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Recovering ultraclean lignins of controlled molecular weight from Kraft black-liquor lignins†

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By operating in a region of liquid–liquid equilibrium, hot acetic acid–water mixtures can be used to simultaneously clean, fractionate, and solvate Kraft black-liquor lignins. Lignin-rich liquid phases of controlled molecular weight with key metals contents reduced to <50 ppm are obtained without a washing step.

Lignin is one of the world's most abundant organic polymers, comprising about 30% of woody biomass on a dry basis. Only cellulose is more abundant. Commercial recovery of the vast majority of lignin is accomplished today in a pulp-and-paper mill, with the Kraft pulping process being dominant with 95% of the market.[1] In particular, during the pulping process the bonds that link lignin and cellulose in the plant cell wall are broken *via* a hot (170 °C) aqueous solution of sodium hydroxide and sodium sulfide, dissolving most of the lignin and freeing the cellulosic fibers from the wood matrix as a pulp that is then used to make paper.[2] The resulting solution forms a by-product stream known as black liquor, which represents a huge potential source of lignin (50 million tons per year[3]). Typically, this lignin-rich black liquor is burned for its heating value in a recovery boiler, as only about 0.2% of the lignin generated from pulp mills is recovered for nonfuel uses.[3] However, lignin potentially has far more value as a renewable biomaterial or biopolymer.[3,4]

Lignin is unique among renewable biopolymers in having significant aromatic character, making it attractive as a ''green'' replacement for petroleum-derived counterparts. Thus, several processes for recovering lignin from black liquor have been developed in recent years. Three that are either commercialized or in advanced development are LignoBoost™, LignoForce System™, and Sequential Liquid-Lignin Recovery and Purification, or SLRP™.[5–7] All are capable of generating lignins from Kraft black liquor (*i.e.*, ''Kraft lignins'') that are relatively low (1–3%) in ash and metals content (*e.g.*, 1500–7500 ppm sodium). Although such purities are suitable for lower-value applications (*e.g.*, phenolic resins, polyurethane foams, and clean-burning biofuels[8]), ''ultraclean'' lignins (*i.e.*, those with metals contents of <100 ppm Na) are required for higher-value applications of significant societal impact. For example, lignin precursors suitable for conversion into carbon fibers for structural automotive applications must be ultraclean, as metal impurities >100–200 ppm create flaws in the fibers upon carbonization, deleteriously affecting their properties.[9–11]

Lignins of low metals content can be obtained with organosolv processes,[12–14] where one starts with the original woody biomass (instead of black liquor), and an aqueous organic solvent (*e.g.*, a hot ethanol–water solution[12]) is used to carry out the pulping process. Because no inorganic pulping chemicals are used, the resulting lignin product has a low ash/metals content. However, companies that produce organosolv lignins have had difficulty competing[15] because the organosolv process is expensive.[8]

We have discovered that when Kraft lignins are combined with hot acetic acid–water mixtures at the appropriate conditions, two equilibrium liquid phases are formed, with the metal salts being extracted into the solvent-rich phase and an ultraclean, lignin-rich phase being obtained as the desired product. <50 ppm Na and <100 ppm total metals content in the isolated ''liquid-lignin'' phase is readily achieved, as the metal salts readily diffuse out of the lignin phase and into the solvent phase. Furthermore, the solvent composition can be ''tuned'' to partition the feed lignin between the solvent-rich and lignin-rich liquid phases according to molecular weight. Finally, the liquid-lignin phase is highly solvated, so that it has the potential to be immediately processed into useful products.

Kubo *et al.*[16] used acetic acid–water mixtures to fractionate lignins obtained from organosolv pulping. The work was carried out at ambient temperatures, so extractions were carried out in a region of solid–liquid equilibrium (SLE). There were no metals to extract in this organosolv lignin, but if this method was applied to a Kraft lignin, the insoluble solid lignin phase would have its original metals content. Lachenal *et al.*[17] used hot acetic acid–water mixtures to extract a residual lignin from pulp, but the pulp still contained unextracted lignin that was discarded untreated.

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No metals information was given. Other workers[18–21] used mixed organic and aqueous solvents at ambient temperatures to fractionate lignin in the SLE region, but did not report on any metals extraction. Zhang and Ogale[22] applied acid washing to Kraft lignin in preparation for carbon-fiber spinning, but even an impractical 25–30 washes with 1N HCl at a 10 : 1 acid : lignin ratio did not achieve the metals removal of our method. In summary, no other lignin treatment methods reported in the literature have exhibited the ability to simultaneously clean, fractionate, and solvate lignins without washing.

In this study, phase-transition temperatures from SLE to liquid–liquid equilibrium (LLE) were determined for the system Kraft lignin–acetic acid–water as a function of solvent composition. Once these phase boundaries were determined, we then measured the distribution of both lignin and metals between the solvent-rich and lignin-rich liquid phases as a function of solvent composition at various temperatures. Molecular weights of the lignin fractions distributed between the two phases were determined *via* gel permeation chromatography (GPC). Finally, a two-stage extraction was carried out to conceptually demonstrate the ranges of purity and molecular weight control attainable with our so-called Aqueous Lignin Purification with Hot Acids (ALPHA) process.

For the phase-transition measurements, specified mixtures of acetic acid (glacial, 99.7% purity), water (distilled and deionized), and lignin (softwood Kraft black-liquor lignin from SLRP process, Kappa no. 25, 80–100 mesh particle size, 1.2% ash, 1400 ppm Na, 690 ppm K + Ca, 2300 ppm total metals) were prepared in sealed, 20 mL, flat-bottom headspace vials (VWR Part No. 66064-348). The compositions of the solvent–lignin mixtures were chosen to cover solvent compositions ranging from pure acetic acid to pure water and solvent-to-lignin ratios from 2 to 9. The prepared vials were placed in a mineral oil bath, and a magnetic stir bar was added to the vials for temperature uniformity and to assist in observation of the phase transition. Continuous stirring of the vial contents was employed at 350 rpm. The temperature of the oil bath was then increased at a rate of 0.5 °C min^{-1} until a phase transition was observed as described below. The temperature in the sample vials was monitored with a Type K 1/32'' o.d. sheathed thermocouple inserted through the silicone septum and read with a digital thermometer. This thermocouple setup was checked against a calibrated secondary standard RTD (Burns Engineering) and is capable of measuring temperatures to within ±0.5 °C.

At ambient temperatures, solid lignin particles were observed in in the vial swirling around in the acetic acid–water ($AcOH/H_2O$) solution. At lower $AcOH/H_2O$ ratios (*e.g.*, 40/60 and lower), the solvent solution was clear, albeit with a tea-like color; at higher $AcOH/H_2O$ ratios (65/35 and above), the solution became darker and more difficult to see through, and a light source was required to see the particles. (The color of the solution was an indication of the extent to which the lignin was soluble in the solvent phase.) As the temperature approached to within ≈10 °C of the SLE to LLE phase-transition temperature, noticeable swelling of the solid particles was observed. This swelling continued to increase with temperature until the swollen particles began adhering to each other to form globules. As these globules continued to increase in size, they became so large that they, being denser than the solvent phase, could no longer be suspended in the solvent by the convective action of the stir bar and fell to the bottom of the vial, where they agglomerated to form a continuous, lignin-rich, liquid phase. The time from which the lignin globules were observed to begin falling from the solvent phase to their agglomeration to form a lignin-rich liquid phase was only ≈5 s. Photographs of the phase transition are given in the ESI† section as Fig. S1.

The temperature at which the globules fell from solution was recorded as the SLE-to-LLE phase transition. Duplicate measurements were taken, and the transition temperatures shown in Fig. 1 as a function of feed solvent composition are believed to be accurate to better than ±1.0 °C. Note that the phase-transition temperature is a strong function of solvent composition: for high $AcOH/H_2O$ ratios the region of LLE begins at temperatures as low as 30–40 °C, whereas at high water concentrations this region does not appear until 100 °C. The increase in temperature for the LLE region when glacial acetic acid is the solvent is not surprising, as the propensity of pure acetic acid to dimerize is well-known.[23] The wt percent lignin present in the starting solid–liquid mixture is also plotted in Fig. 1; here we see that the phase-transition temperature decreases with increasing lignin concentration.

To ensure that the observed transitions were temperature-induced *vs.* reaction-induced and/or a gel-forming phenomenon, the molecular weight of the lignin feedstock was compared to that of the lignin recovered in the lignin-rich phase immediately after the phase transition; no significant increase in the molecular weight was observed.

To determine the distribution of lignin and metals between the solvent-rich and lignin-rich phases in the region of LLE shown in Fig. 1, the experiments described above were carried out as before except with the following changes: The oil bath was preheated to the desired temperature in the LLE region above the SLE–LLE phase-transition temperature (*e.g.*, 70 °C for measurements up to 40/60 $AcOH/H_2O$). The prepared headspace

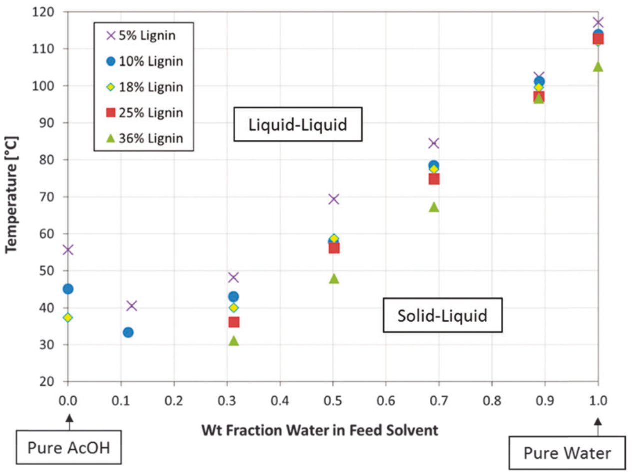

Fig. 1 Solid–liquid to liquid–liquid phase-transition temperatures for lignin in acetic acid–water mixtures at elevated temperatures.

vials were then inserted into the bath, and the desired LLE phase separation occurred within 5–10 min. The phases were then allowed to equilibrate for 15–20 min. Next, the solvent-rich phase was drawn off with a syringe and dried in a vacuum oven at ambient temperatures. The amount of lignin in that phase was determined gravimetrically, and the metals content of the dried lignin was analysed *via* inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Spectro Analytical Instruments spectrometer, model ARCOS. Molecular weight (mol wt) analysis of the dried lignin was performed by GPC, using a Waters Styragel HT4 column followed by an Agilent PolarGel-L column. DMF with 0.05 M lithium bromide was used as the mobile phase, and detection was by UV at a wavelength of 280 nm. Poly(ethylene glycol) standards (PL2080-0101, Agilent) were used as mol wt standards. An identical analytical procedure to that described above was used for the lignin-rich phase.

Fig. 2a presents the distribution of lignin between the two liquid phases. Depending on the solvent composition, we can distribute most of the lignin into either phase. For example, for a 30% water feed, ≈70% of the lignin will be dissolved in the solvent-rich phase; however, by increasing the water concentration to 40%, we can flip the distribution so that ≈70% of the lignin is dissolved in the lignin-rich phase. The region between 30% and 60% water would be expected to be of greatest use for a separation process, as this is where the largest swings in lignin distribution occur.

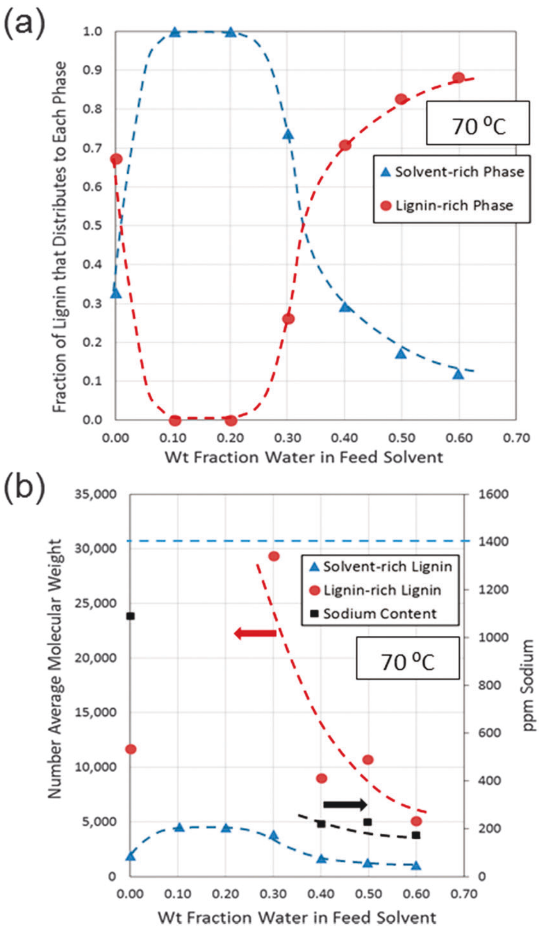

Fig. 2 (a) Distribution of lignin between the solvent-rich and lignin-rich phases when contacted with range of acetic acid–water mixtures at 70 °C and a solvent-to-lignin ratio of 9. (b) LHS: molecular weight of the lignin contained in the lignin-rich and solvent-rich phases; RHS: sodium content of lignin contained in the lignin-rich phase.

One unique advantage of fractionating Kraft black-liquor lignin in the LLE region is that one lignin fraction is cleaned of metals simply by separating the two liquid phases created above; only a drying step with no washing is required. For example, Fig. 2a and b show how 70–90% of the SLRP lignin with an initial sodium content of 1400 ppm (the dashed horizontal line) is cleaned to <200 ppm Na using a single extraction step at 70 °C when using a solvent system of 40–60% AcOH in water. Furthermore, selectivities for the solvent phase to preferentially extract the metals away from the liqnin-rich liquid phase range from 15 to 50,[24] which is on the high side of those present in successful commercial extraction processes.[25] Fig. 2b also shows how the higher mol wt lignins preferentially distribute into the cleaned, lignin-rich phase. With increasing water content in the solvent feed, the solvent becomes weaker, and only the lower mol wt lignins are dissolved in the solvent phase. The large increase in lignin molecular weight with solvent power at 70/30 AcOH/H_2O seen in Fig. 2b may be a result of lignin condensation reactions and will require further investigation. Reducing the residence time for the lignin-rich phase at elevated temperatures, for example *via* continuous processing, may be necessary if such a mol wt increase is seen as undesirable.

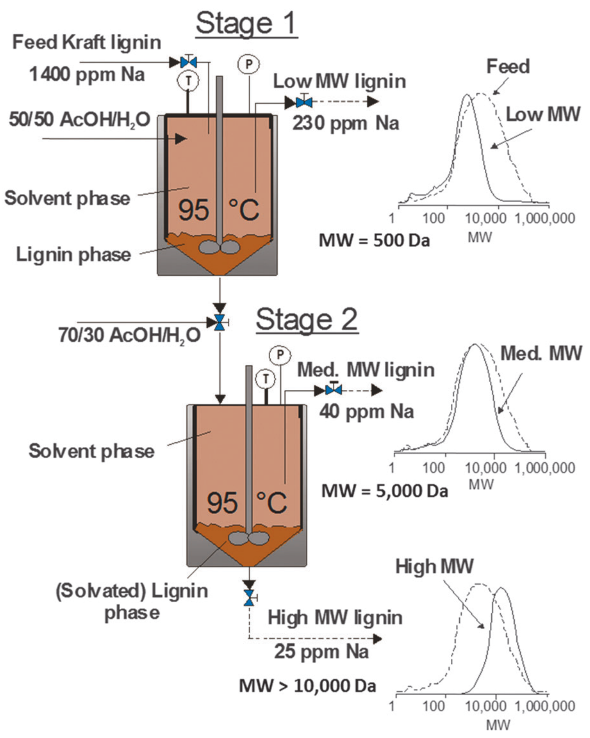

Fig. 3 Multistage lignin fractionation, purification, and solvation (*i.e.*, ALPHA) process for producing ultrapure lignin. The low mol wt (MW) lignin comprised 50% of the feed lignin, the med mol wt 20% and the high mol wt 30%. Different mass ratios of the lignin fractions are readily obtained by varying the AcOH/H_2O feed ratios.

With the above encouraging results for a single-stage extraction, we added a 2nd stage to see just how low we could drive the metals content of the recovered lignin fractions. A 50 mL Parr reactor system (model no. A2236HCEB), with the vessel modified to have a conical bottom, was used for these experiments (see Fig. 3). An operating temperature of 95 °C was chosen so that all stages would be operating in the LLE region. Analysis of the phases was performed as described above. As shown in Fig. 3, a 50/50 AcOH/H_2O solvent system was used for the 1st stage of extraction, splitting the lignin between the solvent-rich and lignin-rich phases, and extracting most of the metals into the solvent phase. The resulting lignin-rich liquid phase from Stage 1 was then contacted with a 70/30 AcOH/H_2O solvent mixture (only a stronger solvent system could be used, as the molecular weight of this lignin fraction was significantly higher than the starting lignin) so as to separate out yet additional solvent- and lignin-rich liquid phases. It is important to note that after this 2nd stage, both the solvent and lignin phases were ultraclean, containing <50 ppm sodium in either phase. Furthermore, as shown by the GPC results, the two ultraclean lignin fractions were significantly different in molecular weight. Finally, the high mol wt fraction from Stage 2 was solvated in a liquid-lignin phase that contained 68 wt% solvent, which could be suitable "as is" for processing. Thus, using only two stages, the ALPHA process generated ultraclean, fractionated, and solvated fractions of lignin. In closing, we note that multiple options of the above 2-stage extraction process can be envisioned, in which different AcOH/H_2O compositions are fed to the two stages in order to obtain ultraclean lignins encompassing a range of molecular weights.

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