

Electronic Supplementary Information (ESI)

For

Eco-friendly additives in acidic pretreatment to boost enzymatic saccharification of hardwood for sustainable biorefinery applications

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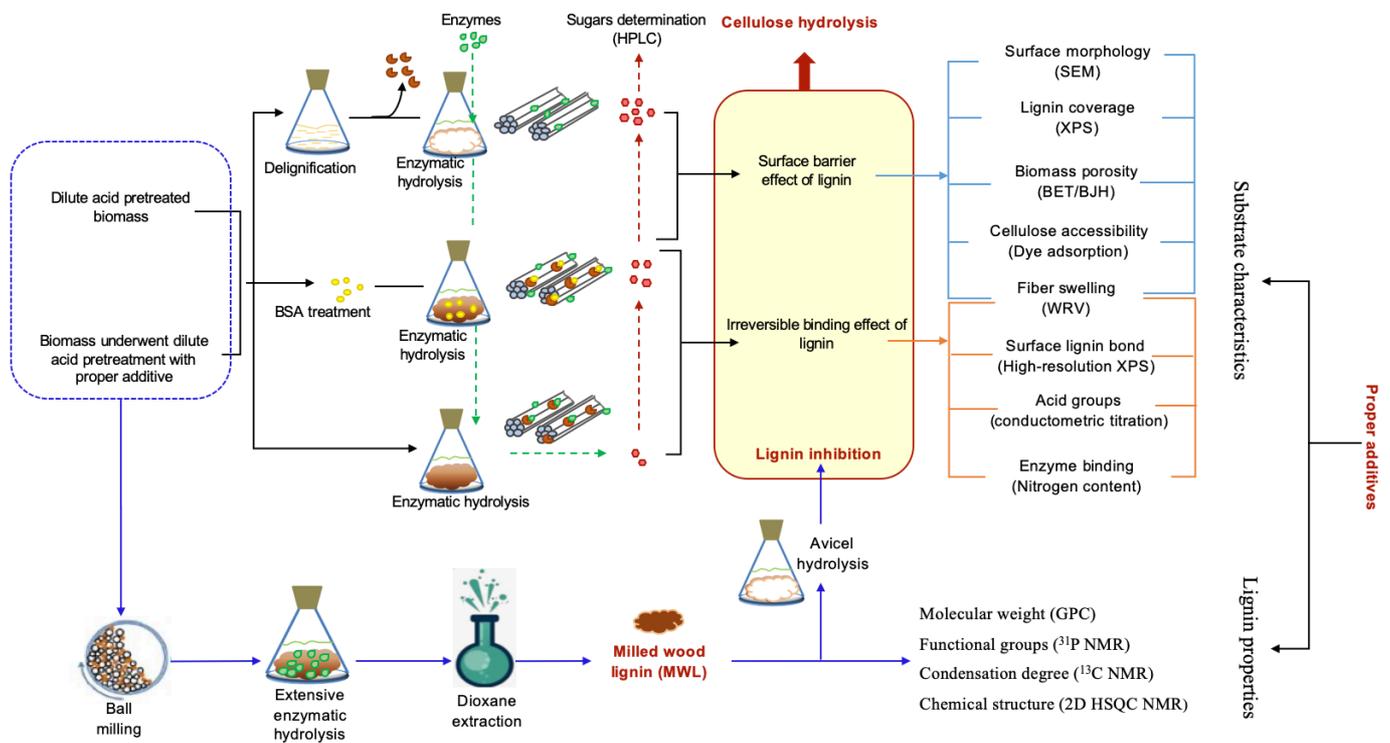


Fig. S1 Overview of experimental configuration for studying effect of additives in DA pretreatment on lignin properties and resulting lignin inhibition on cellulose hydrolysis.

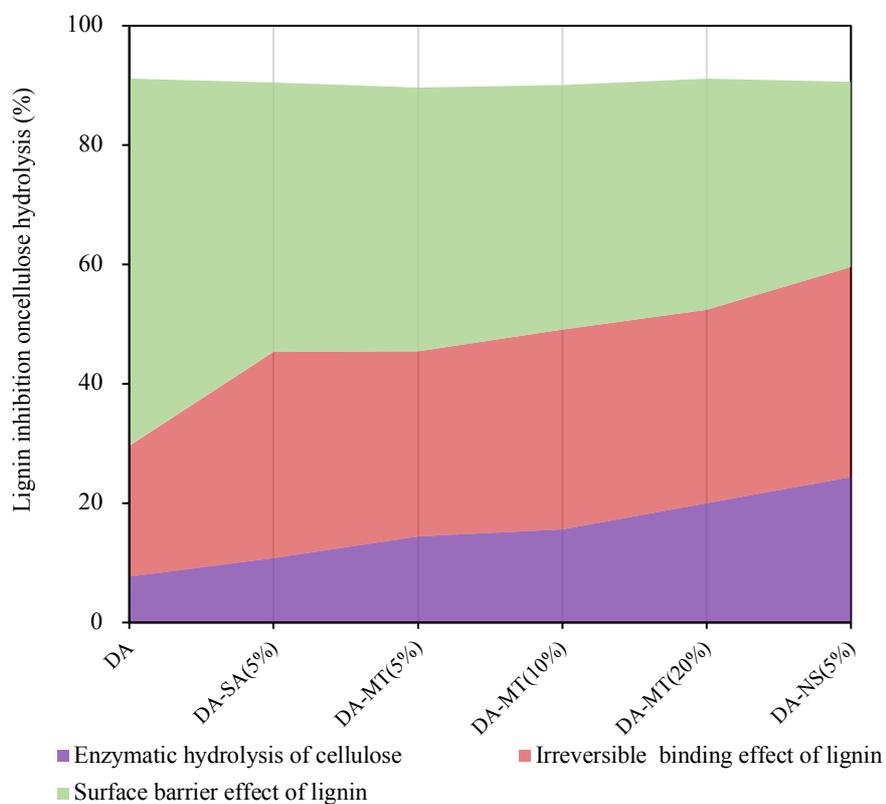


Fig. S2 Surface barrier effect and irreversible binding effect of lignin on enzymatic hydrolysis of cellulose (Enzyme loading: 5 FPU/g) after dilute acid (DA) pretreatment with additives: syringic acid (SA), mannitol (MT), 2-naphthol-7-sulfonate (NS).

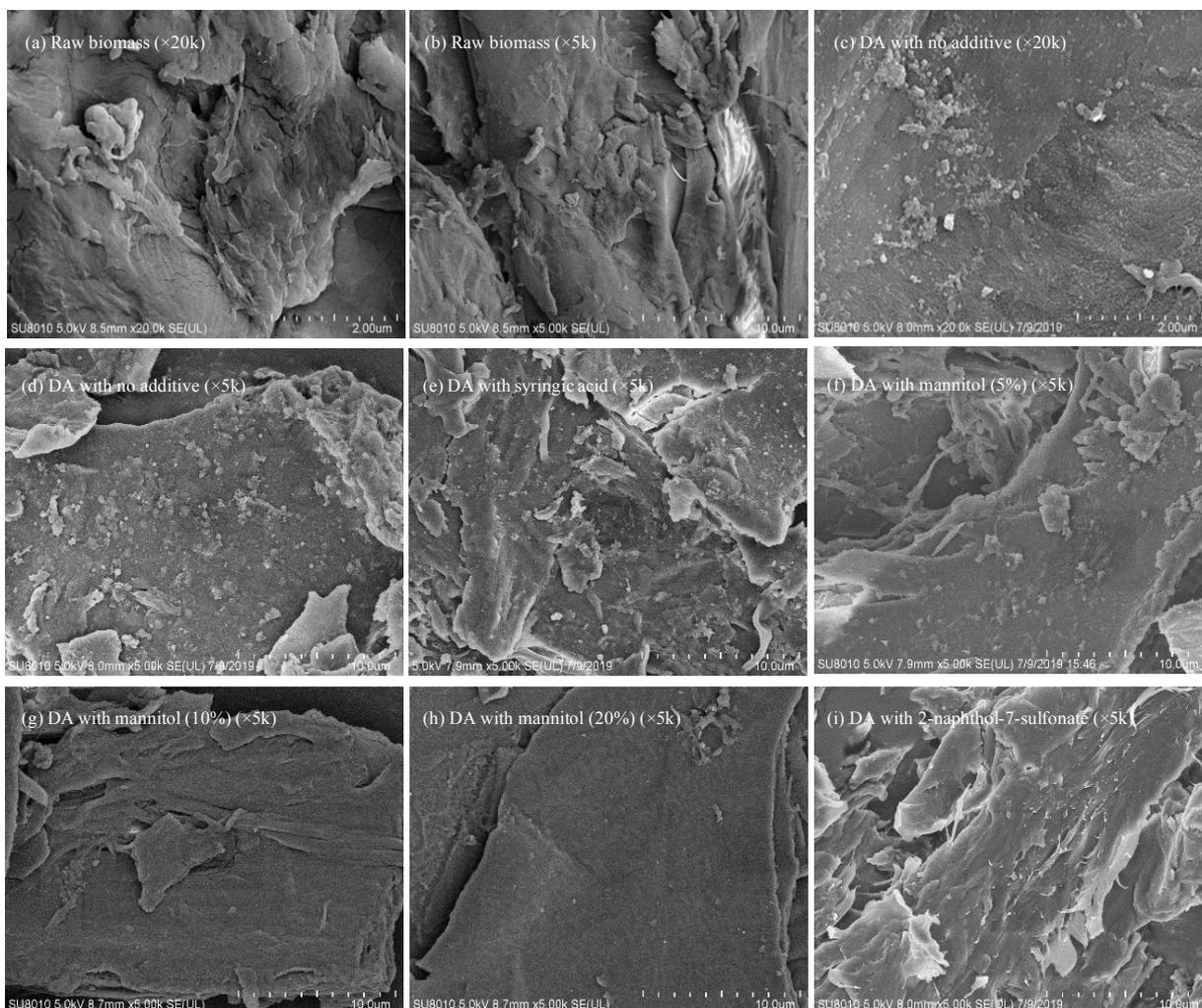


Fig. S3 SEM observations of substrates after dilute acid (DA) pretreatment with various additives at different magnifications.

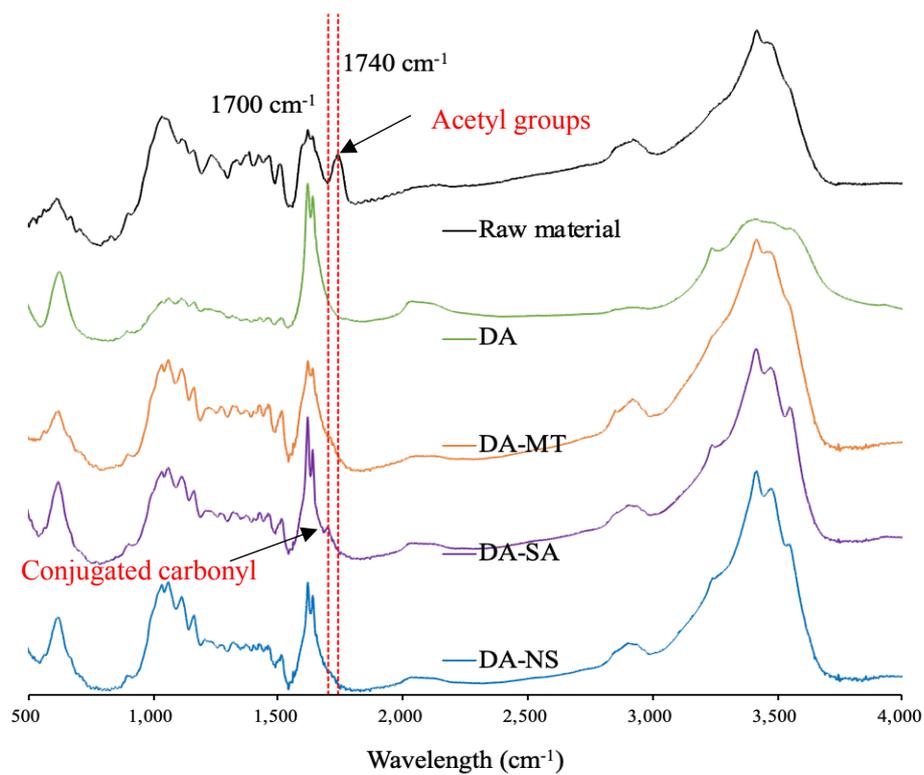


Fig. S4 FTIR spectra for the surfaces of raw biomass and dilute acid (DA) pretreated substrates in the absence and presence of various additives: syringic acid (SA), mannitol (MT), 2-naphthol-7-sulfonate (NS)

Table S1 Pretreatment efficacy of dilute acid (DA) pretreatment with various addition of syrigic acid (SA, 5 %, 10 % and 20 %, w/w, based on dry mass of poplar sawdust), and enzymatic hydrolysis yield of the pretreated substrates.

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Cellulose recovery in solid (%)	Hemicellulose recovery in solid (%)	Hemicellulose recovery in prehydrolysate (%)	Lignin removal (%)	Cellulose hydrolysis yield (%)	BSA treatment + cellulose hydrolysis (%)	Delignification + cellulose hydrolysis (%)
DA	59.30 ±0.51	0.34 ±0.07	38.85 ±1.28	91.71 ±1.66	0.97 ±0.19	39.22 ±1.19	6.83 ±1.08	42.39 ±0.97	72.32 ±1.30	96.59 ±1.09
DA-SA 5%	58.64 ±0.17	0.47 ±0.11	38.52 ±0.80	90.15 ±0.70	1.35 ±0.31	36.67 ±0.01	7.53 ±0.94	56.57 ±0.69	79.46 ±0.05	96.10 ±1.56
DA-SA 10%	58.94 ±1.12	0.66 ±0.00	39.78 ±0.09	87.93 ±1.50	1.83 ±0.02	36.41 ±0.69	9.71 ±0.44	60.07 ±1.10	82.99 ±1.01	97.35 ±0.67
DA-SA 20%	55.41 ±1.03	0.35 ±0.17	41.67 ±1.02	84.37 ±1.37	0.99 ±0.47	32.24 ±2.23	3.48 ±2.30	45.06 ±2.81	82.27 ±0.53	97.16 ±2.03

Table S2 XPS elemental analysis on fiber surface of dilute acid (DA) pretreated substrates in the absence and presence of various additives (5 %, w/w): syringic acid (SA), mannitol (MT), 2-naphthol-7-sulfonate (NS).

	Carbon (C _{1s})			Oxygen (O _{1s})		
	C ₁ (284.7 eV)	C ₂ (286.6 eV)	C ₃ (288.4 eV)	O ₁ (531.3 eV)	O ₂ (532.4 eV)	O ₃ (533.3 eV)
DA	0.70	0.26	0.04	0.11	0.46	0.43
DA-MT (5%)	0.40	0.52	0.08	0.08	0.54	0.38
DA-SA (5%)	0.56	0.38	0.06	0.10	0.47	0.43
DA-NS (5%)	0.49	0.46	0.05	0.12	0.50	0.38

^a Subpeaks in C_{1s} correspond to C₁ (C-C), C₂ (C-S, C-OH or C-O-C) and C₃ (O-C-O or C=O), respectively.

^b Subpeaks in O_{1s} correspond to O₁ (O-C=O and Ar-O-Ar), O₂ (C-O-, C=O, C-O-C and O-C=O), O₃ (Ph-O), respectively.