Stepwise pretreatment involving dilute acid and amine for corn stover fractionation toward full lignocellulose-oriented valorization

Table S1. Experimental design and corresponding results

Run	Factor1(X1): Conc.(%w/v)	Factor 2(X2): Temp.(°C)	Factor3(X3): Time(h)	Response 1: Xylose(mg/g)	Response2: Furfural(mg/g)
1	3	120	2	222.78	10.74
2	1	120	1	167.42	9.10
3	3	120	2	222.78	10.74
4	3	120	2	222.78	10.74
5	5	120	1	220.83	10.75
6	1	130	2	214.07	8.54
7	5	110	2	208.81	8.53
8	1	120	3	212.22	7.67
9	3	110	3	197.72	9.52
10	5	120	3	168.17	31.09
11	3	120	2	222.78	10.74
12	1	110	2	176.41	2.20
13	5	130	2	201.03	27.27
14	3	120	2	222.78	10.74
15	3	130	1	221.59	12.61
16	3	110	1	195.47	0.15
17	3	130	3	211.48	21.84

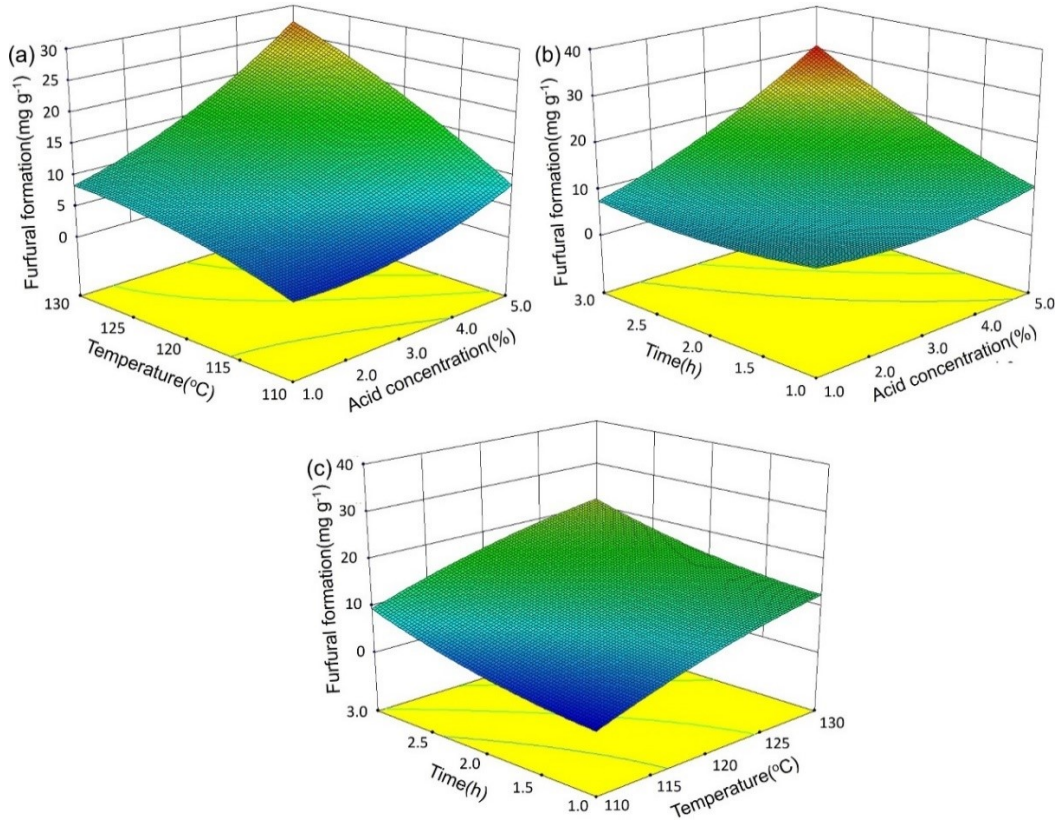

Fig S1. Response surface (3D) and counter plots indicating interaction effects of independent variables on Furfural formation. (a) temperature vs. acid concentration, (b) time vs. concentration, (c) time vs. temperature.

Table S2 Quantification of corn stover constituents and optimal conditions

Conc. (%)	Time (h)	Temp (ºC)	Xylose (mg/g)	Furfural (mg/g)	Araban (mg/g)	Glucose (mg/g)	5-HMF (mg/g)
1	1	120	168.56 ± 0.61	0.7 ± 0.01	27.59 ± 2.16	10.98 ± 0.65	0.10 ± 0.02
2	1	120	193.11 ± 0.72	2.54 ± 0.14	28.81 ± 0.49	18.83 ± 0.17	0.16 ± 0.00
3	1	120	202.24 ± 0.58	5.38 ± 0.1	30.19 ± 0.19	21.77 ± 0.07	0.20 ± 0.00
4	1	120	210.74 ± 1.87	6.7 ± 0.64	32.18 ± 0.46	23.08 ± 1.29	0.22 ± 0.01
5	1	120	220.44 ± 5.87	9.07 ± 0.41	31.65 ± 0.55	25.71 ± 0.55	0.25 ± 0.01
1	2	120	195.87 ± 1.14	3.12 ± 0.22	28.03 ± 1.14	18.10 ± 0.67	0.21 ± 0.03
2	2	120	210.67 ± 2.1	7.79 ± 0.22	37.91± 3.75	26.59 ± 1.77	0.28 ± 0.02
3	**2**	**120**	**221.9 ± 0.92**	**13.53 ± 1.77**	**35.46 ± 0.93**	**29.82 ± 0.47**	**0.37 ± 0.00**
4	2	120	210.96 ± 1.2	16.02 ± 2.01	34.32 ± 3.12	33.83 ± 2.60	0.38 ± 0.04
5	2	120	202.11 ± 2.01	21.14 ± 2.48	32.39 ± 0.47	35.53 ± 0.28	0.35 ± 0.01
1	3	120	208.39 ± 3.67	6.65 ± 0.47	33.70 ± 0.06	23.07 ± 0.11	0.32 ±0.01
2	3	120	203.01 ± 0.38	16.02 ± 0.53	30.73 ± 0.20	28.25 ± 0.16	0.35 ± 0.00
3	3	120	191.89 ± 3.22	22.19 ± 0.64	28.83 ± 0.75	31.83 ± 0.66	0.38 ± 0.02
4	3	120	176.67 ± 0.25	27.53± 0.19	27.67 ± 0.03	35.49 ± 0.11	0.39 ± 0.03
5	3	120	165.81 ± 5.37	33.59 ± 4.13	24.58 ± 0.88	37.28 ± 1.28	0.42 ± 0.04

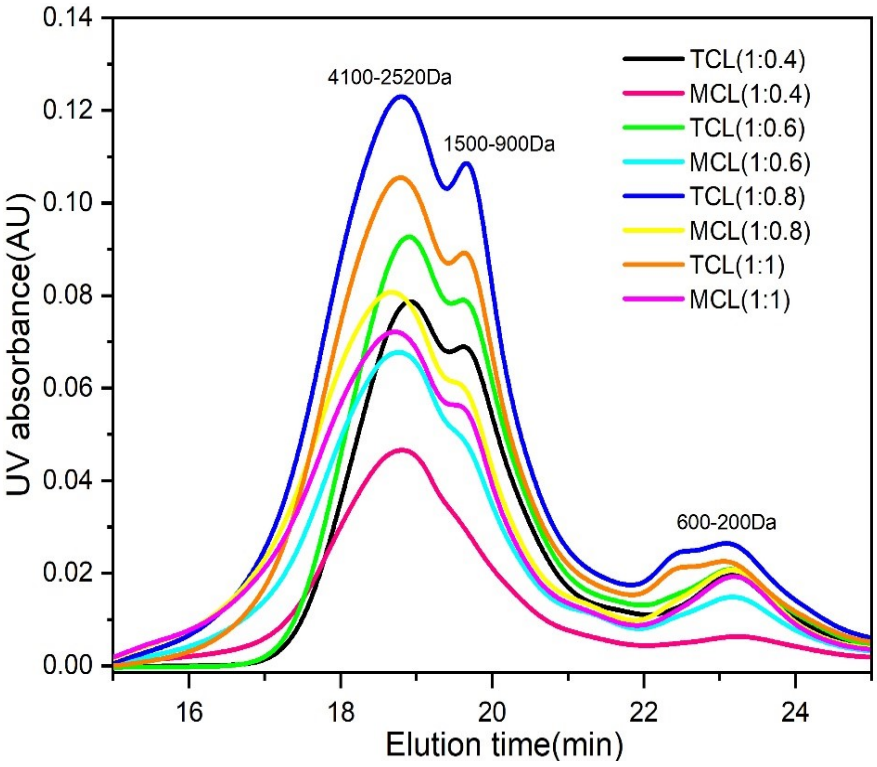

Fig S2. Profile curves as function of elution time vs. absorbance

Table S3. The main ^{13}C-^{1}H cross-signals in HSQC spectra of fractionated lignin

Label	δ_C/δ_H (ppm)	Assignment
Cβ	52.92-50.63/3.71	C_β-H_β in phenylcoumaran substructures (C)
Bβ	53.87/3.20-3.17	C_β-H_β in β-β (resinol) substructures (B)
OMe	55.97/4.11-3.33	C-H in methoxyl(-OCH_3)
Aγ	64.18-58.32/3.81-3.14	C_γ-H_γ in β-O-4 substructures (A)
Cγ	65. 95/3.70	C_γ-H_γ in phenylcoumaran substructures (C)
Bγ	73.58-68.88/4.05-3.86	C_γ-H_γ in β-β (resinol) substructures (B)
Aα	72.6/5.01-4.66	C_α-H_α in β-O-4 substructures(A)
Bα	82.58/4.91	C_α-H_α in β-β (resinol) substructures (B)
Aβ-S	87.70-83.21/4.41-3.94	C_β-H_β in β-O-4 substructures linked to S units (A)
Cα	ND	C_α-H_α in phenylcoumaran substructures (C)
S2/6	104.24/6.75	$C_{2/6}$-$H_{2/6}$ in etherified syringyl units (S)
S'2/6	104.87/7.18	$C_{2/6}$-$H_{2/6}$ in oxidized (C_α=O) syringyl units (S′)
S(condensed)	107.86-104.40/6.51-6.34	$C_{2/6}$-$H_{2/6}$ in condensed syringyl units (S)
FAM2	115.24-111.22/7.39-7.27	C_2-H_2 in Feruloyl amide (FAM)
G2	111.22/6.95	C_2-H_2 in guaiacyl units (G)
H3/5	ND	$C_{3/5}$-$H_{3/5}$ in p-hydroxyphenyl units(H)
G5	115.40/6.94-6.37	C_2-H_2 in guaiacyl units (G)
G6	118.26/6.82-6.61	C_6-H_6 in guaiacyl units (G)
FAMβ	120.89-117.22/6.59-6.29	C_β-H_β in Feruloyl amide (FAM)
pCAMβ	120.89-117.22/6.59-6.29	C_β-H_β in p-Coumaroyl amide(pCAM)
FAM6	124.80-119.69/7.13-6.90	C_6-H_6 in Feruloyl amide (FAM)
H2/6	131.84-126.38/7.27-6.84	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (H)
pCAM2/6	130.98-125.76/7.57-7.32	$C_{2/6}$-$H_{2/6}$ in p-Coumaroyl amide(pCAM)
pCA2/6	130.5-128.15/7.91-7.60	$C_{2/6}$-$H_{2/6}$ in p-Coumarate amide(pCA)
FAMα	144.03-136.93/7.41-7.25	C_α-H_α in Feruloyl amide (FAM)
pCAMα	144.03-136.93/7.41-7.25	C_α-H_α in p-Coumaroyl amide(pCAM)
SBα	187.80-140.11/8.52-7.85	C_α-H_α in Schiff base (SB)

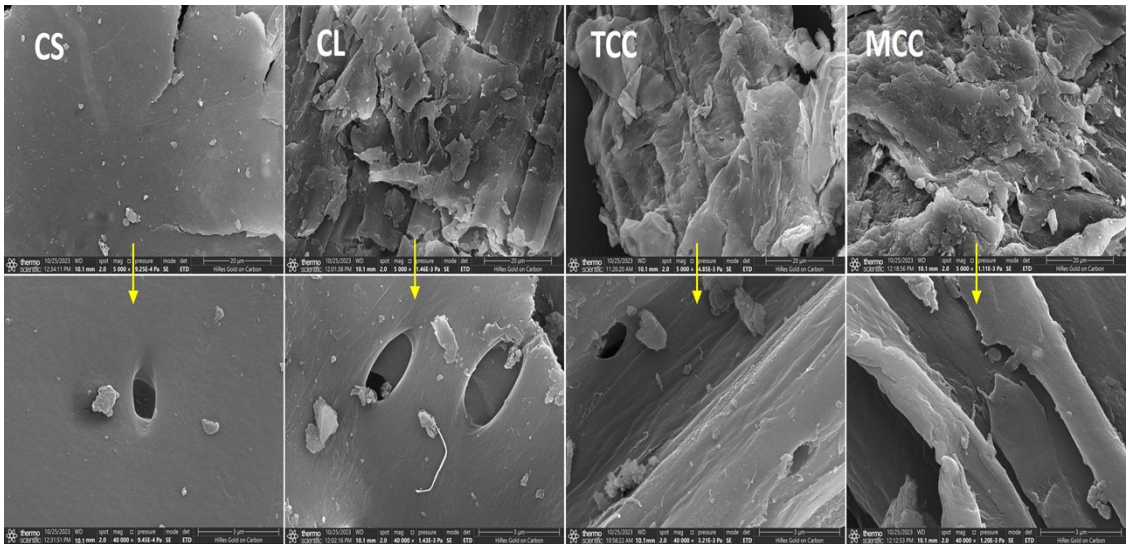

Fig S3. SEM morphologies of CS, CL, TCC and MCC

Table S4: Glucan and residual xylan content of pretreated cellulignin

Pretreatment	CL to EDA ratio	Glucan (mg g^{-1})	Xylan (mg g^{-1})
TC	1:0.4	583.27 ± 15	57.59 ±1.9
MC	1:0.4	678.74 ± 21	55.41 ± 1.7
TC	1:0.6	793.79 ± 19	66.45 ± 2.4
MC	1:0.6	753.75 ± 15	57.16 ± 1.1
TC	1:0.8	837.93 ± 25	66.46 ± 1.7
MC	1:0.8	743.47 ± 21	58.14 ± 1.5
TC	1:1	813.52 ± 16	61.72 ± 1.2
MC	1:1	655.27 ± 18	58.04 ± 1.7