

Starch esterification using deep eutectic solvents as chaotropic agents and reaction promoters

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Supplementary information

Table S1. Experimental design setup for starch acetylation. AA:starch: molar ratio of acetic anhydride to starch, Starch load: amount of wheat starch added to the reaction.

Run No.	Time (h)	Temperature (°C)	AA:Starch	Starch load(g)
1	5	120	15	0.25
2	7	130	20	0.50
3	3	130	20	0.50
4	7	110	20	0.50
5	7	130	10	0.50
6	3	110	20	0.50
7	3	130	10	0.50
8	7	110	10	0.50
9	3	110	10	0.50
10	9	120	15	0.75
11	1	120	15	0.75
12a	5	120	15	0.75
12b	5	120	15	0.75
12c	5	120	15	0.75
12d	5	120	15	0.75
12e	5	120	15	0.75
13	5	120	25	0.75
14	5	120	5	0.75
15	5	140	15	0.75
16	5	100	15	0.75
17	7	130	20	1.00
18	3	130	20	1.00
19	7	110	20	1.00
20	7	130	10	1.00
21	3	110	20	1.00
22	3	130	10	1.00
23	7	110	10	1.00
24	3	110	10	1.00
25	5	120	15	1.25

Table S2. FTIR data for starch and acetylated wheat starch.

Band assignment	Wavenumber (cm ⁻¹)					
	Starch	AcS-1h	AcS-2h	AcS-3h	AcS-4h	AcS-5h
primary N-H		3374	3374			
		3327	3327			
alcohol OH	3275					
	1141					
secondary N-H		3213	3213			
alkane C-H	2920	2958	2958	2958	2958	2958
ester C=O		1733	1733	1733	1733	1733
secondary amide C=O		1662	1662			
methyl C-H		1415	1415	1415	1415	1415
		1367	1367	1367	1367	1367
C-O-C (ester)		1244	1244	1215	1215	1215
C-O-C (acetal)	990	1024	1024	1024	1024	1024

AcS, acetylated wheat starch; AA: Acetic anhydride, S, starch. Reaction conditions: Temp: 120 °C, AA: S: 15, S load: 1.25 g. Reaction was monitored every hour over 5 h.

Table S3. Statistical model term values in coded units of hierarchical quadratic model for optimization of the catalyst-free acetylation reaction. AA: Acetic anhydride, S, starch.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	2.026	0.155124	13.06	<0.0001
Time	0.144583	0.070804	2.04	0.0605
Temperature	0.26875	0.070804	3.8	0.002
AA:S	0.680417	0.070804	9.61	<0.0001
S	0.64375	0.070804	9.09	<0.0001
Time*Temperature	-0.00188	0.086717	-0.02	0.9831
Time*AA:S	0.053125	0.086717	0.61	0.5499
Temperature* AA:S	0.016875	0.086717	0.19	0.8485
Time*S	-0.00438	0.086717	-0.05	0.9605
Temperature*S	0.156875	0.086717	1.81	0.092
AA:S *S	0.496875	0.086717	5.73	<0.0001
Time*Time	-0.26202	0.068097	-3.85	0.0018
Temperature*Temperature	-0.29202	0.068097	-4.29	0.0008
AA:S * AA:S	-0.17202	0.068097	-2.53	0.0242
S*S	-0.15202	0.068097	-2.23	0.0424

Table S4. R^2 and adjusted R^2 (R^2 adj) values for hierarchical quadratic model for optimization of the catalyst-free acetylation reaction.

R^2	0.935517
R^2 Adj	0.904972
Root Mean Square Error	0.334686
Mean of Response	1.29931
Observations	29

Table S5. Statistical model term values in coded units of non-hierarchical quadratic model for optimization of the catalyst-free acetylation reaction. AA: Acetic anhydride, S, starch.

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	2.026	0.138825	14.59	<.0001
Time	0.1445833	0.063365	2.28	0.0349
Temperature	0.26875	0.063365	4.24	0.0005
AA:S	0.6804167	0.063365	10.74	<.0001
S	0.64375	0.063365	10.16	<.0001
Temperature*S	0.156875	0.077606	2.02	0.0584
AA:S *S	0.496875	0.077606	6.4	<.0001
Time*Time	-0.262021	0.060942	-4.3	0.0004
Temperature*Temperature	-0.292021	0.060942	-4.79	0.0001
AA:S * AA:S	-0.172021	0.060942	-2.82	0.0113
S*S	-0.152021	0.060942	-2.49	0.0226

Figure S1. FTIR spectra of evolved gases from degradation peaks at 290 °C, 320 °C, 350 °C and 390 °C. A: Native wheat starch. B: acetylated wheat starch (AcS-128) produced at the reaction conditions of 128 °C, 0.6 h, acetic anhydride: starch ratio of 20, and starch load of 1.25 g (presenting entrapped urea).

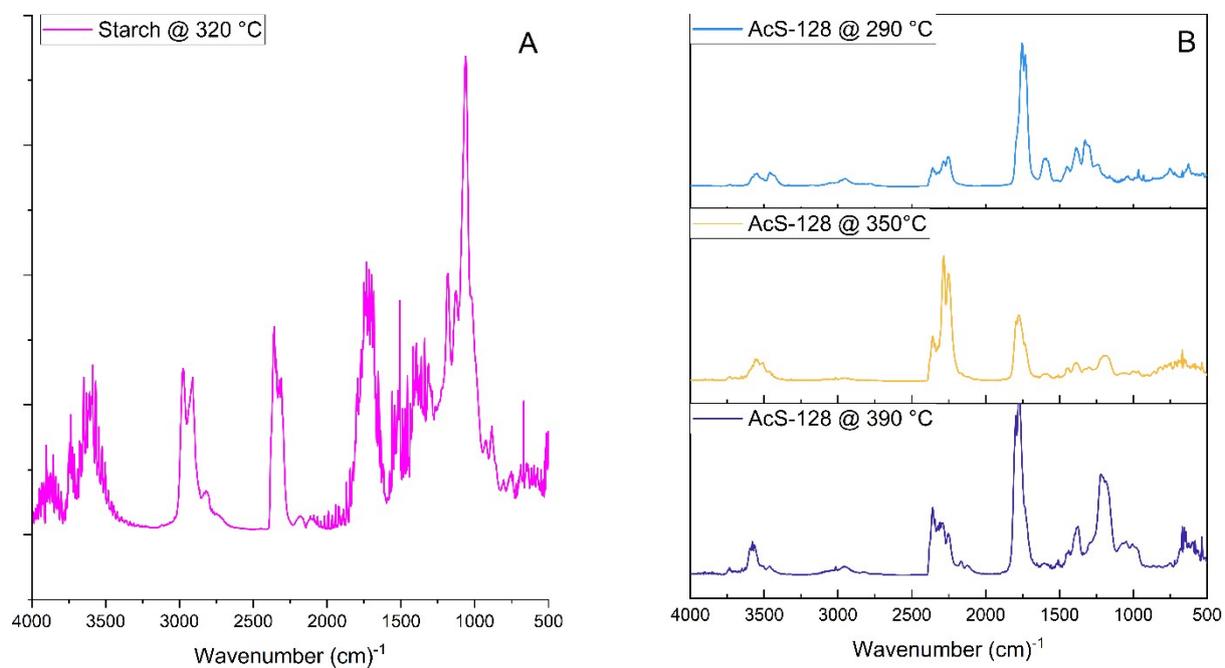


Figure S2. SEM images of acetylated wheat starch (AcS) at 120 °C, acetic anhydride: starch ratio of 15, starch load of 1.25 g, for 1 h (A) and 5 h (B).

