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Fractionating and Purifying Softwood Kraft Lignin with Aqueous Renewable Solvents: Liquid–Liquid Equilibrium for the Lignin–Ethanol–Water System

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Hot ethanol–water solutions can be used to simultaneously fractionate and purify softwood Kraft lignin through the Aqueous Lignin Purification with Hot Agents (ALPHA) process, using the regions of liquid–liquid equilibrium (LLE) that form at selected temperatures and solvent-to-lignin feed (S/F) ratios. Lignin, ethanol, and water compositions are measured for the solvent-rich (SR) and lignin-rich (LR) liquid phases in mutual equilibrium, as well as the lignin and metals mass distributions between the two phases. As depicted in quasi-ternary diagrams for clarity, both temperature and S/F ratio can be used to grow, merge, and even split the regions of LLE, giving significant control over both molecular weight (MW) and lignin purity. For example, a solvent comprising 45:55 EtOH/H_2O at 75 °C and an S/F ratio of 6:1 enables recovery of an ultrapure (95 % of Na removed), higher MW ($M_n = 8400$ Da) lignin fraction in the LR phase. On the other hand, 95:5 EtOH/H_2O at 45 °C and S/F = 3:1 enables recovery of an ultrapure, low MW (1500 Da) lignin in the SR phase.

Introduction

With the growing push for renewable and sustainable manufacturing, the under-utilization of lignin is becoming increasingly difficult to ignore. The value of lignocellulosic biomass as a feedstock is currently dominated by cellulose, the only component recovered in a pulp mill and the key component of interest in a bioethanol refinery. Unfortunately, over 99 % of the lignin generated in these facilities is not recovered, but is simply burned for its heating value.[1] However, if large-scale, higher-value applications for the lignin byproduct could be identified, the economic viability of biorefineries (for paper or ethanol) would be enhanced significantly. For example, as demonstrated in recent techno-economic analyses, the conversion of lignin into higher-value biochemicals[2,3] or its valorization into precursors for polymers and materials applications[4–6] can reduce the price of bioethanol from lignocellulosic biomass to well below the DOE goal[7] of $3/gallon gasoline equivalent. Nevertheless, lignin has thus far proven to be difficult to valorize. Two properties of lignin that need to be controlled, if lignin is to achieve its potential as a renewable biopolymer, are its purity and its molecular weight. For example, lignin suitable as a precursor for high-performance carbon fibers (e.g., for automotive structural applications) must have a metals content below 150–250 ppm metals to minimize fiber flaws,[8] and a molecular weight high enough to build fiber strength and modulus.[9] Furthermore, researchers have also shown that lignins enriched in chemical functionalities such as hydroxyl content can perform better in applications such as phenol-formaldehyde resins[4] and polyurethane foams.[10]

Thies and co-workers[11–13] have discovered that if selected renewable organic solvents that form homogeneous, one-phase mixtures with water, including acetic acid, acetone, or lower-molecular-weight alcohols, are combined with lignin at appropriate temperatures and compositions, two liquid phases with novel properties are created. The less dense, solvent-rich phase contains a lower molecular weight (MW) portion of the lignin, whereas the denser, lignin-rich phase has a higher MW portion. Furthermore, the solvent-rich (SR) phase tends to extract metal salts from the so-called "technical"[14] lignins, which can contain significant amounts of sodium, so that the lignin isolated in the lignin-rich (LR) phase is purified. The unique ability of these one-phase aqueous solvent systems to both purify and fractionate lignin forms the basis of a process that we refer to as Aqueous Lignin Purification using Hot Agents, or ALPHA. A key advantage of ALPHA is that the lignin is always in the liquid state; it is either dissolved in a solvent phase or solvated in a polymer-rich phase. Thus, the process can be operated continuously, which is a significant advantage for scale-up.

ALPHA operating conditions for mixtures of hot aqueous acetic acid with softwood Kraft lignin have been investigated, with liquid–liquid equilibrium (LLE) phase compositions and lignin mass distributions being determined.[12] Similar work has been undertaken for mixtures of hot aqueous acetone.[15] However, to date, no analogous work has been performed with ethanol, one of the greenest solvents of all.[16–18] The motiva-

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tion for investigating the use of hot ethanol–water solutions for fractionating and purifying the lignin recovered from a lignocellulosic bioethanol refinery is obvious. However, thus far, only phase-transition temperatures, at which the lignin–ethanol–water system passes from solid–liquid to liquid–liquid equilibrium upon heating, have been determined.[19] In this study, the LLE that exists for the lignin–ethanol–water system was investigated for a softwood Kraft lignin at two temperatures and solvent-to-lignin mass ratios. In addition, the mass distribution of both lignin and metal salts between the two liquid phases was determined. Such information could then be used to assess the viability of ethanol–water as an ALPHA solvent, enabling comparisons with those aqueous solvents (see above) that have already been investigated.

Although the pulping of whole biomass using organic solvents such as ethanol (called organosolv pulping)[20–23] is a highly researched area, previous work using ethanol–water solutions to fractionate and purify lignin is scarce. Jääskeläinen et al.[14] used an 80:20 ethanol/water solution at ambient temperatures and a solvent/lignin ratio of 10:1 (v/w) to dissolve up to 70% of a Kraft lignin; water was then added sequentially to create a final solution of 10:90 ethanol/water, precipitating out lignin fractions with each addition of water. For all steps, the lignin precipitated as a solid. Ethanol–water solutions can, of course, also be used for the organosolv pulping of biomass to make fuel-grade ethanol.[24] Here, the lignin is recovered as a separate phase, but is neither fractionated nor explicitly purified.

Results and Discussion

Quasi-ternary phase diagrams and liquid–liquid equilibrium phase compositions

Because lignin is not a pure component but is polydisperse, the phase behavior of the quasi-ternary lignin–ethanol–water system changes not only with temperature, but also with the mass ratio of solvent feed to lignin feed, commonly referred to as the solvent-to-feed (S/F) ratio. Thus, three phase diagrams (given as Figures 1, 2, and 3) were generated to elucidate the system phase behavior, using two temperatures (45 and 75 °C) and two S/F ratios (3:1 and 6:1). The liquid–liquid phase-equilibrium compositions and corresponding tie lines in the diagrams for the "Lignin-Rich Phase" and "Solvent-Rich Phase" are presented in Table 1 for 45 °C and a 3:1 S/F ratio, 45 °C and a 6:1 S/F ratio, and 75 °C and a 6:1 S/F ratio. The "Feed" compositions for each measured LLE tie line are also given in Table 1 in terms of the EtOH/H_2O mass ratio for the solvent and the S/F ratio.

Measurements for 45 °C and an S/F ratio of 3:1 are presented in Figure 1. The global phase behavior exhibited at these conditions is qualitatively similar to that previously observed by our group for the lignin–acetic acid–water[12] and lignin–acetone–water systems.[15] As before, there are two liquid–liquid (LL) equilibrium regions, a one-phase liquid (L) region in which lignin and the solvent system are completely miscible, and two regions of solid–liquid (SL) equilibrium, in which

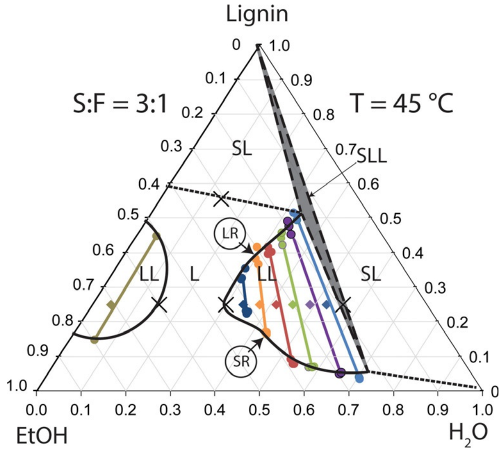

Figure 1. Quasi-ternary phase diagram for lignin–ethanol–water at 45 °C. In determining the two LL regions, the S/F ratio was held constant at 3:1. Circles (●) are phase compositions, diamonds (◆) are feed compositions, and Xs are phase transition points. Binodal/saturation LL curves for the solvent-rich (SR) and lignin-rich (LR) phases were generated by empirical fit.

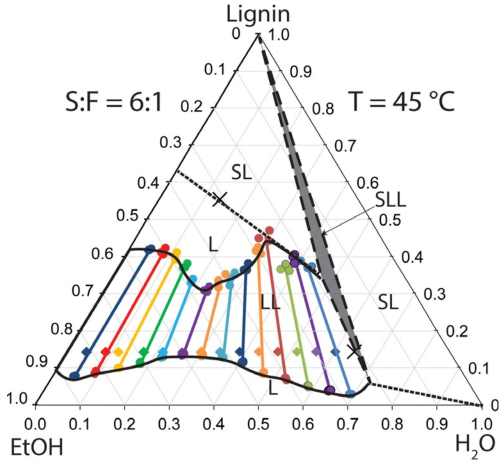

Figure 2. Quasi-ternary phase diagram for lignin–ethanol–water at 45 °C. In determining the LL region, the S/F ratio was held constant at 6:1. Legend and data-fitting information is given in the caption of Figure 1.

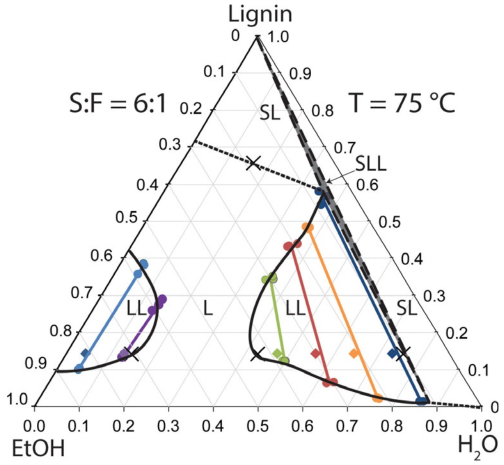

Figure 3. Quasi-ternary phase diagram for lignin–ethanol–water at 75 °C. In determining the LL region, the S/F ratio was held constant at 6:1. Legend and data-fitting information is given in the caption of Figure 1.

Table 1. Feed conditions and measured liquid–liquid equilibrium compositions and tie lines for the lignin–ethanol–water system at 45 and 75 °C.

Feed				Lignin-rich phase			Solvent-rich phase		
T [°C]	tie line [#]	EtOH/H_2O [wt/wt]	S/F [wt/wt]	water [wt %]	EtOH [wt %]	lignin [wt %]	water [wt %]	EtOH [wt %]	lignin [wt %]
45	1	30:70	3.00:1	32.91 ± 0.98	16.57 ± 0.40	50.52 ± 1.22	70.54 ± 0.23	25.72 ± 0.06	3.74 ± 0.23
45	2	35:65	3.00:1	33.23 ± 1.39	19.62 ± 0.50	47.15 ± 1.89	65.78 ± 0.15	29.36 ± 0.34	4.86 ± 0.24
45	3	40:60	3.00:1	33.05 ± 1.03	22.98 ± 0.78	43.97 ± 1.79	58.37 ± 0.63	34.83 ± 0.71	6.80 ± 0.09
45	4	45:55	3.00:1	31.95 ± 0.77	27.57 ± 0.62	40.48 ± 1.08	53.18 ± 0.77	38.47 ± 0.22	8.35 ± 0.78
45	5	50:50	3.00:1	29.99 ± 1.35	31.16 ± 1.27	38.84 ± 2.55	43.06 ± 0.26	40.15 ± 0.16	16.78 ± 0.25
45	6	55:45	2.99:1	29.48 ± 0.37	37.06 ± 1.32	33.46 ± 1.69	35.71 ± 0.28	41.42 ± 0.33	22.86 ± 0.42
45	7	95:5	3.01:1	3.70 ± 0.02	48.21 ± 1.35	48.08 ± 1.38	4.39 ± 0.15	82.49 ± 0.27	13.11 ± 0.22
45	1	30:70	6.00:1	41.99 ± 1.75	20.90 ± 0.24	37.11 ± 1.59	69.21 ± 0.16	27.98 ± 0.38	2.81 ± 0.24
45	2	35:65	5.99:1	38.49 ± 0.66	22.80 ± 0.37	38.71 ± 1.01	64.23 ± 0.23	32.37 ± 0.31	3.40 ± 0.09
45	3	40:60	6.00:1	37.62 ± 1.04	26.25 ± 0.34	36.12 ± 0.95	58.68 ± 0.11	36.55 ± 0.11	4.76 ± 0.09
45	4	45:55	6.00:1	28.90 ± 1.34	27.36 ± 1.24	43.74 ± 1.47	52.53 ± 0.32	40.68 ± 0.20	6.79 ± 0.40
45	5	50:50	6.00:1	29.15 ± 0.91	29.47 ± 0.52	41.37 ± 1.19	46.68 ± 0.08	44.79 ± 0.33	8.53 ± 0.33
45	6	55:45	6.00:1	28.71 ± 0.37	35.15 ± 0.67	36.14 ± 0.39	40.61 ± 0.19	47.95 ± 0.14	11.44 ± 0.10
45	7	60:40	5.99:1	27.07 ± 0.41	39.02 ± 1.41	33.91 ± 1.71	35.65 ± 0.21	51.57 ± 0.13	12.78 ± 0.08
45	8	65:35	6.00:1	24.91 ± 0.52	41.67 ± 1.76	33.42 ± 1.77	30.76 ± 0.09	55.97 ± 0.20	13.28 ± 0.15
45	9	70:30	6.00:1	22.99 ± 0.43	46.14 ± 0.60	30.87 ± 0.55	26.37 ± 0.13	60.19 ± 0.26	13.44 ± 0.19
45	10	75:25	6.00:1	18.48 ± 0.05	48.09 ± 0.57	33.44 ± 0.55	22.06 ± 0.22	65.07 ± 0.32	12.88 ± 0.10
45	11	80:20	6.00:1	14.91 ± 0.25	47.72 ± 0.78	37.37 ± 0.58	17.96 ± 0.17	70.95 ± 0.09	11.09 ± 0.21
45	12	85:15	5.99:1	11.43 ± 0.34	48.49 ± 0.67	40.08 ± 1.00	13.74 ± 0.18	76.39 ± 0.24	9.86 ± 0.07
45	13	90:10	6.00:1	8.13 ± 0.44	50.62 ± 0.88	41.25 ± 0.91	9.20 ± 0.06	82.06 ± 0.36	8.74 ± 0.34
45	14	95:5	6.00:1	4.77 ± 0.20	53.47 ± 0.45	41.76 ± 0.26	4.98 ± 0.24	87.43 ± 0.40	7.59 ± 0.16
75	1	15:85	6.00:1	36.17 ± 1.41	7.42 ± 1.29	56.41 ± 1.84	85.77 ± 0.45	12.80 ± 0.48	1.43 ± 0.04
75	2	25:75	6.00:1	37.03 ± 0.46	14.65 ± 0.41	48.32 ± 0.26	75.62 ± 0.35	22.00 ± 0.29	2.38 ± 0.07
75	3	35:65	6.00:1	35.68 ± 1.00	20.78 ± 1.40	43.54 ± 0.41	62.66 ± 0.82	30.78 ± 0.86	6.56 ± 0.06
75	4	45:55	5.99:1	35.57 ± 0.79	29.89 ± 1.15	34.54 ± 0.57	49.80 ± 0.34	37.93 ± 0.33	12.27 ± 0.04
75	5	85:15	6.00:1	14.04 ± 0.42	58.62 ± 1.90	27.34 ± 1.53	13.11 ± 0.12	73.14 ± 0.45	13.75 ± 0.33
75	6	95:5	6.00:1	5.30 ± 0.17	57.15 ± 1.54	37.55 ± 1.52	4.91 ± 0.07	84.85 ± 0.23	10.24 ± 0.31

lignin exists as a solid phase. A three-phase SLL region separates the two SL regions.

Equilibrium phase compositions were measured only for the lignin-rich (LR) and solvent-rich (SR) phases in the LL regions, with all but one tie line being obtained in the larger LL region in which the ALPHA process is generally practiced.[6,25] These phase compositions were measured in triplicate, and, as seen from the degree of overlap between the compositions in Figure 1 and by the standard deviations reported in Table 1, the data exhibit good reproducibility. End points (not shown) for the equilibrium tie lines (shown in color) were calculated by averaging the triplicates obtained for each phase. The overall feed compositions (shown as colored diamonds) are also shown in Figure 1. A small amount of ethanol volatilizes from the initial feed during experiments, so the diamonds are displaced slightly to the left of the tie lines. Phase transitions from each of the LL regions to a single L phase, measured at an S/F feed ratio of 3:1, are shown as "X"s. The phase boundary on the right-hand side of the larger LL region (denoted with an X) was determined by decreasing the EtOH/H_2O ratio until a solid lignin phase was observed.

The three-phase SLL region (bounded by dashed lines) was difficult to observe, but must exist as a consequence of the adjoining LL and SL regions according to the Gibbs Phase Rule. The SL region to the right of the larger LL region is bounded by both the SLL region and by the lignin and water apexes. Its solvent-rich binodal curve was assumed to be a straight line (shown here as dotted) connecting the two endpoints of the curve. One endpoint must be essentially at the water apex (because the solubility of lignin in water is nil); the other endpoint must be where the water-rich SLL apex and the solvent-rich LL binodal curve meet, according to the Gibbs Phase Rule. The location of this endpoint could be estimated with reasonable certainty, as both the onset of solid lignin (i.e., the X at 25% lignin and 25:75 EtOH/H_2O) and the last SR tie-line endpoint were measured. For the second, EtOH-rich SL region, its binodal curve on the lignin-rich side (i.e., the other dotted line) was estimated from a single measurement: by adding pure EtOH to lignin having a residual water content of 19.7 wt% until the SL mixture transitioned to a single liquid (L) phase, as delineated by the X on the diagram at approximately 56% lignin.

In previous phase-behavior work with the lignin–acetic acid–water and lignin–acetone–water systems,[12,15] the effect of temperature on phase behavior was studied, but not the effect of S/F ratio. (For acetic acid, the effect of S/F ratio on only a single tie line was investigated, and for acetone none were studied.) For both ternary and higher-component systems, the S/F ratio plays an important role in the economic feasibility of any extraction process. However, if the solute is a polymer such as lignin with a broad molecular weight distribution (MWD), changes in S/F can also affect the system phase behavior.[26] Thus, for this study, a second phase diagram was generated at the same temperature as Figure 1, but with an increase in the S/F ratio from 3:1 to 6:1.

As seen in Figure 2, the effect of this change was dramatic. Instead of having two separate LL phase envelopes interrupted by a single-phase L region, we now have one large LL region that extends from a solvent composition of 30:70 EtOH/H_2O (wt/wt) to essentially pure ethanol. One can visualize how the two LL regions in Figure 1 "grow" and then merge with one another as the S/F ratio is increased from 3:1 to 6:1. In addition, note how each binodal curve changes significantly in shape with increasing S/F ratio, developing maxima and minima. This has the potential to affect the choice of ALPHA processing conditions, either in a positive or negative manner. For example, for an S/F ratio of 3:1 (Figure 1), one would want to operate the ALPHA process near an overall solvent composition of 30:70 EtOH/H_2O if the goal was to maximize the lignin content in the LR phase (i.e., at 51%). In general, these higher lignin contents are more appropriate for dry-spinning the LR phase into fibers.[6] In addition, the use of such a high-water solvent as the feed would indeed be quite "green".

On the other hand, operating ALPHA so near to the SLL region, in which lignin also exists as a solid, could be a concern if there were any unexpected perturbations in operating conditions. Therefore, one might prefer to operate ALPHA at an S/F ratio of 6:1 (Figure 2) at the maximum in the binodal curve for the LR phase. More feed solvent would be required, and it would be less "green", comprising 45:55 EtOH/H_2O. Furthermore, the lignin content in the LR phase would be lower at 44%. However, the process would be more robust, with any perturbations having a minimal impact on the composition of the LR product. (We remind the reader that the seemingly adjacent EtOH-rich SL phase exists only at much lower S/F ratios than the LL regions of interest.) Analogous differences in operating conditions between S/F ratios of 3:1 and 6:1 can also be envisioned for the SR phase, in which the binodal curves are also monotonic at 3:1 but exhibit a maximum and minimum at 6:1.

Finally, the effect of increasing the temperature to 75 °C, while keeping the S/F ratio constant, was explored, as shown in Figure 3. Here, we see that a temperature increase can in essence "reverse" the phase-behavior change that occurs with an increase in S/F ratio: once again, as in Figure 1, there are two separate regions of LL equilibrium, with a one-phase L region between them. Additionally, at this increased temperature, LL behavior is possible with an even lower percentage of ethanol (i.e., 15%) in the feed solvent. From a scale-up standpoint, the possibility of using less ethanol by increasing the operating temperature allows even greater latitude in performing an economic assessment of ALPHA technology.

Looking at the overall trends exhibited in all three phase diagrams, the synergistic solvent power of the ethanol–water mixture is clearly exhibited: an approximately 70:30 EtOH/H_2O solvent feed is the most powerful, producing a homogeneous solution for the conditions in both Figures 1 and 3, and reducing the LL region in Figure 2 to its minimum composition range. Figure 2 also shows how the addition of *either* water *or* ethanol to the 70/30 mixture enlarges the LL region, thus reducing the ability of the solvent system to dissolve lignin. Thus, either component can act as the solvent or anti-solvent, depending on the solvent composition. In contrast, if ethanol and water were a classic solvent/anti-solvent pair, pure ethanol would dissolve the most lignin, and the addition of water to this solvent would decrease the amount of solubilized lignin monotonically.

These solvent/anti-solvent trends can be quantified by defining a sort of "pseudo" selectivity, $\beta_{\text{EtOH-H2O}}$, for ethanol with respect to water in the LR (Y) versus the SR (X) phase (see Figure 4), in which $\beta_{\text{EtOH-H2O}} \equiv (Y_{\text{EtOH}}/X_{\text{EtOH}})/(Y_{\text{H2O}}/X_{\text{H2O}})$.[27] Note that for $\beta > 1$, ethanol has a propensity for the LR phase (and thus for lignin vs. H_2O), whereas for $\beta < 1$, it is the water that has the propensity for lignin.

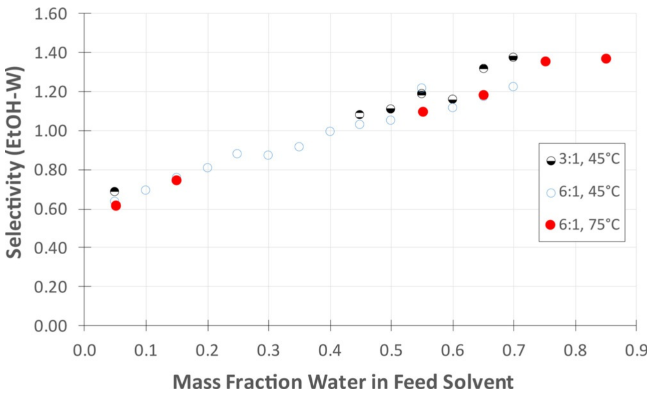

Figure 4. "Selectivity" of ethanol vs. water for the lignin-rich phase vs. the solvent-rich phase. All investigated S/F ratios and temperatures are shown (see legend).

Fractionation of lignin by molecular weight

Historically, progressive precipitation of a polymer from a solvent through addition of an anti-solvent (also called nonsolvent[26]) has been used to isolate solid polymer fractions from homogenous polymer solutions.[28,29] However, ALPHA "precipitates" out the polymer as a polymer-rich *liquid,* which has been shown to be advantageous in terms of both processing and product purity.[25] Because lignin is an inherently polydisperse material, containing chains of varying length and structure, the chains will have different solubilities depending on the solvent system being used. This effect of solvent system has already been observed for the fractionation of lignin through ALPHA with hot aqueous solutions of acetic acid[12] or acetone,[15] with acetone being more effective for isolating lower MW and acetic acid for isolating higher MW lignins.

As shown in Figure 5, the liquid–liquid equilibrium behavior explored in Figures 1–3 can be exploited to fractionate the lignin by molecular weight, with both the S/F ratio and the feed solvent composition being key controlling variables. Although the degree of separation depends on the operating conditions, in every case the lignin-rich (LR) phase generated a higher number average molecular weight (M_n) lignin fraction, and the solvent-rich (SR) phase a lower M_n, relative both to each other and to the feed lignin ($M_n = 4700$). In fact, molecular weights as high as 16000 were obtained with the LR phase and as low as 1500 for the SR phase, an order-of-magnitude

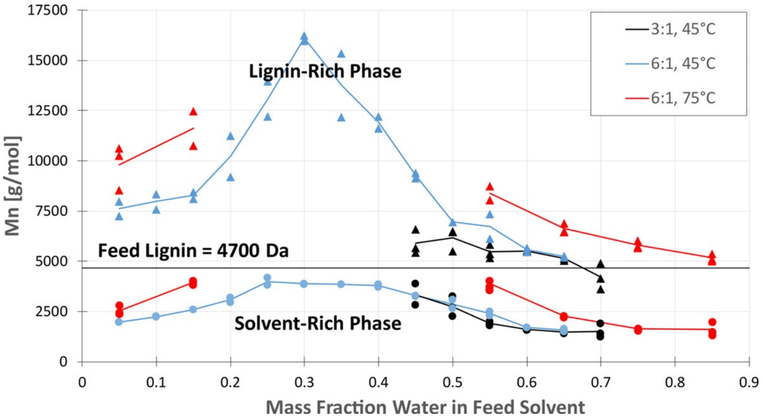

Figure 5. Number average molecular weight (M_n) of the lignin in the LR (△) and SR (●) phases with S/F ratios of 3:1 at 45 °C (see Figure 1), 6:1 at 45 °C (Figure 2), and 6:1 at 75 °C (Figure 3).

difference. The greatest degree of MW separation was obtained at conditions of 6:1 and 45 °C, at which LL equilibrium existed over all solvent feed compositions, see Figure 2. In contrast, at 3:1 and 45 °C, no higher MW fractions were obtained.

On the other hand, the *solubility* of lignin in the EtOH/H_2O system is maximized at an S/F ratio of 3:1. For example, at the S/F ratio of 6:1 and feed solvent composition of 60:40 EtOH/H_2O, the system exhibits LLE (see Figure 2). However, if sufficient lignin is added to decrease the S/F ratio to 3:1, the system is on the LL-L phase boundary and on the verge of becoming a homogenous, one-phase liquid (see Figure 1). This phenomenon occurs because with the addition of polymer, the SR phase can better solubilize the higher MW lignin chains. However, the M_n data in Figure 5 show that the increased solubility at 3:1 comes at a price, as the LR phase indiscriminately pulls in smaller lignin chains, so that M_n never exceeds 6200 for the LR phase.

The fraction of feed lignin that is distributed into each phase (i.e., the lignin yield for each phase) is given in Figure 6. Taken together, Figures 5 and 6 illustrate the general strategy of selecting appropriate operating conditions for the ALPHA process. For example, assume that one wishes to isolate a higher MW lignin fraction (e.g., for carbon fibers[6]); in that case, a mixture of 70:30 EtOH/H_2O at S/F = 6:1 and 45 °C will give the highest MW lignin (M_n = 16 000) at a lignin yield of approximately 15 % (Figure 6) in the LR phase. On the other hand, for an application for which a lower MW lignin at higher yields would be preferred (e.g., for resins or foams[4,10]), a 40:60 EtOH/H_2O solvent system at S/F = 6:1 and 45 °C would give a lignin yield of 20 % in the SR phase, and keep M_n below 2000.

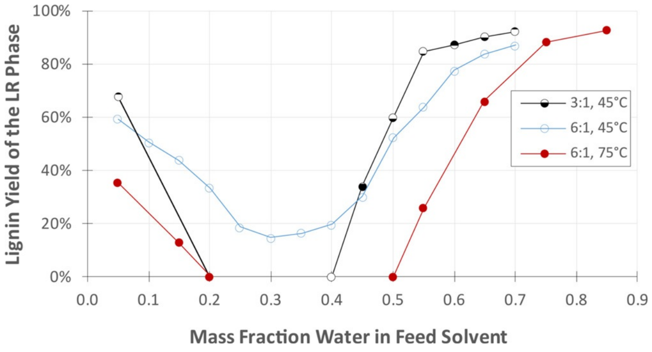

Figure 6. The mass fraction of feed lignin (i.e., yield) that distributes into the LR and SR phases can be controlled with solvent (EtOH/water) composition, S/F ratio, and/or temperature.

Metals removal from lignin

In addition to fractionation by molecular weight, a key advantage of the ALPHA process is the ability to remove metals from lignin.[11,25] As with other ALPHA solvents,[12,15] ethanol–water solutions have also been found to be effective for metals removal. The dominant metals impurity (by a factor of ≈10) is sodium, which originates from the use of NaOH in alkaline pretreatment or pulping processes, including Kraft; our lignin source contained 5700 ppm Na (on a dry basis). The concentration of sodium in each equilibrated (i.e., lignin + EtOH + H_2O) LR and SR phase, for the conditions investigated in Figures 1–3, is plotted as a function of feed solvent composition in Figure 7. Note that these Na ppm levels are on a "wet" basis; normally, the metals contents of lignins are given on a dry basis. However, here we wanted to obtain a more fundamental understanding of how the metals-removal process occurs during ALPHA.

Note that the results in Figure 7 can be divided into two regions: one greater than and one less than 0.40 mass fraction water. Roughly at the intersection of these two regions are the one-phase L regions in Figures 1 and 3 and the narrowest part of the LL region in Figure 2. A mass fraction of water greater than 0.40 corresponds to the LL region in which ALPHA has been practiced previously; below 0.40 mass fraction corresponds to the smaller, solvent-rich LL region in Figures 1 and 3, which to date has not been studied as much, partly because of its smaller size. For the mass fraction region above 0.40, the distribution of Na between the SR and LR phase ranges from 1.5 to 2.0 for the S/F ratio of 6:1. Although such a distribution

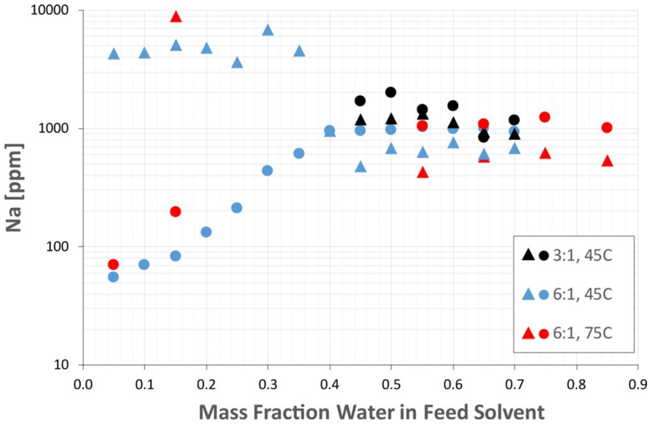

Figure 7. Sodium content in the solvent-rich (●) and lignin-rich (△) phases can be manipulated by changes in solvent mixture (EtOH/H_2O) composition, S/F ratio, and/or temperature.

Table 2. Percentage of feed lignin (yield) and Na content (on a wet basis) in the equilibrated LR and SR phases

Feed				Lignin-rich phase			Solvent-rich phase		
T [°C]	tie line [#]	$EtOH/H_2O$ [wt/wt]	S/F [wt/wt]	lignin yield [%]	Na [ppm]	M_n [$g\,mol^{-1}$]	lignin yield [%]	Na [ppm]	M_n [$g\,mol^{-1}$]
45	1	30:70	3.00:1	92.0	914	4233	8.0	1184	1519
45	2	35:65	3.00:1	90.2	933	5157	9.8	843	1490
45	3	40:60	3.00:1	87.2	1125	5519	12.8	1569	1607
45	4	45:55	3.00:1	84.6	1341	5468	15.4	1446	1891
45	5	50:50	3.00:1	60.0	1228	6151	40.0	2031	2744
45	6	55:45	2.99:1	34.0	1187	5903	66.0	1720	3333
45	7	95:5	3.01:1	67.7	2574.9	N/A	32.3	38.7	N/A
45	8	30:70	6.00:1	86.9	685	N/A	13.1	937	N/A
45	9	35:65	5.99:1	83.7	611	5240	16.4	1008	1574
45	10	40:60	6.00:1	77.5	771	5584	22.5	999	1700
45	11	45:55	6.00:1	63.6	636	6742	36.4	1023	2412
45	12	50:50	6.00:1	52.3	687	6964	47.7	979	2872
45	13	55:45	6.00:1	30.1	479	9277	69.9	965	3291
45	14	60:40	5.99:1	19.5	960	11914	80.5	950	3799
45	15	65:35	6.00:1	16.4	4596	13758	83.6	619	3868
45	16	70:30	6.00:1	14.6	6916	16103	85.4	437	3874
45	17	75:25	6.00:1	18.5	3682	13084	81.5	212	4001
45	18	80:20	6.00:1	33.3	4866	10236	66.7	134	3082
45	19	85:15	5.99:1	43.8	5093	8278	56.2	84	2607
45	20	90:10	6.00:1	50.4	4390	7975	49.6	70	2243
45	21	95:5	6.00:1	59.1	4331	7623	40.9	55	1983
75	22	15:85	6.00:1	92.6	542	5168	7.4	1020	1604
75	23	25:75	6.00:1	88.3	630	5814	11.7	1237	1624
75	24	35:65	6.00:1	66.1	584	6621	33.9	1086	2258
75	25	45:55	5.99:1	25.7	429	8388	74.3	1051	3881
75	26	85:15	6.00:1	12.8	8985	13306	87.2	198	3957
75	27	95:5	6.00:1	35.2	4347	9812	64.8	71	2545

is on the low side for traditional extraction processes, and thus, seems unimpressive at first glance, it can in fact be used to reduce Na levels by a factor of five to ten in the LR phase for each equilibrium stage. Several factors are at play to lead to this result: first, the lignin is present at a much higher wt% in the LR compared with the SR phase (see Table 1 and Figures 1–3); this reduces the Na content in the LR phase per unit of (dry) lignin. Second, the yield of lignin in the LR phase is generally higher than for the SR phase (see Figure 6), and if this is not the case, the selectivity of Na for the SR phase tends to be higher, compensating for the lower yield. The overall result of these synergistic effects are Na recoveries for the SR phase that average over 80% and can exceed 90% for each equilibrium stage. In summary, for feed solvent compositions with a mass fraction of water above 0.40, the ALPHA process can reduce ionic impurities for the LR phase, which concentrates the higher MW molecules in a given feed lignin to very low levels (e.g., <100 ppm) in two to three stages.

Of particular interest in this work, as it has not been investigated previously, is the Na distribution between the LL phases if a mass fraction of water of less than 0.40 is used as the feed solvent. As seen in Figure 7, in this LL region, the SR phase contains monotonically decreasing amounts of sodium with increasing ethanol content, until it approaches extraordinarily low Na levels, but still contains a nontrivial amount of lignin (see Figure 6). For example, as shown in Table 2 for tie lines 19–21, the SR phase contains more than 40% of the feed lignin, but also contains less than 100 ppm sodium. More than 90% of the feed sodium is recovered in the LR phase for these tie lines. We hypothesize that the unusually high selectivity of the LR phase for sodium occurs because the SR phase contains insufficient amounts of water (see Table 1). Thus, lignin is able to dissolve into the SR phase without bringing sodium with it. Such behavior can be exploited to isolate lower MW lignin fractions efficiently with very low levels of metallic impurities in two to three stages.

Conclusions

The global phase behavior for a softwood Kraft lignin with hot ethanol–water solutions has been elucidated. Regions of liquid–liquid equilibrium (LLE) have been identified in which lignin can be simultaneously fractionated and cleaned through the ALPHA process. Both temperature and solvent-to-feed (S/F) ratio can be used to manipulate the phase behavior. For example, with increasing S/F ratio, the two LL regions grow and merge to form a single LL phase. However, the process can be reversed with increasing temperature, which splits the single LL region to re-form two separate LL phases. The solvent synergism discovered previously by our group to exist between water and the renewable solvents acetic acid and acetone continues to be present for mixtures of water with ethanol, the most common renewable solvent. For example, a 70:30 wt/wt $EtOH/H_2O$ solution is the most powerful solvent for lignin, completely dissolving 25 wt% lignin at 45 °C. However, if either water or ethanol is added to this single-phase liquid mixture (e.g., to make an 80:20 or 60:40 $EtOH/H_2O$ solvent mixture), its solvent power is weakened, and the system splits into two liquid phases.

Although the ALPHA process has generally been practiced in the larger LL region, in which ultraclean, higher MW lignins can be isolated, this study demonstrates that order-of-magnitude metals reductions per equilibrium stage can also be obtained in the smaller LL region closer to the EtOH apex, so that ultraclean, lower MW lignins can be isolated. Therefore, we now have methods for the efficient recovery of ultraclean lignins of both low and high molecular weights for materials applications.

Experimental Section

Materials

A softwood Kraft lignin supplied by Domtar Corp. was used for the phase-behavior experiments; it is available commercially under the Biochoice® label and is sold as a low-ash, low-sulfur lignin recovered from a single species of Southern Pine. Because lignin is highly hygroscopic, it had to be dried from its initial, as-received water content of 25–35 % down to the desired 11–15 %. This was accomplished by first reducing the particle size of the (solid) lignin with a mortar and pestle, and then allowing it to dry in the air flow of a chemical hood. The water content of the lignin was determined by dissolving it in anhydrous pyridine ($>$99.8 % pure) at 90:10 w/w pyridine/lignin, and analyzing the resulting solution through Karl Fischer Titration. For the Karl Fischer Autotitrator (Mettler Toledo V20 volumetric KF Titrator), Hydranal$^{\text{TM}}$ Composite 5 k and Hydranal$^{\text{TM}}$ Methanol Rapid were used as the titrant and solvent system, respectively. For GPC analysis, HPLC-grade *N*,*N*-dimethylformamide ($\geq$99.7 % pure, Alfa Aesar) with the additive lithium bromide (99.9 % LiBr, ultra-dry, Alfa Aesar) was used as the mobile phase. All of the above chemicals were purchased from Fischer Scientific. Deionized water (resistivity $>$18.2 MΩ cm) was produced in-house using a Culligan Carbon Initial Regeneration and LTOC (low total organic carbon) mixed-bed deionization system to produce Type 2 water, followed by a Milli-Q Reference System (Millipore Z00QSV0WW) to produce Type 1 water.

Phase-behavior measurements

Phase-behavior measurements for lignin–ethanol–water mixtures were performed in 9.5-dram ($\approx$35 mL) glass vials (VWR part no. 66012-066) charged with lignin (dried down to a known water content) and an ethanol–water stock solvent solution, with the amount of ethanol in the solution varying from 30 to 95 wt %. Depending on the S/F ratio under investigation (3:1 or 6:1), (solid) lignin (either 1 or 2 g) on a dry basis was added to a stock solution ($\approx$6 g). These stock solutions were prepared accounting for the extra water in the dried lignin. A magnetic stirrer bar was then added to the sample vial to ensure adequate mixing and thus facilitate the formation of equilibrated phases. The vials were sealed with polypropylene open-top screw caps fitted with septa (PTFE/silicone; Wheaton part no. W240846, Size 24–400), to allow insertion of a K-type, 1/16th-inch, grounded thermocouple (Omega cat. no. CASS-116G-12) into the vial through a 21-gauge air-tight septum hole. The thermocouple was calibrated to within 0.2 °C using the boiling point and freezing point of water. The temperature of the vial was maintained with an oil bath (Dow Corning 200 silicone heat transfer fluid, A Dimethylpolysiloxane), using a 200 W immersion heater (Glo Quartz Electric, LHP200) controlled by an OMEGA Series CN370 controller.

For a typical experiment, a vial prepared as described above was inserted into a preheated oil bath, with the contents stirred continuously at $\approx$350 rpm and the liquid level in the vial kept at least 4 cm below that of the oil bath. The internal temperature of the vial reached the setpoint within 5 min and was maintained to within $\pm$0.2 °C for the course of the experiment. During this heat-up period, the system would pass through the solid–liquid to liquid–liquid (S-L to L-L) phase-transition temperature for lignin in the presence of ethanol–water solutions. As the contents of the vial were heated, the solid lignin particles swelled with solvent and deformed in response to the shear stress caused by stirring. After crossing the phase-transition temperature, the grains of lignin coalesced into a single liquid phase, falling to the bottom of the vial within seconds. An additional 15 min of continuous stirring was allowed for phase equilibration after the formation of two liquid phases had occurred. After stirring was terminated, a minute of settling was incorporated before the solvent-rich phase was decanted into another vial, retaining the more viscous, lignin-rich phase at the bottom of the original vial. For each overall feed composition investigated, sample vials were generated in triplicate. Previous work by Ding et al.[12] has established that 15 min continuous stirring and 1 min settling are adequate for equilibrium compositions in each phase to be achieved.

Determination of composition

The separated solvent-rich (SR) and lignin-rich (LR) phases were then each homogenized with the addition of acetone (2–6 g), depending on the overall solvent composition (if too much acetone was added relative to the water content, solid lignin would precipitate). Next, each homogenous solution was titrated in duplicate for water content by Karl Fischer titration, with duplicates agreeing on average to within 0.1 wt % absolute water content. With the water content known, the lignin content was then determined by first drying the samples overnight to a solid in a fume hood under excess air flow, and then driving off any residual liquid in a convection oven at 100 °C for 2 h. The remaining dry mass in a pan was recorded as the mass of lignin in the given phase. The mass of ethanol in each phase was then found by difference, as the total mass, the mass of water, and the mass of lignin in each phase were all known.

Both component and overall mass balances were performed to check the validity of the above measurements. In particular, the composition of each component in a given (SR or LR) phase was multiplied by the total mass of that phase to obtain the mass of each component present in a phase. The masses of each component in the SR and LR phases were then added together to obtain the expected mass of each component in the feed. The overall mass balance generally closed to within -0.5 % error, with none exceeding -2 % error. As expected, the overall mass balance error was negative in all cases, reflecting the small amount of solvent lost in the decanting step. The water mass balance generally agreed to within $+2$ %, except for samples containing low water percentages. Thus, for 95:5 and 90:10 EtOH/H_2O feed solvents (e.g., tie lines 21 and 20 in Table 2), mass balance errors for water approached $+15$ % and $+5$ %, respectively. The positive mass balance error is probably caused by a slight over-titration in the Karl Fischer method. The lignin mass balance error was less than $+2$ % in nearly all cases, with a tendency to be positive most, but not all, of the time. Because the ethanol measurements were performed by difference, error in this balance reflects its relative abundance and the errors of the mass balances addressed above. For nearly all samples, the ethanol balance agreed to within −2% error.

Molecular weight analysis

Gel permeation chromatography (GPC) was used to determine the molecular weight of the feed lignin and of the lignin distributing into both the LR and SR liquid phases. The procedure was to start with a lignin sample that had been air-dried in the fume hood as described above, but not dried under heat in the convection oven. This dried lignin (5 mg) was then finely ground and combined with dimethylformamide (DMF, 5.00 mL) containing the additive LiBr (0.05 м), a solution serving as the GPC mobile phase. This lignin/solvent mixture was first sonicated for ≈3 h to obtain complete dissolution, and was then passed through a 0.2 μm Teflon syringe filter (VWR 28145-291) to ensure that no solids were present. The filtered samples were then injected into the mobile phase of 0.05 м LiBr in DMF at a flow rate of 1.00 $\mathrm{mL\,min^{-1}}$, with the stationary phase consisting of a Waters Styragel HT 5 (WAT044214) followed by an Agilent PolarGel-L (PL1117-6830) column. The relative concentration of lignin as a function of elution time was monitored with a Waters 996 UV/Vis photodiode array detector at a wavelength of 280 nm. Molecular weight (MW) calibration was performed using polyethylene glycol (PEG) standards and a Waters Differential Refractometer. Traditionally, lignin GPC analysis is performed using tetrahydrofuran (THF) as the mobile phase in conjunction with polystyrene (PS) standards, with the lignin made soluble by acetylation.[30,31] However, previous work[11,31] has shown that the mobile phase of DMF w/ LiBr allows complete lignin solubility without the need for acetylation. PEG was chosen over traditional polystyrene (PS) for standards because our work has shown that PEG in DMF gives comparable MWs to PS in THF, whereas PS in DMF gives MWs an order of magnitude greater than PS in THF.

Metals analysis

Metals analysis of lignin samples was performed through inductively coupled plasma atomic emission spectroscopy (ICP-AES), using an Ametek Spectro Scientific spectrometer, model ARCOS. As the dominant metal was sodium, only its value was reported. (Potassium averaged about 10% of Na, and all other metals were present in trace amounts.) The Na mass balances closed on average to within 0.7%, with a standard deviation of 18.3%, a typical degree of uncertainty with application of ICP-AES to lignins. Before metals analysis, the samples were both air- and oven-dried as described above in the section "Determination of composition", as any residual water would be considered part of the lignin mass. Because at least 0.1 g sample is required by this lab for analysis, the triplicate samples of each phase were combined to ensure this threshold was met. Details of the ICP method used at ASL are given elsewhere.[15]

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Conflict of interest

The authors declare no conflict of interest.

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