Supporting Information (SI) for

The impact of thermal oxidative stabilization on the performance of lignin-based carbon nanofiber mats

Mijung Cho[1], Frank K. Ko [2] and Scott Renneckar[*1]

[1] Advanced Renewable Materials Lab., Department of Wood Science, University of British Columbia, Vancouver, BC, Canada V6T1Z4

[2] Advanced Fibrous Materials Lab., Departments of Materials Engineering, University of British Columbia, Vancouver, BC, Canada V6T1Z4

Corresponding authors [*] scott.rennecakr@ubc.ca

Supplementary experimental section

Gel Permeation Chromatography (GPC)

Molecular weight of 4th fractionated softwood kraft lignin was measured by GPC with slight modification from the previous work.[1] 5 mg/mL of acetylated lignin was dissolved in tetrahydrofuran (THF, Sigma Aldrich, anhydrous) and incubated at room temperature for 48 h. Lignin samples were then filtrated with a 0.45 μm PTFE syringe filter. GPC measurement was carried out using Agilent 1100 GPC equipment (USA) consisting of a pump, an autosampler, and a column oven set at 35 °C. 100 μL of lignin solution was injected into the system and separated by three columns including Styragel HR4 (5−600 kDa), HR3 (0.5−30 kDa) and HR1 (0.1−5 kDa) with an eluting solvent of THF at a flow rate of 0.7 mL/min. F4SKL was analyzed by the Wyatt Optilab T-Rex refractive index detector (dRI, USA) with 785 nm at 35 °C. All data was collected and analyzed by Wyatt ASTRA 6.0 (USA) installed with standard calibration with seven different polystyrene which had standard molecular weight 1.3, 2,2.7, 5.78, 9, 17.5, and 30 kDa.

Quantitative ^{31}Phosphorus Nuclear Magnetic Resonance (^{31}P NMR) Analysis

The amount of hydroxyl groups on softwood kraft lignin was determined using ^{31}P NMR as described in the previous work.[1] A solution mixture was prepared by mixing pyridine and $CDCl_3$ in a ratio of 1.6/1 v/v. The relaxation reagent and internal standard were prepared by dissolving the chromium (III) acetylacetonate and N-hydroxy-5- norbornene-2,3-dicarboximide into the solution with a concentration of 5.6 and 9.6 mg/mL, respectively. An exact amount of 20 mg of dried F_4SKL lignin powders was then dissolved in 400 μL of the above solution, followed with 40 μL of relaxation reagent solution, the addition of 100 μL of internal standard solution, and 50 μL of 2-chloro- 4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP). This fresh lignin solution was thoroughly mixed until no solid was left in the solution and transferred into a 5 mm NMR tube for immediate analysis. An inverse gated decoupling pulse was employed to obtain quantitative ^{31}P NMR with parameters: number of scans 800, relaxation delay 5 s, acquisition time 1.4 s, pulse length 5.12 μs, and 90° pulse width. The chemical shift of each phosphitylation product was calibrated with a product of TMDP with residual moisture at 132.2 ppm.

Table S1. Analysis of 4th fractionated softwood kraft lignin by ^{31}P NMR and GPC

	Aliphatic OH (mmol/g)	Aromatic OH (mmol/g)	Carboxylic acid(mmol/g)	Total OH (mmol/g)	Mn[a] (kDa)	Mw[b] (kDa)	PDI[c]
F4SKL	2.08	3.28	0.27	5.63	1.6	7.3	4.5

a: number of molecular weight (Mn), b: weight average molecular weight (Mw), and c: polydispersity index (PDI)

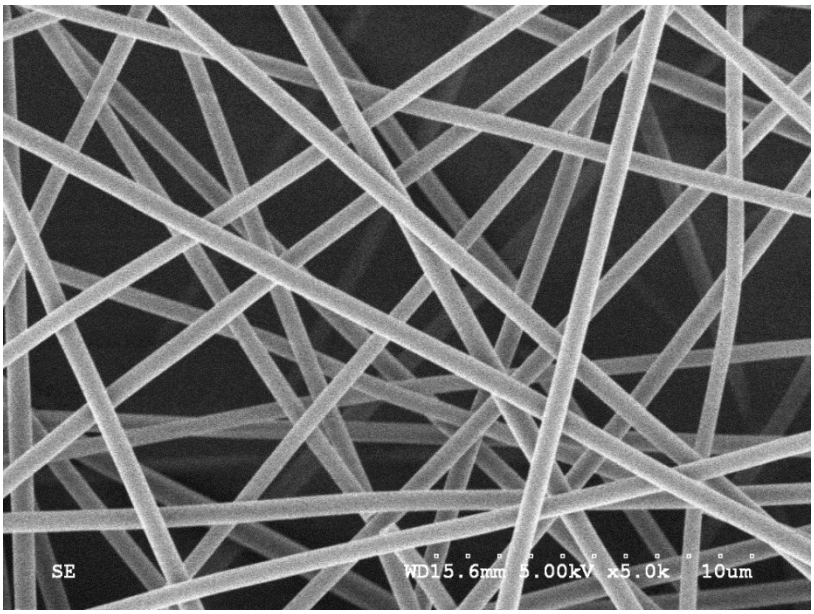


Figure S1. SEM of electrospun lignin based nanofibers

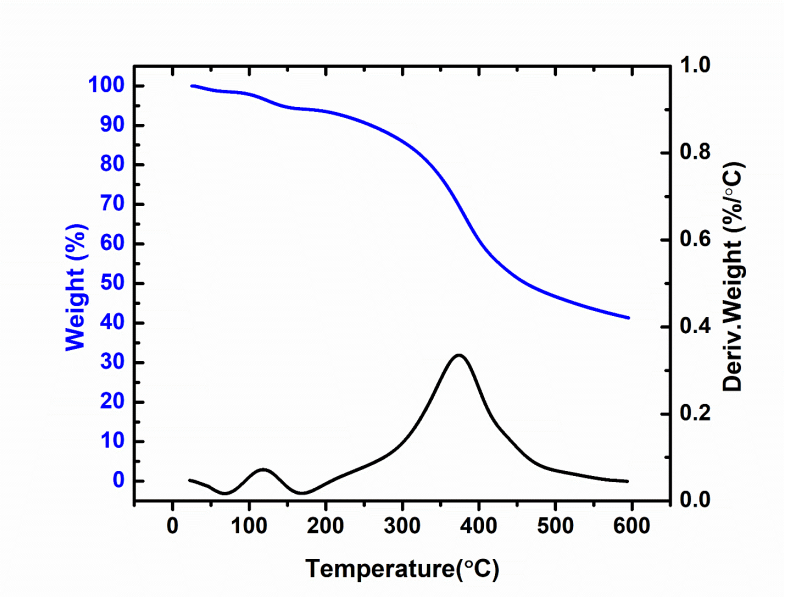
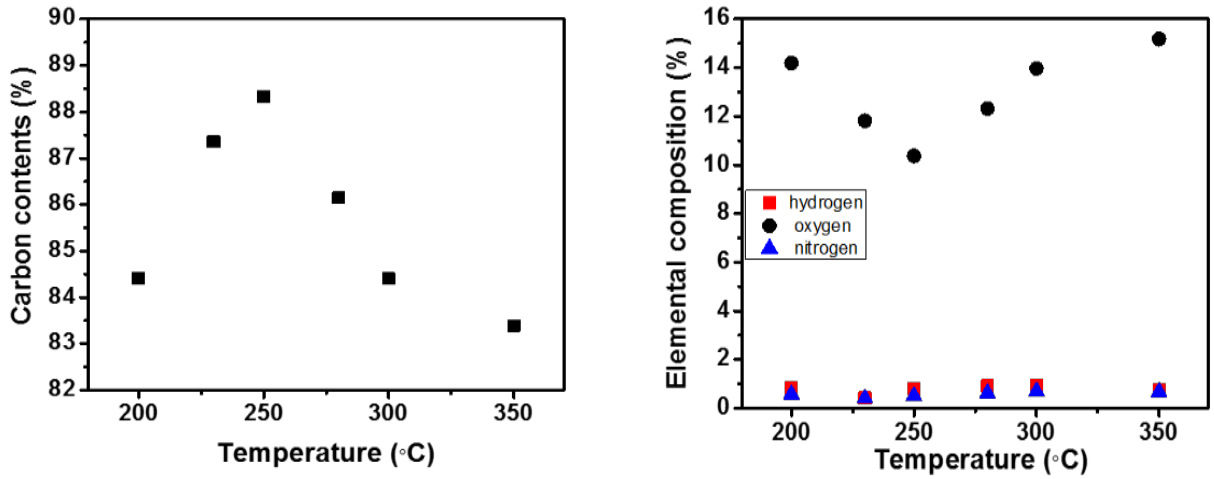


Figure S2. TGA graph of as spun lignin fiber mat



(a) (b)

Figure S3. Elemental analysis of carbonized lignin fiber mats with different final temperatures (a) carbon content and (b) contents of hydrogen, oxygen and nitrogen.

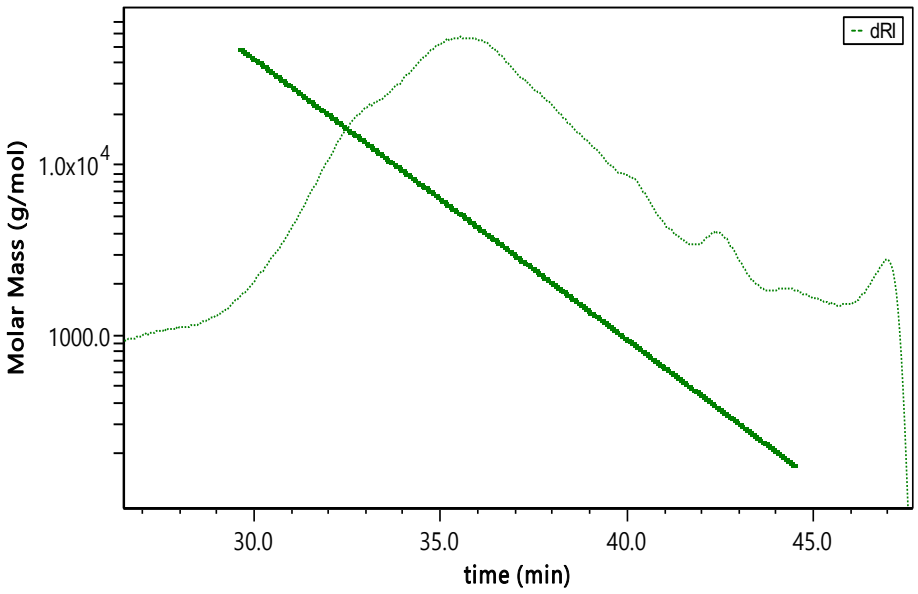


Figure S4. Molecular mass profile of 4th fractionated lignin sample.

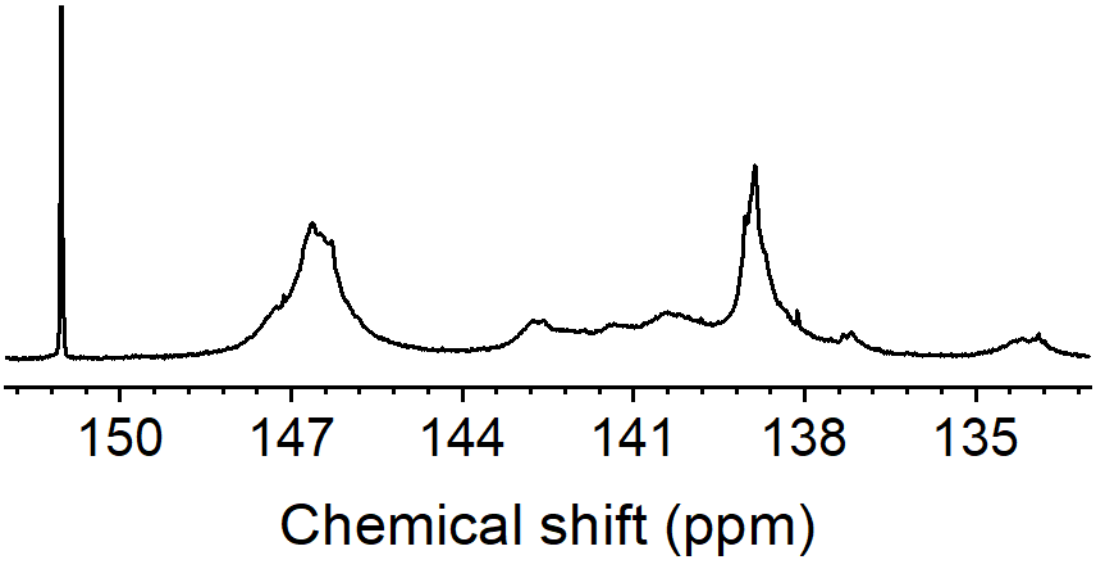


Figure S5. ^{31}P NMR spectrum of F_4SKL

References

(1) Liu, L. Y.; Cho, M.; Sathitsuksanoh, N.; Chowdhury, S.; Renneckar, S. Uniform Chemical Functionality of Technical Lignin Using Ethylene Carbonate for Hydroxyethylation and Subsequent Greener Esterification. *ACS Sustain. Chem. Eng.* **2018**, *6* (9), 12251–12260. https://doi.org/10.1021/acssuschemeng.8b02649.