

Cellulose hydrolysis in acidified LiBr molten salt hydrate (MSH)

media

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Supporting Information

Table S1. Conditions and results for a set of cellulose hydrolysis reactions conducted in molten salt hydrate media

ID	Salt	H ₂ O/Salt (molar)	Salt/Cellul. (molar)	[H ₂ SO ₄] (M)	^a Products yield (%)					
					Dimers	Glucose	Fructose	LG	HMF	Total
1	None	NA	NA	NA	0.01	0.00	0.00	^b ND	ND	0.01
2	None	NA	NA	0.05	ND	ND	0.04	ND	ND	0.04
3	LiBr	3.25	69.35	NA	ND	0.03	0.25	ND	ND	0.28
4	^c LiCl	3.25	69.35	NA	ND	0.21	0.000	ND	ND	0.21
5	ZnBr ₂	3.25	69.35	NA	1.12	1.55	0.36	ND	ND	3.03
6	ZnCl ₂	3.25	69.35	NA	0.12	0.19	0.21	ND	ND	0.52
7	LiBr	3.25	69.35	0.05	9.13	80.17	2.44	0.777	1.99	94.51
8	LiCl	3.25	69.35	0.05	3.548	6.61	0.68	ND	ND	10.84
9	^c LiNO ₃	3.25	69.35	0.05	ND	ND	0.099	ND	ND	0.099
10	^c LiClO ₄	3.25	69.35	0.05	0.49	0.55	0.53	ND	ND	1.58
11	ZnBr ₂	3.25	69.35	0.05	13.01	34.75	1.90	1.96	ND	51.62
12	ZnCl ₂	3.25	69.35	0.05	ND	ND	0.157	ND	ND	0.157
13	^d FeBr ₃	3.25	69.35	0.05	0.87	5.33	1.00	0.65	ND	9.04
14	^d FeCl ₃	3.25	69.35	0.05	11.60	30.60	9.20	2.87	ND	59.23
15	^c Mg(ClO ₄) ₂	3.25	69.35	0.05	0.18	0.27	0.53	ND	ND	0.98
16	LiBr	3.25	69.35	0.05	10.15	78.94	2.42	1.40	1.27	94.18
17	LiBr	3.80	69.35	0.05	13.89	66.72	2.29	1.02	ND	83.91
18	LiBr	4.40	69.35	0.05	10.10	26.82	1.33	0.28	ND	38.53
19	LiBr	5.00	69.35	0.05	2.041	3.825	0.83	ND	ND	6.69
20	LiBr	6.75	69.35	0.05	0.06	0.19	0.24	ND	ND	0.48
21	^e LiCl	3.25	69.35	1	2.927	62.62	1.38	0.53	7.15	74.61
22	^e ZnCl ₂	3.25	69.35	0.5	3.422	78.58	2.34	6.67	ND	91.01

Reaction conditions: all reactions listed in Table 1 were based on 2.5ml water or diluted acid solution, conducted at 85°C for 30minutes under vigorous stirring. Reactions stopped by ice quenching.

- ^a Small amount of organic acids (formic acid and levulinic acid, less than <1% in total yield) may be produced from some reactions.
- ^b Beyond the detection limit of HPLC used for this work.
- ^c Salt solutions with water/salt molar ratio of 3.25 couldn't be prepared at room temperature due to their solubility, however, homogeneous solutions could be achieved at reaction temperature, which was 85°C.
- ^d Small amount of formic acid (with yield of 1.19 and 4.96% for FeBr₃ and FeCl₃, respectively) produced.
- ^e HCl was used for these reactions

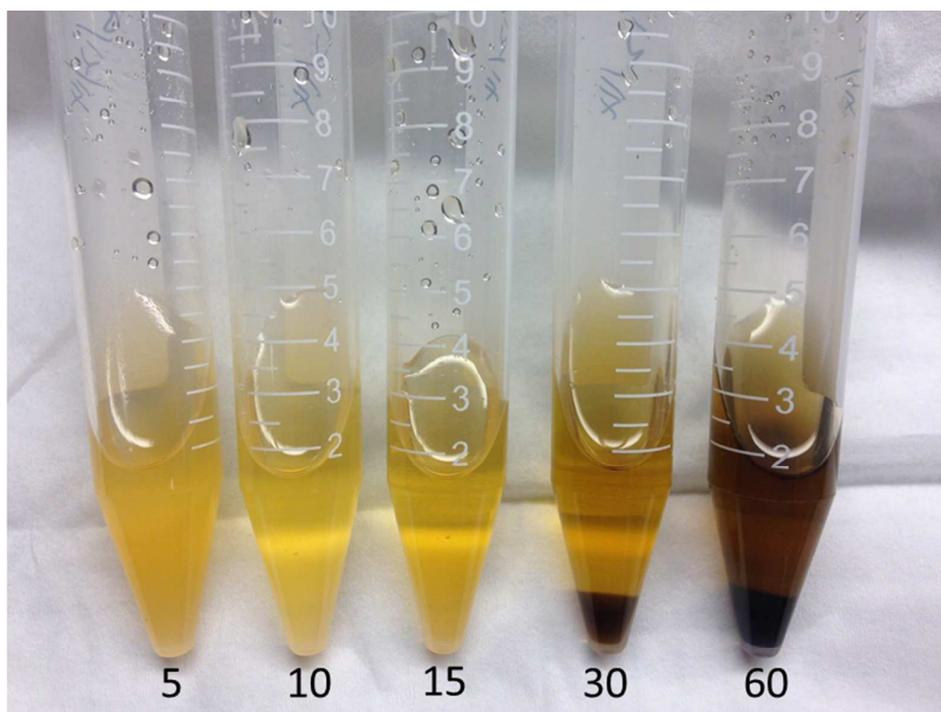


Figure S1: Photos of the cellulose mixture in LiBr MSH at different reaction times in minutes (shown underneath each vial). Reaction conditions: $T=85^{\circ}\text{C}$, $0.05\text{M H}_2\text{SO}_4$ in water/ salt ratio = 3.25, salt/cellulose ratio = 69. The yellow color corresponds to that of LiBr in H_2SO_4 solutions.

Table S.2: Reproducibility studies of cellulose hydrolysis in LiBr MSH. Carbon yields of water soluble products after 30 min at 85°C . ($0.05\text{M H}_2\text{SO}_4$ in water/ salt ratio = 3.25, salt/cellulose ratio = 69)

ID	Dimers	Glucose	Fructose	Levoglucosan	HMF	HPLC Yield
1	9.127	80.174	2.438	0.777	1.997	94.513
2	10.158	77.622	2.441	1.332	0.562	92.115
3	9.280	81.642	2.472	1.574	1.263	96.232
4	9.329	77.703	2.376	1.490	1.071	91.969
5	8.784	79.631	2.426	1.518	1.434	93.793
6	10.706	81.771	2.594	1.495	1.169	97.735
7	10.847	80.015	2.492	1.462	1.095	95.911
8	10.408	81.623	2.428	1.406	1.104	96.969
9	10.151	78.940	2.422	1.403	1.267	94.183
10	9.088	79.072	2.375	1.424	0.961	92.920
STDEV	0.75	1.54	0.06	0.23	0.37	2.02

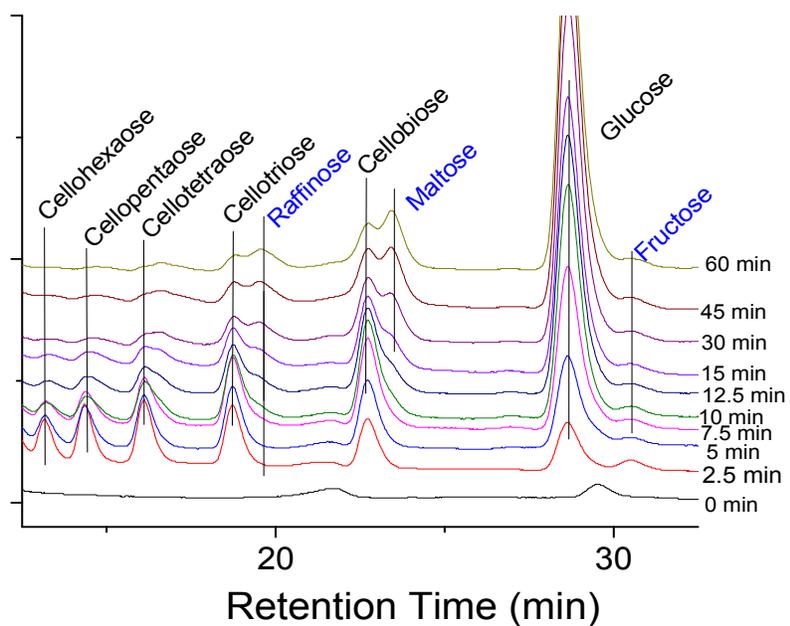


Figure S2: HPLC plots for reaction mixtures taken from a kinetic reaction as shown in Figure 5 with 6.05wt% cellulose initial load, 0.05M H₂SO₄ solutions (water/ salt ratio = 3.25, T=85°C), analysis was conducted using the same HPLC separation unit and detectors as described in the manuscript but using an Agilent Hi Plex Na type Column at 85°C, with 0.3ml/min water as mobile phase, the samples were ~100 times diluted by water in order to reduce the effect of salt on HPLC column.

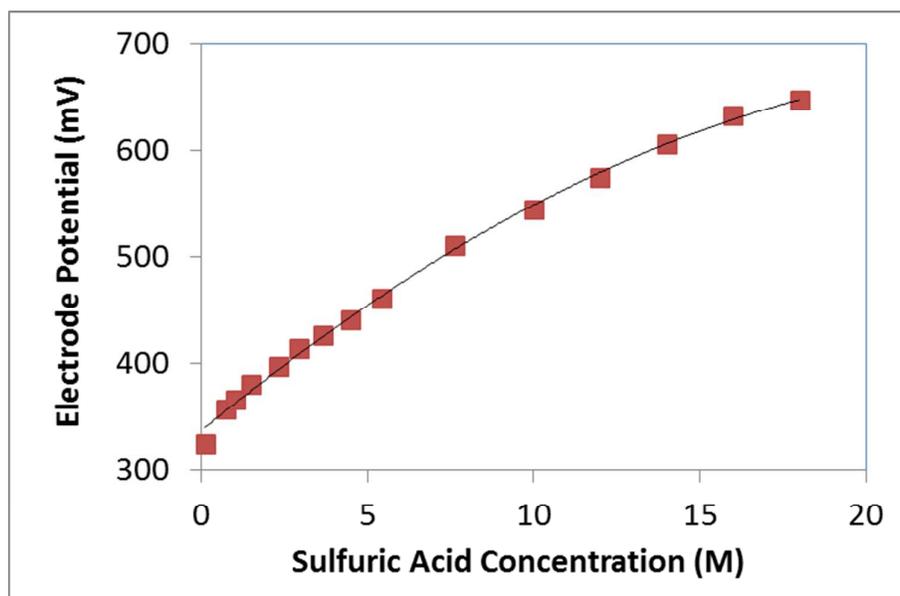


Figure S3: Correlation between pH electrode potential and sulfuric acid concentration.

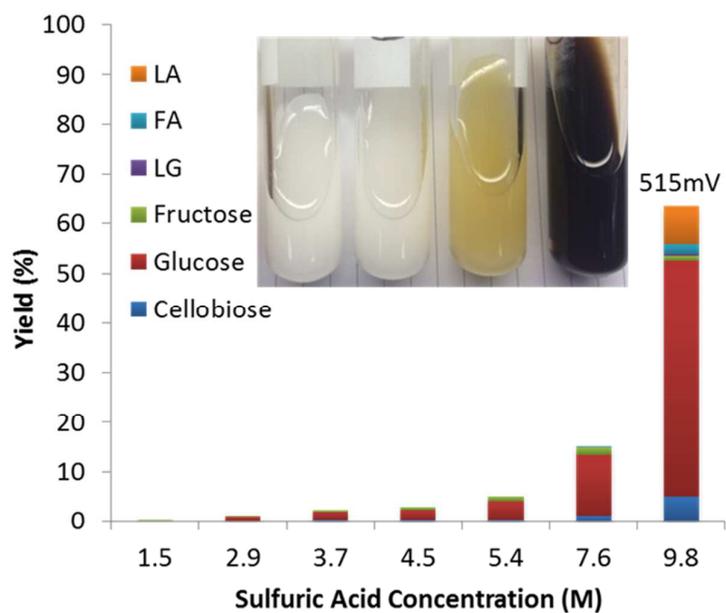


Figure S4: Carbon yields of cellulose hydrolysis carried out in concentrated H_2SO_4 acid solutions. ($T=85^\circ C$, $t=30$ mins)

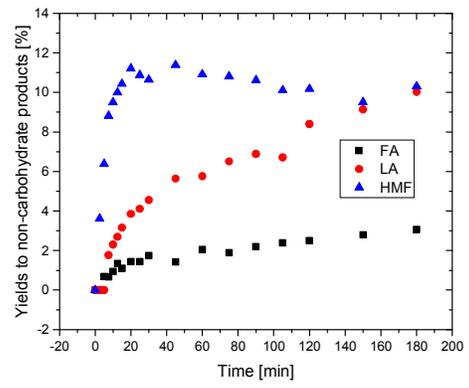
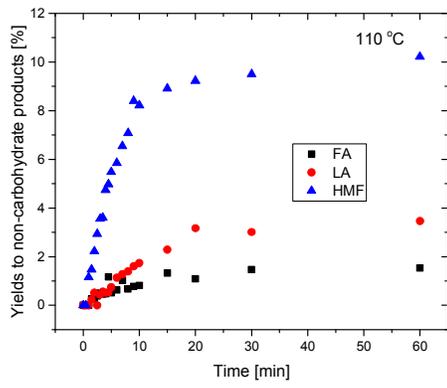


Figure S5: Carbon yields to soluble non-carbohydrate products at 110°C (left) and 115°C (right)

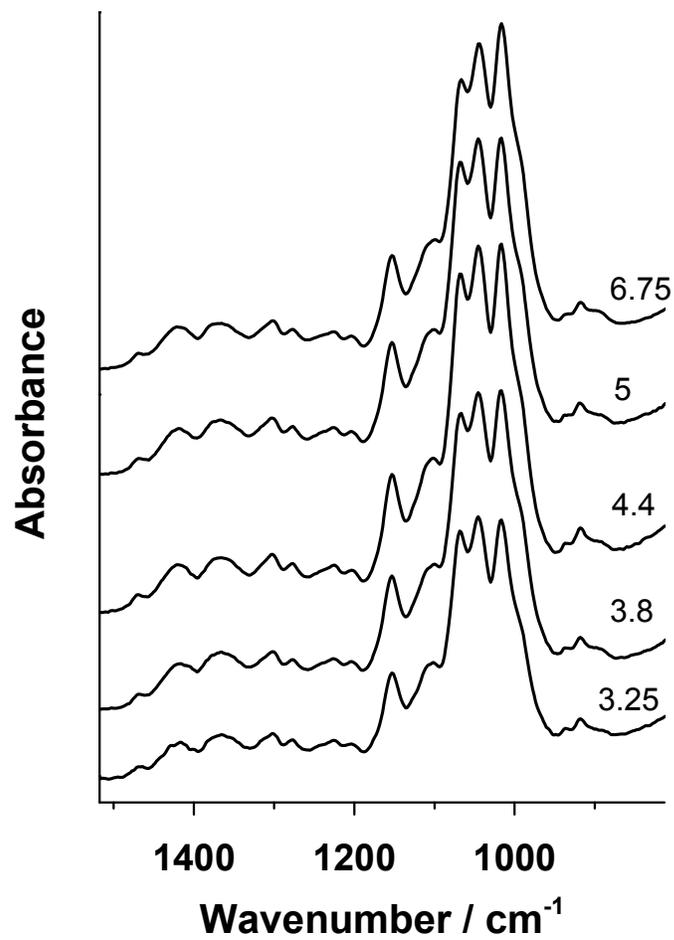


Figure S6: ATR-FTIR spectrum of cellulose treated using molten salt hydrates with various water/ LiBr ratios