Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary for:

Enhancing Multifunctional Properties of Renewable Lignin Carbon Fiber via Defining Structure-Property Relationship Using Different Biomass Feedstock

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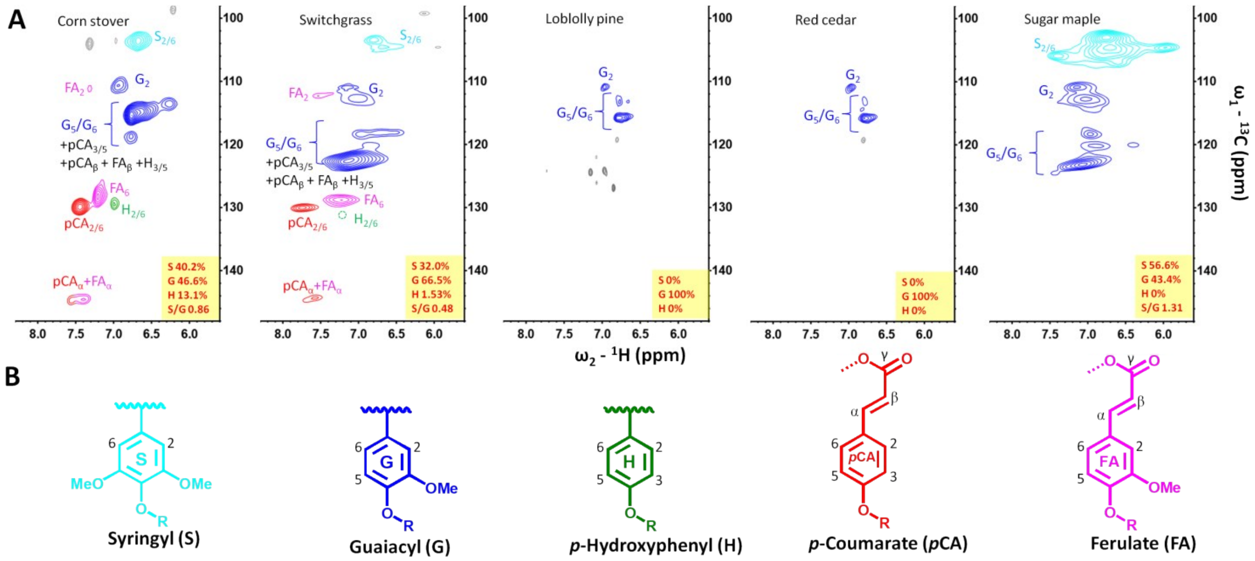


Fig S1. Aromatic region of 2D HSQC NMR spectra of lignin. S/G/H ratios were semi-quantified from the volume integration. The chemical structures of S, G, H, *p*CA and FA are in panel B. The chemical shifts of these structures were in Table S1.

Table S1. Assignments of lignin chemical structures in 2D HSQC NMR.[1,2]

Lignin structures*	F2 (ppm)	F1 (ppm)
Iα (α position in β–*O*–4')	5.0	74.5
IIα (α position in β–5')	5.5	87.7
IIIα (α position in β–β')	4.7	85.0
C_2/H_2 in guaiacyl units (G_2)	6.8	111.3
$C_{2,6}/H_{2,6}$ in *p*-hydroxyphenyl units ($H_{2/6}$)	7.3	127.2
$C_{2,6}/H_{2,6}$ in syringyl units ($S_{2/6}$)	6.7	103.8
$C_{2,6}/H_{2,6}$ in *p*-Coumarate ($pCA_{2,6}$)	7.6	130.0
C_α/H_α in *p*-Coumarate (pCA_α)	7.6	145.0
C_2/H_2 in Ferulate (FA_2)	7.5	111.5
C_6/H_6 in Ferulate (FA_6)	7.3	128.3
C_α/H_α in Ferulate (FA_α)	7.5	144.5

*Lignin linkages and units are shown in Fig. S1 and Fig. 7, respectively.

Table S2. Ash content of lignin samples.

Lignin samples	Ash content (%)
Corn stover	0.52
Switchgrass	0.10
Loblolly pine	0.10
Red cedar	0.11
Sugar maple	0.10

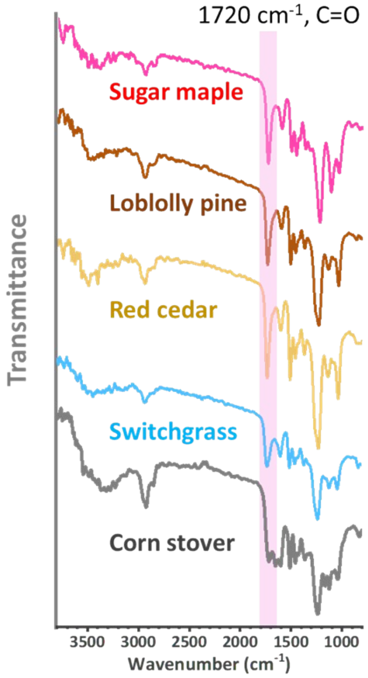


Fig. S2. FTIR spectra of lignin (3800-800 cm^{-1}). The peaks at about 1720 cm^{-1} were assigned to the stretching vibrations of carbonyl groups in lignin.

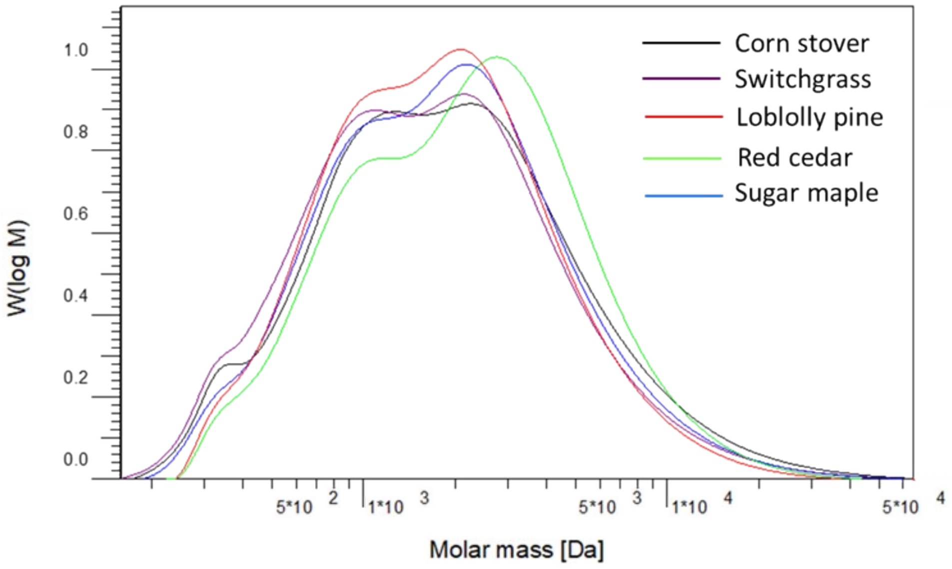


Fig. S3. GPC spectra of lignin from different biomass.

Table S3. Molecular weight and polydispersity index (PDI) of lignin.

Lignin samples	Mn	Mw	PDI
Corn stover	1245	3056	2.45
Switchgrass	1127	2633	2.33
Loblolly pine	1270	2533	1.99
Red cedar	1462	3096	2.11
Sugar maple	1257	2791	2.22

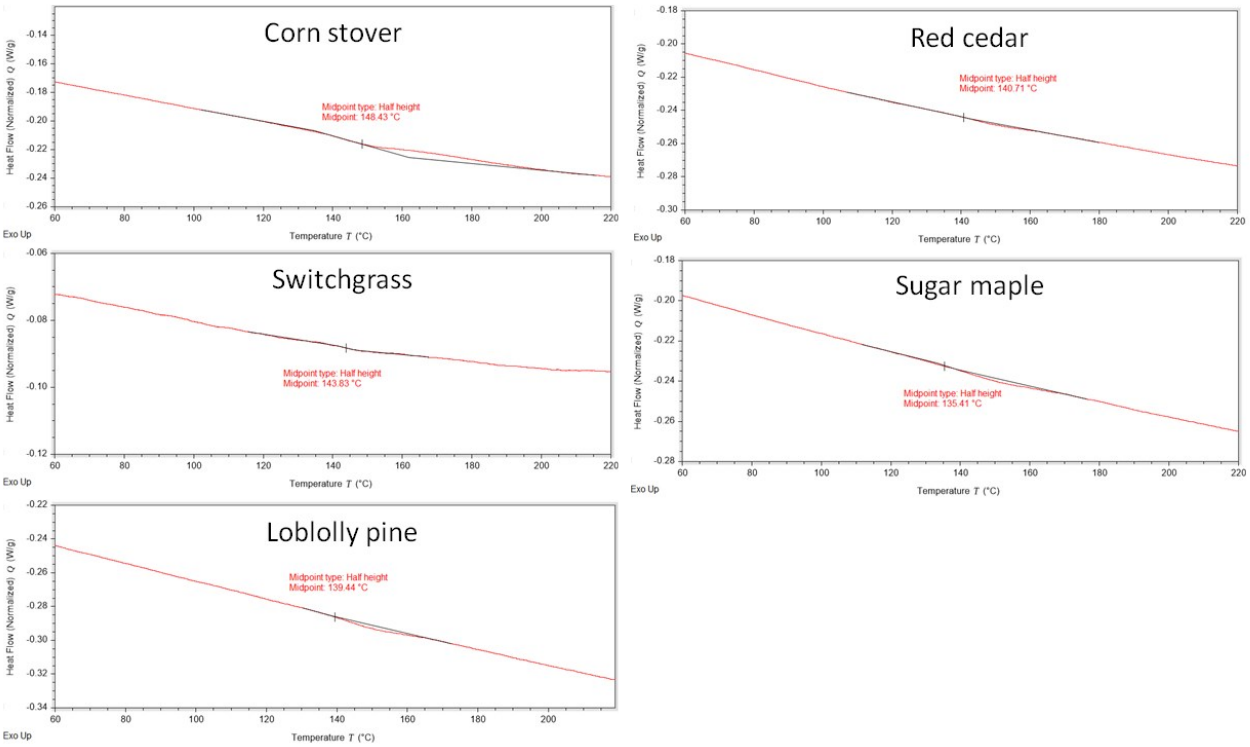
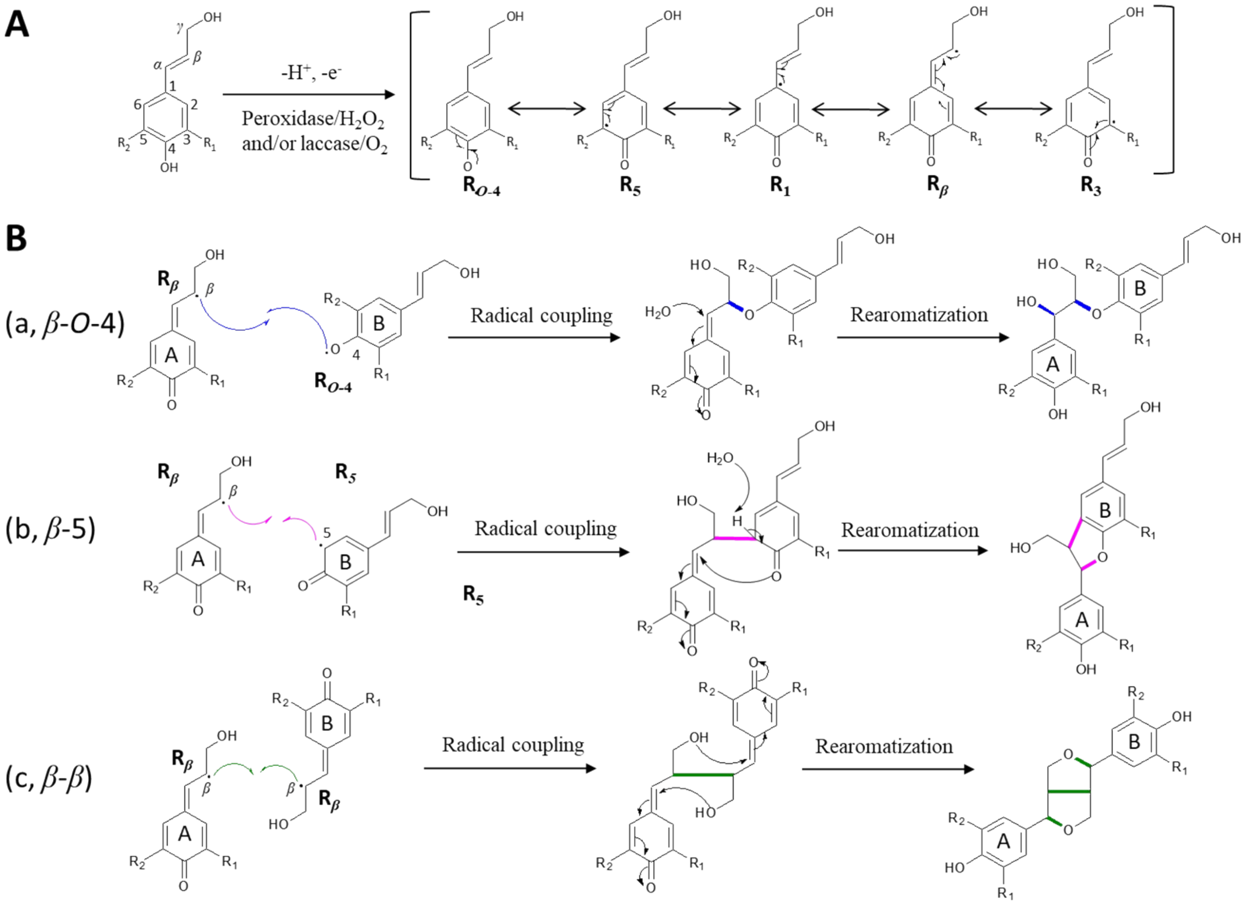


Fig. S4. The second heating cycles (60-220 ^{o}C) of DSC thermograms of lignin-based fibers. The glass transition temperatures (T_g) were calculated using TRIOS software (TA Instrument) and given in each figure.



R_1 = H, R_2=H: *p*-coumaryl alcohol (formed H lignin)
R_1= OMe, R_2 = H: coniferyl alcohol (formed G lignin)
R_1 = OMe, R_2 = OMe: sinapyl alcohol (formed S lignin)

Fig. S5. Formation of lignin interunitary linkages during lignin polymerization. A, radical formation by monolignol oxidation with oxidase and followed by radical delocalization. $R_{O\text{-}4}$, R_5, R_1, R_β, and R_3 represented radicals formed on C_4-O, C_5, C_1, C_β, and C_3 positions, respectively. B, radical-radical coupling to form *β*-*O*-4, *β*-5, and *β*-*β* linkages using monolignol dimerization as an example. The newly formed bonds in radical coupling and re-aromatization were highlighted in bold. The image was drawn based on the Morreel et al (2010)[3] and Vanholme et al (2010).[4]

Table S4. The yields of carbon fibers made from different biomass.

Lignin samples	Carbonization (%)[a]
Corn stover	51.3
Switchgrass	52.6
Loblolly pine	56.6
Red cedar	57/0
Sugar maple	59.4

[a] % is based on as-spun fibers.

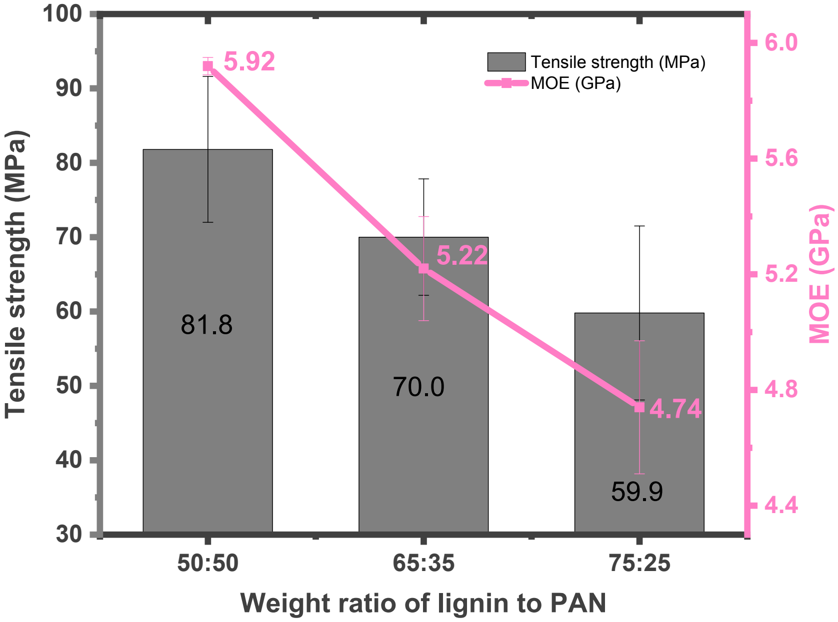


Fig. S6. Mechanical properties of the as-spun fibers made of lignin/PAN at different weight ratios of 50:50, 65:35, and 75:25.

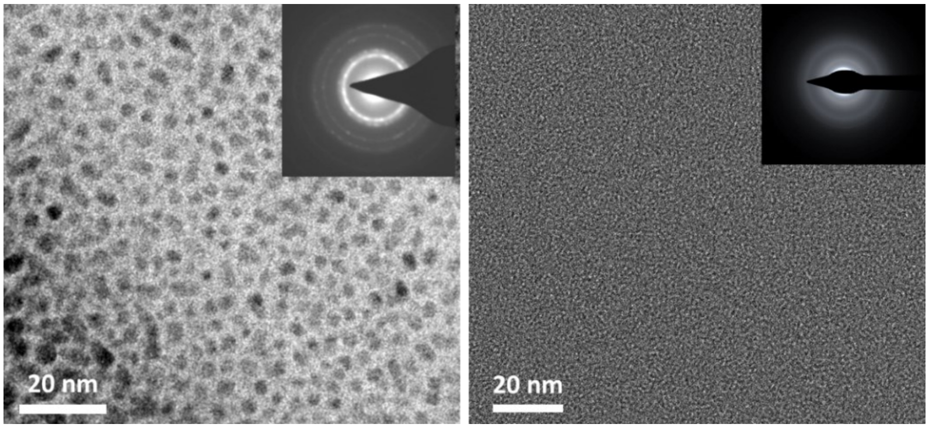


Fig. S7. TEM and electronic diffraction image of carbon fibers made of pure PAN (left) and hardwood lignin/PAN blend (right).

Table S5. Comparisons of lignin-based carbon fiber (CF-Lig) with pure PAN-based carbon fiber (CF-PAN) as obtained in this study and in other reports.

Ref.	Lignin	Blend	Lignin / blend	Spin	**MOE (GPa)**			**Tensile strength (MPa)**			**Elongation (%)**		
					CF-Lig	CF-PAN	**Ratio[a]**	CF-Lig	CF-PAN	**Ratio[a]**	CF-Lig	CF-PAN	**Ratio[a]**
Lin et al (2014)[5]	SW PEG lignin	n.d.	n.d.	Melt spin	26.2	200-500	**0.131[b]**	457	3500-6300	**0.131[b]**	**2.11**	**0.8-2.2**	**2.638[b]**
Thunga et al (2014)[6]	SW Kraft lignin	PLA	1:1	Extrusion	0.0225	6.4	**0.004**	17.5	41	**0.427**	n.d.	n.d.	n.d.
Ding et al (2016)[7]	CS organosolv lignin	PAN (MW 150K)	1:1	Electro-spin	2.4	6.4	**0.375**	22	41	**0.537**	**1.2**	**0.8**	**1.50**
Liu et al (2017)[8]	Soda lignin	PAN (MW 250K)	3:7	Gel spin	194	193	**1.005**	1370	1540	**0.890**	**0.72**	**0.83**	**0.867**
Jin et al (2018)[9]	SW Kraft lignin	PAN (MW 233K)	1:1	Wet spin	105.7	155.2	**0.681**	1200	1380	**0.870**	**1.1**	**0.9**	**1.222**
This paper	**HW AA lignin**	**PAN (MW 150K)**	**1:1**	**Wet spin**	**40.4**	**40.5**	**0.998**	**472**	**453**	**1.042**	**1.51**	**1.40**	**1.079**

a, the ratioes in the table represented the ratio of CF-Lig mechanical properties to that of the CF-PAN; b, calculated from the low end of PAN-based carbon fiber. CF-Lig, lignin-based carbon fiber; CF-PAN, PAN-based carbon fiber; MOE, modulus of elasticity; PLA, polylactic acid; MW, molecular weight; AA lignin, acetic acid lignin; PEG, polyethylene glycol; n.d., no data.

Reference

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