Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Production of levoglucosenone and 5-hydroxymethylfurfural from cellulose in polar aprotic solvent-water mixtures

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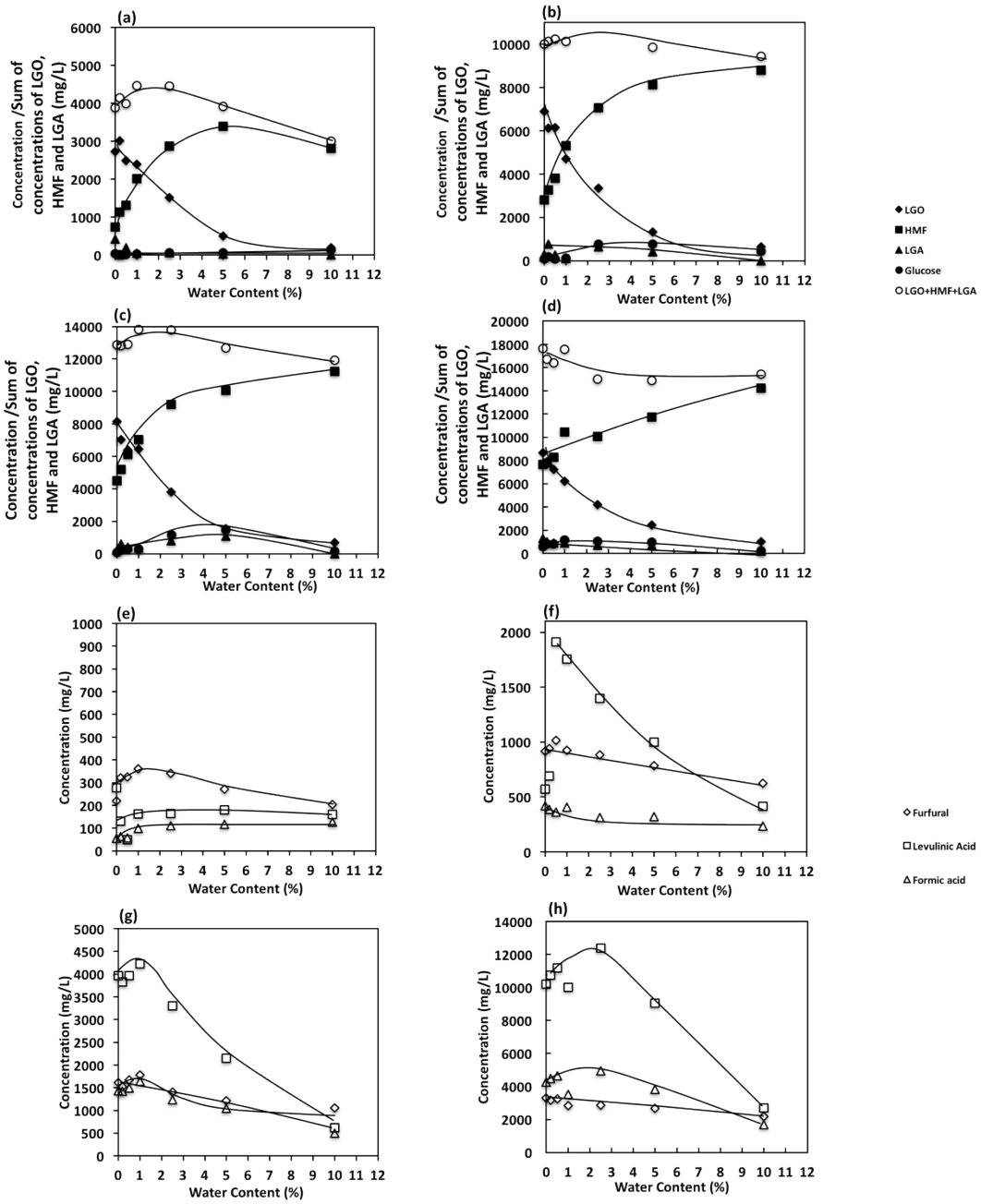


Figure S1 Influence of water content on the product concentrations. Reaction conditions: THF (60 mL), 210 ˚C, 1000 psi H_2, 700 rpm. Cellulose loading: (a, e) 1 wt.% (b, f) 3 wt.% (c, g) 5 wt.% (d, h) 10 wt.%. Reaction time for maximum yields of LGO and HMF are listed in **Table S2**.

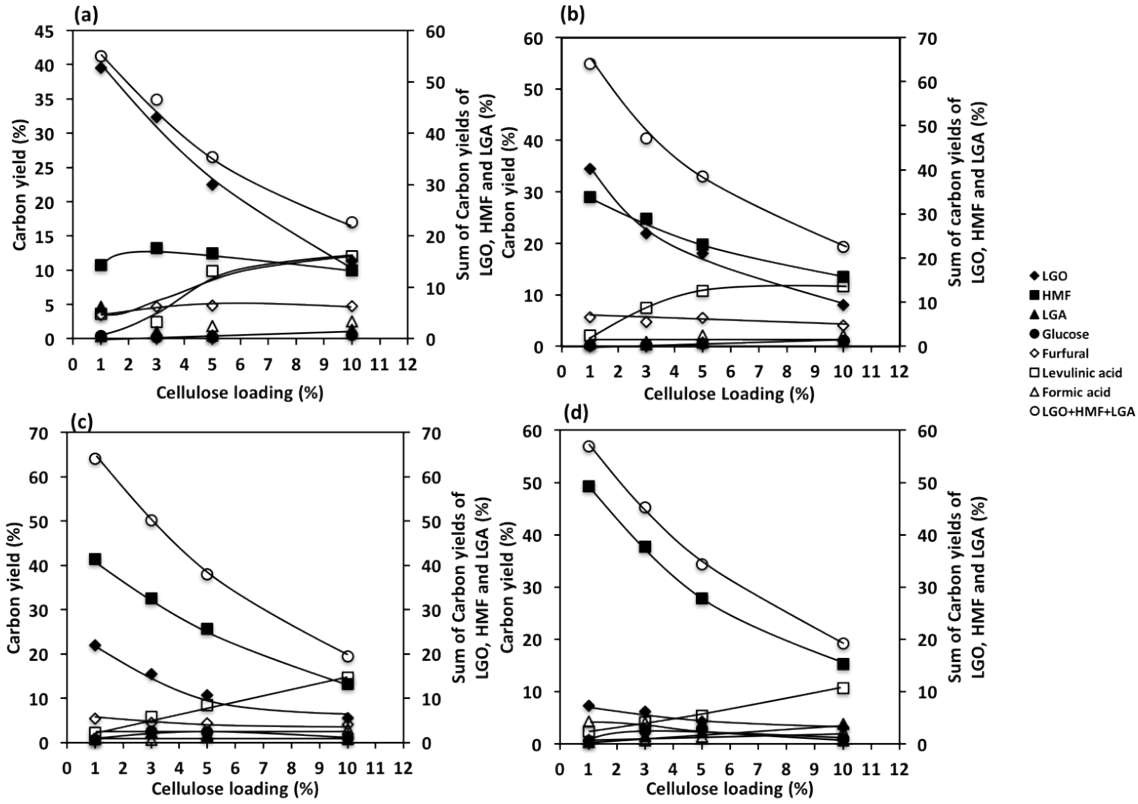


Figure S2. Influence of water content and cellulose loading on the product yields for cellulose conversion. Reaction conditions: THF (60 mL), 210 ˚C, 1000 psi H_2, 700 rpm. Water content: (a) 1 wt.% (b) 2.5 wt.% (c) 5 wt.% (d) 10 wt.%. Reaction time for maximum yields of LGO and HMF are listed in **Table S2**.

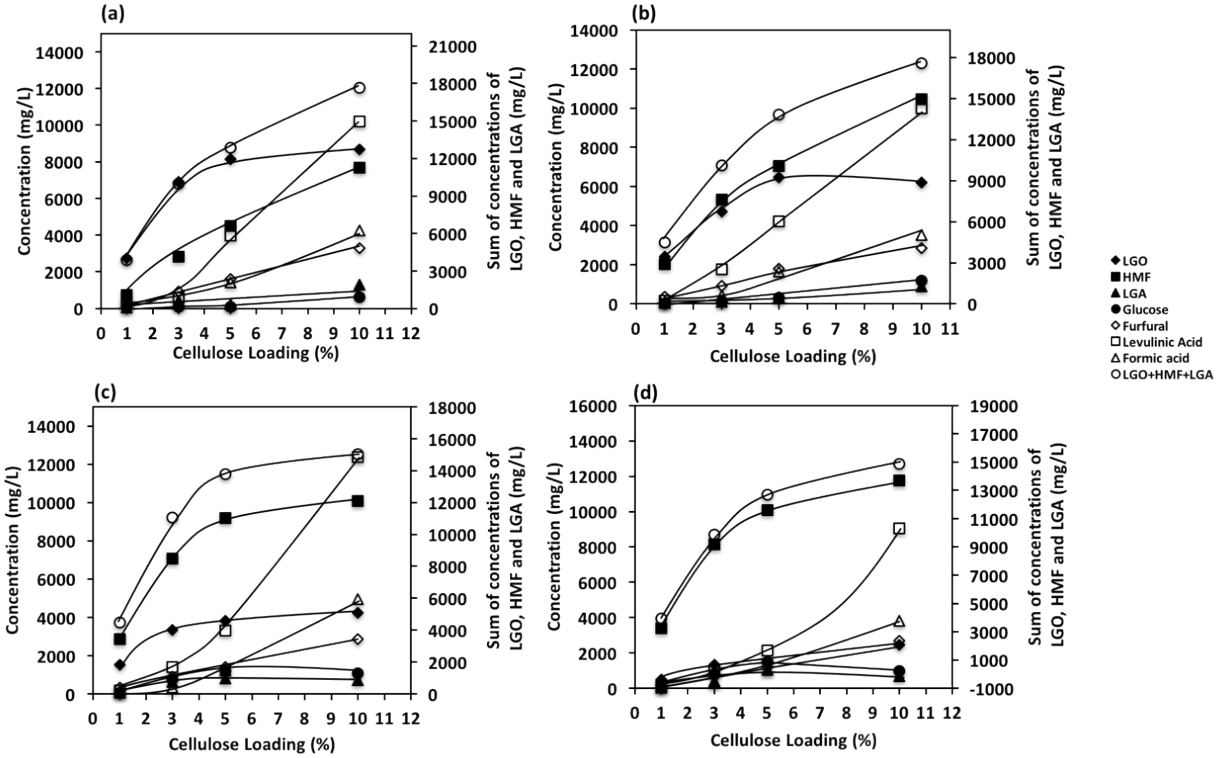
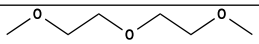
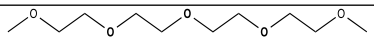
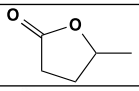
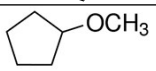


Figure S3. Influence of cellulose loading on product concentrations in the presence of various cellulose loadings. Reaction conditions: THF (60 mL), 210 ˚C, 1000 psi H_2, 700 rpm. Water content: (a) 1 wt.% (b) 2.5 wt.% (c) 5 wt.% (d) 10 wt.%. Reaction time for maximum yields of LGO and HMF are listed in **Table S2**.

Table S1. Physical properties of polar aprotic solvents.

Solvent	Chemical structure	Dipole moment (D)	Polarity[f]	Water solubility	Boiling point (˚C)
THF		1.7[a]	0.207	Miscible	66
Diglyme		1.92[b]	0.224	Miscible	162
Tetraglyme		1.92[c]	0.224	Miscible	275
GVL		5.3[d]	-	>=100 mg/mL	208
CPME		1.27[e]	-	0.011 mg/mL	106
DMSO		4.1[a]	0.444	Miscible	189
1,4-dioxane		0.45[a]	0.164	Miscible	101

a. http://macro.lsu.edu/howto/solvents/Dipole%20Moment.htm
b. http://www.stenutz.eu/chem/solv6.php?name=bis(2-methoxyethyl)%20ether
c. Estimated from the dipole moment of diglyme
d. http://www.patentgenius.com/patent/8354365.html
e. http://www.zeon.co.jp/business_e/enterprise/spechemi/spechemi5-13.html
f. *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed., 2003.

Table S2 Reaction time (minutes) for maximum yields of LGO and HMF at various water content and cellulose loading at 210 ˚C.

Time (min.) / Cellulose Loading (wt%)	Water content (wt.%)						
	0	0.19	0.5	1	2.5	5	10
1	48	45	45	46	45	44	61
3	55	48	47	51	48	42	45
5	50	50	50	50	47	47	60
10	50	50	50	52	50	50	60

Reaction conditions: THF (60 mL), H_2SO_4 (64 μL Conc., 20 mM), 1000 psi He, 700 rpm.

Table S3. Aspen Plus material balance information for selected streams (from flowsheet in Figure 6)

Component	Units	1	2	4	5	6	7	8	9
Mass flow	kg/hr	17,000	567	620,337	428	620,765	64,145	556,620	8,739
Temperature	˚C	25	25	170	25	58	57	57	57
Pressure	atm	1	1	68	1.2	1.2	1.1	1.1	1.1
Vapor fraction		0	0	0	0	0.1	1	0	0
HMF	kg/hr	0	0	4,985	0	4,985	0	4,985	0
LGO	kg/hr	0	0	807	0	807	0	807	0
H2O	kg/hr	0	0	33,868	0	34,076	2,278	31,798	0
THF	kg/hr	0	0	543,994	0	543,994	49,297	494,698	0
H2SO4	kg/hr	0	567	567	0	0	0	0	0
GLUCOSE	kg/hr	0	0	472	0	472	0	472	472
LGA	kg/hr	0	0	255	0	255	0	255	0
FURFURAL	kg/hr	0	0	408	0	408	1	407	0
FACID	kg/hr	0	0	233	0	233	4	229	0
LACID	kg/hr	0	0	511	0	511	0	511	0
CH2O	kg/hr	0	0	26,758	0	26,758	12,565	14,192	0
CELLULOSE	kg/hr	17,000	0	0	0	0	0	0	0
CASO4	kg/hr	0	0	0	0	787	0	787	787
LIME	kg/hr	0	0	0	428	0	0	0	0
HUMINS	kg/hr	0	0	7,480	0	7,480	0	7,480	7,480

Component	Units	10	11	13	15	16	17	18
Mass flow	kg/hr	547,881	538,775	493	602,771	9,106	3,113	5,994
Temperature	C	57	55	25	47	113	59	40
Pressure	atm	1.1	1.1	1.1	1	1.1	0.2	1.1
Vapor fraction		0	0	0	0	0	0	0
HMF	kg/hr	4,985	0	0	0	4,985	50	4,935
LGO	kg/hr	807	0	0	0	807	8	798
H2O	kg/hr	31,798	29,855	0	32,110	1,943	1943	0
THF	kg/hr	494,698	494,698	493	543,994	0	0	0
H2SO4	kg/hr	0	0	0	0	0	0	0
GLUCOSE	kg/hr	0	0	0	0	0	0	0
LGA	kg/hr	255	0	0	0	255	0	255
FURFURAL	kg/hr	407	4	0	5	403	403	0
FACID	kg/hr	229	26	0	30	203	203	0
LACID	kg/hr	511	0	0	0	511	506	5
CH2O	kg/hr	14,192	14,192	0	26,632	0	0	0
CELLULOSE	kg/hr	0	0	0	0	0	0	0
CASO4	kg/hr	0	0	0	0	0	0	0
LIME	kg/hr	0	0	0	0	0	0	0
HUMINS	kg/hr	0	0	0	0	0	0	0

Table S4. Cost parameters used for calculating capital charge factor

Plant life	30 years
Discount rate (Internal rate of return)	10%
General plant depreciation	200% declining balance (DB)
General plant recovery period	7 years
Federal tax rate	35%
Financing	10% equity
Loan terms	10-year loan at 8% APR
Construction period	3 years
First 12 months' expenditures	8%
Next 12 months' expenditures	60%
Last 12 months' expenditures	32%
Start-up time	6 months
Revenues during startup	50%
Variable costs incurred during startup	75%
Fixed costs incurred during startup	100%

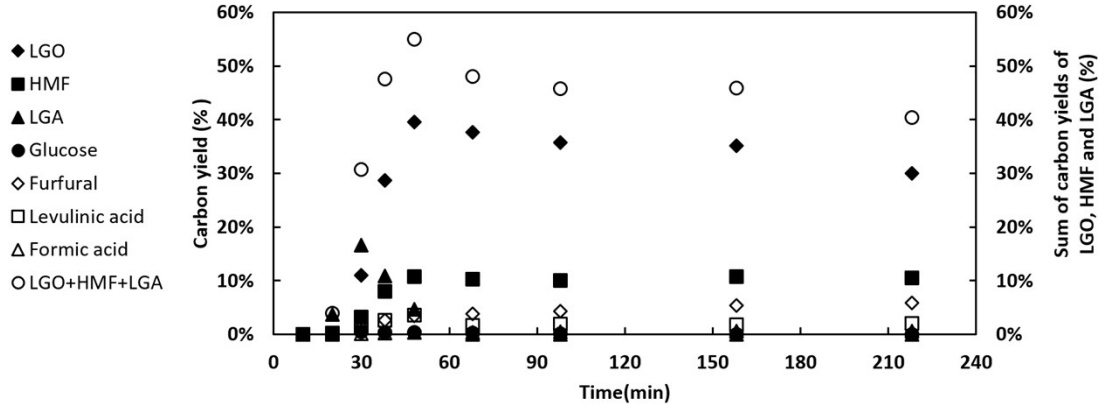


Figure S4 THF as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1 wt%, 0.53 g), THF (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi He, 210 ˚C, 700 rpm.

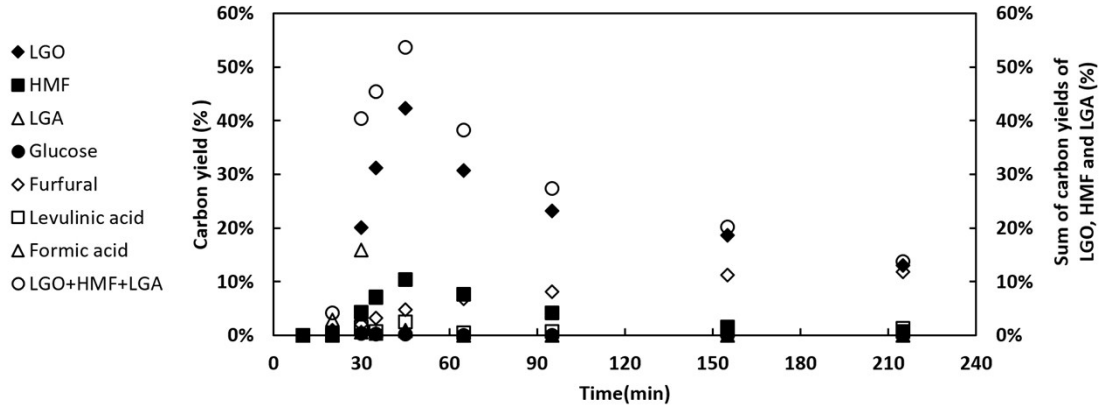


Figure S5 Diglyme as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1 wt%, 0.57 g), Diglyme (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi He, 210 ˚C, 700 rpm

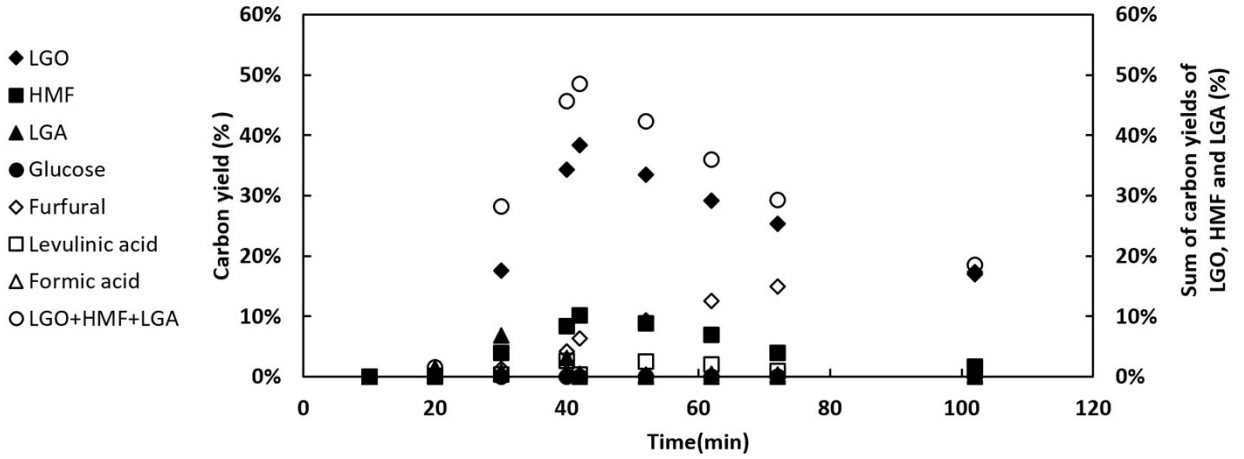


Figure S6 Tetraglyme as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1 wt%, 0.61 g), Tetraglyme (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi. He, 210 ˚C, 700 rpm.

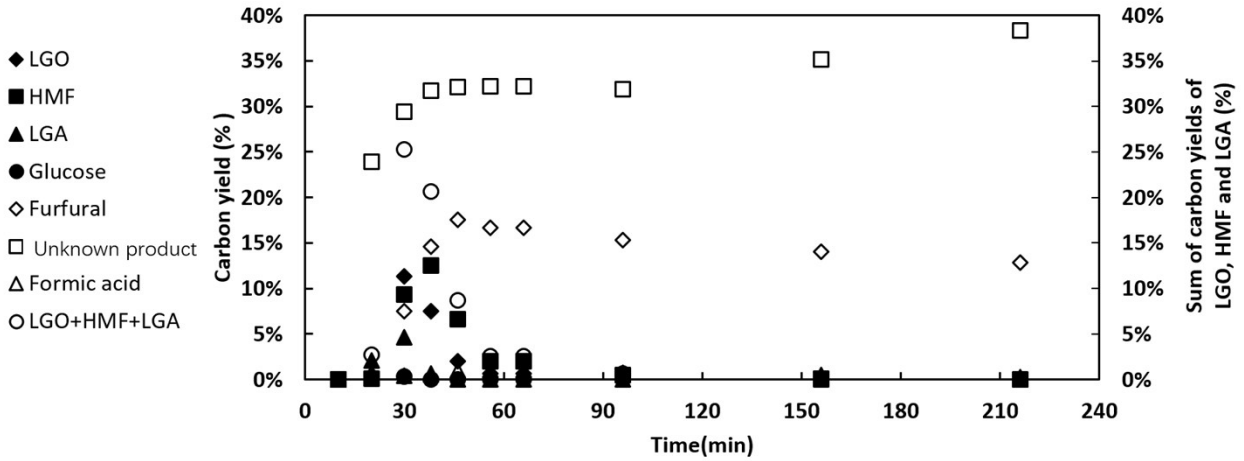


Figure S7 GVL as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1 wt%, 0.63 g), GVL (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi He, 210 ˚C, 700 rpm.

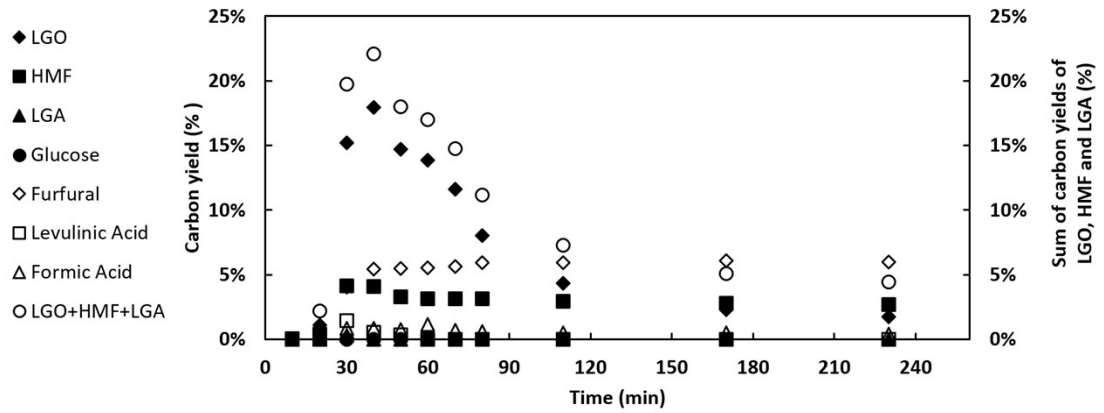


Figure S8 Cyclopentyl methyl ether (CPME) as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1 wt%, 0.53 g), CPME (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi He, 210 ˚C, 700 rpm.

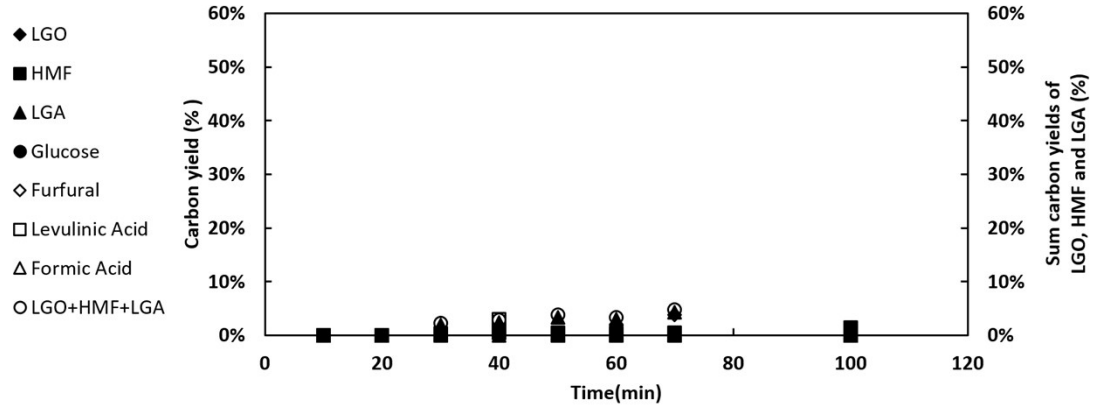


Figure S9 DMSO as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1.0 wt%, 0.6669 g), H_2SO_4 (64 µL Conc., 20 mM), DMSO (60 mL), 1000 psi He, 210 ˚C, 700 rpm.

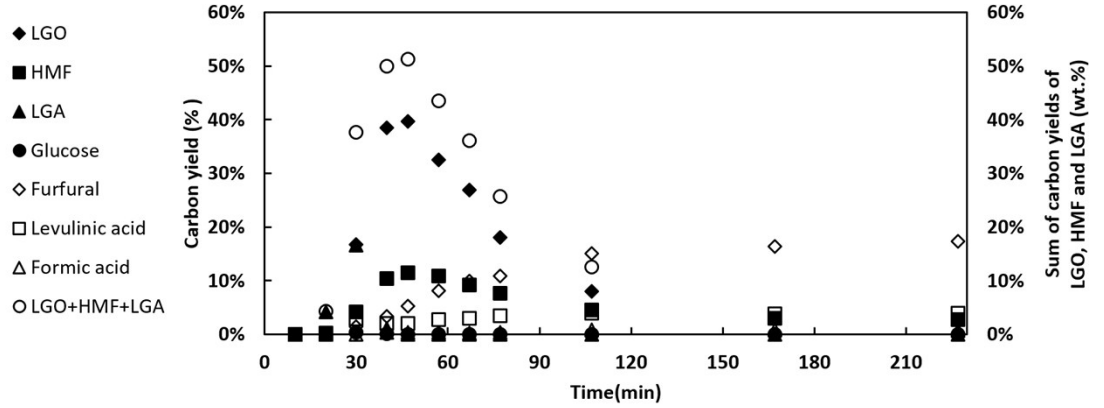


Figure S10 1,4-dioxane as a solvent for cellulose dehydration. Reaction conditions: Cellulose (1.0 wt%, 0.6267 g), H_2SO_4 (64 µL Conc., 20 mM), 1,4-dioxane (60 mL), 1000 psi He, 210 ˚C, 700

rpm.

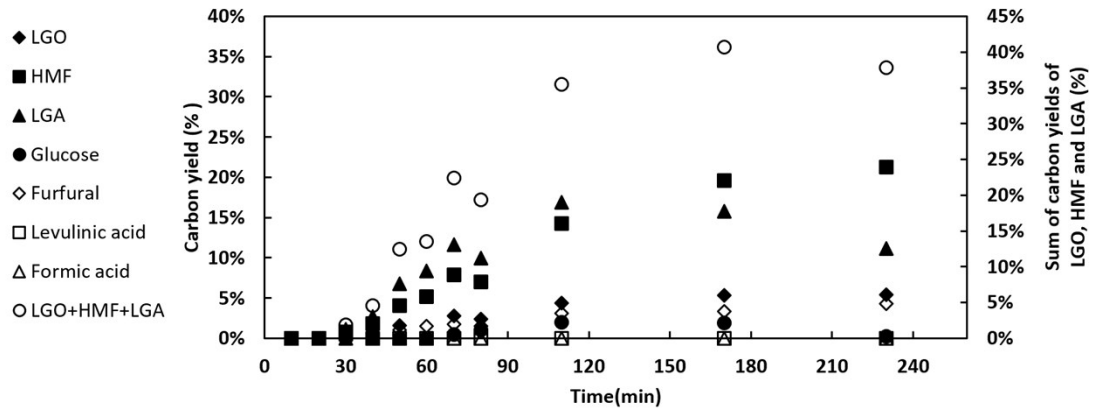


Figure S11 Cellulose dehydration in the presence of HCl. Reaction conditions: Cellulose (1.0 wt%, 0.5389 g), HCl (20 mM, 98 μL), THF (60 mL), 1000 psi He, 210 ˚C, 700 rpm.

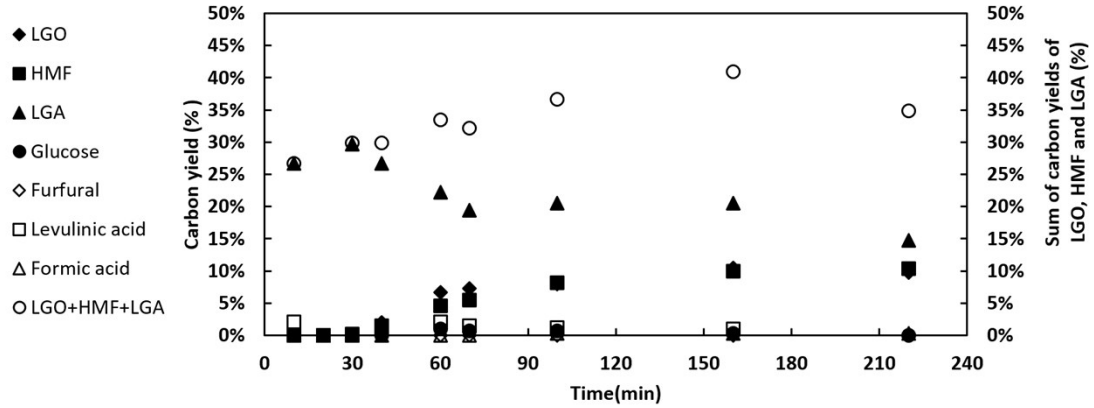


Figure S12 Cellulose dehydration in the presence of H_3PO_4. Reaction conditions: Cellulose (1.0 wt%, 0.5389 g), H_3PO_4 (20 mM, 82 μL), THF (60 mL), 1000 psi He, 210 ˚C, 700 rpm.

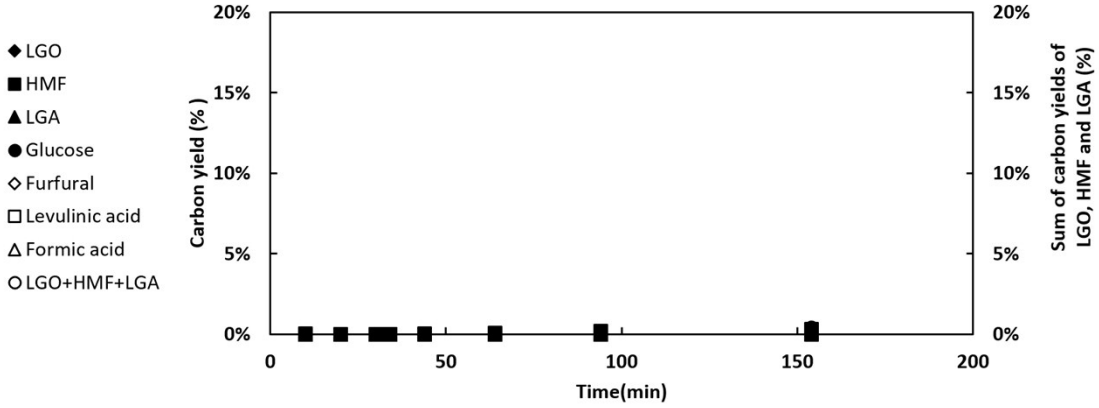


Figure S13 Cellulose dehydration in the presence of HCOOH. Reaction conditions: Cellulose (1.0

wt%, 0.5389 g), HCOOH (20 mM, 46 μL), THF (60 mL), 1000 psi He, 210 ˚C, 700 rpm.

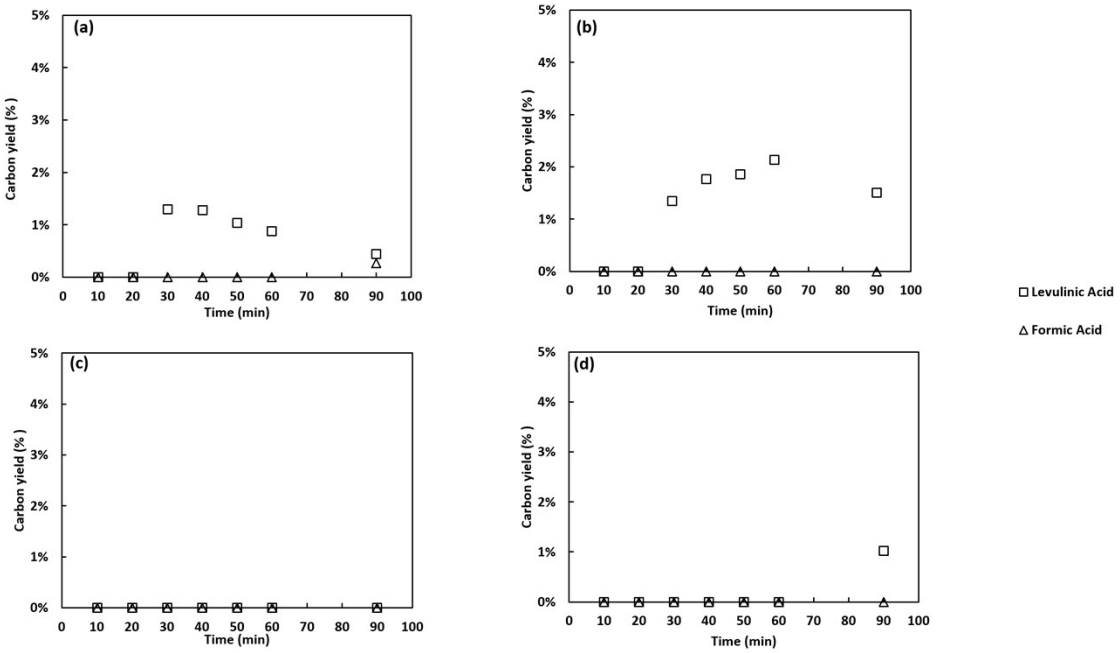


Figure S14 Influence of water on the conversion of (a) cellulose in pure THF (b) cellulose with 1 wt% H_2O in THF (c) LGA in pure THF (d) LGA with 1 wt% H_2O in THF. Reaction conditions: Cellulose (1 wt%, 0.53 g) or LGA (0.4 wt%, 0.2143 g), THF (60 mL), H_2SO_4 (24 μL Conc., 7.5 mM), 1000 psi He, 170 ˚C, 700 rpm.