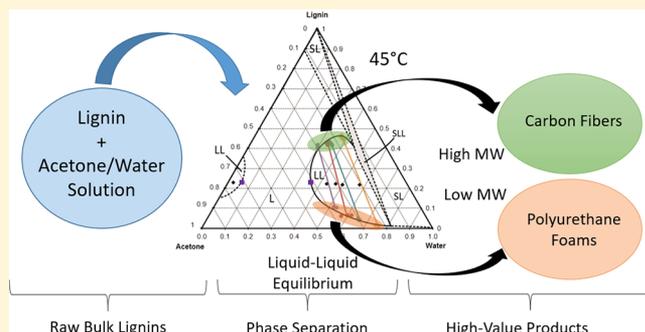


Liquid–Liquid Equilibrium Compositions and Global Phase Behavior for Lignin–Acetone–Water Ternary at 25, 45, and 65 °C

Spencer C. Temples, Sallye R. Gathmann, Junhuan Ding,^{1b} and Mark C. Thies*^{1b}

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

ABSTRACT: Liquid–liquid equilibrium (LLE) phase compositions and tie lines were measured for the lignin–acetone–water system in the region of LLE where the aqueous lignin purification with hot agents (ALPHA) process can be practiced. The surrounding one-phase, solid–liquid (SL), SLL, and acetone-rich LL regions were also identified, mapping out the global phase behavior for this system. Solvent compositions (on a lignin-free basis) in the coexisting solvent-rich and lignin-rich liquid phases are quite similar and the one-phase region extends to ~50/50 wt/wt acetone/water, indicating affinity between acetone + water with respect to the lignin polymer. This renewable pseudoternary system exhibits properties useful in isolating low-molecular-weight (MW) fractions of lignin. For example, a 45/55 acetone/water mixture at a solvent-to-lignin ratio of 3:1 can be used to isolate a lignin with a number-average MW (\bar{M}_n) of 1000 Da at 15% yield from a feed with a \bar{M}_n of 5300.



1. INTRODUCTION

Lignin is unique among biopolymers in that it has significant aromatic character, making it potentially useful for a wide range of materials applications, including resins, foams, and carbon fibers.^{1–4} Furthermore, lignin is second only to cellulose in abundance among organic compounds, further enhancing its attractiveness as a biorenewable material. Unfortunately, the lignins available on the market today (e.g., (alkali) Kraft and others) are bulk lignins, and thus have a broad molecular weight (MW) distribution. However, recent research indicates that the molecular weight and polydispersity of a lignin can significantly affect its performance for a given application. For example, carbon fibers made from higher MW lignins have been shown to exhibit significantly higher strength and modulus,⁴ and lower MW lignins with higher hydroxyl content have been shown to be more effective substitutes for polyols in polyurethane foams.³ In addition, for many applications a reduction in the metals content of lignin would also be desirable, as Kraft lignins typically contain ~10 000 ppm total metals (mostly Na and K), with ash analyses being in the 1–3% range.

Thies and co-workers^{5,6} have developed a process, known as aqueous lignin purification with hot agents (ALPHA), for simultaneously fractionating and purifying bulk lignins, including those recovered from pulp-and-paper mills (i.e., Kraft lignins) and from lignocellulosic biorefineries (e.g., corn-stover lignins). The key discovery⁷ behind ALPHA is that when these so-called “technical” lignins are combined with hot, one-phase mixtures of water with acetic acid, two liquid phases are formed: one solvent-rich and the other lignin-rich. Lignin preferentially distributes between the two phases, with lower MW lignin dissolving in the solvent-rich phase, and higher

MW lignin forming a separate, highly solvated, lignin-rich phase. Furthermore, the solvent-rich phase preferentially extracts the metal salts, so that the lignin in the lignin-rich phase is purified.^{5,6} Liquid–liquid equilibrium phase compositions and tie lines have been measured for the lignin–acetic acid–water system,⁸ and the strongest carbon fibers from lignin reported to date were made from the purified, high MW lignin isolated within the lignin-rich phase.

Recently, another one-phase solvent mixture that forms two liquid phases when combined with lignin has been discovered, namely mixtures of acetone with water. The use of acetone–water mixtures to fractionate lignin is certainly not new to lignin researchers; for example, several groups^{9–12} have recently used acetone/water mixtures on a lab scale to fractionate and characterize a range of technical lignins. Generally speaking, in those investigations initially a 60/40 acetone/water mixture was used at a solvent:lignin (v/w) ratio of 10:1 to dissolve a large percentage (if not all) of the lignin; then water was added to the solution in order to precipitate out lignin fractions sequentially, until the final solution being used contained 10–40% acetone. In all cases, the lignin fractions were designated as either being “soluble” or “insoluble” in the single-phase solvent mixture. Only solid lignin precipitates were noted. The presence of a solvated,

Special Issue: Chuck Eckert Festschrift

Received: June 27, 2019

Revised: August 13, 2019

Accepted: August 29, 2019

Published: September 10, 2019

lignin-rich liquid phase, which is a key to the uniqueness of ALPHA, was not reported.

Several motivating factors exist for measuring liquid–liquid equilibrium (LLE) phase behavior for the lignin–acetone–water system. First, as with the lignin–acetic acid–water (L–AcOH–W) system, there is the advantage of a solid-free process for fractionating and purifying lignin, in terms of both scale-up and cost. Second, acetone–water would be another green solvent system^{13,14} that would be attractive for commercially producing lignin streams of high value via ALPHA. Third, our results for lignin–acetic acid–water indicated that the molecular weight of the lignin-rich phase increased as equilibration times were increased above 15 min.⁸ On the basis of the literature,^{15,16} we hypothesize that this is being caused by acid-catalyzed reactions. Such reactions would not be expected for lignin–acetone–water (L–Ace–W), allowing us to investigate a system where the MW differences of lignin between the two liquid phases are exclusively due to phase equilibrium.

2. EXPERIMENTAL METHODS

2.1. Materials. A softwood Kraft lignin with an ash content of ~1% was recovered at Clemson from a softwood black liquor (Kappa number = 25; solids content = 42%) via the sequential liquid-lignin recovery and purification (SLRP) process.^{17,18} This “SLRP” lignin is representative of other commercially available lignins (referred to as “technical lignins”), such as BioChoice from Domtar and West Fraser’s lignin. Prior to an experiment, the lignin was vacuum-dried down to 8–14% water (at ambient, it ranges from 25 to 40% water), with the precise amount of water determined by Karl Fischer titration of lignin dissolved in pyridine in a 10:1 w/w ratio.⁸ Acetone, certified ACS 99.7% purity, was obtained from Fischer Chemical, and distilled and deionized water with a resistance >18.2 M Ω was made in-house, utilizing distillation followed by a Milli-Q Academic filter. Acetone-suitable, Karl–Fischer chemicals (Hydranal Titrant Composite 5 k, cat. no. 34816; Hydranal Solvent, cat. no. 37817) were used for water titrations. For GPC analysis, HPLC-grade (99.7+%) N,N-dimethylformamide (DMF; cat. no. AA22915-K7) and ultradry lithium bromide (LiBr; cat. no. AA35705–14) were obtained from VWR.

2.2. LLE Experiments. Solvent mixtures ranging from 50/50 to 20/80 w/w acetone/water and combined with SLRP lignin at a solvent-to-lignin (S/L) ratio (w/w) of 3:1 were used to measure equilibrium tie lines in the liquid–liquid region of interest for ALPHA processing. A lower S/L ratio was chosen (compared to the 9:1 ratio previously used for the L–AcOH–W system⁸) so as to lower the solid–liquid to liquid–liquid phase transition temperature curve for L–Ace–W to temperatures less than 5–10 °C above the boiling point (= 56.1 °C) of acetone (as was done for L–AcOH–W⁵). With this change, our phase-behavior measurements could be performed at ambient pressures. An additional advantage of the change was that the economically optimal version of ALPHA would likely operate at S/L ratios closer to 3:1 than 9:1. Experiments were conducted in 9.5-dram (~35 mL) glass vials (VWR part no. 6012–066) capped with PTFE/silicon septa (VWR part no. 89042–292) and containing magnetic stir bars (Fischer part no. 14–512–121) for constant stirring at 270 rpm. The temperature of the vial contents was monitored with a K-type 1/16th inch grounded thermocouple (Omega cat. no. CASS-116G-12) inserted through the airtight septum via a 21-gauge

needle hole. The thermocouple was calibrated to within an accuracy of 0.1 °C using the ice point of water and the boiling point of acetone as reference points.

For a typical experiment, a vial containing ~4.00 g of the lignin + solvent mixture was submerged into a stirred oil bath, with the mixture level being ~1/2 in. below that of the oil to ensure a constant and uniform sample temperature. The bath was heated by a 200W quartz heater (VWR part no. 470122–464) interfaced to an Omega CN8500 controller. The temperature of the mixture was measured every 3 min after the solution had reached the desired set point (on average 5 min into the run). 15 min runs were found to be adequate for the L–Ace–W system to undergo its transition from solid–liquid to liquid–liquid equilibrium, when the lignin-rich (LR) and solvent-rich (SR) phases were formed. Vial temperatures were held to within 0.1 °C of the reported values for 25 °C and to within 0.3 °C for 45 and 65 °C. Minor acetone losses from the vials (averaging 0.06, 0.12, and 0.18 g) occurred for the experiments (at 25, 45, and 65 °C, respectively) by leakage around the thermocouple inserted through the septum cap. However, because the leaks were small and the two liquid phases were well-mixed in the vial after their formation, we assumed that perturbations from equilibrium were small enough so that true LLE was present for the phase compositions that existed at the end of the run. With 1 min remaining, stirring was terminated to allow the phases to settle and separate. The thermocouple was then removed, and the SR phase was decanted into a clean, preweighed glass vial. The large volume of the vial relative to the sample volume aided in the decantation process, as did the large differences in the density and viscosity between the SR and LR phases. However, those differences did decrease at higher Ace/W solvent ratios as the tie lines approached the plait point, which is why tie lines were not obtained near this region. Also, the viscous LR phase was nearly black, whereas the watery, SR phase ranged from dark brown to nearly clear in color. Thus, any “stray” LR phase that was inadvertently decanted was easily spotted, and that run was terminated.

Finally, consistent, accurate measurement of the mass of the sample vials, both empty and containing SR or LR phase, was critical to the overall accuracy of the results. Thus, after decantation of the SR phase, the outside of the original sample vial now containing just the LR phase was first rinsed with water to cool the contents, and was then cleaned with degreaser to remove any bath oil adhering to the outside of the vial. This vial-cleaning process has been demonstrated to be highly reproducible, with the average weight difference of a clean vial before and after oil bath submersion being 0.0005 ± 0.0009 g. The cooled and cleaned vials were then weighed at ambient temperature to determine the mass of each separate phase.

For liquid–liquid equilibrium measurements at 25 °C, a modified setup was employed, allowing for both heating of the bath with the above-mentioned quartz heater and cooling of the bath with an ice–water condenser.

2.3. Determination of LLE Phase Compositions. The SR and LR phases were each homogenized with ~4 g of acetone, and the water content of each phase was determined in triplicate via Karl–Fischer (KF) titration, using a Mettler Toledo V20 volumetric KF Titrator. The water content of the homogenizing acetone (~0.3 wt %) was periodically determined and taken into account. A 1 wt % water standard (Aquastar) was periodically used to calibrate the KF titrator.

Table 1. Measured Liquid–Liquid Equilibrium Tie-Line Compositions for the Lignin–acetone–water System at 25, 45, and 65 °C^a

temp. (°C)	feed parameters		lignin-rich phase			solvent-rich phase		
	acetone:water solvent composition ^b	S:L ratio (wt:wt)	lignin (%)	acetone (%)	water (%)	lignin (%)	acetone (%)	water (%)
25	50:50	3.004:1	46.90 ± 2.62	25.53 ± 1.96	27.55 ± 0.65	7.657 ± 0.67	43.21 ± 0.54	49.12 ± 0.15
	45:55	3.003:1	47.23 ± 0.48	23.72 ± 0.06	29.04 ± 0.53	3.550 ± 0.83	39.81 ± 0.63	56.63 ± 0.20
	40:60	3.020:1	46.08 ± 3.78	21.02 ± 2.52	32.89 ± 1.26	1.733 ± 0.24	35.86 ± 0.65	62.39 ± 0.74
	35:65	3.006:1	40.49 ± 1.68	21.03 ± 1.02	38.46 ± 0.66	0.781 ± 0.04	31.31 ± 0.25	67.90 ± 0.26
45	50:50	2.995:1	40.83 ± 0.62	29.19 ± 0.36	29.96 ± 0.27	10.26 ± 0.20	37.09 ± 0.55	52.64 ± 0.75
	45:55	3.002:1	44.42 ± 2.49	22.06 ± 2.29	33.50 ± 0.47	6.519 ± 0.36	33.66 ± 2.43	59.81 ± 2.10
	40:60	3.001:1	42.64 ± 2.24	21.74 ± 1.74	35.60 ± 0.50	4.161 ± 0.64	29.55 ± 0.01	66.28 ± 0.65
	30:70	3.001:1	48.59 ± 1.07	13.25 ± 0.32	38.14 ± 0.92	1.255 ± 0.06	23.04 ± 0.81	75.69 ± 0.88
65	45:55	3.003:1	45.21 ± 0.16	24.17 ± 0.38	30.60 ± 0.23	7.337 ± 0.15	34.22 ± 0.26	58.43 ± 0.19
	40:60	3.002:1	44.07 ± 0.33	22.65 ± 0.47	33.26 ± 0.29	4.825 ± 0.10	30.31 ± 0.84	64.86 ± 0.90
	30:70	3.006:1	53.92 ± 0.89	14.46 ± 0.65	31.61 ± 0.72	2.192 ± 0.17	20.57 ± 2.56	77.23 ± 2.73
	20:80	3.009:1	47.77 ± 0.74	11.68 ± 0.63	40.53 ± 1.37	1.222 ± 0.06	16.10 ± 0.77	82.67 ± 0.77

^aPhase compositions are given in weight percent. S:L ratio = solvent-to-lignin mass ratio. Uncertainties are $\pm 1\sigma$ (each tie-line was measured in triplicate). ^bSolvent compositions are nominal and do not include water content of feed lignin.

The lignin content of each phase was determined gravimetrically by removing all solvent from this highly hygroscopic material. Specifically, aliquots (~3g) of each homogenized phase were dried in aluminum weighing dishes (VWR cat no. 25433–020), with the more volatile portion of the solvent (mostly acetone) being removed by drying in a hood overnight, and the less volatile portion (mostly water) being removed by drying in an oven with desiccant at 50 °C for 24 h. Afterward, the dried lignin was immediately placed in a desiccator to cool before weighing, to prevent any water absorption from the air. Finally, KF titration was used to confirm that the final lignin sample was water-free.

With the mass of lignin determined gravimetrically and the mass of water determined by KF titration as described above, the mass of acetone was determined by difference, giving the overall composition of the LR or SR phase. As stated above, the small acetone losses did not affect the system LLE, so phase-composition calculations for the SR and LR phase were unaffected. However, these acetone losses were used to adjust the feed compositions originally obtained for each run from weighing the lignin and solvent mixture placed into the vial.

2.4. Molecular Weight and Metal Analyses. The relative molecular weight of the lignin in each phase was determined with a Waters 600GPC using two columns in series: a Waters Styragel HT and an Agilent PolarGel-L column, respectively. GPC samples were prepared as follows: 5 mg of the dried homogenized samples, both the SR and LR phases, were dissolved in 5 mL of DMF containing 0.05 M LiBr. Once dissolved, the samples were passed through a 0.2 μ m nylon filter (VWR, part no 28145–487) to remove insoluble contaminants such as dust and cellulose, and were then analyzed at a mobile-phase flow rate of 1 mL/min. The GPC was calibrated with polyethylene glycol (PEG) standards detected by a Waters differential refractometer, and the lignin samples were detected with UV–vis using a Waters 996 PDA detector at 280 nm.

The metals content of the feed lignin and of the lignin from the SR and LR phases was determined via inductively coupled plasma atomic emission spectroscopy (ICP–AES) by the Agricultural Service Laboratory at Clemson University. Analyses were carried out using an Ametek Spectro Scientific spectrometer, model ARCOS. To prepare a sample for ICP, we

dried an aliquot of the feed lignin, SR phase, or LR phase under 29–30" of vacuum for at least 24 h to reduce the moisture content as much as possible, as any residual water would be considered as part of the original lignin mass. Next, up to 0.5 g of this dried lignin sample was predigested in 5 mL of concentrated nitric acid at ambient temperature for 30 min. Sample digestion was then started by heating to 125 °C for 90 min, followed by the addition of 3 mL of 30% hydrogen peroxide and heating to 125 °C for 60 min. An additional 3 mL of 30% hydrogen peroxide were added, and the sample was heated at 125 °C for 60 min. Finally, the sample was heated to dryness at 200 °C for 1 h. The above dried samples were diluted in 10 mL of 1.6 M nitric acid and, after cooling, brought up to 50 mL volume with deionized water and mixed thoroughly. The resulting liquids were then transferred to a test tube for analysis by ICP–AES.

3. RESULTS AND DISCUSSION

3.1. Phase Compositions and Phase Diagrams. The measured LLE phase compositions are given in Table 1 and are plotted along with the accompanying tie lines and feed compositions in lignin–acetone–water (L–Ace–W) pseudo-ternary phase diagrams at 25, 45, and 65 °C in Figures 1–3, respectively. We use the term “pseudo” because lignin is not pure but polydisperse. Thus, the diagrams are not true ternaries and will change with the MW and chemical functionality of the lignin. Nevertheless, plotting the data in this manner is still one of the most useful ways to depict the results. Each set of tie-line compositions was measured in triplicate, so one can see that there is much overlap, and thus good reproducibility, in much of the data. As mentioned in Section 2.2, there was some loss of acetone from the samples, and we can see this in the figures for those feed compositions that are slightly displaced from their feed line toward the acetone apex. The reader is also reminded that the feed SLRP lignin contained 8–14 wt % water even after drying; thus the feed compositions are located slightly below 25% lignin in the phase diagrams. In addition to making quantitative LLE measurements, we either qualitatively observed or estimated the other types of phase behavior that exist for this system, consistent with the Gibbs phase rule, to map out the global phase behavior.

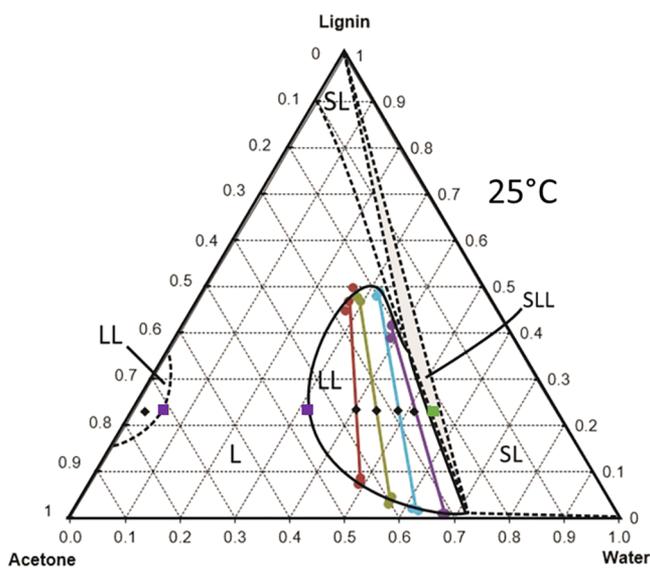


Figure 1. Pseudoternary phase diagram for the lignin–acetone–water (L–Ace–W) system at 25 °C and a solvent-to-lignin (S/L) feed ratio of 3:1 (25 wt % lignin). Diamonds (\diamond) are feed compositions, circles (\circ) are tie-line compositions, and squares (\square) are for phase-boundary compositions—purple for L/LL and green for LL/SLL.

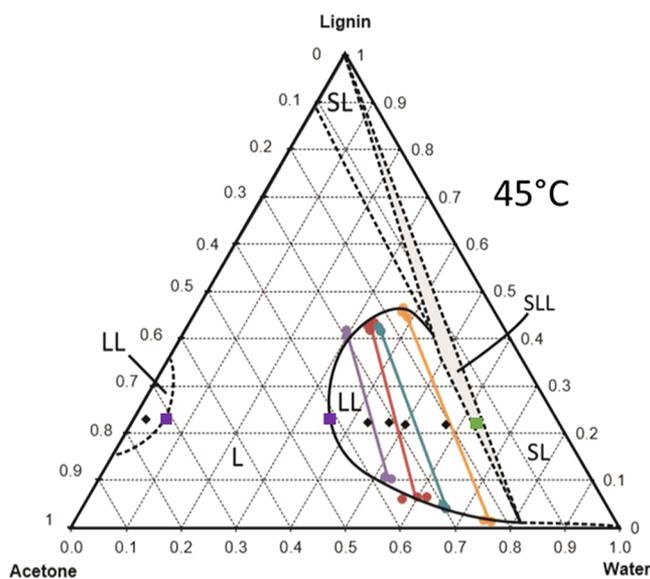


Figure 2. Pseudoternary phase diagram for L–Ace–W at 45 °C and a S/L feed ratio of 3:1 (25 wt % lignin). The legend is given in Figure 1.

The key feature of interest at each temperature is the large liquid–liquid (LL) region where the ALPHA process is practiced. The phase boundary/bimodal curve (i.e., the solid curved line) for this region was created from an empirical fit to the measured tie-line compositions, with the left-most (Ace-rich) part of the curve being located from LLE experiments (Section 2.2) in which the Ace/H₂O wt/wt ratio of the solvent was increased by ~ 2 wt % increments until the one-phase L region was attained. (Recall that the LL critical point for a multicomponent system will occur at only one unique overall phase composition, so one would not expect to obtain this point unless multiple S/L ratios were investigated.) The phase boundary for the right-hand side (RHS) of the LL region was determined by decreasing the Ace/H₂O ratio until a solid

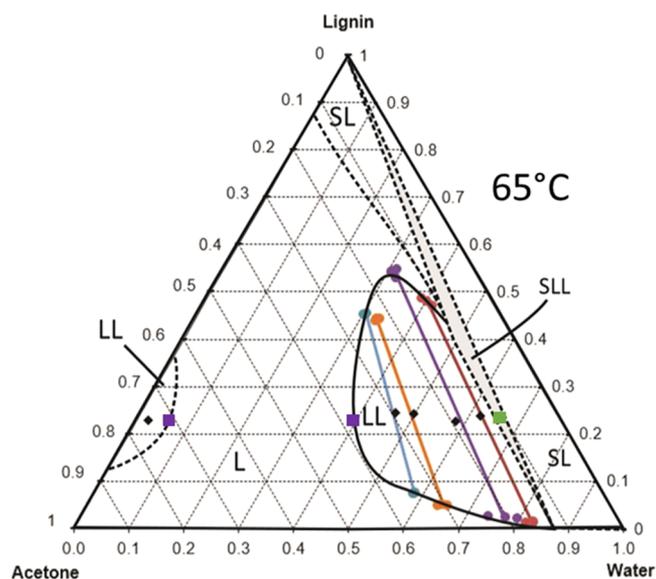


Figure 3. Pseudoternary phase diagram for L–Ace–W at 65 °C and a S/L feed ratio of 3:1 (25 wt % lignin). The legend is given in Figure 1.

phase (instead of LLE) was observed. Observation of the LR and SR liquid phases in the presence of the solid phase was difficult, but from the Gibbs Phase Rule such a three-phase SLL region must be present there, even though it encompasses only a small area. The SL region to the right of the SLL region, indicating that lignin is insoluble in a high-water liquid phase, was readily observed. The phase transition from SL to LL phase behavior with temperature is an important variable that establishes the minimum temperature at which ALPHA can be practiced for a given solvent mixture composition.

The acetone-rich SL region near the lignin apex and to the left of the SLL region was not actually observed, but is the simplest phase behavior that can exist consistent with the Gibbs phase rule. Such SL phase behavior is commonly observed in this region for systems where one component is a solid.¹⁹ The small liquid–liquid (LL) phase split on the left-hand (i.e., Ace-rich) side of the diagram was qualitatively located by obtaining two liquid phases for a 97/3 Ace/H₂O solvent mixture with lignin, and by locating the phase boundary for this region at 93/7 Ace/H₂O.

Comparing the ternaries at 25, 45, and 65 °C, note how the right-hand phase boundary of the LL region extends to higher water concentrations with increasing temperature, as the SL region “retreats”. However, the one-phase L region to the left of the LL region also moves to higher water concentrations with temperature; thus, the net area of LL region where ALPHA can be practiced does not appreciably change with temperature. However, the solvent mixtures that can be used for ALPHA do become “greener” with increasing temperature; for example, at 65 °C ALPHA can be practiced with a 20/80 Ace/H₂O solvent mixture (see Figure 3).

For the LL region where ALPHA can be practiced, feed solvent compositions (Ace/H₂O wt/wt), S/L ratios, and average phase compositions for each component/pseudocomponent (wt %) are tabulated for each temperature in Table 1. Mass balance closure for the lignin and water (feed vs the sum of the two phases) averaged better than 4%. On the basis of an error analysis incorporating the uncertainties in mass-balance closure, component compositions, and temperatures, the reported phase compositions are estimated to be accurate to

within 5% relative error for the minor component (acetone) in the lignin-rich phase and to within 6% relative error for the minor component (lignin) in the solvent-rich phase.

This LL region exhibits several interesting characteristics. First, selectivities for the partitioning of acetone and water between the LR and SR phases are relatively low, that is, close to 1, with $\beta_{\text{Ace-H}_2\text{O}}$ averaging 1.13, 1.27, and 1.50 at 25, 45, and 65 °C, respectively. Thus, the slopes of the feed lines and tie lines do not differ significantly. It is instructive to note that Flory–Huggins (F–H) theory can be used to predict this phase behavior. In particular, for the polymer (3)–solvent (2)–nonsolvent (1) model ternary system (analogous to lignin–acetone–water), Flory²⁰ proved that if the non-solvent–polymer and solvent–polymer interactions are identical (i.e., if $\chi_{13} = \chi_{23}$), and the solvent–nonsolvent interactions χ_{12} are equal to zero (i.e., the case for an ideal solution), then the tie lines and feed lines are parallel for such a ternary system (i.e., in other words, $\beta_{\text{Ace-H}_2\text{O}} = 1.0$). Per Flory, in this situation the mixed solvent behaves as a single solvent, and the so-called “single-liquid approximation” applies. To some extent, then, it appears that our acetone–water system behaves in this manner in the presence of lignin.

Another interesting feature of our phase diagrams is the prominent maximum on the lignin-rich side of the binodal curve. McHugh and co-workers²¹ showed that this behavior can also be predicted with F–H theory by having the nonsolvent–solvent parameter χ_{12} take on negative values (instead of zero as above). Negative values of χ_{12} indicate a high degree of affinity between the two solvent components, with the sharpness of the maximum increasing as χ_{12} becomes more negative. In summary, then, both our LLE work and the work of others in dissolving solid lignin into acetone/water mixtures^{9–12} indicate this kind of synergistic interaction between the acetone and water, as the best lignin solubilities have been observed for mixtures of acetone with water—and not with pure acetone.

3.2. Mass Distributions, Molecular Weight, and Metal Content of Lignins. The mass distribution of lignin between the LR and SR phases for the measured tie lines as a function of the feed solvent composition (calculated from the mass of lignin in each phase per Section 2.2) is given in Figure 4. Here

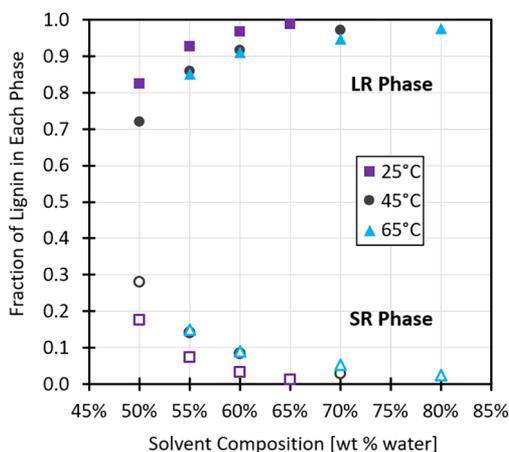


Figure 4. Mass distribution of lignin between the lignin-rich (LR) and solvent-rich (SR) phases at 25, 45, and 65 °C. Solvent compositions are nominal, as they do not include the water present in the feed lignin.

we see that a maximum of ~30% of the feed lignin can be dissolved into the SR phase (and 70% of the lignin forms the solvated, LR liquid phase) at a nominal solvent concentration of 50/50 Ace/H₂O. SR phases containing more lignin/LR phases containing less lignin were observed at higher Ace/H₂O ratios within 2–3 wt % of the measured data point on the L–LL phase boundary (see Figures 1–3), but the SR and LR phase densities were too similar to allow for clean phase separation and the measurement of tie lines and lignin mass distributions. (It appears that a S/L ratio of 3:1 gives an overall composition that is relatively close to the liquid–liquid critical point for this system). With increasing water content in the solvent, Figure 4 indicates that there is a steady decline in the lignin content of the SR phase.

Figure 5 illustrates how the acetone–water system can be used to partition the lignin by molecular weight (MW)

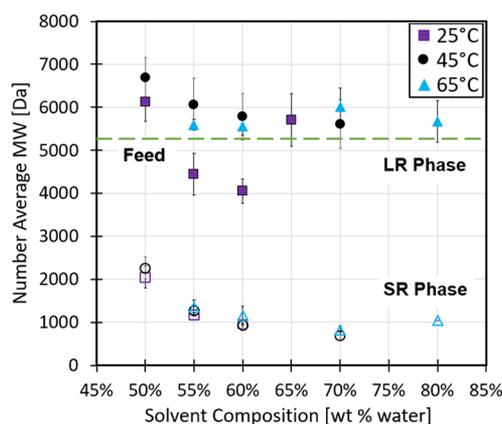


Figure 5. Distribution of lignin between the LR and SR phases by molecular weight (MW) at 25, 45, and 65 °C. The number average MW of the feed is 5270 Da. Solvent compositions are nominal.

between the LR and SR phases. Although the scatter in the data is less than desirable, it is clear that lignins of significantly lower MW than the feed can be isolated in the SR phase, and that lignins of significantly higher MW can be isolated in the LR phase. For example, for the tie line obtained with a nominal solvent composition of 50/50 Ace/H₂O and a lignin mass distribution of ~70/30 LR/SR (from Figure 4 above), this is clearly the case. On the other hand, if one’s focus is on isolating the lowest-MW portion of the lignin, then operating at 55/45 or 60/40 Ace/H₂O at 45 or 65 °C would be preferable, as lignins with MWs no greater than ~1000 are obtained in the SR phase at yields of 10–15%. Above 60/40 Ace/H₂O, yields in the SR phase drop significantly without commensurate drops in MW.

The sodium content in the LR phase for the measured tie lines is given in Figure 6 (~90% of the metals in Kraft lignin is sodium from the NaOH used in wood pulping). A significant decrease in the metal content compared to the feed was obtained at 45 and 65 °C, but the extraction of sodium into the SR phase was much less at 25 °C.

3.3. Comparison with Lignin–Acetic Acid–Water System. Comparison of the above results with our previous work with lignin–acetic acid–water⁸ reveal similarities, yet also important differences. Both systems exhibit the global phase behavior shown in Figure 7 and have a pronounced maximum in the binodal curve for the LR phase, which Flory–Huggins theory predicts will occur when the two solvents (here, organic

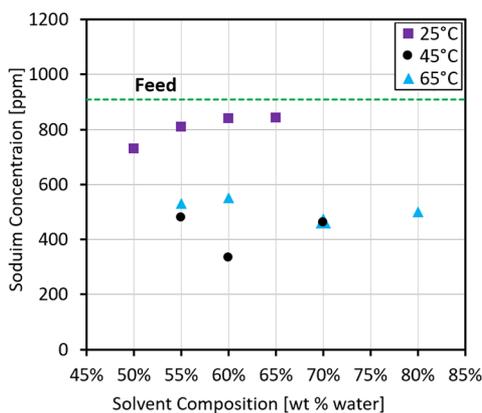


Figure 6. Sodium content of the LR phase at 25, 45, and 65 °C. Solvent compositions are nominal.

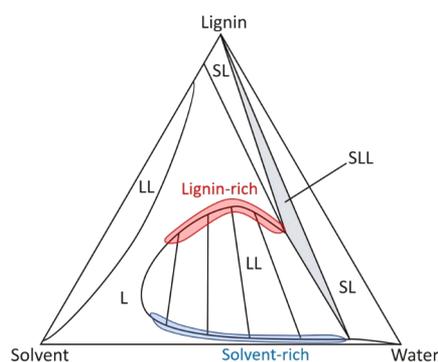


Figure 7. Global ternary phase behavior measured for L–Ace–W and L–AcOH–W systems. Reprinted with permission from ref 4. Copyright 2018 American Chemical Society.

and water) have an affinity for each other. However, with acetone, the one-phase L region is significantly larger, extending to 40–50 wt % water, whereas for acetic acid, the L–LL phase boundary begins at 28–35 wt % water for the temperatures investigated. As a result, with acetone the LL region where ALPHA can be practiced is smaller. Part of the reason for the above differences may be that with acetone, the S/L ratio was held at 3:1, while for AcOH it was 9:1. Selected additional tie-line and phase-boundary measurements for L–Ace–W and L–AcOH–W at the same S/L ratios (i.e., acetone at 9:1 and acetic acid at 3:1) would be useful in addressing this issue.

For both systems, the lignin isolated in the LR phase is significantly higher in MW than the lignin dissolved in the SR phase. However, with acetic acid the MW of the LR phase is more than double (i.e., ~15 000 vs 6700) than that obtained with acetone, even while holding key variables across the two systems (i.e., the water content of the solvent at ~50% and the SR/LR mass distribution at 30/70) constant. This result thus provides compelling evidence that condensation reactions are occurring in the LR phase for the L–AcOH–W system. Finally, with acetic acid, the SR phase preferentially extracts the metals from the feed lignin, so that the metals content in the LR phase is 0.5–1.0 order of magnitude less than that of the feed. With acetone, metals are reduced less effectively in the LR phase, that is, by no more than about 50%.

4. CONCLUSIONS

The ALPHA process for fractionating and purifying lignin can be practiced with the Ace–W system, as the required phase split into a LR and SR phase occurs. The overall global phase behavior for Ace–W with lignin is analogous to that observed for AcOH–W; nevertheless, significant differences exist between the two systems. First, the molecular weight of the lignin recovered in the LR phase is much lower for Ace–W, as no condensation reactions occur with the nonacidic acetone. Second, metal removal from the LR phase with Ace–W is less effective, with an aprotic ketone being used as the organic solvent. In summary, each solvent system exhibits characteristics for ALPHA that may be useful for a given lignin application. For example, for applications favoring higher-MW lignins and low impurities levels, such as carbon fibers,⁴ acetic acid–water would be a preferable ALPHA solvent for lignin. However, for applications where lower-MW lignins are preferred and high purity is not a key requirement, such as PF resins¹ or the feed to lignin depolymerization,³ acetone–water could be preferred.

AUTHOR INFORMATION

Corresponding Author

*Email: mcths@clemson.edu. Tel. +1-864-656-5424.

ORCID

Junhuan Ding: 0000-0003-1251-807X

Mark C. Thies: 0000-0002-2833-485X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under Grant IIP-1701128. The authors acknowledge Anne Mason for her assistance with the phase-composition measurements, Dr. Shannon Alford and the Agricultural Service Laboratory at Clemson for the metals analysis via ICP-AES, the Calhoun Honors College at Clemson for funding Sallye Gathmann and Spencer Temples through Departmental Honors Research Grants, and the Center for Advanced Engineering Fibers and Films at Clemson for equipment support. Last but not least, MCT thanks Chuck (and MEP) for instilling in him a life-long love of phase equilibria.

REFERENCES

- (1) Kalami, S.; Arefmanesh, M.; Master, E.; Nejad, M. Replacing 100% of phenol in phenolic adhesive formulations with lignin. *J. Appl. Polym. Sci.* **2017**, *134*, 45124.
- (2) Baroncini, E. A.; Kumar Yadav, S.; Palmese, G. R.; Stanzione, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *J. Appl. Polym. Sci.* **2016**, *133*, 44103.
- (3) Mahmood, N.; Yuan, Z.; Schmidt, J.; Xu, C. Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. *Renewable Sustainable Energy Rev.* **2016**, *60*, 317–329.
- (4) Jin, J.; Ding, J. H.; 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) 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.

(6) Klett, A. S.; Payne, M.; Thies, M. C. Continuous-Flow Process for the Purification and Fractionation of Alkali and Organosolv Lignins. *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 6689–6694.

(7) Thies, M. C.; Klett, A. S.; Bruce, D. A. Solvent and recovery process for lignin. U.S. Patent 10 053 482, Aug 21, 2018.

(8) 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.

(9) Domínguez-Robles, J.; Tamminen, T.; Liitiä, T.; Peresin, M. S.; Rodríguez, A.; Jääskeläinen, A.-S. Aqueous acetone fractionation of kraft, organosolv, and soda lignins. *Int. J. Biol. Macromol.* **2018**, *106*, 979–987.

(10) Jääskeläinen, A.-S.; Liitiä, T.; Mikkelsen, A.; Tamminen, T. Aqueous organic solvent fractionation as means to improve lignin homogeneity and purity. *Ind. Crops Prod.* **2017**, *103*, 51–58.

(11) Sadeghifar, H.; Wells, T.; Le, R. K.; Sadeghifar, F.; Yuan, J. S.; Ragauskas, A. J. Fractionation of Organosolv Lignin Using Acetone:–Water and Properties of the Obtained Fractions. *ACS Sustainable Chem. Eng.* **2017**, *5*, 580–587.

(12) Boeriu, C. G.; Fițișău, F. I.; Gosselink, R. J.A.; Frissen, A. E.; Stoutjesdijk, J.; Peter, F. Fractionation of five technical lignins by selective extraction in green solvents and characterization of isolate fractions. *Ind. Crops Prod.* **2014**, *62*, 481–490.

(13) Capello, C.; Fischer, U.; Hungerbühler, K. What is a green solvent? *Green Chem.* **2007**, *9*, 927–934.

(14) Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C. R.; Abou-Shehadeh, S.; Dunn, P. J. CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.* **2016**, *18*, 288–296.

(15) Yasuda, S.; Ito, N. Behavior of lignin in organic acid pulping. I. Reaction of arylglycerol- β -aryl ethers with acetic acid. *Mokuzai Gakkaishi* **1987**, *33* (9), 708–715.

(16) 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- β -aryl ethers in lignins with aqueous acetic acid containing H₂SO₄. *J. Wood Sci.* **1998**, *44*, 217–221.

(17) Lake, M. A.; Blackburn, J. C. Process for recovering lignin. U.S. Patent 9 260 464, Feb. 16, 2016.

(18) Velez, J.; Thies, M. C. Solvated liquid-lignin fractions from a Kraft black liquor. *Bioresour. Technol.* **2013**, *148*, 586–590.

(19) Yang, H.; Rasmuson, Å. C. Phase equilibrium and mechanisms of crystallization in liquid–liquid phase separating system. *Fluid Phase Equilib.* **2015**, *385*, 120–128.

(20) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1967; pp 548–554.

(21) Yilmaz, L.; McHugh, A. J. Analysis of nonsolvent–solvent–polymer phase diagrams and their relevance to membrane formation modeling. *J. Appl. Polym. Sci.* **1986**, *31* (4), 997–1018.