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Supplementary Material

Acidic $ZnCl_2/ZnBr_2$ Molten Salt Hydrates for Cellulose Deconstruction and Selective Conversion to 5-Hydroxymethylfurfural

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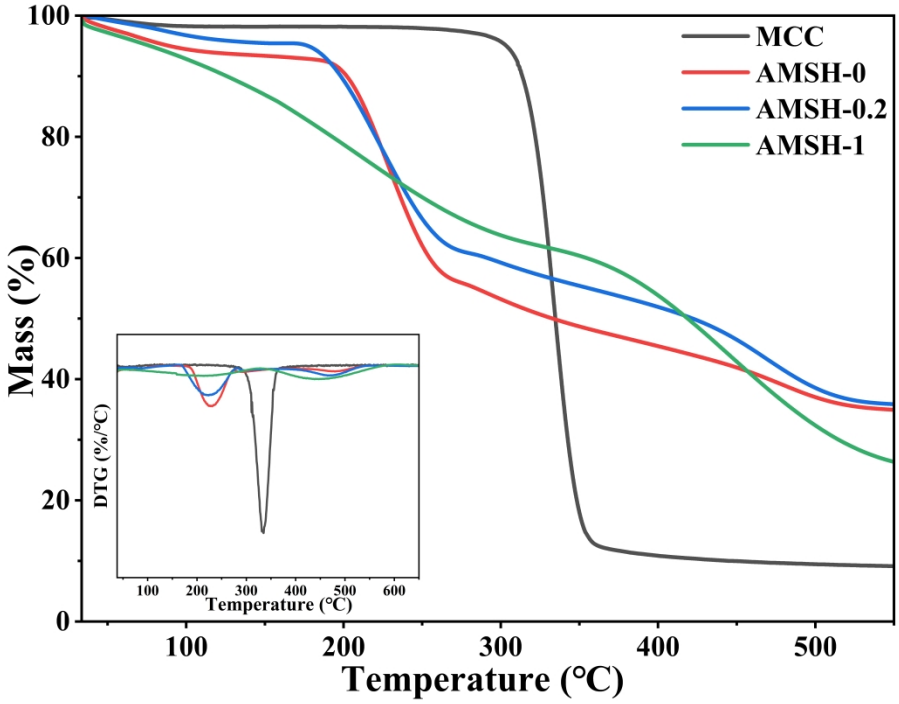


Fig. S1 TGA curves of MCC before and after AMSH treatment

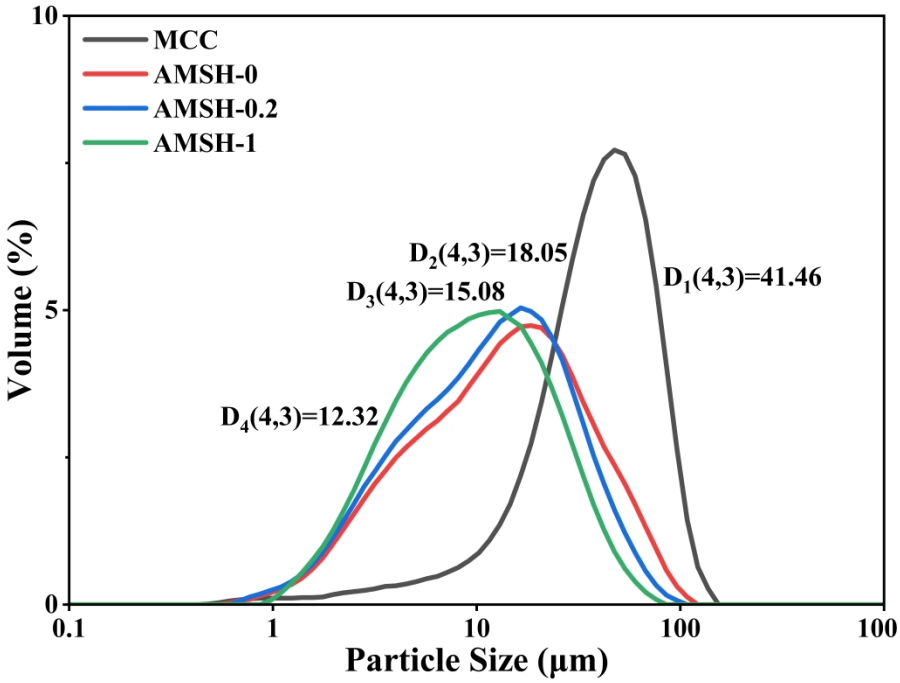


Fig. S2 Particle size distributions of MCC before and after AMSH treatment

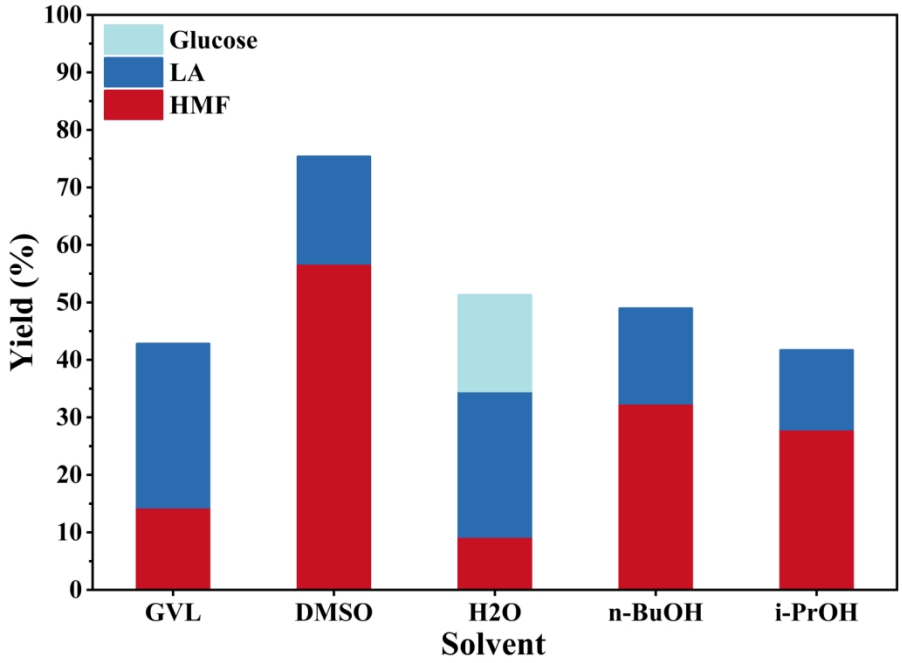


Fig. S3 Effects of solvent type on the product distribution during cellulose conversion. Reaction conditions: MCC 0.1 g, AMSH 1.0 g, $ZnBr_2$ 20 mol%, HCl 2 wt%, pretreatment at 80 °C for 10 min, solvent dosage 3 mL, 170 °C for 120 min

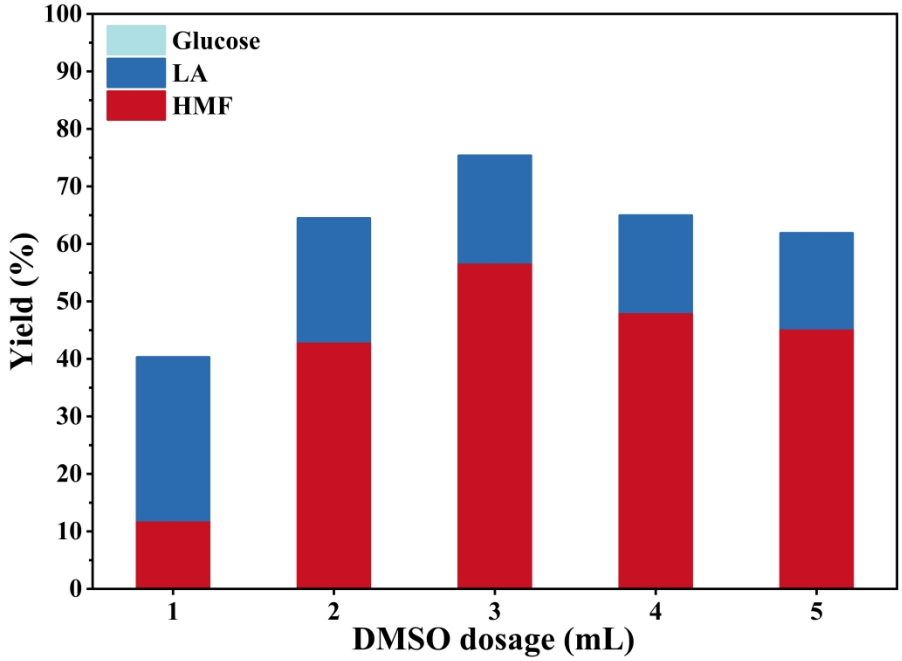


Fig. S4 Effects of DMSO dosage on the product distribution during cellulose conversion. Reaction conditions: MCC 0.1 g, AMSH 1.0 g, $ZnBr_2$ 20 mol%, HCl 2 wt%, pretreatment at 80 °C for 10 min, 170 °C for 120 min

Table S1 Variables and levels in the response surface design

level	A-temperature (°C)	B-reaction time (min)	C-HCl mass fraction (wt%)	D-$ZnBr_2$ molar content (mol%)
-1	160	90	1	10
0	170	120	2	20
1	180	150	3	30

Table S2 Experimental and predicted results of the RSM design

run	factor				HMF yield (%)	
	A	B	C	D	Predicted	Experimental
1	160	90	2	20	47.94	45.27
2	180	90	2	20	36.95	36.18
3	160	150	2	20	52.28	50.80
4	180	150	2	20	43.96	44.38
5	170	120	1	10	31.97	28.62
6	170	120	3	10	47.60	44.57
7	170	120	1	30	40.75	41.53
8	170	120	3	30	29.08	30.18
9	160	120	2	10	51.01	54.41
10	180	120	2	10	40.19	41.03
11	160	120	2	30	44.98	47.01
12	180	120	2	30	36.49	35.95
13	170	90	1	20	37.76	40.26
14	170	150	1	20	39.20	41.02
15	170	90	3	20	35.50	36.54
16	170	150	3	20	45.42	45.78
17	160	120	1	20	28.69	27.49
18	180	120	1	20	38.93	38.41
19	160	120	3	20	50.57	50.51
20	180	120	3	20	21.01	21.63
21	170	90	2	10	44.74	46.08
22	170	150	2	10	55.80	56.62
23	170	90	2	30	45.25	43.85
24	170	150	2	30	45.55	43.63
25	170	120	2	20	55.88	55.22
26	170	120	2	20	55.88	54.69
27	170	120	2	20	55.88	57.76

Table S3 ANOVA for the response surface model of HMF yield

Source	Sum of Squares	df	Mean Square	F-value	P-value	Remarks
Model	2150.1	14	153.58	24.45	<0.0001	significant
A-Reaction temperature	279.46	1	279.46	44.49	<0.0001	—
B-Reaction time	96.62	1	96.62	15.38	0.0020	—
C-HCl wt%	11.76	1	11.76	1.87	0.1963	—
D-$ZnBr_2$ mol%	70.96	1	70.96	11.3	0.0057	—
AB	1.78	1	1.78	0.2837	0.6040	—
AC	396.01	1	396.01	63.04	<0.0001	—
AD	1.35	1	1.35	0.2142	0.6518	—
BC	17.98	1	17.98	2.86	0.1165	—
BD	28.94	1	28.94	4.61	0.0530	—
CD	186.32	1	186.32	29.66	0.0001	—
A^2	310.83	1	310.83	49.48	<0.0001	—
B^2	46.94	1	46.94	7.47	0.0181	—
C^2	964.87	1	964.87	153.6	<0.0001	—
D^2	137.79	1	137.79	21.94	0.0005	—
Residual	75.38	12	6.28	—	—	—
Lack of Fit	69.99	10	7	2.60	0.3097	Not significant
Pure Error	5.39	2	2.70			
Cor Total	2225.48	26				
R^2	—	—	0.9661	—	—	—

HPLC Calibration Curves

Calibration curves for 5-hydroxymethylfurfural (HMF), glucose, and levulinic acid (LA) were established using the external standard method. Analytical standards (purity ≥ 99%) were accurately weighed and dissolved in ultrapure water to prepare stock solutions, which were subsequently diluted into a series of gradient calibration standards. The standard solutions were analyzed by high-performance liquid chromatography (HPLC) in order of increasing concentration. Linear regression of peak area against analyte mass concentration (mg mL^{-1}) yielded the respective calibration curves with correlation coefficients (R^2) of at least 0.999

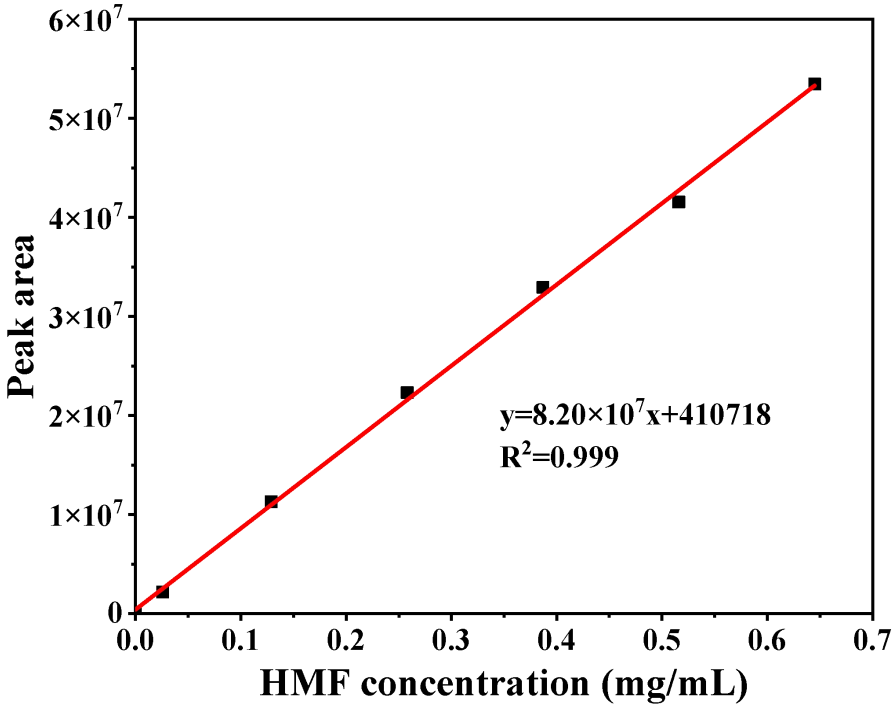


Fig. S5 External standard HPLC calibration curve for 5-hydroxymethylfurfural (HMF)

The calibration curves for glucose and levulinic acid were constructed using the same procedure.

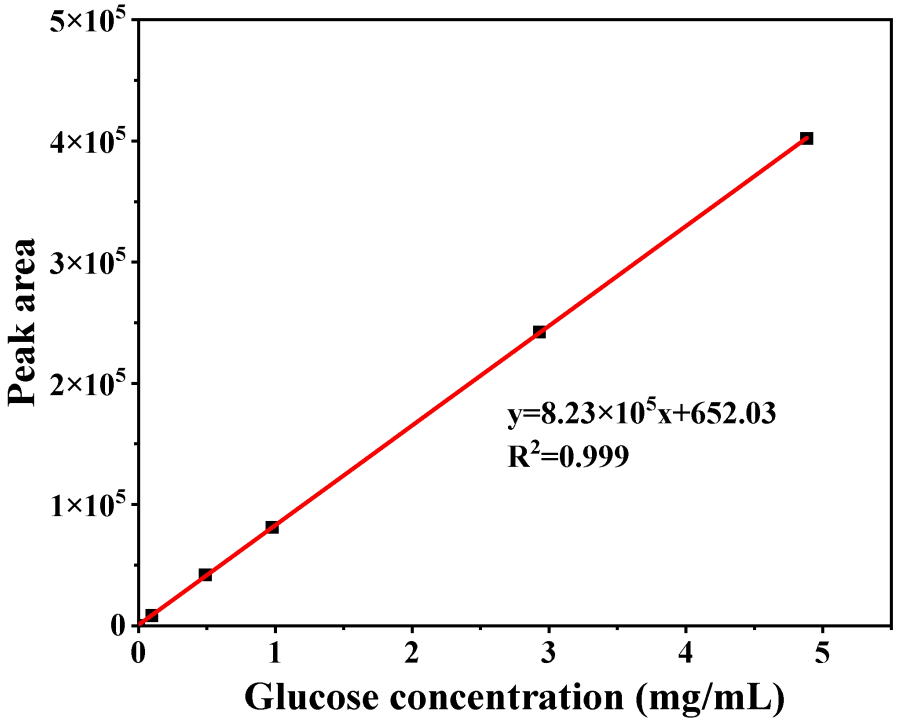


Fig. S6 External standard HPLC calibration curve for glucose

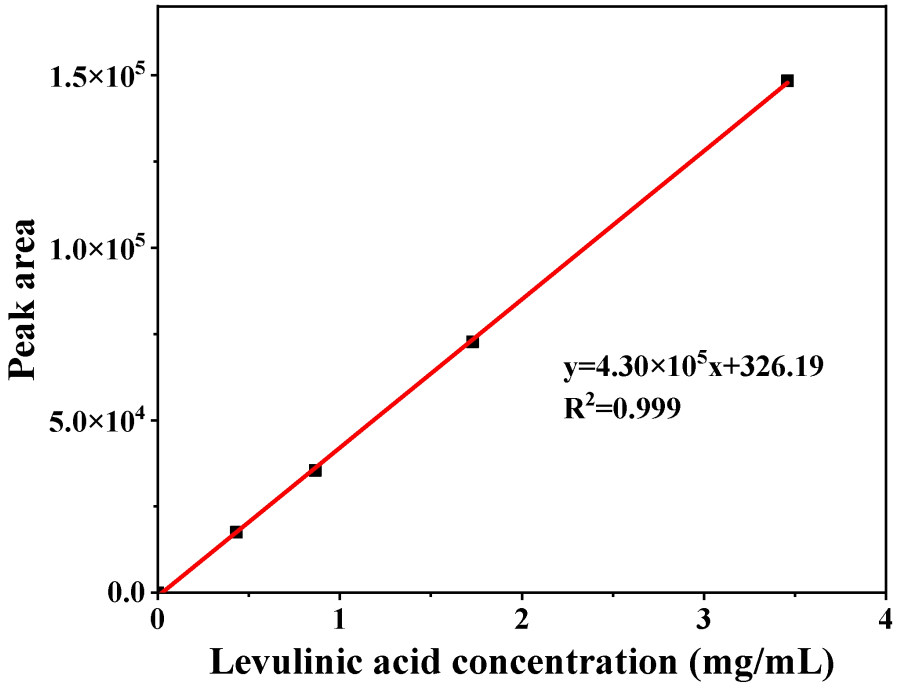


Fig. S7 External standard HPLC calibration curve for levulinic acid (LA)