Supporting Information

Stepwise fractionation extracted lignin for high strength lignin-based carbon fibers

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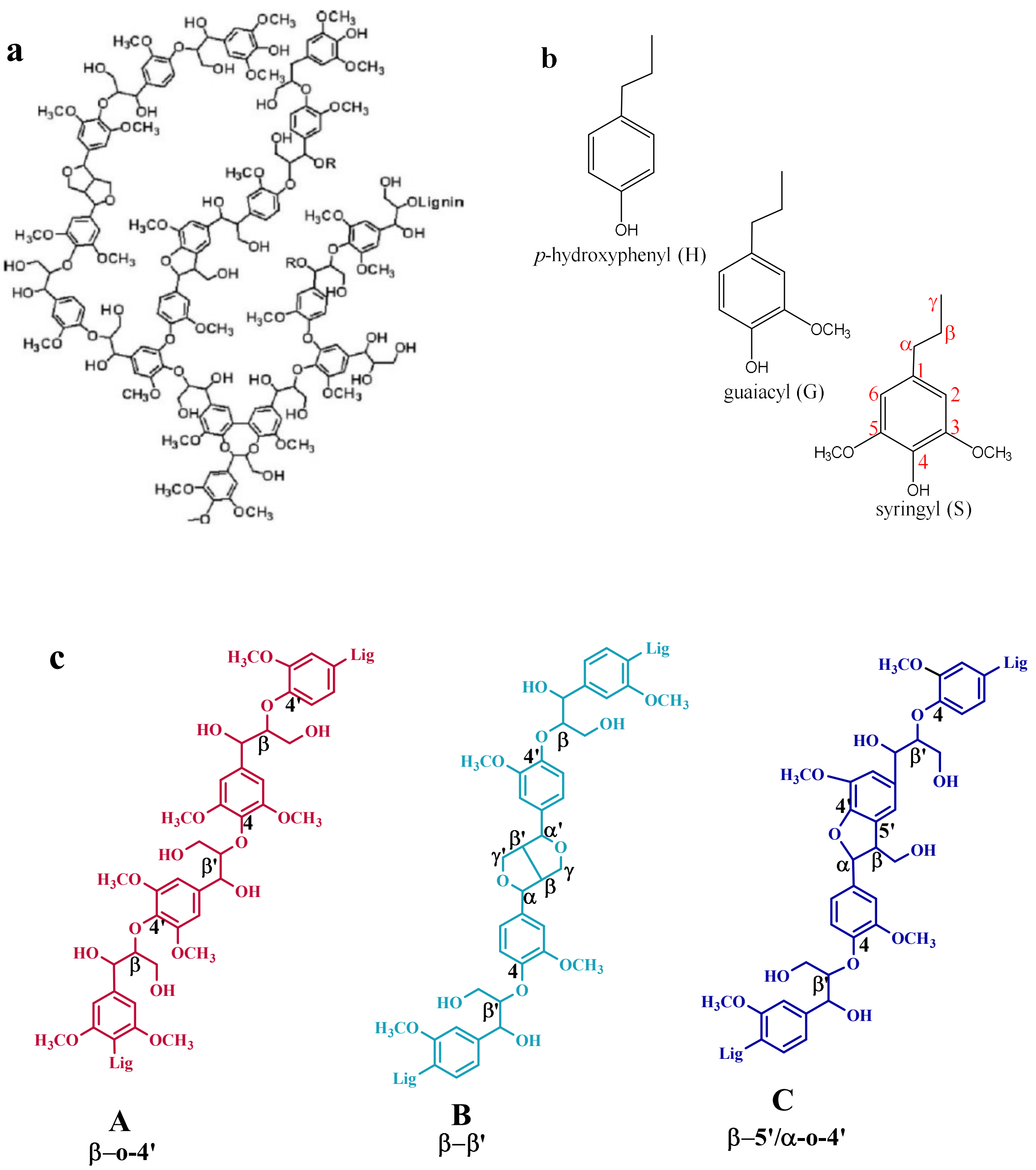

Fig.S1 (a) **A example of lignin structure; (b) Structural units of lignin; (c) display linear structure in lignin macromolecule**

Table S1 Molecular weight and PDI of lignin samples

Lignin samples	M_n (g/mol)	M_w (g/mol)	PDI
AL	2779	6768	2.44
1-step lignin	1593	3530	2.22
2-step lignin	2002	4777	2.39
FAL	3575	6966	1.95

▲XRD data analysis was based on the following Bragg Equation and Scherrer Equation:

$$d_{002}(\mathrm{nm}) = \frac{\lambda}{2\sin\theta} \quad \text{(Equation S1)}$$

$$\mathrm{L_c}(\mathrm{nm}) = \frac{k\lambda}{\beta_{002}\cos\theta} \quad \text{(Equation S2)}$$

Where d_{002} is distance between two crystalline lattices, θ is the Bragg angle, λ is wavelength of X-ray (0.1540598nm), L_c is graphite microcrystalline stacking thickness, k is the shape factor (set as 0.94), β_{002} is the full width at half maximum of diffraction peak (in radian).

Table S2 Assignments of ^{13}C-^{1}H cross-signals in 2D-HSQC spectra of lignin

Lable	δ_C/δ_H(ppm)	Assignments
C_β	53.7/3.47	C_β–H_β in phenylcoumaran (C)
B_β	55.0/3.10	C_β–H_β in β-β (resinol) (B)
$-OCH_3$	56.0/3.72	C-H in methoxyls
I_γ	60.2/4.03	C_γ–H_γ in cinnamyl alcohol end-groups (I)
A_γ	60.3/3.55	C_γ–H_γ in β-O-4 substructures (A)
A'_γ	63.8/3.93	C_γ–H_γ in γ-acylated β-O-4 (A')
C_γ	62.9/3.70	C_γ–H_γ in phenylcoumaran (C)
A_α	72.6/4.86	C_α–H_α in β-O-4 substructures (A)
B'_α	83.2/4.98	C_α–H_α in β-β substructures (B')
A_β(G/H)	84.1/4.38	C_β–H_β in β-O-4 linked to G/H (A)
A_β(S)	86.6/4.13	C_β–H_β in β-O-4 linked to S (A)
C_α	87.2/5.45	C_α–H_α in phenylcoumaran (C)
$S_{2,6}$	104.4/6.71	$C_{2,6}$–$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	105.2/7.31	$C_{2,6}$–$H_{2,6}$ in oxidized S units (S')
FA_2	111.7/7.26	C_2–H_2 in ferulate (*p*-FA)
G_2	111.5/6.92	C_2–H_2 in guaiacyl units (G)
G_5	115.6/6.67	C_5–H_5 in guaiacyl units (G)
G_6	119.6/6.74	C_6–H_6 in guaiacyl units (G)
$PCE_{3,5}$	116.0/6.86	$C_{3,5}$–$H_{3,5}$ in p-coumarate (PCE)
PCE_8	114.3/6.24	C_8–H_8 in p-coumarate (PCE)
FA_6	122.9/7.13	C_6–H_6 in ferulate (*p*-FA)
$H_{2,6}$	128.3/7.11	$C_{2,6}$–$H_{2,6}$ in H units (H)
$PCE_{2,6}$	130.8/7.44	$C_{2,6}$–$H_{2,6}$ in p-coumarate (PCE)
X_2-X_5	62-77/3.1-3.6	polysaccharides

The relative quantification of β-*O*-4, β-β, or β-5 linkages and S/G ratio were calculated according to following formulas:

$$I(\mathrm{X})\% = \frac{I(\mathrm{X})}{0.5I(\mathrm{S}_{2,6}) + I(\mathrm{G}_2) + 0.5I(\mathrm{H}_{2,6})} \times 100\% \qquad \text{(Equation S3)}$$

Where I(X) is the integration of α-position of A(β-*O*-4), B(β-β), or C(β-5) linkages, and the integration of B_α needs to be divided by 2 because there are two α-positions in B structures. $I(S_{2,6})$ is the integration of $S_{2,6}$, including S and S' . $I(G_2)$ is the integration of G_2. $I(H_{2,6})$ is the integration of $H_{2,6}$. The integration should be in the same contour level.

$$S/G = 0.5I(S_{2/6})/I(G_2) \qquad \text{(Equation S4)}$$

Where $I(S_{2,6})$ is the integration of $S_{2,6}$, and $I(G_2)$ is the integration of G_2.