Electronic Supplementary Material (ESI) for Energy & Environmental Science

Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst

Supplementary Information

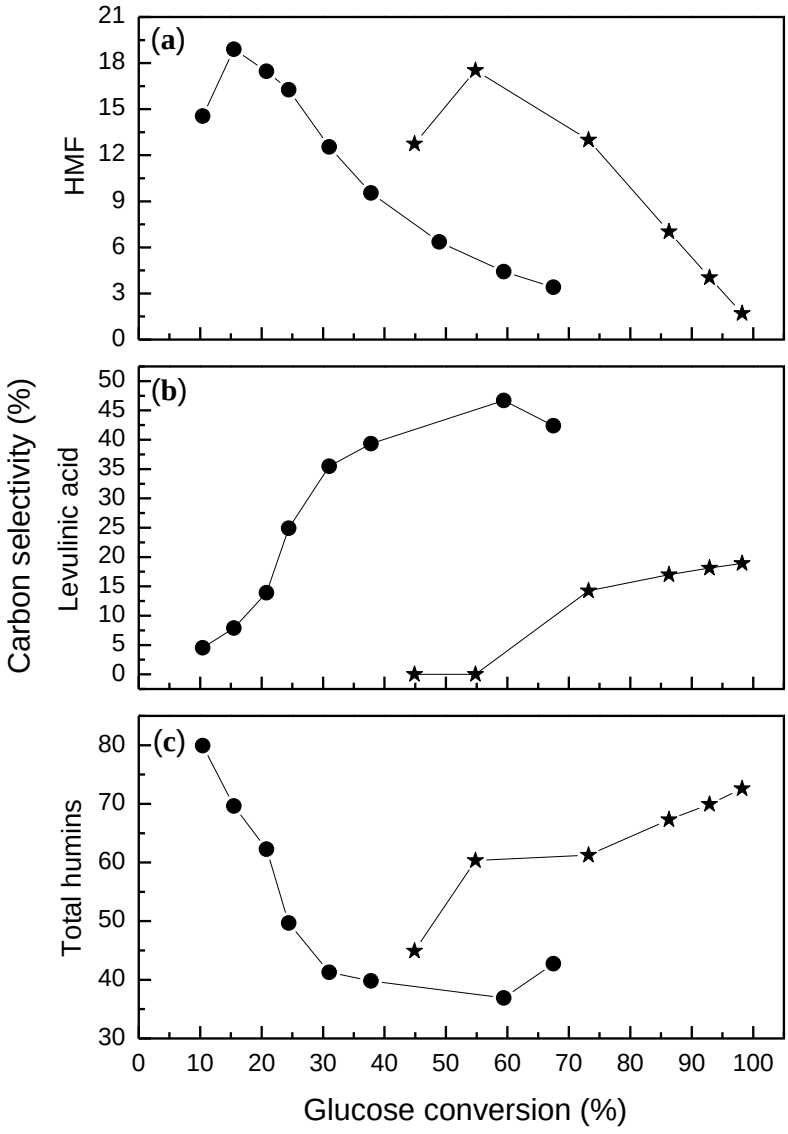

Fig. S1 Aqueous phase glucose dehydration in a stirred batch reactor with homogeneous acid catalysts at 160 °C. Effect of type of acid site on carbon selectivity for (**a**) HMF; (**b**) levulinic acid; (**c**) humins. Feed was 10 wt% glucose aqueous solution and acid concentration was 0.1 M. Acid catalyst type = Brønsted: HCl (,), Lewis: $Yb(OTf)_3$ (ξ).

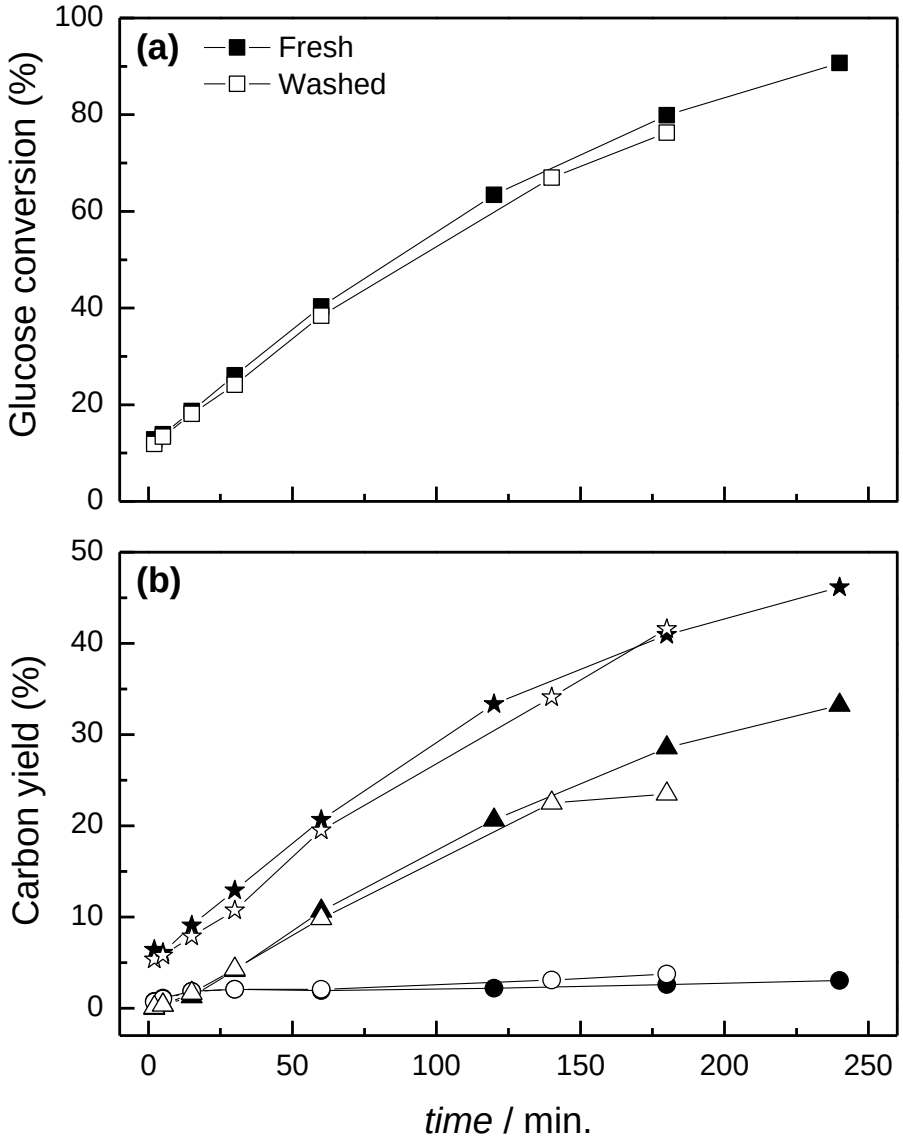

Fig. S2 Stability test with Amberlyst 70 for aqueous phase acid-catalyzed glucose dehydration in a stirred batch reactor at 160 °C. (**a**) glucose conversion; (**b**) carbon yield of major products: HMF (,), levulinic acid (7), soluble and solid humins (ξ). Feed was 10 wt% glucose aqueous solution. Catalyst concentration was 0.1 M total acid sites (taken from manufacturer). Closed symbols denote reaction with fresh catalyst. Open symbols denote reaction with washed catalyst.

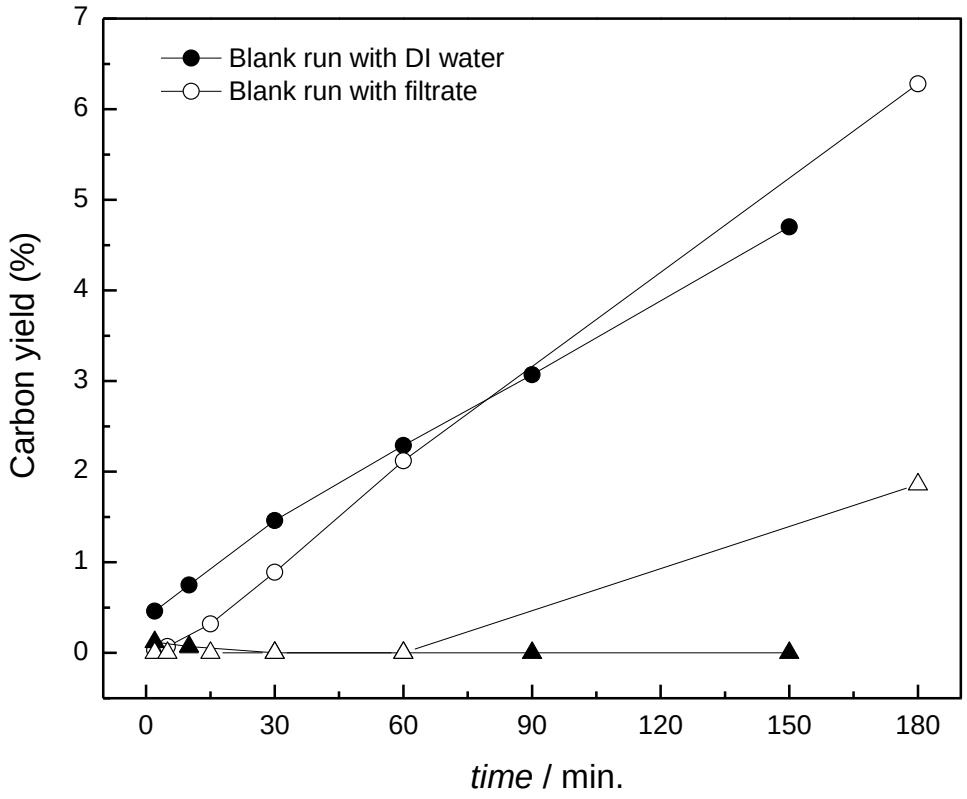

Fig. S3 Non-catalyzed aqueous phase glucose dehydration in a stirred batch reactor at 160 °C. Carbon yield of major products as a function of reaction time: HMF (,), levulinic acid (7). Feed was 10 wt% glucose aqueous solution. Closed symbols denote reaction with clean DI water as solvent. Open symbols denote reaction with aqueous filtrate obtained after exposure to Amberlyst 70.

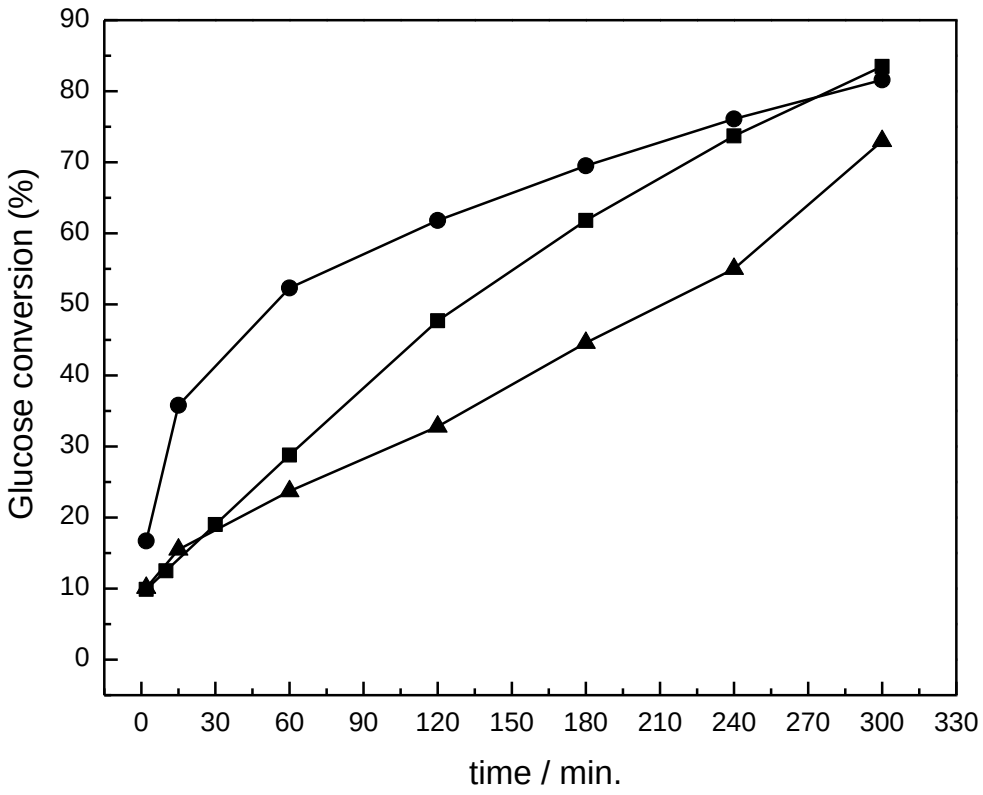

Fig. S4 Recycle test with Amberlyst 70 for aqueous phase acid-catalyzed glucose dehydration in a stirred batch reactor at 160 °C. Glucose conversion as a function of reaction time for: fresh catalyst (!), recycled catalyst (,), regenerated catalyst (7). Feed was 10 wt% glucose aqueous solution. Catalyst concentration of fresh batch was 0.1 M total acid sites (taken from manufacturer).

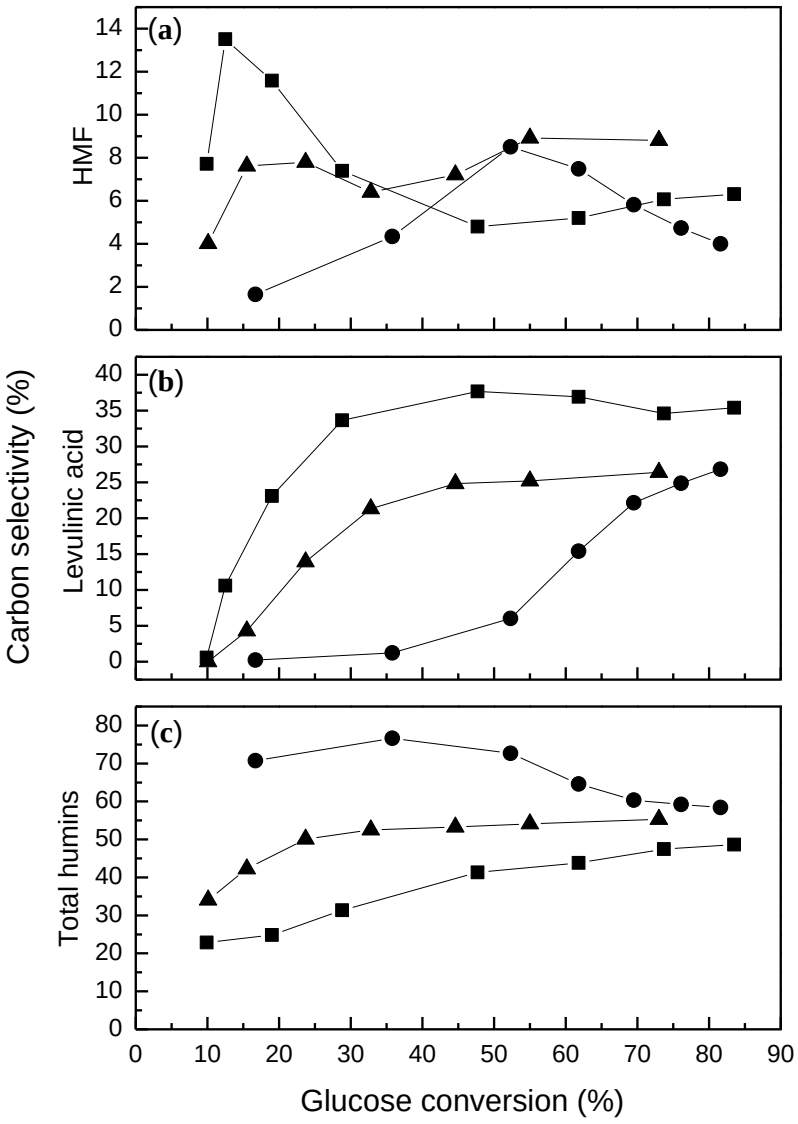

Fig. S5 Recycle test with Amberlyst 70 for aqueous phase acid-catalyzed glucose dehydration in a stirred batch reactor at 160 °C. Effect on carbon selectivity for (**a**) HMF; (**b**) levulinic acid; (**c**) total humins. Feed was 10 wt% glucose aqueous solution. Catalyst concentration of fresh batch was 0.1 M total acid sites (taken from manufacturer). Fresh catalyst (!), recycled catalyst (,), regenerated catalyst (7).

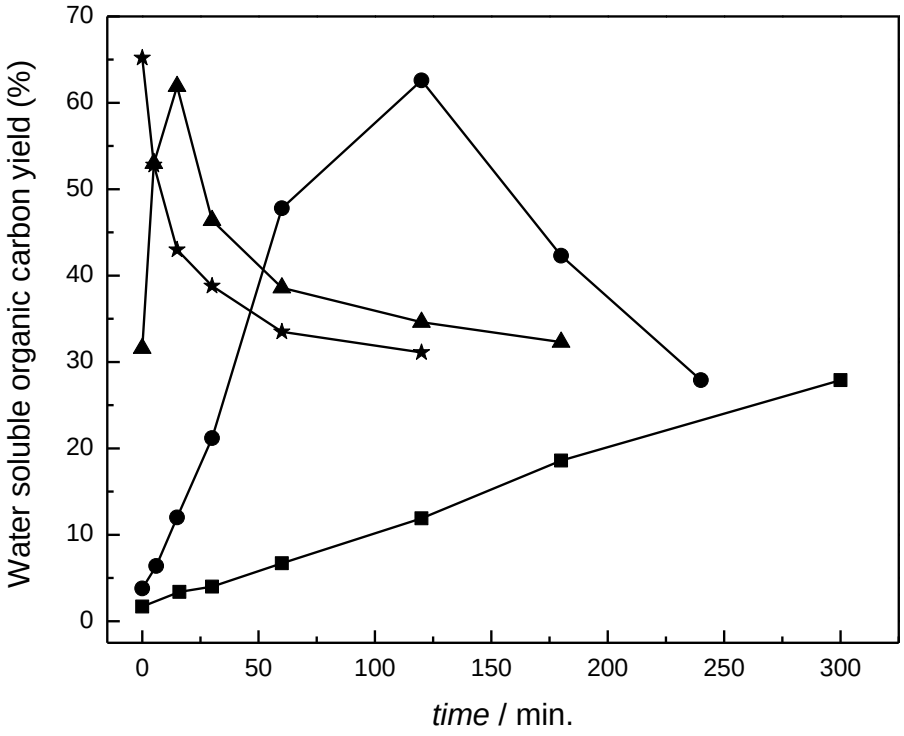

Fig. S6 Hydrothermal decomposition of cellulose without a solid acid catalyst in a stirred batch reactor. Total water-soluble organic carbon yield as a function of reaction time. Initial cellulose loading was 4 wt% of total. T / °C = 190 (!), 220 (,), 250 (7), 270(ξ).

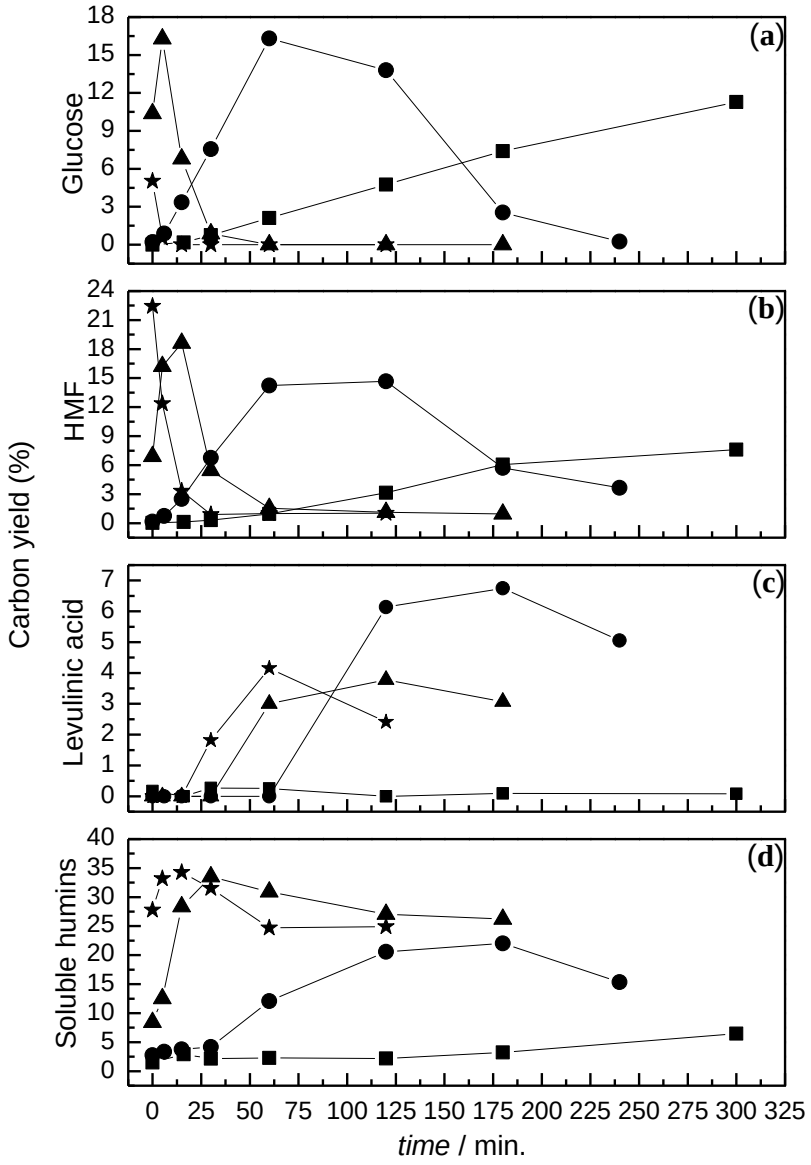

Fig. S7 Hydrothermal decomposition of cellulose without a solid acid catalyst in a stirred batch reactor. Water-soluble organic carbon yield for (**a**) glucose, (**b**) HMF, (**c**) levulinic acid, (**d**) soluble humins. Initial cellulose loading was 4 wt% of total. *T* / °C = 190 (!), 220 (,), 250 (7), 270(ξ).

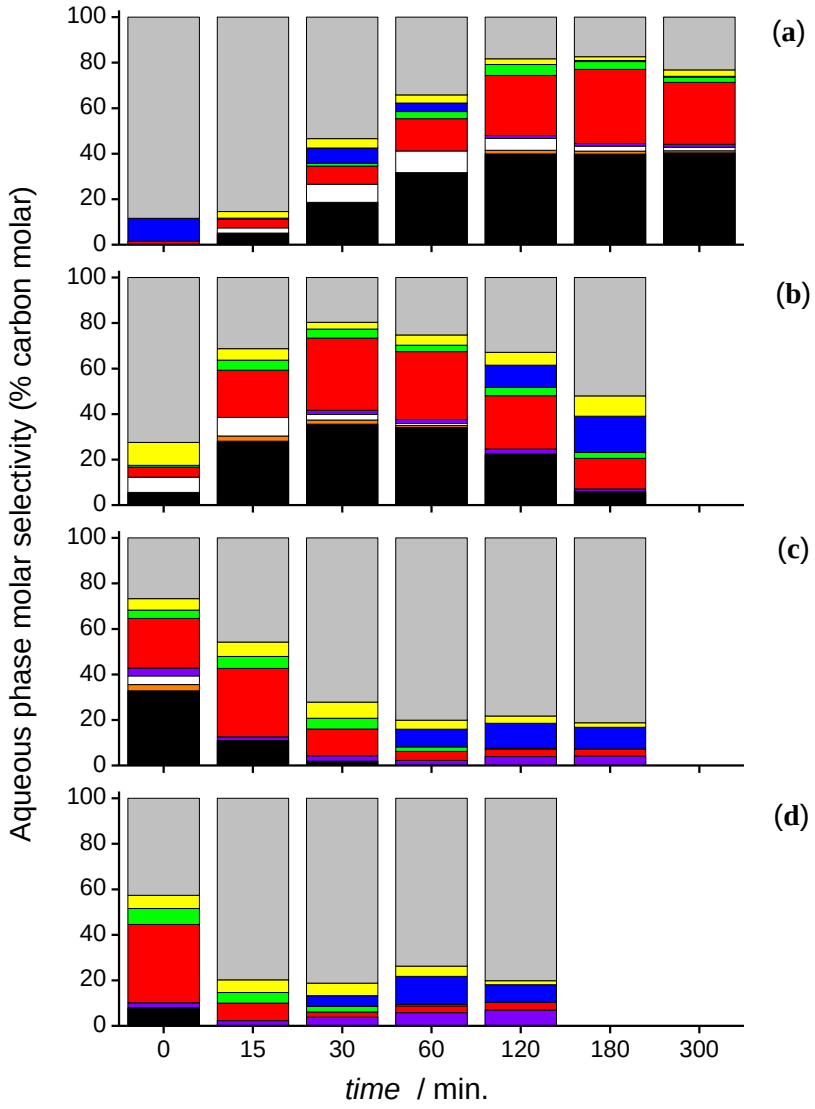

Fig. S8 Water-soluble organic carbon product selectivity for the aqueous phase cellulose decomposition without a solid acid catalyst in a stirred batch reactor for *T* / °C = (**a**) 190 (**b**) 220, (**c**) 250, (**d**) 270. Initial cellulose loading was 4 wt% of total. ■ glucose; ■ fructose; □ cellobiose; ■ levoglucosan; ■ HMF; ■ furfural; ■ levulinic acid; ■ formic acid; ■ humins.

Table S1 Product distribution from non-catalyzed hydrothermal decomposition of cellulose in a stirred batch reactor at 170 °C with recycling of solids. Initial solids loading for each cycle was 29 wt%. Each cycle reaction time was 4 h.

Cycle	Cumulative cellulose conversion (%)	Cumulative carbon selectivity (%)			Cumulative carbon yield (%)		
		Usable organics [a]	Water-soluble humins	Solid humins	Usable organics	Water-soluble humins	Solid humins
1	7.4	70.5	20.5	9.1	5.2	1.5	0.7
2	18.1	70.1	16.9	13.0	12.7	3.1	2.3
3	25.8	62.0	14.5	23.5	16.0	3.7	6.1
4	31.1	59.3	15.1	25.6	18.4	4.7	7.9
5	36.2	57.0	14.7	28.3	20.6	5.3	10.2
6	41.8	53.8	14.4	31.8	22.5	6.0	13.3

[a] includes: glucose, fructose, cellobiose, levoglucosan, HMF, furfural, levulinic acid, formic acid

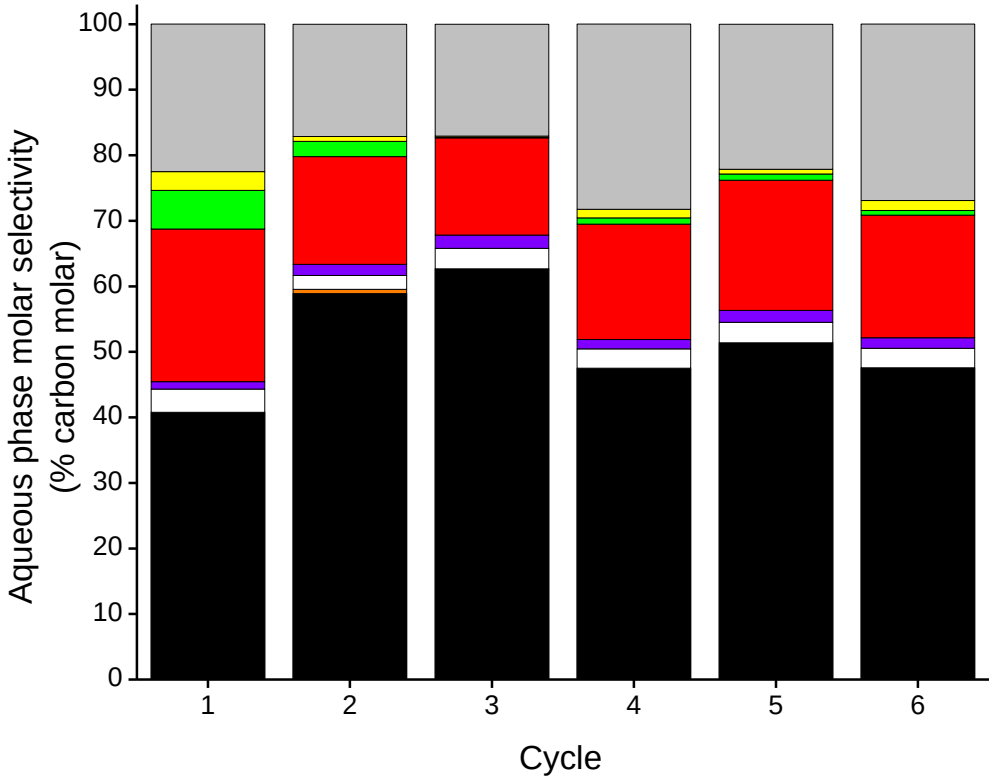

Fig. S9 Water-soluble organic carbon product selectivity for each recycle run from non-catalyzed hydrothermal decomposition of cellulose in a stirred batch reactor at 170 °C. Initial solids loading for each cycle was 29 wt%. Each cycle reaction time was 4 h. ■ glucose; ■ fructose; □ cellobiose; ■ levoglucosan; ■ HMF; ■ furfural; ■ levulinic acid; ■ formic acid; ■ humins.

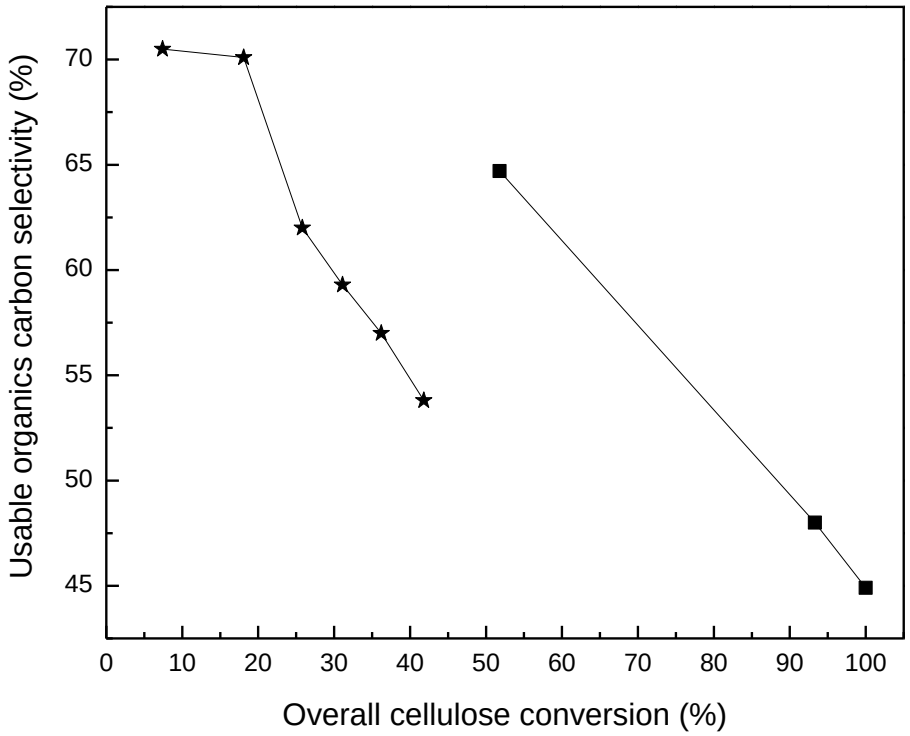

Fig. S10 Cumulative carbon selectivity of usable organics obtained from hydrothermal decomposition of cellulose with recycling of solids. Initial solids loading for each cycle was 29 wt%. Reaction conditions: 220 °C for 30 min. each cycle (!); 170 °C for 4 h each cycle (ξ).