I&EC research
Industrial & Engineering Chemistry Research

pubs.acs.org/IECR Research Note

Liquefying Lignins: Determining Phase-Transition Temperatures in the Presence of Aqueous Organic Solvents

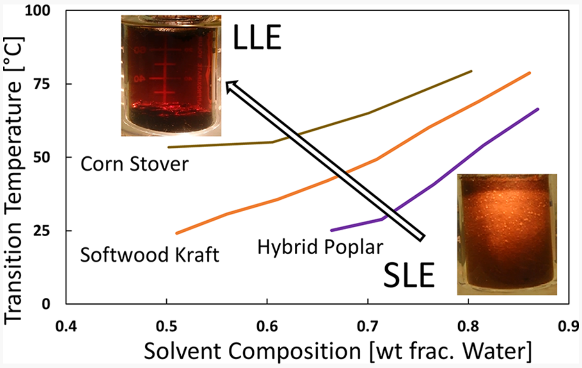
Graham W. Tindall,[∇] Spencer C. Temples,[∇] Mikhala Cooper, Villő Enikő Bécsy-Jakab, David B. Hodge, Mojgan Nejad, and Mark C. Thies[*]

Cite This: *Ind. Eng. Chem. Res.* 2021, 60, 17278−17282

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Under appropriate conditions of temperature and solvent composition, single-phase aqueous organic solvents are capable of liquefying lignin to form a lignin-rich liquid phase separate from the solvent phase, creating liquid−liquid equilibrium. The extent to which this phenomenon occurs when Kraft lignin is combined with the solvents methanol, ethanol, isopropanol, and acetone was determined, with solid−liquid (SL) to liquid−liquid (LL) phase-transition temperatures being measured over the range of applicable organic−water compositions. Lignins tested from a variety of biomass sources were all discovered to form this liquid−liquid equilibrium with aqueous ethanol solutions. The formation of such phase behavior between lignin and economical, green solvents creates new opportunities for the large-scale purification and fractionation of raw bulk (i.e., technical) lignins.



INTRODUCTION

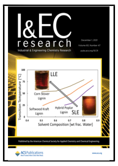
Although lignin is the world's second most abundant biopolymer and the only common one with aromaticity, it remains very much an underutilized material. One of the issues impeding the use of this amorphous polymer is its poor processability. With glass-transition temperture (T_g) values ranging from 90 °C to 150 °C,[1] lignin typically does not liquefy, but instead starts to degrade before the viscosity becomes low enough to process as a liquid. Several of the techniques that have been applied to lignin to improve its processability, including chemical modification and dry-spinning, have been discussed by Ogale and co-workers.[2]

Thies and co-workers[3] discovered that when Kraft lignin is combined with acetic acid (AcOH)−water solutions, the undissolved solid lignin can liquefy (i.e., solvate) upon heating to form a second, lignin-rich liquid phase, similar to a polymer melt, in terms of both density and viscosity. This "liquid-lignin" phase was found to be up to 5 times higher in molecular weight and 7 times lower in impurities[4] versus the starting lignin. When isolated, this phase was also shown to be useable for downstream applications, as it was dry-spun and converted to carbon fibers, having the highest mechanical properties ever obtained for lignin-based carbon fibers.[4] The process of using the liquid-lignin phase behavior to simultaneously fractionate, purify, and solvate lignins is called aqueous lignin purification with hot agents (ALPHA).

Typically, when lignin is combined with a solvent, or solvent mixture, in which it partially dissolves, the insoluble fraction remains in the solid state. A wide range of solvents, including alcohols, ketones, ethers, and alkanes, exhibit this conventional solid−liquid phase behavior and have been used to practice sequential lignin fractionation.[5−7] In contrast, the formation of a liquid-lignin phase is unusual, and the temperatures at which the system undergoes a transformation from a solid−liquid equilibrium to liquid−liquid equilibrium, as a function of solvent composition, have been reported only for AcOH−water solutions.[8] Preliminary estimates of a few phase-transition temperatures have been derived from measured acetone−water and ethanol−water isotherms with lignin.[9,10] Of equal importance is the fact that these solid−liquid to liquid−liquid equilibrium (SL−LL) phase transitions have been investigated for only one type of lignin, namely, a softwood Kraft lignin.

It is critical to distinguish this type of liquid−liquid phase behavior from a more traditional aqueous−organic biphasic system. Here, a one-phase solvent (i.e., ethanol−water) is added to solid lignin, and upon heating, a polymer-rich phase and a solvent-rich phase evolve. In contrast with previous work (e.g., refs 11 and 12), there is neither a distinct organic nor a distinct aqueous phase. Instead, the solvent-rich phase behaves as a dilute polymer solution, while the polymer-rich phase

Received: May 27, 2021
Revised: September 28, 2021
Accepted: September 29, 2021
Published: October 4, 2021



https://doi.org/10.1021/acs.iecr.1c02044

(∼50% lignin by mass) behaves as a plasticized polymer. Previous work has found the composition of EtOH−water, acetone−water, and AcOH−water remain approximately equal in both phases, suggesting that the solvents *cooperatively* suppress the temperature needed for the lignin chains to become mobile, crossing from a glassy state into a rubbery one.

Thus, there were two objectives to this study: First, to determine the extent to which SL−LL phase-transition temperatures and, thus, the desired liquid-lignin phase, exist for organic−water mixtures, with the focus being on biorenewable solvents (i.e., those that can be produced solely from biomass). With the ease of processing the liquid-lignin phase, one could envision a scenario whereby the manufacture of a lignin-based product was largely or completely "green". Thus, temperature versus composition diagrams were generated for softwood Kraft lignin with aqueous methanol, ethanol, and isopropanol. Aqueous acetone was also investigated. The second objective was to determine the extent to which lignins from plant sources other than softwood pine also exhibit the desired SL−LL phase transition. Thus, hybrid poplar (a hardwood) and corn stover (a herbaceous plant) were also investigated, along with Kraft lignin from a second recovery method, to assess variability.

■ MATERIALS AND METHODS

The base-case lignin was a Southeastern softwood pine Kraft lignin (sold under the BioChoice label), which was obtained from Domtar Corp. A second Southeastern pine Kraft lignin was recovered from the black liquor obtained from a pulp mill via the Sequential Lignin Recovery and Purification (SLRP) process.[13] A corn stover lignin was extracted from lignin cake obtained from POET, following the method of Abächerli and Doppenberg.[14] Finally, a hybrid poplar lignin was obtained as a byproduct from the alkaline pretreatment of wood chips, with the lignin being recovered from the resultant alkaline liquor via precipitation with sulfuric acid. The ash and sugar contents of these lignins (typical of bulk lignins), along with the number-average molecular weight of each (M_n), are given in Table 1.

Table 1. Selected Properties of Lignins Used in This Study

lignin label	biomass source	ash (wt %)	sugar (wt %)	M_n (Da)	softening point (°C)
HP	hybrid poplar	0.8	2.6	1300	140
BioChoice	southeastern pine	2.0	1.3	2200	175
SLRP	southeastern pine	1.3	0.4	5000	185
CS POET	corn stover	1.7	2.1	35000	–

Because the lignins had initial water contents ranging from 25 wt % to 35 wt %, they were dried at 10 mmHg and ambient temperatures for at least 24 h so that solvent−water solution compositions would be accurately known. The final water content of the lignins as determined by Karl Fischer titration[15] was 6.1 ± 2.7 wt %. Ash was determined by TGA, heating to 750 °C, using air as a purge gas with a heating rate of 10 °C/min. Sugar was measured in accordance with the procedure outlined in NREL Technical Report No. TP-510-42618,[16] and is the sum of xylose, glucose, arabinose monomers originating as hemicellulose and/or cellulose. The relative M_n value was determined by GPC with two columns in series: a Waters Styragel HT5 column, followed by an Agilent PolarGel-L column, using a mobile phase of dimethylformamide containing 0.05 M LiBr. Elution time was calibrated to a molecular weight value using polyethylene glycol standards. Lignin concentration was monitored with a UV/vis photodiode array detector at 280 nm, and the polyethylene glycol standards were monitored by refractive index. Furthers details are given elsewhere.[15] The softening point was measured on a Fisher−Johns melting point apparatus. Lignin powder was heated at a rate of ∼10 °C/min until it was sufficiently softened, such that it formed a smooth and optically translucent film when deformed with a spatula against the heated plate.

For the phase-transition measurements, solvent−water mixtures ranging from 30 wt % to 90 wt % water were prepared. These homogeneous solvent mixtures were then mixed with the lignins described above at nominal solvent (mixture)-to-lignin ratios of 3:1 and/or 6:1 (w/w). Experiments were performed in 35 mL glass vials charged with a nominal 1 g of lignin and the appropriate amount of solvent. A magnetic stir bar was added to the vial to facilitate mixing and to ensure that the contents were maintained at equilibrium. The vial was submerged in an oil bath so that the liquid in the vial was ∼1.5 cm below the surface of the oil. The internal temperature of the liquid(s) in the vial was measured using a sheathed, grounded, and calibrated 1 mm outer diameter (o.d.) T-type thermocouple that pierced the septum cap. Once the vial reached thermal equilibrium with the oil bath, the bath was heated at a ramp rate of 1 °C/min. As the temperature approached within 5−10 °C of the phase-transition temperature, the solid lignin particles in the solvent solution became sticky and thus started coagulating on the surface of the thermocouple probe and stir bar. The SL−LL phase transition was recorded as the temperature at which the coagulated lignin particles completely melted to form a continuous glossy phase that flowed and deformed to take the shape of the container. Typically, the bottom liquid-lignin phase was easy to see, as it was denser and nearly black, while the top, less-dense solvent phase was light brown and translucent. The brief removal of the vial from the bath for phase observation had a negligible impact on the internal temperature of the vial. In just a few cases, the phase transition was difficult to observe (typically the high-water region), so the contents of the heated vial would be quickly poured into an aluminum pan under a fume hood to observe the discrete phases without obstruction. Phase-transition temperatures for each composition were measured in at least duplicate, with temperatures for replicate compositions having an average standard deviation of ±0.8 °C.

■ RESULTS AND DISCUSSION

In Figure 1, SL−LL phase-transition temperatures for the different aqueous solvent systems are compared, all while holding the source of the lignin (BioChoice, BC) and the solvent (mixture)-to-lignin ratio constant. Below the dotted line for each system and composition, solid−liquid equilibrium (SLE) is present; above this line, liquid−liquid equilibrium (LLE) exists. To the right of each dotted line, LLE ends and there is only SLE, because of an excess of water; to the left, the SLE-to-LLE phase boundary still exists down to ambient temperatures, where the last measurements were made.

Acetone (Ace) forms LLE at the lowest temperature and highest water content (wt %), suggesting that it is the strongest organic solvent of those investigated. However, from a separations standpoint, the strongest solvent is not necessarily the best option. For example, Ace has the smallest range of

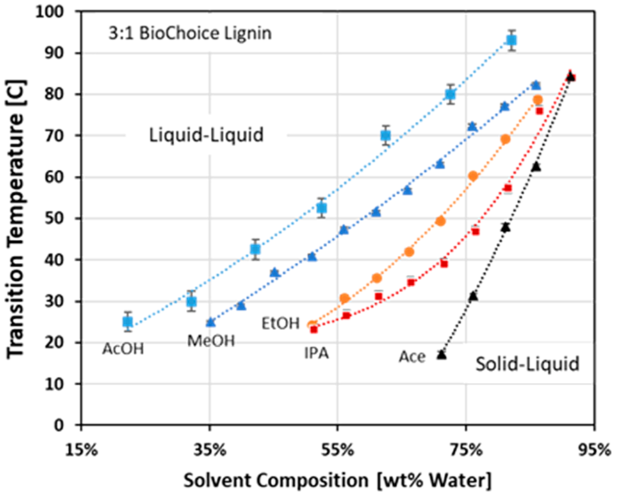


Figure 1. Phase-transition temperatures for Bio-Choice (BC) lignin in various aqueous solvents at a 3:1 solvent-to-feed ratio. From left to right: acetic acid (light blue square, ■), methanol (blue triangle, ▲), ethanol (orange circle, ●), isopropanol (dark orange square, ■), and acetone (black triangle, ▲).

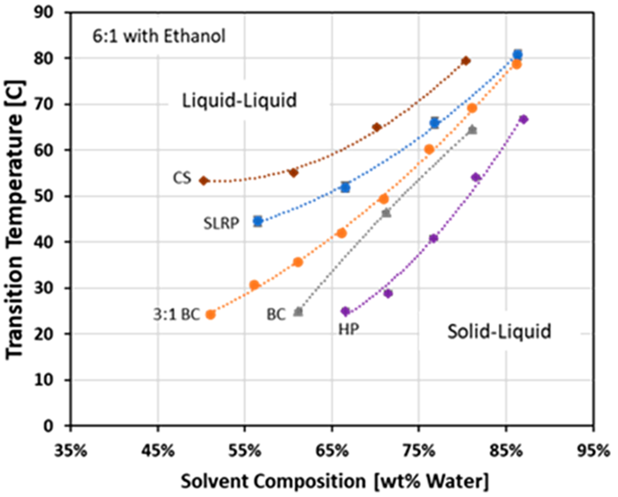


Figure 2. Phase-transition temperatures for various lignins in ethanol−water solutions at a S:F ratio of 6:1. From top to bottom: corn stover (dark orange, ◆), SLRP (blue circle, ●), 3:1 BioChoice (orange circle, ●), 6:1 BioChoice (gray triangle, ▲), and hybrid poplar (purple diamond, ◆).

solvent−water compositions for forming the desired LLE phase separation. On the other hand, the LLE region for what appears to be the weakest solvent, acetic acid (AcOH), is significantly larger; in fact, it has been used to isolate useful lignin fractions of high purity and controllable molecular weight.[5,17] Aqueous mixtures of methanol (MeOH), ethanol (EtOH), and isopropanol (IPA) are similarly capable of forming LLE with lignin, with the transition temperature decreasing as the alkyl chain on the alcohol increases in length. Finally, it is interesting to note that, as a group, the organic solvents follow the trend of decreasing phase-transition temperatures and increasing slope of the phase-transition lines with increasing dipole moment, from 1.3 D for AcOH, to 1.7 D for the alcohols, to 2.9 for Ace.

To determine the prevalence of the desired "ALPHA" liquid−liquid phase behavior among a variety of lignins, two lignins recovered from Kraft papermill black liquor and two recovered from bioethanol-refinery-type waste streams were selected, as described earlier. Ethanol was chosen as the biorenewable solvent for this investigation, since lignocellulosic bioethanol refineries have a readily available supply of both ethanol and lignin-rich waste streams. Diverting a small portion of the primary product from a bioethanol refinery to upgrade the lignin into a higher-value coproduct stream could fundamentally change the techno-economics of renewable ethanol production.

Figure 2 shows the effect, for the lignin−ethanol−water system, of two variables integral to the ALPHA process: solvent-to-feed (S:F) ratio and lignin source. The relationship between the phase-transition temperature and the S:F ratio for BC−ethanol−water (3:1 vs 6:1) is consistent with what was previously observed for AcOH−water with SLRP lignin,[3] where, at higher water concentrations, the temperature difference between similar S:F ratios was no more than 3−4 °C. As the solvent composition shifts toward higher amounts of the organic component, a higher S:F results in a higher temperature needed to achieve LLE.[3,10] The limits of the effect of changing the S:F ratio were also explored in the course of this work, with the ratio of 9:1 generally differing by no more than a few degrees from the ratio of 6:1, and higher S/F ratios approaching an asymptotic phase-transition temperature. On the other hand, by decreasing the S/F ratio from 3:1, one eventually reaches the point (e.g., <1:1) where there is not enough solvent left to liquefy the lignin, and SLE is obtained.

As far as the effect of lignin source, all lignins exhibited the desired SL−LL phase-transition behavior over a relatively wide range of solvent−water compositions, starting at ∼50/50 EtOH−water and extending to ∼15/85. As described above, only SLE exists to the right of the SLE/LLE line, and to the left SLE/LLE exists until at least ambient temperatures. However, the phase behavior for the SLRP and corn stover (CS) lignins was an exception to this rule, because, on the left, their SLE/LLE lines terminated at SLE, when the two liquid phases merged to form one at the higher solvent compositions.

Figure 2 also shows how the phase-transition temperatures are strongly dependent on lignin type. The observed trends can be qualitatively explained in terms of the thermodynamic theory for solid−liquid solutions,[18] which indicates that the higher the melting point of a solid, the higher the temperature required to completely dissolve that solid in a given solvent solution. Thus, hybrid poplar (HP) lignin, with a softening point of 140 °C, exhibited the lowest SLE-to-LLE phase-transition temperature of the lignins investigated. Hardwood lignin generally is known to have a relatively low melting point, so it stands to reason that the intermolecular forces of this polymer would be easiest to disrupt with heat and solvent, such that a liquid-lignin phase is formed. BioChoice lignin was next at 175 °C, followed by SLRP lignin at 185 °C. As both BC and SLRP are softwood Kraft lignins and thus were exposed to similar processing conditions (albeit from different pulp mills with different paper/cardboard requirements), one would expect similar phase-transition temperatures. However, as anticipated, the SLRP lignin transition temperature is higher, because this particular SLRP run had an increased residence time, and research for this has been shown[19] to be able to increase the molecular weight of the lignin. For the corn-stover lignin, which had the highest phase-transition temperature for a given solvent solution, no actual softening point was observed; instead, the lignin started to degrade at ∼225 °C—discoloring and off-gassing appreciable amounts of volatiles. This result was not unexpected, as lignin from the POET process has been exposed to dilute-acid (DA) pretreatment, which catalyzes carbon−carbon condensation reactions and can make the lignin intractable if allowed to proceed too far.[20]

The agreement between softening point and molecular weight in Table 1 is not surprising, as one would expect these two properties to be linked. The impact of the different chemical functionalities possessed by hardwood, softwood, and herbaceous lignins (the H, G, and S monomer units differ in prevalence in each) would also be expected to affect the location of the observed phase boundaries. However, both the lignin molecular weight and pretreatment method would have to be held constant in order to isolate this effect. Regardless, these results confirm the hypothesis of this work: the ALPHA process can be practiced on Kraft lignin using a wide variety of aqueous organic solvents, most of which are biorenewable. Furthermore, lignins from a variety of biomass sources and pretreatment processes form liquid−liquid equilibria when exposed to aqueous ethanol solutions over specific temperatures, establishing a new avenue for the large-scale purification and fractionation of biomass lignins using economical and green solvents via the ALPHA process. Finally, SL-LL phase-transition temperatures, if they indeed are found to exist, should be measured for a wide variety of lignins in aqueous organic solvents other than ethanol.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c02044.

> Data table showing the transition temperatures (plus/minus one standard deviation), the composition of the solvent on a lignin-free basis, and the overall composition of the vial (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Mark C. Thies − *Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634-0909, United States;* orcid.org/0000-0002-2833-485X; Email: mcths@clemson.edu

Authors

Graham W. Tindall − *Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634-0909, United States;* orcid.org/0000-0002-2431-2282

Spencer C. Temples − *Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634-0909, United States*

Mikhala Cooper − *Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634-0909, United States*

Villő Enikő Bécsy-Jakab − *Department of Chemical & Biological Engineering, Montana State University, Bozeman, Montana 59717, United States*

David B. Hodge − *Department of Chemical & Biological Engineering, Montana State University, Bozeman, Montana 59717, United States;* orcid.org/0000-0002-9313-941X

Mojgan Nejad − *Department of Forestry, Michigan State University, East Lansing, Michigan 48824, United States;* orcid.org/0000-0003-1306-6108

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.1c02044

Author Contributions

$^{\nabla}$These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based on work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) (under Bioenergy Technology Office Award No. DE-EE0008502), the National Science Foundation (under Grant No. CBET-1915787), and the Department of Education Graduate Assistance in Areas of National Need (GAANN) Fellowship (Award No. P200A180076 to G.W.T.).

■ REFERENCES

(1) Irvine, G. The Glass Transitions of Lignin and Hemicellulose and Their Measurement by Differential Thermal-Analysis. *Tappi J.* **1984**, *67* (5), 118−121.

(2) Ogale, A. A.; Zhang, M.; Jin, J. Recent Advances in Carbon Fibers Derived from Biobased Precursors. *J. Appl. Polym. Sci.* **2016**, *133* (45), 43794.

(3) Klett, A. S.; Chappell, P. V.; Thies, M. C. Recovering Ultraclean Lignins of Controlled Molecular Weight from Kraft Black-Liquor Lignins. *Chem. Commun.* **2015**, *51* (64), 12855−12858.

(4) Jin, J.; Ding, J.; Klett, A.; Thies, M. C.; Ogale, A. A. Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 14135−14142.

(5) Morck, R.; Reimann, A.; Kringstad, K. P. Fractionation of Kraft Lignin by Successive Extraction with Organic-Solvents, III. Fractionation of Kraft Lignin from Birch. *Holzforschung* **1988**, *42* (2), 111−116.

(6) Duval, A.; Vilaplana, F.; Crestini, C.; Lawoko, M. Solvent Screening for the Fractionation of Industrial Kraft Lignin. *Holzforschung* **2016**, *70* (1), 11−20.

(7) Jiang, X.; Savithri, D.; Du, X.; Pawar, S.; Jameel, H.; Chang, H.; Zhou, X. Fractionation and Characterization of Kraft Lignin by Sequential Precipitation with Various Organic Solvents. *ACS Sustainable Chem. Eng.* **2017**, *5* (1), 835−842.

(8) Klett, A. S.; Gamble, J. A.; Thies, M. C.; Roberts, M. E. Identifying Thermal Phase Transitions of Lignin-Solvent Mixtures Using Electrochemical Impedance Spectroscopy †. *Green Chem.* **2016**, *18*, 1892.

(9) Temples, S. C.; Gathmann, S. R.; Ding, J.; Thies, M. C. Liquid − Liquid Equilibrium Compositions and Global Phase Behavior for Lignin − Acetone − Water Ternary at 25, 45, and 65° C. *Ind. Eng. Chem. Res.* **2019**, *58* (50), 22619−22625.

(10) Tindall, G. W.; Chong, J.; Miyasato, E.; Thies, M. C. Fractionating and Purifying Softwood Kraft Lignin with Aqueous Renewable Solvents: Liquid−Liquid Equilibrium for the Lignin−Ethanol−Water System. *ChemSusChem* **2020**, *13* (17), 4587−4594.

(11) Smink, D.; Kersten, S.; Schuur, B. Comparing multistage liquid−liquid extraction with cold water precipitation for improvement of lignin recovery from deep eutectic solvents. *Sep. Purif. Technol.* **2020**, *252*, 117395.

(12) Xin, Q.; Pfeiffer, K.; Prausnitz, J. M.; Clark, D. S.; Blanch, H. W. Extraction of lignins from aqueous−ionic liquid mixtures by organic solvents. *Biotechnol. Bioeng.* **2012**, *109* (2), 346−352.

(13) Velez, J.; Thies, M. C. Liquid Lignin from the SLRP TM Process: The Effect of Processing Conditions and Black-Liquor Properties. *J. Wood Chem. Technol.* **2016**, *36* (1), 27−41.

(14) Abacherli, A.; Doppenberg, F. Method for Preparing Alkaline Solutions Containing Aromatic Polymers. U.S. Patent No. 6,239,198 B1, 2001.

(15) Ding, J.; Klett, A. S.; Gamble, J. A.; Tindall, G. W.; Thies, M. C. Liquid−Liquid Equilibrium Compositions and Global Phase Behavior for the Lignin−Acetic Acid−Water System at 70 and 95 °C. *Fluid Phase Equilib.* **2018**, *461*, 8−14.

(16) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass: Laboratory Analytical Procedure (LAP)*; National Renewable Energy Laboratory: Golden, CO (revised July 2011).

(17) Chakraborty, S.; Ding, J.; Thies, M. C.; Kitchens, C. L. More Elongated Solution Structures in Lignin Precursors Improve Properties of Resultant Carbon Fibers. *ACS Appl. Polym. Mater.* **2019**, *1* (10), 2561−2565.

(18) Sandler, S. *Chemical, Biochemical, and Engineering Thermodynamics*, 5th Edition; John Wiley and Sons, Inc., 2017.

(19) Velez, J.; Thies, M. C. Temperature Effects on the Molecular Properties of Liquid Lignin Recovered from Kraft Black Liquor. *ACS Sustainable Chem. Eng.* **2015**, *3* (6), 1032−1038.

(20) Sano, Y.; Shimamoto, S.; Enoki, M.; Konno, H. Fractionation of Woody Biomass with Boiling Aqueous Acetic Acid Containing a Small Amount of Mineral Acid at Atmospheric Pressure: Reactivity of Arylglycerol-Aryl Ethers in Lignins with Aqueous Acetic Acid Containing H_2SO_4. *J. Wood Sci.* **1998**, *44*, 217−221.