Unlocking the Graphitization Potential of Lignin: Insights into its Transformation through Hot Pressing and Carbonization

Wangda Qu[a, #, *], Xiao Han[a, #], Jing Liu[b], Linghong Yin[a], Chen Liang[c], Pengyu Hu[a]

a. Laboratory of Lignin-based Materials, College of Life Sciences, Qingdao Agricultural University, Qingdao 266109, China

b. College of New Materials and New Energies, Shenzhen Technology University, Shenzhen, 518116, China

c. College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, China

*Corresponding author: Wangda Qu, e-mail: wqu@qau.edu.cn.

[#]Authors contributed equally to this work.

Supporting Information

Supplementary Figures

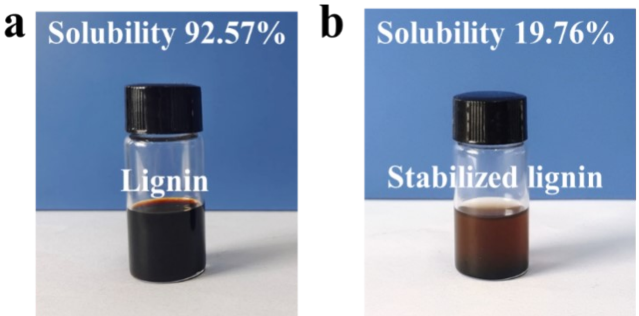

Figure S1. a) Lignin and b) stabilized lignin dissolved in THF.

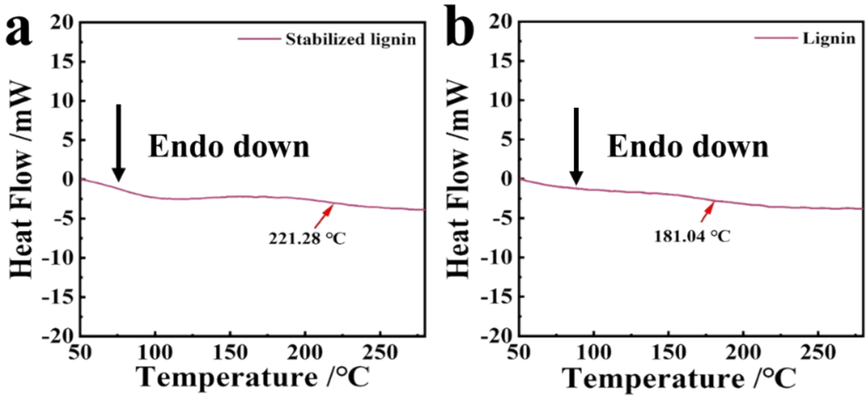

Figure S2. a) DSC curve of lignin; b) DSC curve of stabilized lignin.

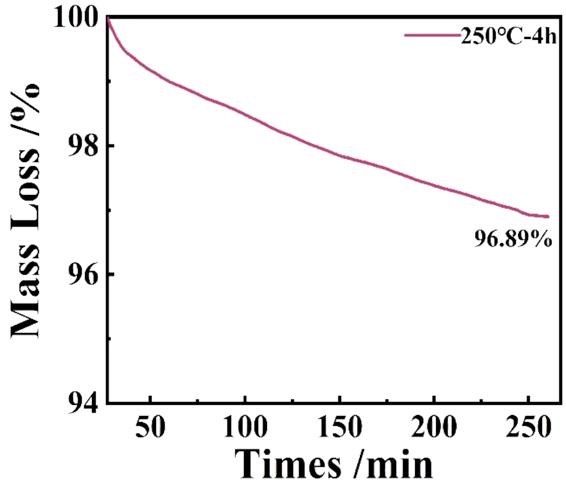

Figure S3 TG-DTG curves of stabilized lignin.

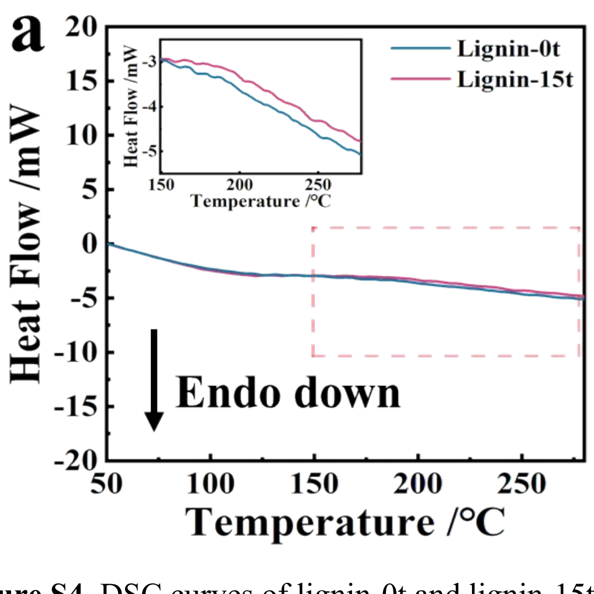

Figure S4. DSC curves of lignin-0t and lignin-15t.

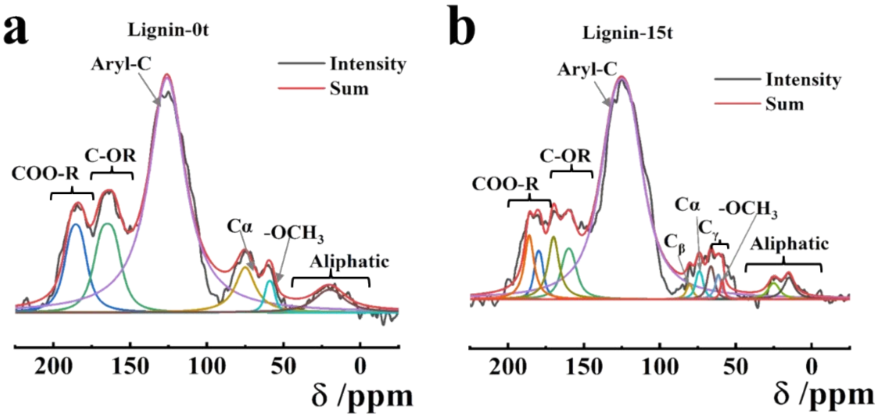

Figure S5. The deconvoluted peaks for quantitative fraction of carbon moieties. a) Lignin-0t; b) Lignin-15t.

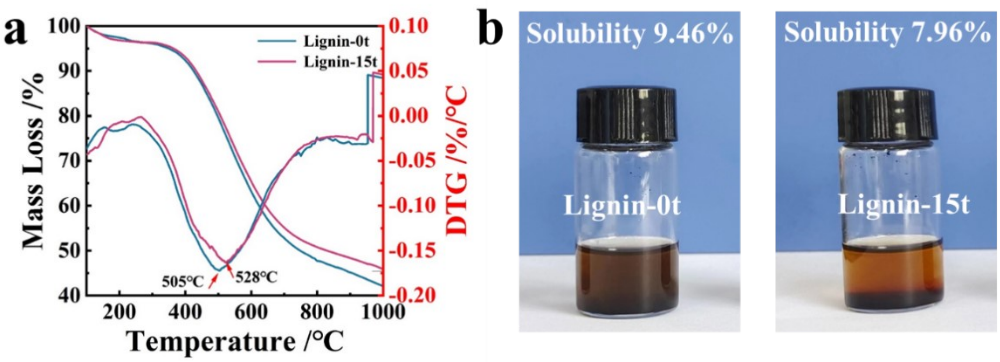

Figure S6. a) TG-DTG curves of lignin-0t and lignin-15t; b) Lignin-0t and lignin-15t dissolved in THF.

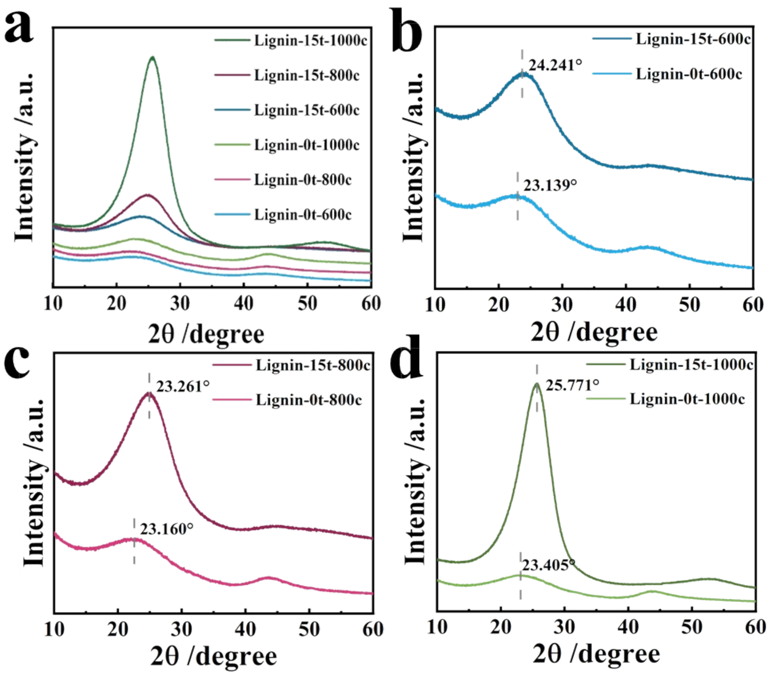

Figure S7. a) XRD profiles of carbonized lignin-0t and carbonized lignin-15t samples at different temperatures; b) XRD profiles of lignin-0t-600c and lignin-15t-600c; c) XRD profiles of lignin-0t-800c and lignin-15t-800c; d) XRD profiles of lignin-0t-1000c and lignin-15t-1000c.

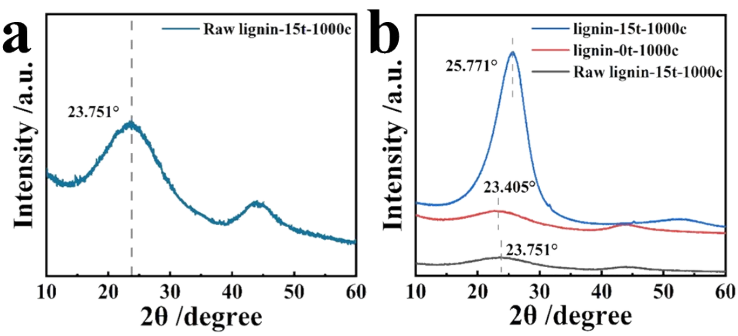

Figure S8. a) XRD profile of raw lignin-15t-1000c; b) XRD profiles of raw lignin-15t-1000c, lignin-0t-1000c and lignin-15t-1000c.

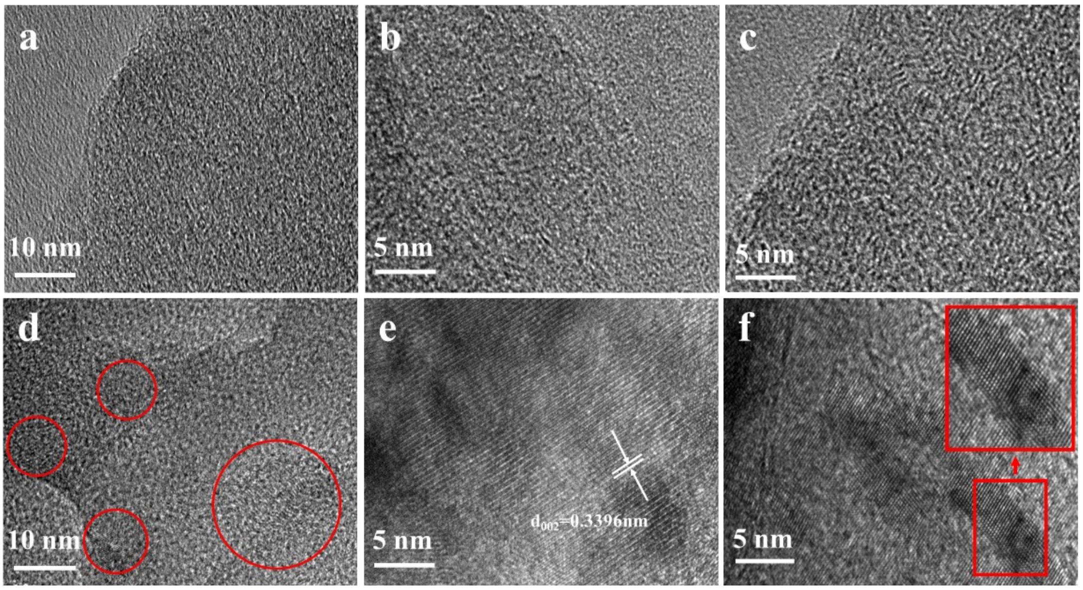

Figure S9. TEM images of a-c) lignin-0t-1000c; d-f) lignin-15t-1000c.

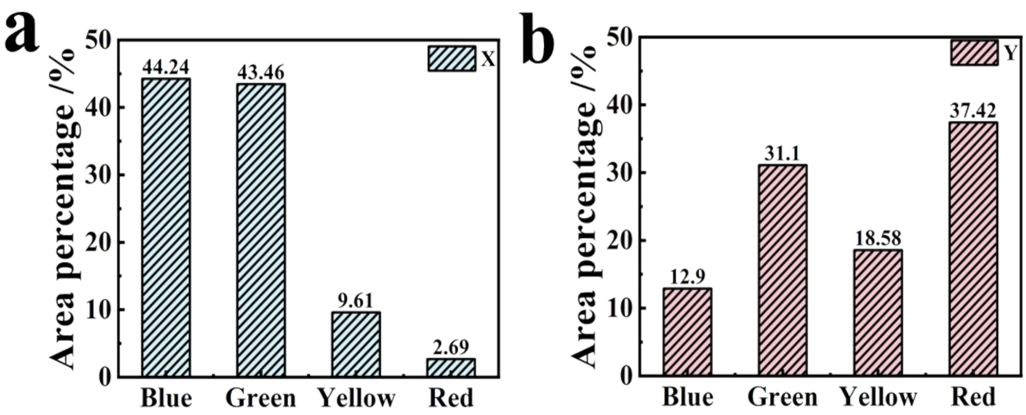

Figure S10. a) Color distribution histogram of X side for lignin-15t-1000c; b) Color distribution histogram of Y side for lignin-15t-1000c.

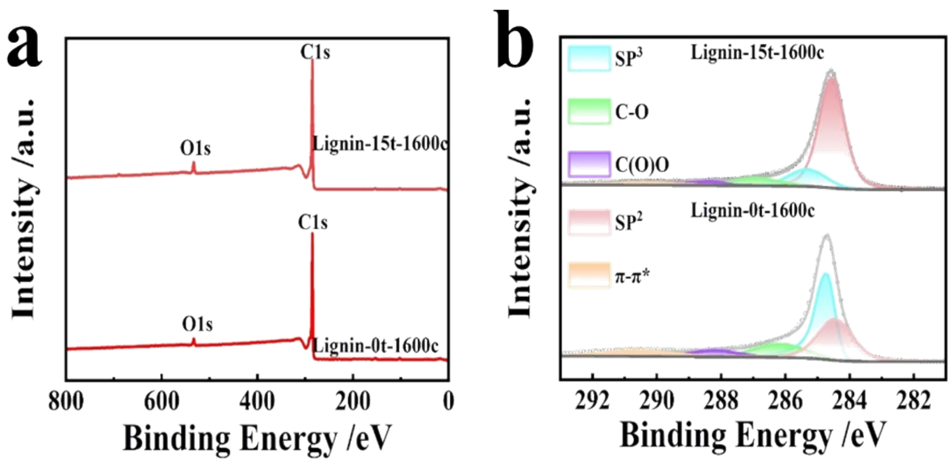

Figure S11. a) XPS survey spectra of lignin-0t-1600c and lignin-15t-1600c; b) C1s peak deconvolution results for lignin-0t-1600c and lignin-15t-1600c.

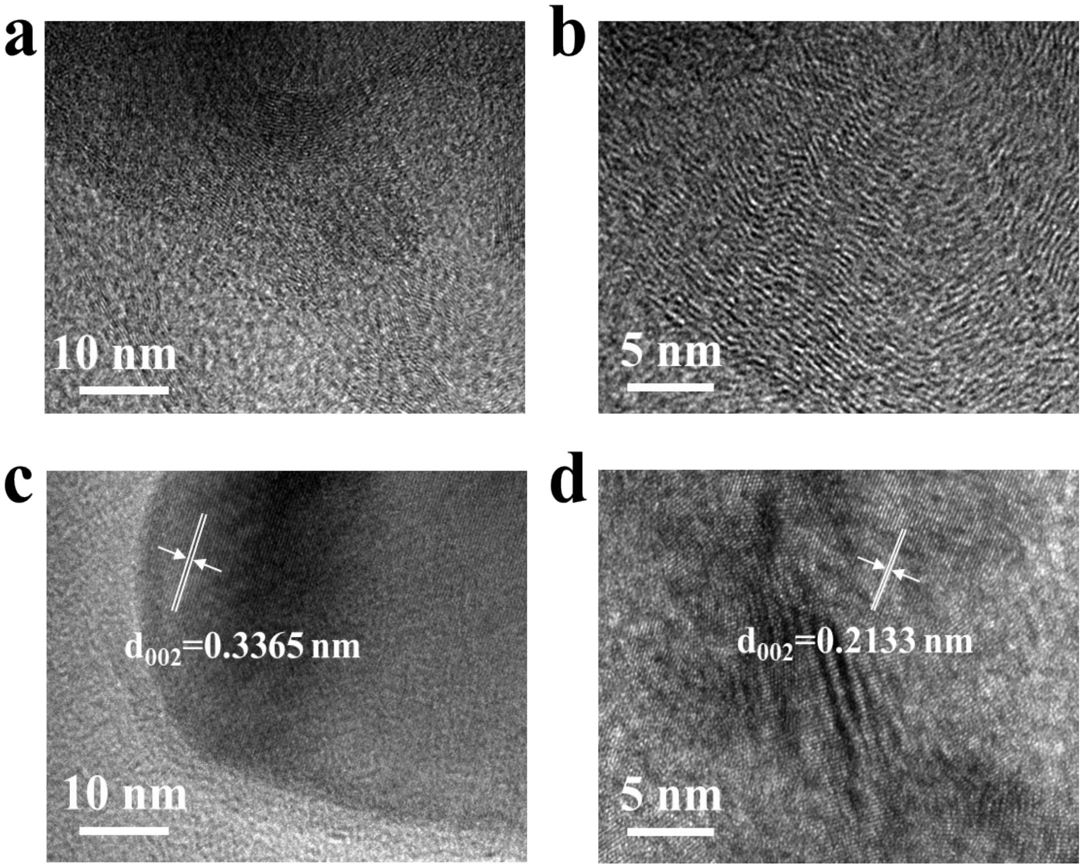

Figure S12. TEM images of a-b) lignin-0t-1600c; c-d) lignin-15t-1600c.

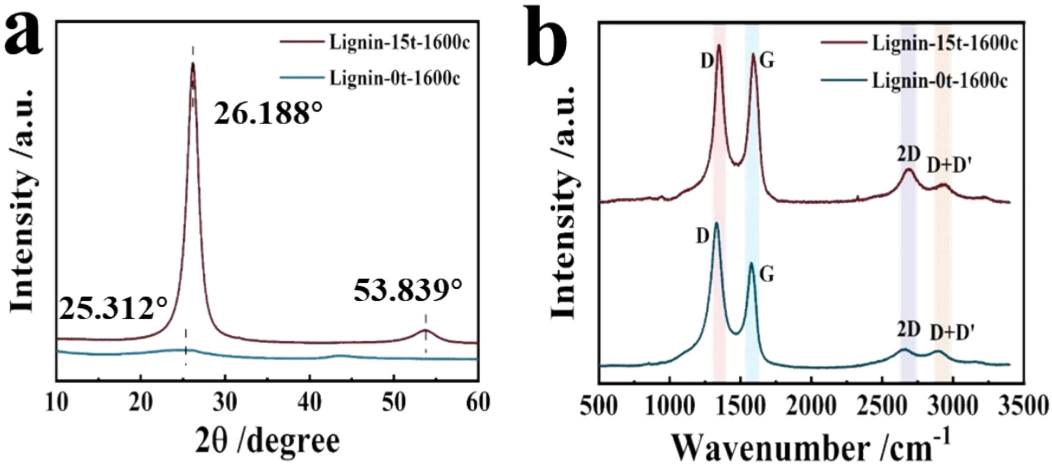

Figure S13. a) XRD profiles of lignin-0t-1600c and lignin-15t-1600c; b) Raman spectra of lignin-0t-1600c and lignin-15t-1600c.

Supplementary Tables

Table S1. Elemental analysis of lignin and lignin-derived samples.

Sample	C (%)	H (%)	O (%)	N (%)	S (%)
Lignin	63.20±0.18	5.01±0.12	31.38±0.09	0.17±0.03	0.24±0.02
Lignin-0t	61.51±0.12	1.80±0.09	36.29±0.35	0.31±0.12	0.10±0.03
Lignin-15t	62.60±0.12	1.98±0.09	34.99±0.36	0.34±0.12	0.10±0.03
Lignin-0t-600c	80.06±0.13	2.17±0.09	16.75±0.20	0.68±0.10	0.34±0.06
Lignin-15t-600c	83.84±0.13	2.06±0.08	12.94±0.31	0.70±0.08	0.47±0.22
Lignin-0t-800c	86.07±0.11	1.22±0.08	11.70±0.18	0.74±0.12	0.28±0.10
Lignin-15t-800c	90.24±0.11	0.85±0.08	8.02±0.32	0.79±0.09	0.11±0.04
Lignin-0t-1000c	90.85±0.12	0.53±0.10	6.60±0.21	1.55±0.08	0.49±0.08
Lignin-15t-1000c	93.12±0.13	0.25±0.09	5.82±0.15	0.64±0.13	0.18±0.06

Table S2. Carbon type assignments of lignin, lignin-0t, and lignin-15t characterized by solid-state ^{13}C NMR.

Lignin-0t	**δ (ppm)**	**Height**	**Width (Hz)**	**Area**	**Area ratio (%)**
Aliphatic-C	20.00	0.32	2615	40.48	4.48
-O-CH_3	59.00	0.45	1130	22.69	1.88
Aliphatic-C_α-O	75.00	0.64	2376	82.33	6.82
Aryl-C	126.00	3.33	4242	752.56	62.32
Aryl-C-OR	164.81	1.26	2920	157.36	13.03
COOR	185.42	1.25	2449	138.40	11.47

Lignin-15t	**δ (ppm)**	**Height**	**Width (Hz)**	**Area**	**Area ratio (%)**
Aliphatic-C	15.00	0.23	1068.59	15.35	3.75
	25.00	0.19	1270.33	11.90	
-O-CH_3	59.00	0.24	296.72	3.80	0.52
Aliphatic-C_γ-O	61.50	0.34	752.81	10.09	3.32
	66.5	0.39	717.78	14.04	
Aliphatic-C_α-O	73.96	0.38	980.29	12.23	1.69
Aliphatic-C_β-O	80.41	0.21	496.79	6.29	0.87
Aryl-C	125.10	2.19	4666.64	499.68	68.85
Aryl-C-OR	159.93	0.62	2182.25	43.32	12.10
	170.00	0.45	1226.09	44.51	
COOR	179.74	0.48	2089.22	24.54	8.90
	186.00	0.41	2431.12	40.03	

Table S3. Yields of carbonized lignin-0t and carbonized lignin-15t at different temperatures.

Sample	Stabilization Yield (%)	Hot pressing Yield (%)	Carbonization Yield (%)	Total Yield (%)
Lignin-0t-600c	49.50±0.30	98.64±0.31	54.18±3.12	26.45±0.29
Lignin-0t-800c			51.53±1.96	25.16±0.18
Lignin-0t-1000c			50.62±1.96	24.72±0.18
Lignin-15t-600c	49.50±0.30	96.71±0.52	59.91±2.85	28.68±0.44
Lignin-15t-800c			53.06±3.42	25.40±0.53
Lignin-15t-1000c			52.65±3.16	25.20±0.49

Table S4. Ratio of different carbon types determined by XPS analysis of carbonized lignin-0t samples and carbonized lignin-15t samples at different temperatures.

Sample	SP^2 Carbon (%)	SP^3 Carbon (%)	C-O (%)	C(O)O (%)	π-π* (%)	SP^2+SP^3 (%)
Lignin-0t-600c	11.20	53.86	24.19	10.74	-	65.06
Lignin-15t-600c	47.83	29.07	22.02	7.21	-	76.90
Lignin-0t-800c	20.08	48.47	22.02	9.43	-	68.55
Lignin-15t-800c	55.67	23.13	14.57	6.63	-	78.80
Lignin-0t-1000c	24.26	45.86	18.43	7.21	4.24	70.36
Lignin-15t-1000c	62.34	18.49	10.31	5.43	3.43	80.83

Table S5. Comparison of the yield of lignin-0t-1600c and lignin-15t-1600c.

Sample	Mass residual during carbonization (%)
Lignin-0t-1600c	32.53
Lignin-15t-1600c	41.42

Table S6. Elemental analysis of lignin-0t-1600c and lignin-15t-1600c.

Element	Lignin-0t-1600c	Lignin-15t-1600c
C (%)	95.39±0.18	96.47±0.12
H (%)	0.35±0.09	0.23±0.06
O (%)	4.06±0.35	3.09±0.06
N (%)	0	0
S (%)	0.20±0.08	0.21±0.003

Table S7. Ratio of different carbon types determined by XPS analysis of lignin-0t-1600c and lignin-15t-1600c.

Sample	SP^2 carbon (%)	SP^3 carbon (%)	C-O (%)	C(O)O (%)	π-π^* （%）	SP^2+SP^3 (%)
Lignin-0t-1600c	32.49	39.63	13.84	5.88	8.16	72.12
Lignin-15t-1600c	70.05	13.90	7.20	4.81	4.04	83.95

Table S8. Lattice parameters of lignin-0t-1600c and lignin-15t-1600c.

Sample	**2θ (002) (°)**	**2θ (004) (°)**	**FWHM (002) (°)**	**Lc (nm)**	**d_{002} (nm)**
Lignin-0t-1600c	25.312	N/A	5.80	1.404	0.3516
Lignin-15t-1600c	26.188	53.84	1.89	4.316	0.3399