Supplementary Information for The Degradation of Lignin in *Phyllostachys Heterocycla* cv. var. *Pubescens* in Ethanol Solvothermal System

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1. Elemental analysis of *pubescens*

Elemental composition of *pubescens* (Table S1)

Table S1. The elemental analysis of *pubescens*

	Weight percentage of elements (%)					
	C	**H**	**N**	**O[a]**	**S[b]**	**ash**
Pubescens	47.29	5.89	0.58	46.07	-	0.17

[a] O%=100%-C%-H%-N%-ash%; [b] less than detection limit.

2. XRD analysis of solid samples

Instrument parameter

The XRD measurement was operated on a DANDONG FANGYUAN DX-1000 instrument (Cu Kα radiation; k=0.1540 nm; 40 kV and 50 mA). The diffracted intensity was measured over the 2θ ranged from 5° to 40°. The diffraction peak at 2θ of 22° was assigned to the (002) lattice plane of cellulose. The crystalline index (CI) of cellulose in samples was calculated by the following equation[S1]:

$$CI = \frac{I_{002} - I_{AM}}{I_{002}} \times 100\%$$

Thereinto, I_{002} was the diffraction intensity of the (002) lattice plane, which represented both crystalline and amorphous parts of cellulose. I_{AM} referred to the peak intensity at 2θ of 18° which represented amorphous part only.[S2]

XRD graph (Figure. S1)

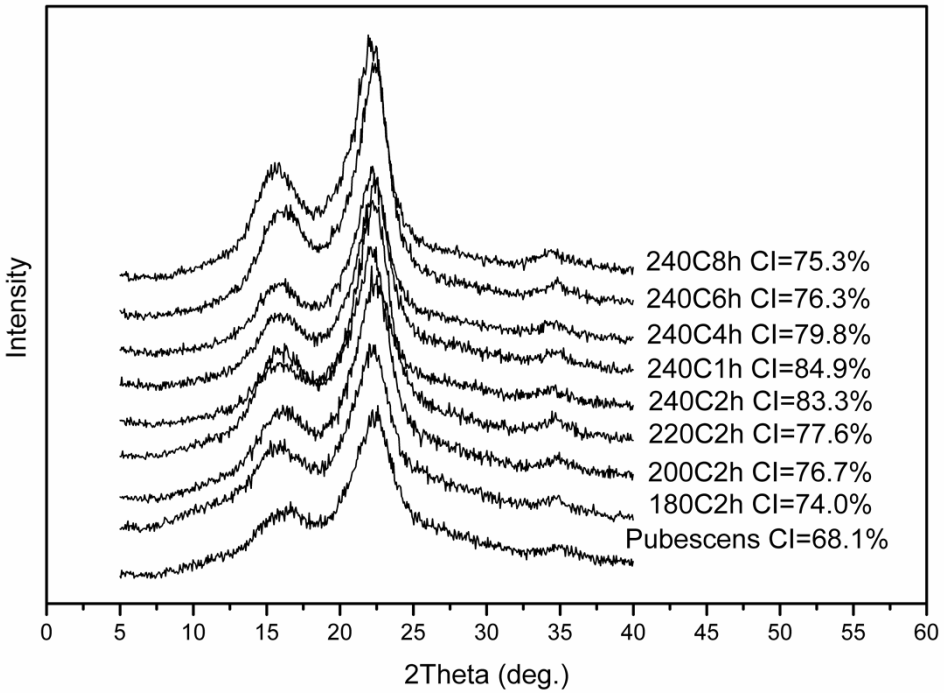

Figure S1. The XRD patterns of *pubescens* and residues obtained under different solvothermal conditions.

As shown in Fig. S1, four characteristic peaks at 2θ=14.6°, 16.5°, 22.4°, and 34.6° were observed which could be assigned to the (**Error!**10), (110), (002) and (040) lattice planes of cellulose Ⅰ, respectively [S3]. All samples had strong diffraction intensity. Compared to the *pubescens* feedstock, the samples after reaction in ethanol gained a sharper diffraction peak than *pubescens*, which suggested that crystal structure in residue maintained well. In terms of CI, the maximum CI of 84.9% was obtained for the residue of 240 °C for 1 h. It indicated that the ethanol treatment made the cellulose crystal more ordered. The cellulose fibers are surrounded by non-celluloses polysaccharides such as hemicellulose and lignin matrix. The increase of CI was attributed to the degradation of the amorphous cellulose mainly during the chemical treatment [S4]. The CI value increased from 74.0% to 83.3% with the reaction temperature increasing, which declared that higher temperature was better for the selective removal of hemicellulose and lignin. However, the CI values became to decrease at 240 °C when the reaction time was extended. It demonstrated that the cellulose crystal structure started to be destroyed for longer reaction time. The XRD data demonstrated that lignin and hemicellulose were selectively removed from the *pubescens* during the ethanol solvothermal treatment, which was coincided with the titration results well.

3. SEM images of solid samples

Instrument parameter

The SEM images were collected by JEOL JSM-7500F (acceleration voltage, 5 kV). The samples were coated with gold to improve the conductivity and the images quality.

SEM images (Figure. S2)

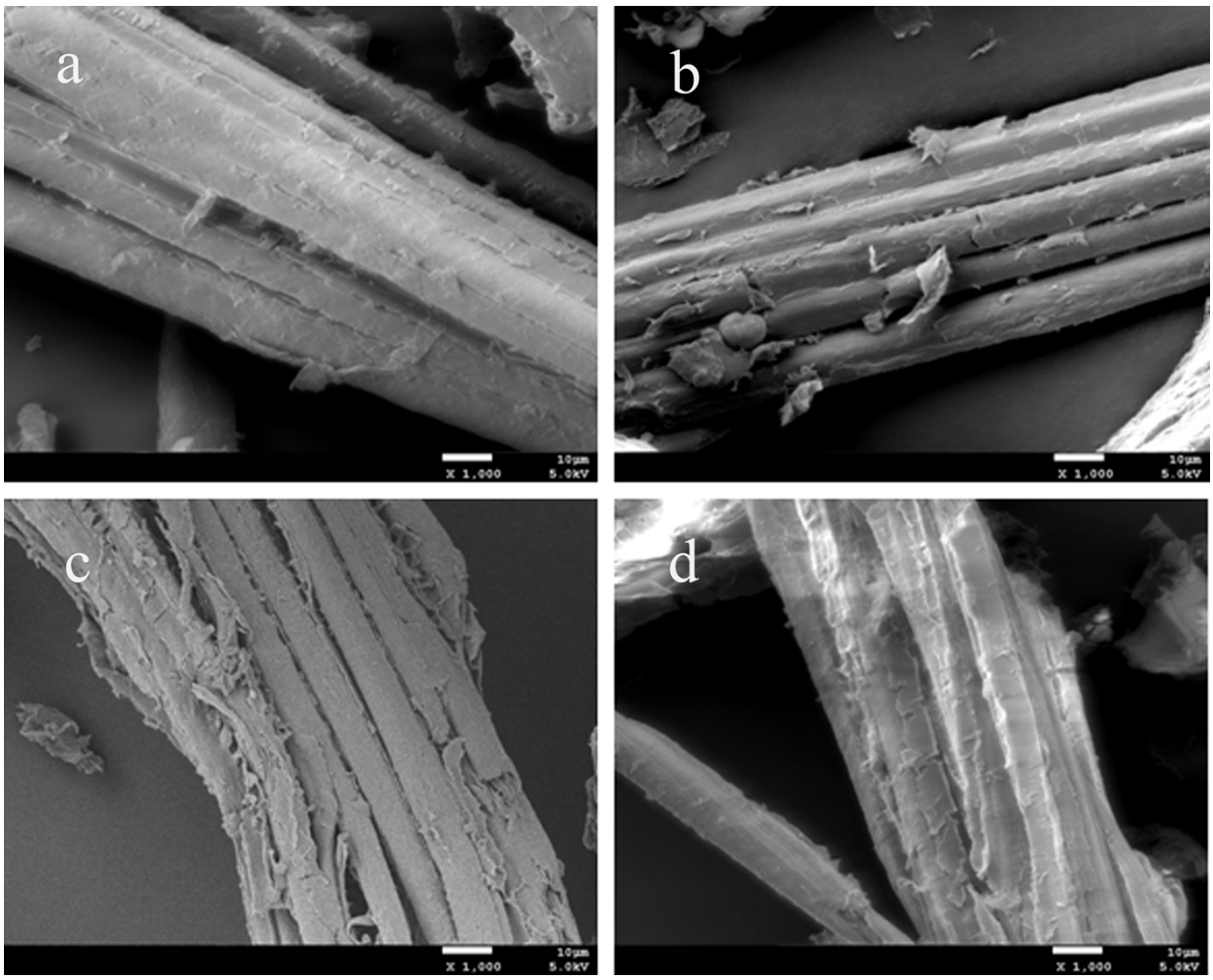

Figure S2. The SEM images of (a) *pubescens*, (b) residue after 220 °C reaction for 2 h, (c) residue after 240 °C reaction for 2 h, (d) residue after 240 °C reaction for 8 h.

The pubescesn was a cellulosic complex mainly composed of hemicellulose, cellulose and lignin. In **Fig. S2(a)**, the obvious cellulose bundles were observed with a rough surface, which was attributed to the coating of cellulose fibers by non-cellulosic materials, that is, hemicellulose-lignin composite. In Poulomi Sannigrahi's work, [S5] discrete spherical balls or droplets were presented on the surface of hybrid poplar residues pretreated by ethanol, which was concluded to be the "lignin droplet". Spheric droplet was observed on the surface of residue after reaction at 220 °C for 2 h, as illustrated in **Fig. S2(b)**. It showed that the some hemicellulose-lignin composite was peeled from the cellulose bundles, while the cellulose bundles existed well. As to **Fig. S2(c)**, the cellulose bundles seemed to be more isolated while hemicellulose-lignin composite was mostly

degraded. The comparison of **Fig. S2 (a), (b)** and **(c)** showed that the ethanol treatment promoted the removal of hemicellulose and lignin without breaking the cellulose structure. However, in **Fig. S2(d)**, the cellulose bundles were obviously damaged after 240 ^{o}C reaction for 8h. It indicated that the exposure of cellulose to ethanol solvent could also make cellulose degrade with the removal of hemicellulose and lignin which protected the cellulose from damage.[S6] Therefore, the SEM images indicated that the hemicellulose and lignin was converted prior to cellulose in ethanol system, which matched the titration and XRD results well.

4. 2D HSQC NMR spectra

Table S2. Assignment of main lignin ^{13}C-^{1}H correlation signals in HSQC spectra of liquid fraction according to the literature.

Labels	**δ_C/δ_H (ppm)**	**Assignment**
MeO	56.0/3.71	C-H in methoyls
A_α	72.4/4.85	C_α-H_α in β-O-4’ structures (A)
A_β(G)	84.9/4.32	C_β-H_β in β-O-4’ structures linked to a G unit (A)
A_β(S)	86.2/4.11	C_β-H_β in β-O-4’ structures linked to a G unit (A)
A_γ	59.8-60.2/3.23-3.71	C_γ-H_γ in β-O-4’ structures (A)
B_α	84.6/4.66	C_α-H_α in β-β’ structures (B)
B_β	53.8/3.07	C_β-H_β in β-β’ structures (B)
B_γ	71.3/4.18, 3.82	C_γ-H_γ in β-β’ structures (B)
C_α	86.2/5.51	C_α-H_α in β-5’ structures (C)
C_β	52.8/3.47	C_α-H_α in β-5’ structures (C)
C_γ	62.7/3.73	C_γ-H_γ in β-5’ structures (C)
E_α	144.5/7.50	C_α-H_α in cinnamate structures (E)
E_β	113.7/6.30	C_α-H_α in cinnamate structures (E)
G_2	111.2/7.00	C_2-H_2 in guaiacyl units (G)
G'_2	111.5/7.35	C_2-H_2 in oxidized (C_α=O) guaiacyl units (G)
G_5	114.9-115.9/6.75	C_5-H_5 in guaiacyl units (G)
G_6	119.5/6.83	C_6-H_6 in guaiacyl units (G)
$S_{2,6}$	104.4/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.4/7.30	$C_{2,6}$-$H_{2,6}$ in (C_α=O) syringyl units (S)
$H_{2,6}$	128.2/7.19	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (H)
Xyl	102-110/4.0-5.5	C-H in xylose derived from hemicellulose

5. GC-FID analysis of liquid fractions

GC-FID data (Table S3-S6)

Table S3. Phenolic compounds in liquid products obtained at different temperature.[a]

	Reaction temperature (°C)				
	160	**180**	**200**	**220**	**240**
Benzofuran	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**
2,3-2*H*-benzofuran	0.0	0.0	0.0	0.0	0.1
Phenols	**0.0**	**0.1**	**0.1**	**0.5**	**1.0**
guaiscol	0.0	0.0	0.0	0.1	0.2
phenol	0.0	0.0	0.0	0.0	0.1
2,6-dimethoxyl phenol	0.0	0.1	0.1	0.4	0.7
4-ethyl phenols	**0.0**	**0.1**	**0.1**	**0.2**	**0.5**
4-ethyl-2-methoxyl phenol	0.0	0.0	0.0	0.1	0.1
4-ethyl phenol	0.0	0.1	0.1	0.1	0.4
Aromatic aldehydes	**0.2**	**0.3**	**0.8**	**1.40**	**2.1**
vanillin	0.1	0.1	0.3	0.5	1.0
syringaldehyde	0.1	0.2	0.5	0.9	1.1

[a] wt% based on the content of lignin in the *pubescens*. The amount of products (furfual, HMF, levulinic acid) from cellulose and hemicellulose was very small (totally less than 1wt%) and was not given in the table.

Table S4. Phenolic compounds in liquid products obtained at 240 °C for different time.[a]

	Reaction time (h)				
	1	**2**	**4**	**6**	**8**
Benzofuran	**0.1**	**0.1**	**0.1**	**0.1**	**0.2**
2,3-2*H*-benzofuran	0.1	0.1	0.1	0.1	0.2
Phenols	**0.4**	**1.0**	**1.1**	**1.9**	**2.2**
guaiscol	0.2	0.2	0.2	0.5	0.7
phenol	0.1	0.1	0.1	0.2	0.2
2,6-dimethoxyl phenol	0.1	0.7	0.8	1.2	1.3
4-ethyl phenols	**0.2**	**0.5**	**0.6**	**1.3**	**1.6**
4-ethyl-2-methoxyl phenol	0.0	0.1	0.2	0.2	0.4
4-ethyl phenol	0.2	0.4	0.4	1.1	1.3
Aromatic aldehydes	**1.2**	**2.1**	**2.2**	**2.4**	**1.6**
vanillin	0.7	1.0	1.1	1.4	0.8
syringaldehyde	0.5	1.1	1.1	1.0	0.8

[a] wt% based on the content of lignin in the *pubescens*. The amount of products (furfual, HMF, levulinic acid)

from cellulose and hemicellulose was small (totally less than 5wt%) and was not given in the table. The selectivity of degradation of lignin in *pubescens* was very low at 240 °C. Thus, the liquid fraction obtained at 220 °C for 2 h was selected for the further degradation at higher temperature, as shown in Table S5-S6.

Table S5. The influence of temperature on the second-step for 2 h.[a,b]

	Temperature (°C)				
	220	**240**	**260**	**280**	**300**
Benzofuran	**0.1**	**0.1**	**0.1**	**0.1**	**0.0**
2,3-2*H*-benzofuran	0.1	0.1	0.1	0.1	0.0
Phenols	**0.6**	**0.7**	**1.1**	**2.2**	**2.0**
guaiscol	0.2	0.2	0.2	0.3	0.4
phenol	0.1	0.1	0.1	0.2	0.3
2,6-dimethoxyl phenol	0.3	0.4	0.8	1.7	1.3
4-ethyl phenols	**0.4**	**1.1**	**1.4**	**1.8**	**4.8(10.6)[b]**
4-ethyl-2-methoxyl phenol	0.2	0.2	0.3	0.4	0.5
4-ethyl phenol	0.2	0.9	1.1	1.4	4.3(9.6)[b]
Aromatic aldehydes	**1.5**	**1.3**	**1.0**	**0.5**	**0.3**
vanillin	0.9	0.7	0.8	0.4	0.2
syringaldehyde	0.6	0.6	0.2	0.1	0.1

[a] wt% based on the content of lignin in the *pubescens*. [b] wt% based on the content of lignin converted.

Table S6. The influence of time on the second-step at 280 °C.[a]

	Time (h)				
	1	**2**	**4**	**6**	**8**
Benzofuran	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
2,3-2*H*-benzofuran	0.1	0.1	0.1	0.1	0.1
Phenols	**0.6**	**2.2**	**0.6**	**0.6**	**0.6**
guaiscol	0.2	0.3	0.2	0.2	0.2
phenol	0.1	0.2	0.1	0.1	0.1
2,6-dimethoxyl phenol	0.3	1.7	0.3	0.3	0.3
4-ethyl phenols	**0.8**	**1.8**	**2.1**	**2.5**	**2.7**
4-ethyl-2-methoxyl phenol	0.2	0.4	0.6	0.7	0.8
4-ethyl phenol	0.6	1.4	1.5	1.8	1.9
Aromatic aldehydes	**0.7**	**0.6**	**0.4**	**0.3**	**0.2**
vanillin	0.5	0.4	0.3	0.2	0.1
syringaldehyde	0.2	0.2	0.1	0.1	0.1

[a] wt% based on the content of lignin in the *pubescens*.

6. References (S1-S6)

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