	
1	DIO	98.7	-	-	35.4	22.9	-	1.5	-	2.7	44.0
2	MeOH-DIO	98.1	28.4	-	25.1	14.5	2.5	0.5	1.6	2.1	61.7
3	i-PrOH-DIO	98.4	-	0.8	37.3	12.7	-	-	-	3.7	44.9

Reaction conditions: 20 *wt.*% fructose, 5 mL solvent ($V_{alcohol}:V_{DIO}$ = 1:4), 0.1 g HND-580, 120 ^{o}C, 0.5 h.

It was observed that the total yield of furanics was increased from 35.4% to 53.5% by adding MeOH as the co-solvent, accompanied with the decrease of total yield of FA and MF (methyl formate) from 22.9% to 17.0% and slight increase of total yield of LA and ML (methyl levulinate) from 1.5% to 2.1%. These variations in product yields decreased the stoichiometric excess between FA+MF and LA+ML from 21.4 mol% to 14.9 mol%, thereby revealing the similar inhibiting role of MeOH on the degradative condensation of fructose and/or HMF to humins owing to its stabilizing role on the key intermediates (DFAs) for humin formation. As a result, the carbon balance was increased from 44.0% to 61.7%. However, different situation was found in the mixed solvent of i-PrOH and DIO, as both the total yield of HMF/i-PMF and carbon balance were not improved significantly. This result might be ascribed to the difficulty in stabilizing DFAs caused by the large steric resistance of i-PrOH.

Table S2. Product distributions after the acid-catalyzed conversion of high-concentration fructose in a glass or SiC tube.

Entry	Solvent	microwave reaction tube	Conv. of fruc. /%	Yield /%								Carbon balance /%
				HMF	EMF	FA	EF	LA	EL	(FA+EF)-(LA+EL)	FF	
1	DIO	glass tube	98.7	35.4	-	22.9	-	1.5	-	21.4	2.7	44.0
2		SiC tube	98.6	37.5	-	21.9	-	1.2	-	20.7	3.5	46.5
3	EtOH-DIO[a]	glass tube	98.6	40.6	15.0	9.2	5.0	0.8	1.6	11.8	1.8	62.9
4		SiC tube	97.8	36.7	18.0	8.5	6.0	0.8	2.3	11.4	2.2	63.7
5	EtOH	glass tube	97.0	21.7	20.2	6.6	6.4	0.3	3.6	9.1	0.8	51.0
6		SiC tube	97.6	20.0	22.2	6.2	6.5	0.2	3.8	8.7	0.9	50.1

Reaction conditions: 20 *wt.*% fructose, 5 mL solvent, 0.1 g HND-580, 120 ^{o}C, 0.5 h. [a] V_{EtOH}/V_{DIO} = 1/4.

Table S3. Number-average (*Mn*) and weight-average (*Mw*) molecular weights of the liquid products after fructose conversion in the mixed solvent of EtOH-DIO with various $V_{\mathrm{EtOH}}/V_{\mathrm{DIO}}$.[a]

Entry	$V_{\mathrm{EtOH}}/V_{\mathrm{DIO}}$	*Mn*	*Mw*
1	0:1	361	16179
2	1:4	222	3275
3	1:1	244	6795
4	4:1	269	10340
5	1:0	331	15519
6[b]	1:4	196	3140
7[c]	1:4	190	2980

[a] Reaction conditions: 20 *wt.*% fructose, 5 mL solvent, 0.1 g HND-580, 120 ^{o}C, 0.5 h. [b] 10 *wt.*% fructose. [c] 5 *wt.*% fructose.

Table S4. Product distributions for the acid-catalyzed conversion of fructose with various substrate concentrations in the mixed solvent of EtOH and DIO.

Entry	Fruc. conc. /*wt*. %	Conv. /%	Yield /%						Carbon balance /%
			EMF	HMF	FA+EF	LA+EL	(FA+EF) - (LA+EL)	FF	
1	5	99.7	39.7	29.8	16.9	7.9	9.0	4.3	82.8
2	10	99.8	26.5	38.0	15.5	6.0	9.5	3.0	74.8
3	20	98.6	14.9	40.6	14.2	2.4	11.8	1.8	62.9

Reaction conditions: 5 mL solvent (V_{EtOH}:V_{DIO} = 1:4), 0.1 g HND-580, 120 ^{o}C, 0.5 h.

Table S5. The possible structural formula of the ionic species deconvoluted from the ESI-MS spectrum of humins **I**.

m/z	Possible structural formula	m/z	Possible structural formula
207	$[HMF+Fru-FA-3H_2O+H]^+$	401	$[2HMF+EL-H_2O+Na]^+$
235	$[2HMF-H_2O+H]^+$	411	$[3HMF+EtOH-2H_2O+Na]^+$
257	$[2HMF-H_2O+Na]^+$	429	$[2HMF+EL+EtOH-2H_2O+Na]^+$
273	$[2HMF-H_2O+K]^+$	447	$[3HMF+EtOH+Na]^+$
321	$[HMF+EL+EtOH-H_2O+Na]^+$	475	$[3HMF+2EtOH-H_2O+Na]^+$
331	$[2HMF+2EtOH-2H_2O+Na]^+$	527	[4HMF+Na]+
349	$[HMF+EL+2EtOH-2H_2O+Na]^+$	555	$[4HMF+EtOH-H_2O+Na]^+$

Table S6. The possible structural formula of the ionic species deconvoluted from the ESI-MS spectrum of humins **II**.

m/z	Possible structural formula	m/z	Possible structural formula
231	$[Fru+EtOH-H_2O+Na]^+$	437	$[3Fru-7H_2O+Na]^+$
301	$[2Fru-FA-2H_2O+Na]^+$	445	$[3Fru-FA-4H_2O+Na]^+$
311	$[2Fru-4H_2O+Na]^+$	455	$[3Fru-6H_2O+Na]^+$
327	$[2Fru-4H_2O+K]^+$	471	$[3Fru-6H_2O+K]^+$
329	$[2Fru-3H_2O+Na]^+$	473	$[3Fru-5H_2O+Na]^+$
347	$[2Fru-2H_2O+Na]^+$	491	$[3Fru-4H_2O+Na]^+$
363	$[2Fru-2H_2O+K]^+$	509	$[3Fru-3H_2O+Na]^+$
405	$[3Fru-FA-5H_2O+H]^+$	563	$[4Fru-10H_2O+Na]^+$
419	$[3Fru-8H_2O+Na]^+$	581	$[4Fru-9H_2O+Na]^+$

Table S7. The possible structural formula of the ionic species deconvoluted from the ESI-MS spectrum of humins **III**.

m/z	Possible structural formula	m/z	Possible structural formula
253	$[HMF+Fru-3H_2O+H]^+$	435	$[2HMF+Fru-2H_2O+K]^+$
271	$[HMF+Fru-2H_2O+H]^+$	447	$[2HMF+Fru+EtOH-3H_2O+Na]^+$
293	$[HMF+Fru-2H_2O+Na]^+$	463	$[2HMF+Fru+EtOH-3H_2O+K]^+$
311	$[HMF+Fru-H_2O+Na]^+$	465	$[2HMF+Fru+EtOH-2H_2O+Na]^+$
339	$[HMF+Fru+EtOH-2H_2O+Na]^+$	483	$[2HMF+Fru+EtOH-H_2O+Na]^+$
361	$[2HMF+Fru-4H_2O+H]^+$	491	$[2HMF+Fru+2EtOH-4H_2O+K]^+$
379	$[2HMF+Fru-3H_2O+H]^+$	493	$[2HMF+Fru+2EtOH-3H_2O+Na]^+$
383	$[2HMF+Fru-4H_2O+Na]^+$	527	$[2HMF+2Fru-6H_2O+Na]^+$
409	$[HMF+2Fru-FA-3H_2O+Na]^+$	573	$[2HMF+2Fru+EtOH-6H_2O+Na]^+$
419	$[2HMF+Fru-2H_2O+Na]^+$		

Table S8. The possible structural formula of the ionic species deconvoluted from the ESI-MS spectrum of humins **IV**.

m/z	Possible structural formula	m/z	Possible structural formula
281	$[2HMF+EtOH-H_2O+H]^+$	377	$[2HMF+3EtOH-2H_2O+Na]^+$
285	$[2HMF+EtOH-2H_2O+Na]^+$	383	$[2HMF+Fru\text{-}FA+EtOH-4H_2O+Na]^+$
303	$[2HMF+EtOH-H_2O+Na]^+$	411	$[3HMF+EtOH-2H_2O+Na]^+$
309	$[2HMF+2EtOH-2H_2O+H]^+$	439	$[3HMF+2EtOH-3H_2O+Na]^+$
321	$[2HMF+EtOH+Na]^+$	447	$[3HMF+EtOH+Na]^+$
331	$[2HMF+2EtOH-2H_2O+Na]^+$	475	$[3HMF+2EtOH-H_2O+Na]^+$
349	$[2HMF+2EtOH-H_2O+Na]^+$		

Table S9. Weight-average and number-average molecular weight of the liquid products after reaction under different conditions.

Entry	Reaction temperature /^{o}C	Reaction time / h	Catalyst dosage / g	*Mn*	*Mw*
1	120	0.5	0.1	222	3275
2	120	1.5	0.1	1210	26611
3	140	0.5	0.1	1213	22328
4	120	0.5	0.3	1210	27941

Reaction conditions: 20 *wt*.% fructose, 5 mL solvent (V_{EtOH}/V_{DIO} = 1:4).