Supporting Information

The production of xylooligosaccharide, nanolignin and nanocellulose through a fractionation strategy of corncob for biomass valorization

Qixuan Lin[+], Yuhuan Yan[+], Xinxin Liu, Bei He, Xiaohui Wang, Xiaoying Wang, Chuanfu Liu, Junli Ren[*]

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, Guangdong, China

[+]The authors contributed equally to this work.

*Corresponding author. E-mail address: renjunli@scut.edu.cn

Current address: State Key Laboratory Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China.

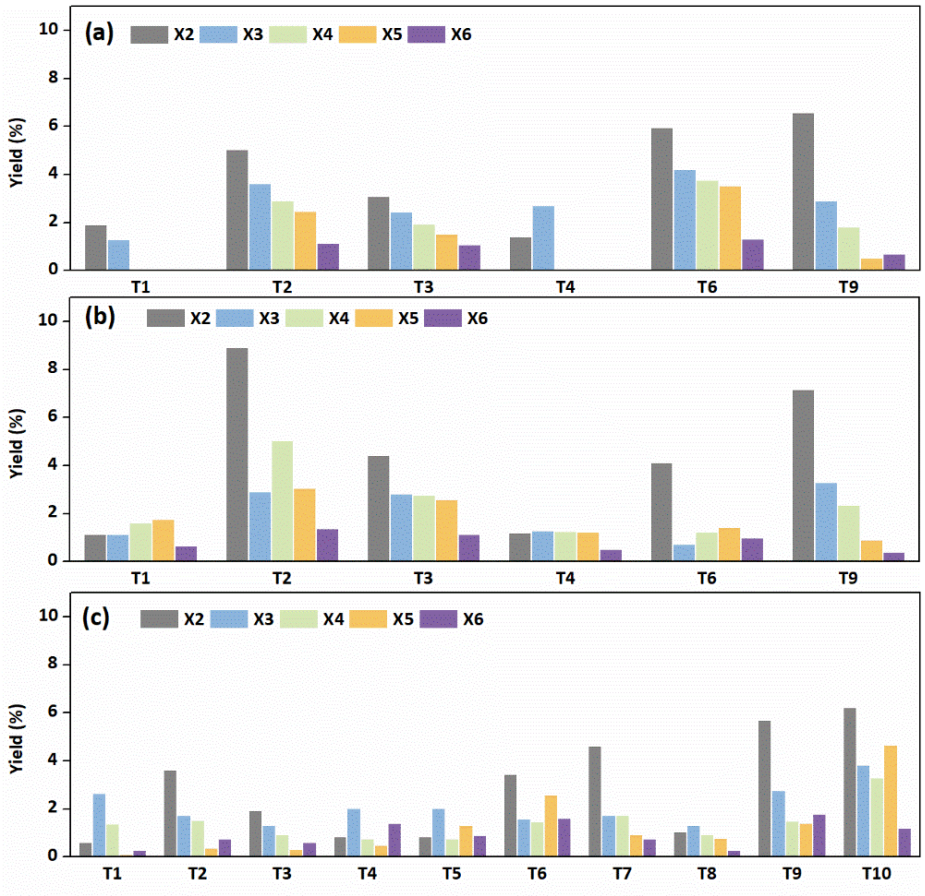

Figure S1. Yields of X2, X3, X4, X5 and X6 in hydrolysate. Reaction condition: 0.5 g of dewaxed corncob, 10 mL citric acid solution, (a) 140°C; (b) 150°C; (c) 160°C.

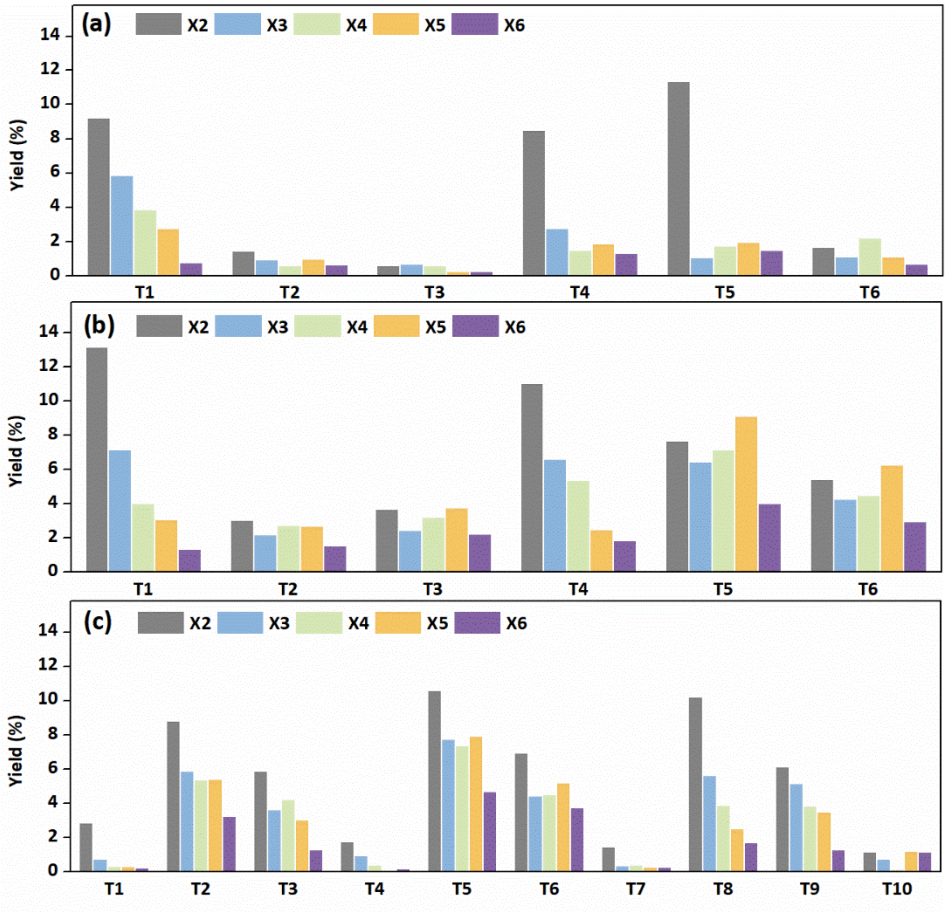

Figure S2. Yields of X2, X3, X4, X5 and X6 in hydrolysate. Reaction condition: 0.5 g of dewaxed corncob, 10 mL formic acid solution, (a) 140℃; (b) 150℃; (c) 160℃

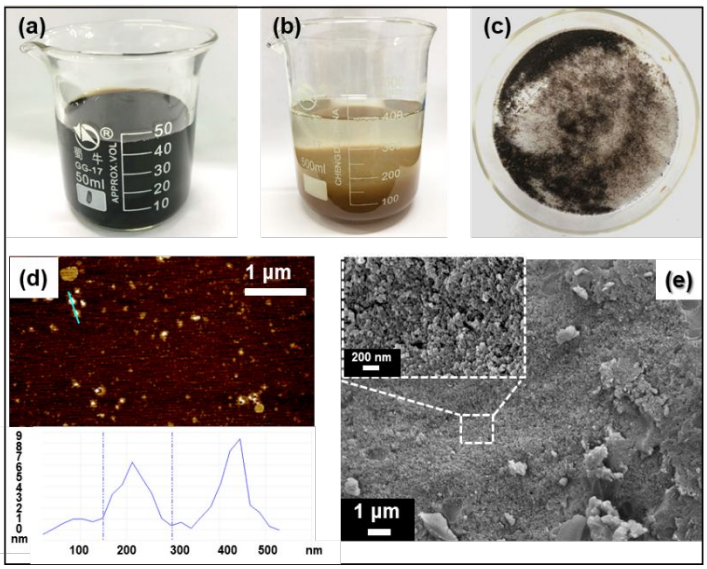

Figure S3. The structure and morphology of isolated lignin (a) in 30 wt% *p*-TsOH solution; (b) in 4 wt% *p*-TsOH solution after 1 h standing; (c) after freeze-drying; (d) AFM image of *p*-TsOH extracted lignin; (e) SEM image of *p*-TsOH extracted lignin

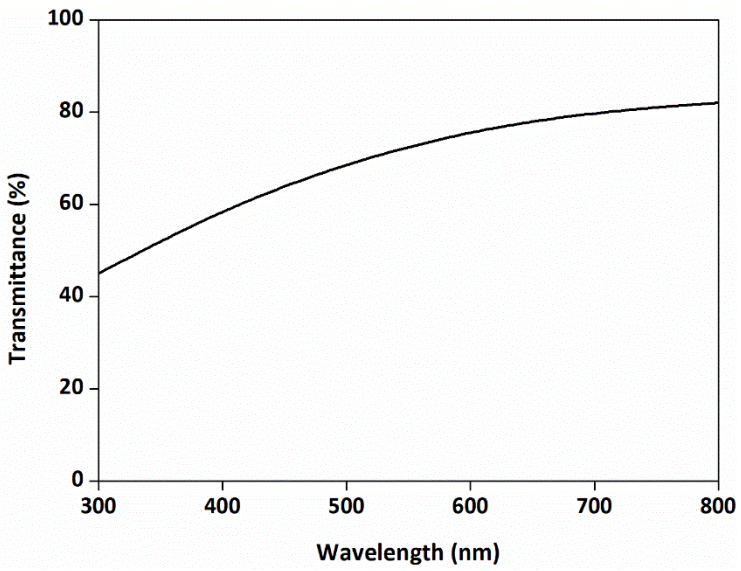

Figure S4. UV–Vis transmittance spectra of 0.1% corncob TEMPO-oxidized cellulose nanofibrils dispersed in water

Table S1 The yields of composition in hydrolysate after citric acid-NaOH pretreatment

Yield (%)		T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
140℃	Xylose	18.4	0.6	0.4	24.7	-	1.6	-	-	2.3	-
	XOS	3.2	15.2	10.1	4.1	-	18.8	-		12.5	-
	WSX	0.1	4.6	7.8	1.2	-	3.9	-	-	5.8	-
	Glucose	0.3	0.3	0.1	0.8	-	0.5	-	-	0.4	-
	Furfural	2.3	*	*	3.6	-	*	-	-	*	-
150℃	Xylose	28.6	5.8	10.2	38.1	-	20.3	-	-	14.0	-
	XOS	6.3	21.3	13.7	5.5	-	8.5	-	-	14.1	-
	WSX	3.0	12.3	15.6	*	-	13.4	-	-	12.6	-
	Glucose	1.4	1.0	1.1	2.2	-	1.5	-	-	1.0	-
	Furfural	3.8	*	*	4.0	-	0.1	-	-	*	-
160℃	Xylose	32.8	16.2	15.6	29.9	27.6	16.5	13.5	26.9	17.6	7.4
	XOS	5.0	9.2	4.2	5.5	5.8	10.6	9.7	4.4	13.0	19.2
	WSX	4.2	15.6	19.3	7.1	7.3	14.0	12.5	9.1	10.8	9.5
	Glucose	2.1	1.2	1.0	2.0	2.1	1.5	1.0	2.0	1.4	1.1
	Furfural	4.2	1.1	0.4	4.8	3.0	1.0	0.5	2.9	0.6	0.2

XOS: Xylooligosaccharides; WSX: Water-soluble xylan. * < 0.045%.

Table S2 The yields of composition in solid residue after citric acid-NaOH pretreatment

Yield (%)		T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
140℃	SR	57.9	60.0	49.9	54.3	-	63.6	-	-	47.1	-
	Hemicellulose	7.6	11.2	12.6	0.5		8.9			11.8	
	Cellulose	32.4	34.6	33.5	32.0		34.8			32.2	
	Lignin	15.6	12.9	2.3	16.2		13.9			2.1	
150℃	SR	49.8	58.3	43.0	47.8	-	53.0	-	-	42.5	-
	Hemicellulose	*	0.1	0.1	*		*			0.1	
	Cellulose	32.8	33.9	32.2	31.4		34.1			32.6	
	Lignin	15.5	16.2	7.2	15.3		14.9			5.5	
160℃	SR	47.9	50.1	49.0	50.0	56.8	52.8	47.9	48.6	42.4	38.2
	Hemicellulose	*	*	0.1	*	*	*	0.2	*	*	0.2
	Cellulose	32.4	33.6	33.5	32.0	32.3	33.8	32.5	32.6	32.3	32.0
	Lignin	14.6	14.1	13.9	16.5	16.0	11.3	7.5	8.2	5.2	0.9

SR: Solid residue. Dewaxed Corncob: hemicellulose 34.3%, cellulose 37.0%, lignin 16.4%. * < 0.045%.

Table S3 The yields of composition in hydrolysate after formic acid-NaOH pretreatment

		T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
140℃	Xylose	10.2	0.2	*	27.7	0.7	0.3				
	XOS	22.4	4.6	2.4	15.9	17.5	6.7				
	WSX	0.4	3.4	5.8	*	2.4	3.7				
	Glucose	0.1	0.6	0.7	0.6	0.7	1.0				
	Furfural	*	*	*	2.0	*	*				
150℃	Xylose	19.1	4.5	2.1	34.6	6.0	3.3				
	XOS	28.7	12.1	15.3	25.7	34.4	23.4				
	WSX	*	10.4	12.8	*	9.1	9.9				
	Glucose	1.8	1.5	1.4	2.0	1.2	0.9				
	Furfural	1.6	*	*	3.2	*	*				
160℃	Xylose	20.1	13.2	13.0	23.6	11.9	10.0	26.3	11.1	5.0	4.7
	XOS	4.5	28.7	18.1	3.4	38.3	24.8	2.8	23.9	19.9	4.3
	WSX	*	5.7	10.4	*	3.3	5.3	*	2.2	3.5	6.3
	Glucose	2.0	1.5	1.6	2.4	2.0	1.0	2.4	2.3	2.2	1.1
	Furfural	2.4	0.1	*	4.5	0.2	0.2	4.8	1.0	0.4	*

XOS: Xylooligosaccharides; WSX: Water-soluble xylan. * < 0.045%.

Table S4 The yields of composition in solid residue after formic acid-NaOH pretreatment

Yield (%)		T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
140℃	SR	62.0	75.3	65.6	59.6	64.3	53.1				
	Hemicellulose	2.3	25.8	26.0	*	13.5	17.1				
	Cellulose	36.2	36.6	36.8	36.0	36.3	35.4				
	Lignin	17.4	12.5	2.6	17.5	14.3	0.2				
150℃	SR	57.5	63.2	61.2	55.2	59.2	51.7				
	Hemicellulose	*	7.3	4.0	*	*	2.1				
	Cellulose	35.9	36.1	36.0	35.9	36.5	35.4				
	Lignin	17.8	17.2	15.4	16.1	16.5	10.3				
160℃	SR	49.8	52.0	41.3	50.2	54.6	47.9	50.8	58.0	55.6	48.7
	Hemicellulose	*	*	*	*	*	*	*	*	*	*
	Cellulose	32.1	35.6	35.2	32.3	34.6	34.9	32.0	34.9	34.5	34.1
	Lignin	15.6	15.0	4.6	16.4	16.5	11.0	17.1	17.5	16.4	10.4

SR: Solid residue. Dewaxed Corncob: hemicellulose 34.3%, cellulose 37.0%, lignin 16.4%. * < 0.045%.

Table S5. The crystallinity of corncob before and after the organic acid-NaOH pretreatment

Sample	*I_{am}(a.u.)	I_{002}(a.u.)	CrI(%)
Raw material	1622.1	2553.3	36.5
CA 0.1-0	1301.4	3020.2	56.9
CA 0.1-0.8%	1131.5	2672.5	57.7
CA 0.2-0	955.0	2121.0	55.0
FA 0.2-0	1515.4	3241.1	53.2
FA 0.2-0.2%	1414.7	3101.9	54.4
FA 0.2-0.4%	1198.2	2733.0	56.2
FA 0.3-0.4%	1351.8	2980.8	54.6
FA 0.3-0.6%	1301.9	3066.0	57.5
FA 0.3-0.8%	1231.0	2905.6	57.6
Residue after two treatment	1455.9	4136.9	64.8

*I_{am} (2θ=18.3°). CA: citric acid; FA: formic acid.

Table S6. Assignments of the HSQC spectra of *p*-TsOH extracted lignin from corncob

Lable	δ_C/δ_H (ppm)	Assignments
Aγ	59.1/3.54	Cγ-Hγ in β-O-4' substructures (A)
A'γ/A"γ	62.3/4.22	Cγ-Hγ in γ-acylated β-O-4' substructures (A'/A")
Aα	71.4/4.86	Cα-Hα in β-O-4' substructures (A)
$S_{2,6}$	103.9/6.73	$C_{2,6}$-$H_{2,6}$ in etherified syringyl units (S)
$T'_{2,6}$	104.2/7.34	$C_{2',6'}$-$H_{2',6'}$ in tricin (T)
T_3	104.6/7.05	C_3-H_3 in tricin (T)
G_2	110.6/6.98	C_2-H_2 in guaiacyl units (G)
FA_2	111.2/7.32	C_2-H_2 in ferulate (FA)
pCA_β/FA_β	113.6/6.28	C_β-H_β in *p*-coumarate (PCA) and ferulate (FA)
G_5	115.0/6.95	C_5-H_5 in guaiacyl units (G)
$pCA_{3,5}$	115.2/6.76	$C_{3,5}$-$H_{3,5}$ in *p*-coumarate (PCA)
G_6	118.5/6.82	C_6-H_6 in guaiacyl units (G)
$H_{2,6}$	127.9/7.22	$C_{2,6}$-$H_{2,6}$ in hydroxyphenyl units (H)
$pCA_{2,6}$	129.9/7.46	$C_{2,6}$-$H_{2,6}$ in *p*-coumarate (PCA)
*p*CAα/FAα	144.7/7.45	Cα-Hα in *p*-coumarate (PCA) and ferulate (FA)