

Table S1. Assignments of ^{13}C - ^1H cross-peaks in HSQC spectra of the lignin fractions isolated from *Eucalyptus* wood under different pretreatment conditions.

label	$\delta_{\text{C}}/\delta_{\text{H}}$	assignments
C_{β}	52.4/3.51	C_{β} - H_{β} in phenylcoumaran substructures (C)
B_{β}	53.5/3.07	C_{β} - H_{β} in β - β (resinol) substructures (B)
OMe	55.6/3.73	C-H in methoxyls
A_{γ}	59.4/3.65	C_{γ} - H_{γ} in β - O -4 substructures (A)
C_{γ}	62.3/3.70	C_{γ} - H_{γ} in phenylcoumaran substructures (C)
B_{γ}	71.0/3.80-4.18	C_{γ} - H_{γ} in β - β resinol substructures (B)
A_{α}	71.7/4.83	C_{α} - H_{α} in β - O -4 linked to a S unit (A)
$\text{A}_{\beta(\text{G})}$	83.5/4.32	C_{β} - H_{β} in β - O -4 linked to G/H unit (A)
B_{α}	84.9/4.64	C_{α} - H_{α} in β - β resinol substructures (B)
$\text{A}_{\beta(\text{S})}$	85.8/4.11	C_{β} - H_{β} in β - O -4 linked to a S unit (A)
C_{α}	87.1/5.44	C_{α} - H_{α} in phenylcoumaran substructures (C)
$\text{S}_{2,6}$	103.6/6.67	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in syringyl units (S)
$\text{S}'_{2,6}$	106.2/7.29	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in oxidized S units (S')
G_2	110.7/6.93	C_2 - H_2 in guaiacyl units (G)
G_5	114.8/6.92	C_5 - H_5 in guaiacyl units (G)
G_6	118.8/6.79	C_6 - H_6 in guaiacyl units (G)
$\text{I}_{\alpha\beta}$	125.6/6.99	$\text{C}_{\alpha\beta}$ - $\text{H}_{\alpha\beta}$ instilbenes units
I_2	106.2/7.31	C_2 - H_2 instilbenes units

Table S2. The yield of the lignin fractions isolated from *Eucalyptus* wood under different pretreatment conditions.

	L-180-0	L-180	L-170	L-160	L-150	L-140	L-130
Yield of lignin ^a (%)	28.52	48.69	35.41	45.29	29.82	38.48	20.95

^aYield of the lignin = (weight of lignin precipitated / weight of lignin in the raw biomass) × 100%.

Results and Discussion

1. The yield of lignin

After same precipitation process, the lignin fractions were obtained and the corresponding yields varied from 20.95% to 48.69% (Table S2), and the highest value (48.69%) was achieved at 180 °C for 60 min with AlCl_3 catalyst, while the lowest yield (20.95%) of lignin was obtained at 130 °C for 60 min with AlCl_3 catalyst. In addition, it was observed that the yield of the lignin distinctly decreased from 38.48% to 29.82% with the temperature increased from 140 °C to 150 °C, while the delignification ratio reached to the maximum value at 150 °C, suggesting that the significant dissociation of the lignin occurred under this temperature and impeded the subsequent precipitation and acquisition, and the lowest molecular weight (690 g/mol) of the lignin obtained at 150 °C also provides some evidence for this phenomenon. However, the yield of lignin was then increased to 35.41-45.29% at 160-180 °C, which was probably attributed to the condensation of lignin at these conditions (temperatures higher than 150 °C), and it would be detailedly discussed in the following GPC and NMR sections. Interestingly, the yield of lignin obtained at 180 °C without AlCl_3 was only 28.52%, which was obviously lower than that catalyzed by AlCl_3 (48.69%) at the same temperature. The result implied that the addition of AlCl_3 in EWS has significantly improved the delignification ratio and yield of lignin.

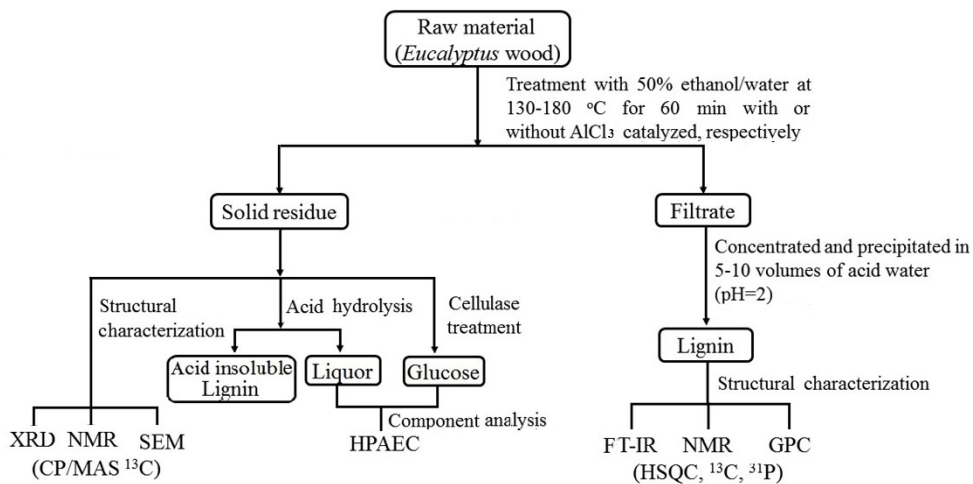


Fig. S1. Schematic illustration of the experimental procedure.

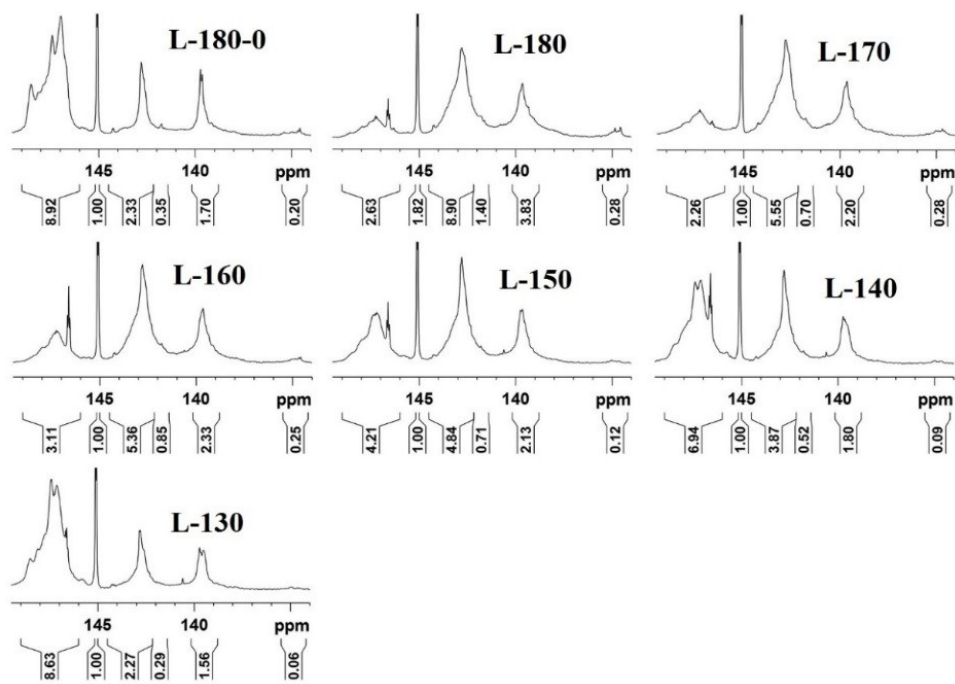


Fig. S3. ^{31}P -NMR of the lignin fractions isolated from *Eucalyptus* wood under different pretreatment conditions.

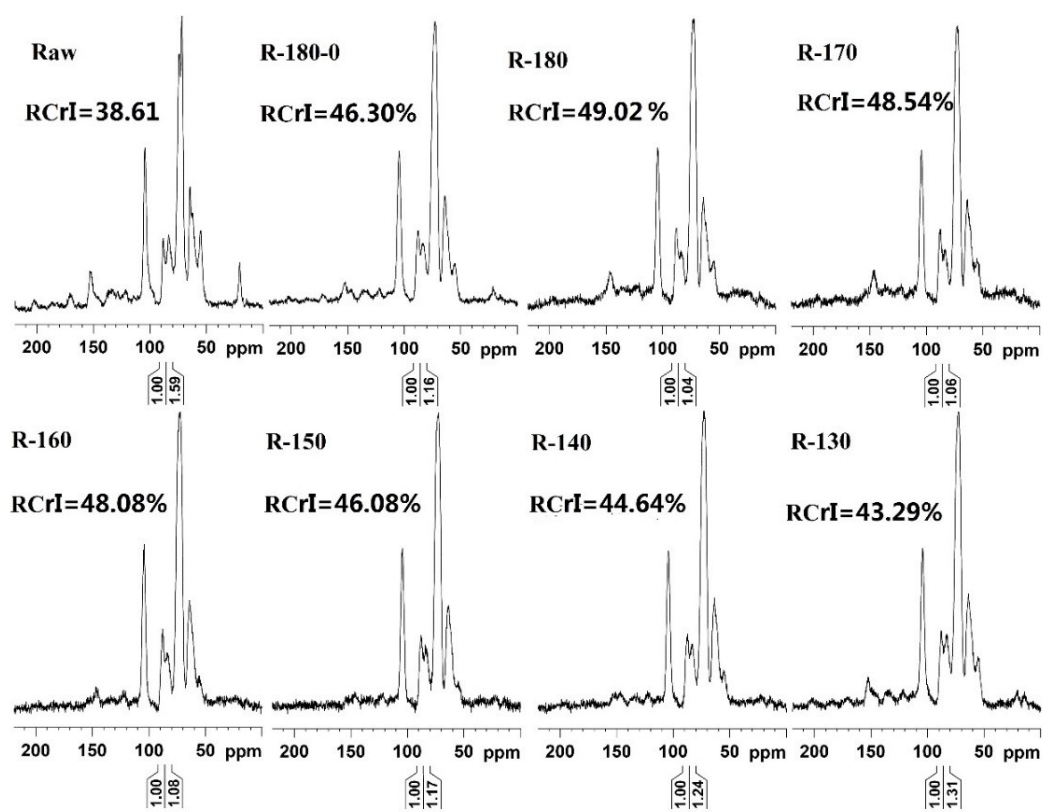


Fig. S4. CP/MAS ^{13}C NMR characterization of the raw material and pretreated substrates.