Supporting Information

Cascade fractionation of poplar into xylose, glucan oligomers and less-condensed lignin via synergistic formic acid–LiBr molten salt hydrate pretreatment

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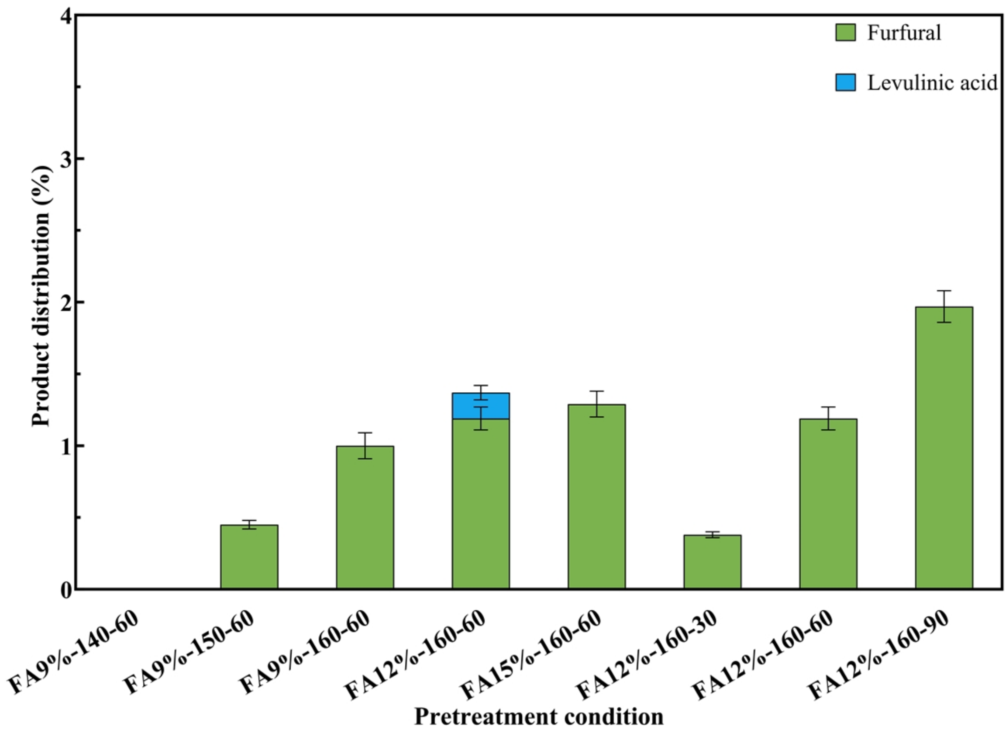

Fig. S1 The content of furfural and levulinic acid in the hydrolysate during FA pretreatment

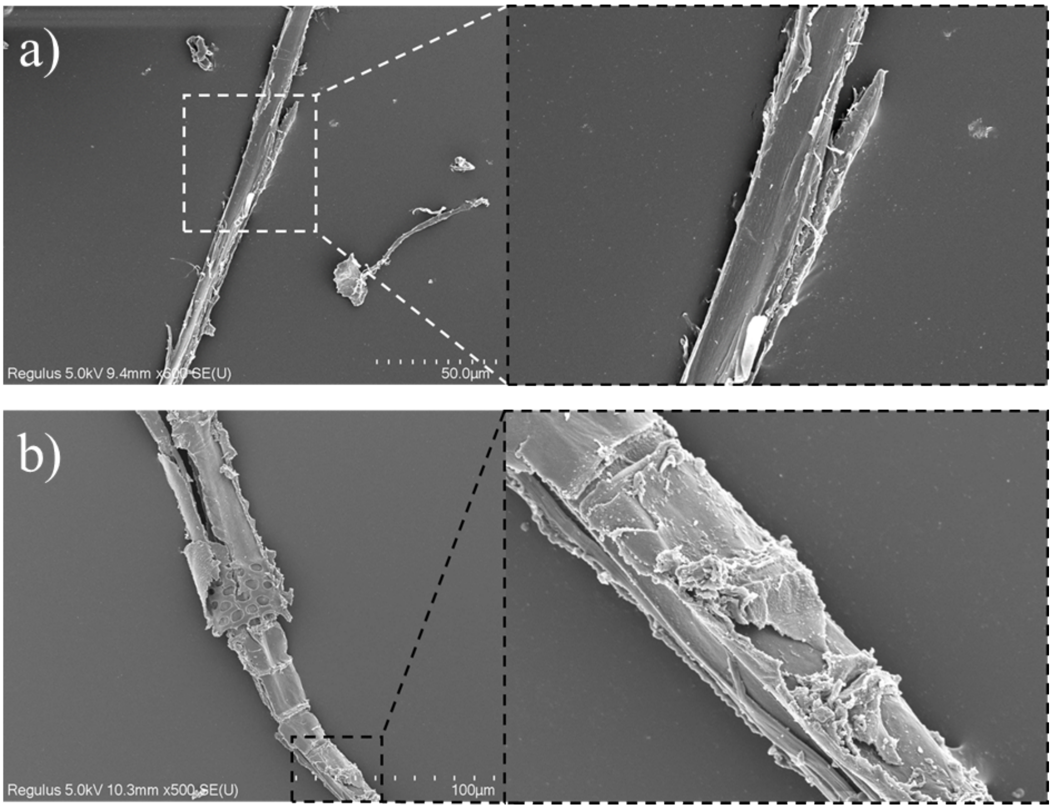

Fig. S2 Morphological characteristics of the control poplar (a) and FA-pretreated substrate (b)

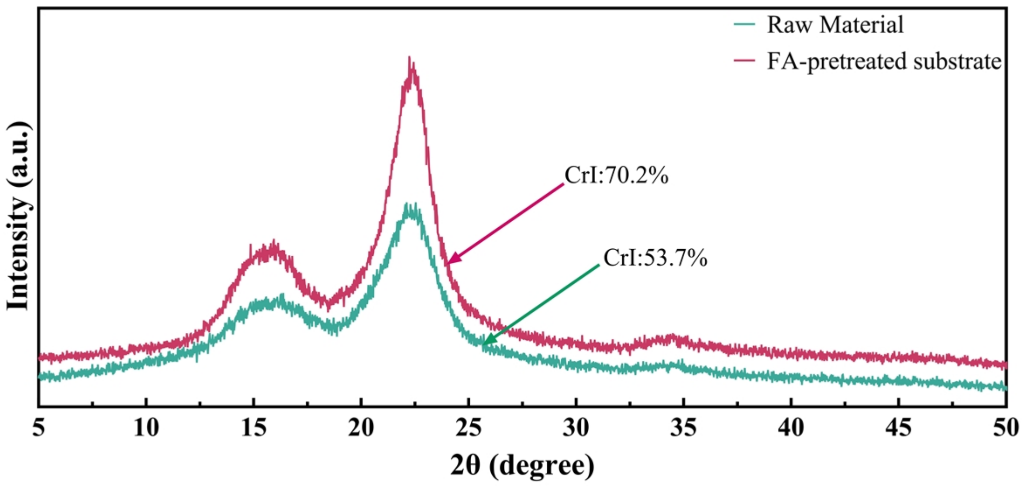

Fig. S3 The XRD pattern of raw material and FA-pretreated substrate

Table S1 Comparison of results of different treatment

	Ref [1]	Ref [2]	This Work
Raw material	Corn stover	Cellulose	Poplar
Pretreatment	Auto-hydrolysis	/	12 wt% FA
Reaction conditions	190 °C, 20 min	/	160 °C, 1h
Hemicellulose removal rate	94.4%	/	91.24%
MSH	60 wt% LiBr	60 wt% LiBr	60 wt% LiBr
Reaction conditions	130 °C, 2h	130 °C, 5h	100°C, 0.5h, 30mM HCl
Glucan oligomers yield	59.9%	90.4%	42.68%
Glucose yield	21.4%		41.87%

Table S2 The purity and yield of lignin samples

Lignin samples ($L_{a/b-c}$)	Yield of acid-insoluble lignin (%)	Yield of acid-soluble lignin (%)	Purity (%)
$L_{C/40\ mM-110℃}$	81.35	6.18	87.53
$L_{FA/20\ mM-90℃}$	40.77	3.32	44.09
$L_{FA/20\ mM-100℃}$	73.22	3.57	76.79
$L_{FA/20\ mM-110℃}$	88.80	3.32	92.12
$L_{FA/30\ mM-90℃}$	62.84	3.66	66.50
$L_{FA/30\ mM-100℃}$	91.73	3.84	95.57
$L_{FA/30\ mM-110℃}$	91.86	3.44	95.30
$L_{FA/40\ mM-90℃}$	69.09	3.58	72.67
$L_{FA/40\ mM-100℃}$	92.68	3.70	96.38
$L_{FA/40\ mM-110℃}$	94.04	3.34	97.38

$L_{a/b-c}$: a-Conventional or Formic Acid, b-HCl concentration, c-Temperature

Table S3 2D HSQC NMR data for the signal assignments in lignin

Lable	δ_C/δ_H(ppm)	Assignment
A_α	71.58/4.86	C_α-H_α in β-O-4 (A)
OMe	56.63/3.72	C-H in Methoxy
A_γ	59.46/3.23-3.64	C_γ-H_γ in β-O-4 (A)
I_γ	61.42/4.09	C_γ-H_γ in *p*-hydroxycinnamyl alcohol end-groups
C_α	86.48-87.61/5.44-5.59	C_α-H_α in Phenylcoumarin substructure
C_γ	62.49/3.70	C_γ-H_γ in Phenylcoumarin substructure
B_α	83.19-84.87/4.81-4.65	C_α-H_α in β-β resinol substructures (B)
B_β	53.25/3.03	C_β-H_β in β-β resinol substructures (B)
B_γ	70.18-71.10/3.82-4.19	C_γ-H_γ in β-β resinol substructures (B)
X_2	69.68/3.51	C_2-H_2 in β-D-xylopyranoside (X)
X_3	72.27/3.21-3.43	C_3-H_3 in β-D-xylopyranoside (X)
X_4	74.17/3.22-3.50	C_4-H_4 in β-D-xylopyranoside (X)
A_β(G/H)	83.47/4.26-4.45	C_β-H_β in β-O-4 linked to G/H (A)
A_β(S)	85.72-87.11/3.96-4.08	C_β-H_β in β-O-4 linked to S (A)
BD_α	75.48/4.89	C_α-H_α in benzodioxane substructures
HK_α	44.34/3.65	C_α-H_α in Hibbert ketone
HK_γ	66.99/4.15	C_γ-H_γ in Hibbert ketone
$S_{2,6}$	103.42/6.70	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.41/7.30	$C_{2,6}$-$H_{2,6}$ in oxidized S units (S')
$S''_{2,6}$	106.68/6.49	$C_{2,6}$-$H_{2,6}$ in condensed S units (S'')
G_2	110.47/6.96	C_2-H_2 in guaiacyl units (G)
G_5	114.69/6.78	C_5-H_5 in guaiacyl units (G)
G_6	118.74/6.78	C_6-H_6 in guaiacyl units (G)
$PB_{2,6}$	131.17/7.50-7.87	$C_{2,6}$-$H_{2,6}$ in benzoate
I_α	128.18/6.22	C_α-H_α in acylated cinnamyl alcohol
I_β	128.39/6.45	C_β-H_β in acylated cinnamyl alcohol
I'_γ	125.95/6.77	C_γ-H_γ in acylated *p*-hydroxycinnamyl alcohol end-groups

References

1. Q. Liu, L. Zhou, X. Xie, D. Fan, X. Ouyang, W. Fan and X. Qiu, *Green Chem.*, 2022, **24**, 8812-8819.
2. Q. Liu, Q. Ma, S. Sabnis, W. Zheng, D. G. Vlachos, W. Fan, W. Li and L. Ma, *Green Chem.*, 2019, **21**, 5030-5038.