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Research Letter

Ultraclean hybrid poplar lignins via liquid–liquid fractionation using ethanol–water solutions

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Abstract

As recovered from the byproducts stream of a cellulosic ethanol biorefinery, the renewable biopolymer lignin is too impure and polydisperse for many proposed applications. By mixing a hybrid poplar lignin with hot ethanol–water solutions, two liquid phases, one polymer-rich and one solvent-rich, are created. This liquid–liquid equilibrium phenomenon was used to generate solvated (and thus liquefied) lignin fractions of controlled molecular weight for which the impurities analyses for sugars and ash were near or below the limits of detection. Additionally, those carbohydrates and metals impurities end up highly concentrated in a single process stream also having potential value.

Introduction

An ever-increasing population on the planet and irrefutable environmental consequences have elevated the aspirations of renewability and sustainability to become the new bare minimum. When looking for inspiration to convert existing industrial monoliths into green processes, perhaps the most obvious examples are the plants and primitive lifeforms that have populated the planet for billions of years. After all, these hardy and robust biochemical reactors have been a mainstay of the chemical industry since its inception. Aside from the obvious use of harvesting biomass as a food source, much of industrial biomass utilization has focused on the material properties of cellulose in applications ranging from fabrics to paper. In more recent decades, the processing of inedible biomass into combustible ethanol for use as an energy currency has emerged.[1] In contrast to using expensive and human-edible biomass as feedstock, the use of inexpensive lignocellulosic biomass is a more lucrative value proposition.[2] Cellulose may continue to be the primary material of interest in these resource streams, but fully realizing the potential of lignocellulosic biorefineries also requires maximizing the value of the lignin.

Lignin is a biomolecule synthesized by plants to provide structural support in conjunction with cellulose and hemicellulose.[3] More abundant in woody biomass than other plant parts, lignin is an aromatic polymer, comprised three different monomer units connected via a variety of possible linkages.[4] Due to its aromatic nature, variety of hydroxyl groups, relative abundance, and low cost, lignin has been a target of valorization efforts for decades. These efforts have historically focused on the lignin by-product of a paper mill, as this already exists in massive quantities. To reduce the energy and chemical needs of the process, Kraft paper mills burn this lignin to recoup pulping salts and produce process steam.[5] While lignin processing has yet to reach full maturity, lignin has nevertheless shown promise as a precursor for materials applications such as carbon fibers, polyurethane construction foams, and phenol–formaldehyde resins.[6–8] Other strategies for lignin valorization focus on it use as a source of commodity chemicals through targeted depolymerization.[9]

In almost all cases, the heterogenous, impure, and variable nature of lignin significantly impedes the upgrading process. Energy recovery boilers have a wide tolerance on what can be burned, but higher-value applications are less forgiving. For example, lignin for materials or chemical applications can suffer from inorganic impurities that disrupt structure or affect reaction pathways. Furthermore, the polydisperse nature of lignin causes conventional polymeric properties such as the glass-transition point or degradation temperature to appear as broad windows. For applications such as carbon fibers[6] and polyurethane foams,[10] the properties of the final product have been found to improve when fractionation is applied to tailor the properties of the lignin-based precursor. The improvement in properties conferred by fractionation stands to increase the value gained through lignin utilization, as long as this separation can be performed in an economical and environmentally benign manner.

While earlier lignin fractionation involved harsh solvents such as dioxane and chloroform,[10, 11] more recent research has focused on less expensive and greener alternatives. For example, both aqueous acetone[12–14] and aqueous ethanol[14–16] have been used to fractionate a wide range of lignins, including those derived from Kraft, organosolv, and enzymatic hydrolysis processes. However, in all of the above work the fractionation was always carried out by partitioning the lignin between a

solid lignin phase and a solvent phase, and always at ambient temperatures. Furthermore, the wt/wt ratio of solvent to lignin (*S*/*L*) used for fractionation was typically quite large, that is, *S*/*L* ≥10:1, so that the solvent system was always in significant excess.

Thies et al. have taken a different approach to lignin fractionation. They have discovered[17, 18] that by combining aqueous organic solvents with lignins at elevated temperatures and within certain unique ranges of solvent composition, two *liquid* phases are formed, one solvent-rich and one lignin-rich, in the manner of polymer–solvent phase separation behavior.[19] Furthermore, the *S*/*L* ratios that exhibit this liquid–liquid phase behavior can be relatively low, with 3:1 and 6:1 frequently being used in our work.[18, 20] With solvent use being more modest and both phases being processable liquids, this method of lignin fractionation, which we refer to as Aqueous Lignin Purification using Hot Agents (ALPHA), has been shown by techno-economic analysis (TEA)[21] to be viable for commercial scale-up. Another significant advantage of processing lignins in a region of liquid–liquid (versus solid–liquid) phase equilibrium, and which is a key focus of this work, is the ability to both remove and concentrate impurities, such as metal salts and sugars, into/out of either liquid phase, as diffusion in liquids is typically orders of magnitude more rapid than in solids.[22]

In this study, liquid–liquid equilibrium (in the form of ALPHA) was used to both fractionate and purify a hybrid poplar technical lignin[23] with hot, ethanol–water solutions. The objective of this separation process was the generation of extremely clean (we refer to as "ultrapure") lignin fractions of controlled molecular weight. Alkaline pretreatment was used to recover the hybrid poplar (HP) lignin from the starting biomass, as this type of pretreatment has been found to be relatively benign to lignin versus dilute acid pretreatment.

Compared to the previous work of our group with softwood Kraft lignin,[20] HP was significantly lower in sodium and sulfur content; however, it had greater levels of calcium, potassium, and xylan. With this different set of impurities and the differing chemical properties of a biorefinery versus a Kraft lignin, the previously applied ALPHA fractionation strategies were found to be less effective in removing non-lignin impurities from HP. To address this issue, a wide range of conditions and separation schemes were investigated, and an ALPHA setup was developed that not only produced ultrapure lignin fractions of controlled molecular weight but was also amenable to commercial scale-up.

Materials and methods

Materials

The procedure for generating HP from biomass was as follows: chips of hybrid poplar wood (*Populus nigra* var. *charkowiensis* × *P. nigra* var. *caudina* cv. NE19) were loaded into a digester comprising one 20-L chamber (model AU/E-20, RegMed, Osasco, Brazil) along with NaOH at an 18 wt% loading on biomass at a liquor-to-wood wt/wt ratio of 5:1. The reactor vessel was heated via a temperature-controlled steam jacket to 150°C and held at temperature for 3 h. After the 3-h reaction time, the steam in the jacket was flashed and the vessel was allowed to cool to < 100°C prior to opening. The resulting alkaline liquor was decanted from the biomass solids, and the still-wet wood chips were pressed to remove any entrained liquor. Lignin recovery from the black liquor was achieved by acidifying the liquor to a pH of 2.0 using 96.6 wt% sulfuric acid. An ice bath was used at this stage for cooling. The resulting slurry of aqueous lignin was left at 4°C overnight, then centrifuged for 2 h at 8000 rpm. The supernatant was decanted, and the lignin solids were then collected and washed twice with deionized water (at a lignin-to-water ratio of 1:5 by mass). Finally, the lignin was dried under ambient conditions for 24 h, and then in a vacuum oven at 50°C for 24 h.

For the ALPHA experiments, deionized water (> 18.2 MΩ/cm) was produced using a Culligan deionization system followed by a Milli-Q Reference system (Model No. Z00QSV0WW). Molecular biology grade, 200 proof ethanol was supplied from Fisher Scientific (Cat. No. BP28184). Whatman Grade 4 filter paper (particle retention of 25 µm at 98% efficiency) was purchased from Millipore Sigma (WHA100409). For molecular weight analysis, dimethyl formamide (BDH83634) was purchased from VWR, and lithium bromide (13408) was purchased from Alfa Aesar. Sulfuric acid (96.6 wt%, A300-212) used for carbohydrate analysis was purchased from Fisher.

Lignin fractionation

Successive fractionation of lignin was performed to recover 16 lignin fractions, with fifteen being lignin-rich phase fractions (L1–L15) and one being solvent-rich (S15), see Fig. 1. First, ~ 300 g of lignin was added to a 2-L Parr reactor fitted with a helical-ribbon impeller. Next, an 80 wt% ethanol solution was added at a 3:1 solvent-to-feed lignin ratio by weight. The reactor was then sealed, heated to 60°C, and allowed to mix for 30 min, well above the 5 min that has been found from previous work to be adequate for achieving liquid–liquid equilibrium. As a result of this process, two liquid phases were formed: a denser, lignin-rich liquid phase (L1) that quickly settled to the bottom of the reactor when agitation was halted, and a less-dense, solvent-rich phase (S1) that occupied the remaining volume of the reactor. In addition to the solvated lignin, plasticized by the ethanol–water solution, L1 was also observed to contain undissolved solid impurities. To separate L1 from the inviscid, solvent-rich phase S1, the heated contents of the reactor were vacuum-filtered with filter paper. The lignin-rich phase (~ 15% of the starting lignin on a dry basis) and the insoluble impurities remained on the filter paper, while S1 passed through and cooled to room temperature in the process. The filtrate (S1, still a homogenous liquid with no signs of phase splitting) was then collected in a separate vessel. Water was then added incrementally to S1 so that the ability to use this scheme for lignin fractionation could be studied. Upon the addition of 50 g of

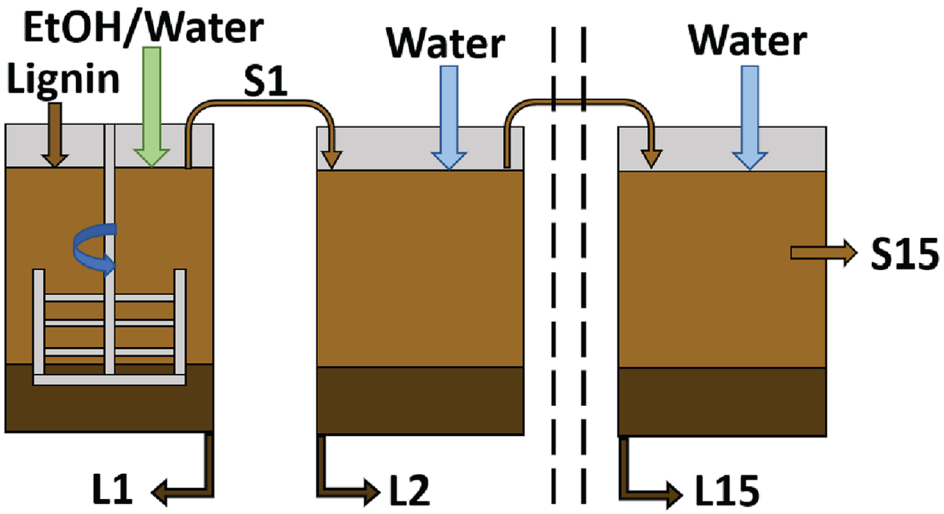

Figure 1. Depiction of multistage ALPHA fractionation process. **Lx** denotes the lignin-rich phase product of the numbered stage **x**. **Sx** denotes the solvent-rich phase product of the same numbered stage **x**.

water, a second liquid-rich phase precipitated (L2). As shown in Fig. 1, this process was repeated, collecting **L(x+1)** from **Sx**. After L11, the quantity of water added was increased to 100 g to compensate for the decreasing yield of the lignin-rich phases. This process was then repeated until a total of 15 lignin-rich fractions (including L1, the retentate from the filtration step) were collected. Only in the first precipitate, L1, were any solid impurities observed. After removal from the vessel, the plasticized, dough-like, lignin-rich phase was thoroughly kneaded to collapse and thus eliminate any pockets of residual, solvent-rich phase. This kneading process was performed until solvent stopped weeping from the molten polymer mass, about 3–5 min. All exuded solvent was then added to the accompanying solvent-rich phase sample.

The lignin-rich fractions, along with the lignin still in S15 at the end of the water addition, were dried at 120°C under atmospheric pressure for 2 h and characterized as described below. Additionally, the dried fractions were weighed to generate a curve of cumulative yield as a function of vessel composition (on a lignin-free basis). To assess reproducibility, the overall fractionation process delineated above was performed twice to generate a set of independent replicate samples.

Analytical methods

To measure sugar content, a method similar to the carbohydrates analysis section of NREL/TP-510-42618 was used[24] and is described below. First, 100±10 mg of lignin were added to a 35-mL, pressure-rated tube to which 1 mL of 72% sulfuric acid had been introduced. The tube was then maintained in a 30°C water bath for 1 h, mixing every 15 min with a glass stir rod. Next, 28 mL of deionized water was added to the tube, washing what lignin could be washed off the stir rod in the process. The tubes were then capped and placed in an autoclave set at 121°C for 60 min on the liquid setting. After being cooled to ambient temperature, the samples were passed through a 0.2 µm syringe filter. Separation of the digested sugars was performed with an Aminex HPX-87H Column (300×7.8 mm), using a mobile phase of 5 mM sulfuric acid in water at 65°C and 0.6 mL/min. A Waters 2414 Refractive Index Detector, calibrated to standard solutions of xylose, glucose, and arabinose, was used for the determination of sugars concentration. The mass of water added via hydrolysis was accounted for in all three sugar measurements. A set of sugar standards was also exposed to digestion conditions to account for undesired monosaccharide degradation.

To measure ash content, ~1 g of dried lignin was weighed into a crucible and placed in a muffle furnace. The sample was heated to 750°C at a rate of ~25°C/min and held at 750°C for 5 min before the heating was turned off and the furnace allowed to cool. After the furnace cooled to room temperature, the crucibles were removed and weighed. Thermogravimetric analysis (TGA) at a heating rate of 10°C/min, a final temperature of 750°C, and with air as a purge gas was also used for independent confirmation of characteristic high-ash, medium-ash, and low-ash lignin samples. This allowed us to see if residual moisture in dried samples was enough to affect the results. TGA also afforded us a finer resolution and limit of detection to ensure that the low-ash values obtained from the primary procedure were valid.

Softening points of finely powdered samples were measured using a Fisher–Johns melting point apparatus. To minimize the impact of thermal degradation on measurements, two heating schedules were implemented. For the first, the sample was heated from room temperature to softening at a rate of ~25°C/min. Next, the heating plate was preheated to within 20°C of the first measurement and then heated at a rate of ~5°C/min. The latter measurement was repeated in triplicate; only this measurement is reported here. Softening point was defined as the first temperature where plastic deformation with a spatula resulted in the formation of a smooth, translucent layer of lignin on the heated plate.

Dried lignin feed and samples L1–L15 and S15 were analyzed via gel permeation chromatography (GPC), with filtered multiangle light scattering (MALS) (DAWN—Wyatt Technologies) being used for absolute weight average molecular weight (M_w) and refractive index (RI, Optilab-WREX-08) being used for concentration. Separation was performed using Styragel (Waters, HT5 WATO-44214) and Polargel-L (Agilent, PL1117-6830) columns in series, using HPLC-grade DMF containing 0.05 M LiBr as the mobile phase at a flowrate of 0.6 mL/min. Samples were prepared by dissolving lignin in the mobile phase at a concentration of 1.5 mg/mL. After complete dissolution, the samples were passed through a 0.20 μm PTFE syringe filter before analysis.

Results

Shown in Table I are the ash and xylan concentrations of the unfractionated feed, along with the same properties of the dried lignin fractions. It is important to note that as produced, the lignin-rich phases are 50–60% solids and the solvent-rich phase is ~5% solids. The solvent in **Lx** is an ethanol–water solution that decreases from ~80% EtOH for L1 down to ~35% EtOH for L15 as water is added. Previous work[20] indicates that the lignin-free solvent compositions in **Lx** and **Sx** differ little, typically from 0.1 to 2.5 wt%.

The first stage of separation was carried out with the intention of dissolving as much lignin as possible, while retaining insoluble impurities (i.e., metal salts and long-chain carbohydrates) behind on the filter. As shown in Table I, L1 (the retentate from the filtration stage) is highly concentrated in ash and xylan. In contrast, the lignin fractions that precipitate from water additions (L2–L15) contain levels of ash and xylan that are either at or below the limits of detection of our analytical methods. Although the lignin fraction recovered by drying down solvent-rich phase S15 was enriched in ash compared to the feed, it was still depleted in xylan versus the feed—but still higher than the previous lignin-rich-phase fractions.

In Fig. 2, the cumulative fraction of recovered lignin is plotted against the lignin-free solvent composition for the stage of interest. Here we define recovered lignin as the lignin recovered in L1–L15 and in S15. Figure 1 shows that in principle the mass of the feed and of the recovered lignin should be the same. However, in practice a nontrivial portion (~20%) of L2–L15 is inevitably lost (e.g., on the sides of the vessel and on the helical impeller) during the II. Lignin Fractionation procedure described above. Approximately half of the losses of the lignin-rich phase occur during the first separation stage when L1 is removed from the vessel. Analogous experiments in which only 3 product streams (L1, L2, and S2) are produced have ~10% losses. The remaining losses are directly attributable to the high number of individual stages and the large degree of handling that such a process necessitates. As the 2-L reactor weighs almost 20 kg, eliminating losses by weighing the reactor before and after a given stage is impractical. Finally, the focus of this work was the determination of the molecular weights and relative yields of **Lx** phases as a function of ALPHA solvent composition. Neither M_w nor yield trends were affected by consistent minor losses of **Lx.**

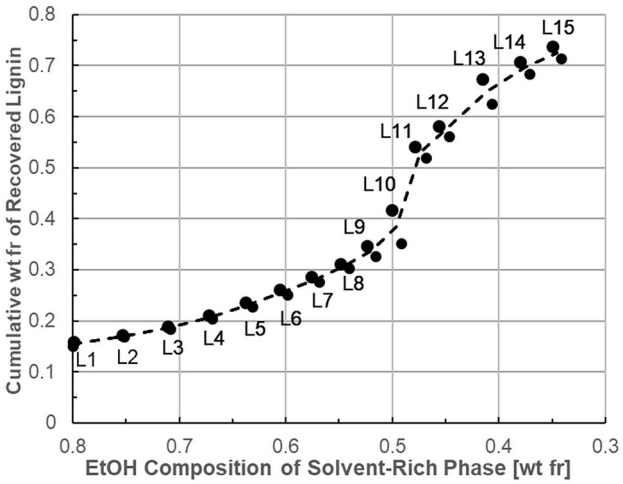

Figure 2. Cumulative fraction of recovered lignin plotted vs. ethanol composition of the solvent. All runs were duplicated and plotted. Recovered lignin is 20% less than the feed lignin due to **Lx** losses on reactor walls and impeller.

Table I. Ash and xylan compositions for the feed lignin and dried lignin fractions (average of duplicates and standard deviation are given).

ID	Ash (wt%)	Xylan (wt%)	ID	Ash (wt%)	Xylan (wt%)
Feed	0.47±0.01	2.65±0.08	L9	0.04±0.03	0.05±0.01
L1	2.80±0.37	24.94±0.49	L10	0.01±0.01	0.03±0.01
L2	0.01±0.02	0.07±0.00	L11	0.02±0.01	0.10±0.03
L3	0.01±0.02	0.11±0.01	L12	0.00±0.00	0.07±0.00
L4	0.00±0.03	0.07±0.02	L13	0.03±0.01	0.06±0.00
L5	0.00±0.00	0.05±0.00	L14	0.03±0.02	0.06±0.02
L6	0.02±0.02	0.05±0.03	L15	0.00±0.00	0.06±0.01
L7	0.03±0.01	0.06±0.01	S15	0.47±0.01	0.26±0.00
L8	0.04±0.02	0.05±0.01			

Solvent compositions for L2–L15 were calculated by material balance, taking into account the water added to each stage and the solvent removed from each stage in the lignin-rich phase, which was assumed to have the same EtOH/water composition as the solvent-rich phase. For reference, the initial feed was 300 g of lignin and 900 g of 80/20 EtOH/water solution, and 50 g of water was added to stages 2–11 and 100 g to stages 12–15, resulting in a total addition (excluding the starting solvent) of 850 g of water and a final composition of 35% EtOH.

As shown in Fig. 2, the precipitation of lignin via water addition for this system is sigmoidal in nature. When the solvent composition reaches 60% EtOH, only 10% of the lignin has precipitated as high-purity fractions. However, as the composition passes 50% EtOH, the rate of precipitation increases significantly. Thus, 20% of the recovered lignin precipitates

from 52 to 47% EtOH. Precipitation then begins to plateau as the composition passes 40% EtOH, with the drop to 35% EtOH resulting in the recovery of only an additional 6% of the lignin.

The absolute weight average molecular weights (M_w) of the dried lignin fractions are given in Fig. 3(a). The first precipitated fraction L1 (not plotted for scaling reasons) had the highest M_w (44,000 ± 900 Da). If this dried fraction were purely lignin (and chemically identical to the lignin found in the other fractions), one would expect it to have the highest M_w. However, the presence of a unique peak in the GPC-MALS measurements (that is not observed in low sugar samples) suggests that residual xylan or lignin aggregates could be further driving the M_w upward. Referring to Fig. 3(a), the molecular weight trend exhibited by the dried, lignin-rich phases L2–L15 is complex and counterintuitive. Although the first samples (L2–L10) that precipitate upon water addition have higher M_w than the feed lignin, they are not the highest M_w samples. Instead, the maximum is not observed until L11, which precipitates at 47% EtOH. This fraction not only has the highest observed M_w of the high-purity fractions, but also the highest yield by mass (see Fig. 2) of any one fraction. Moving past L11, there is a dramatic drop in M_w, such that these later fractions now have a lower M_w than the feed. However, the declining trend of M_w in these fractions is observed to neither be smooth nor monotonic. Lastly, the diamond (◆) represents the S15 fraction, the lignin that was still in solution after the composition had reached 35% EtOH. As expected, this fraction has the lowest observed M_w—although only slightly lower than L14.

Because of the somewhat surprising trend in the observed M_w, softening point (SPt) measurements were performed as a simple yet useful validation check. The highest M_w fraction L1 did not soften below 300°C; instead, significant off-gassing of volatiles occurred, indicating that thermal degradation occurs before softening for this fraction—an observation consistent with the measured M_w. For the subsequent fractions,

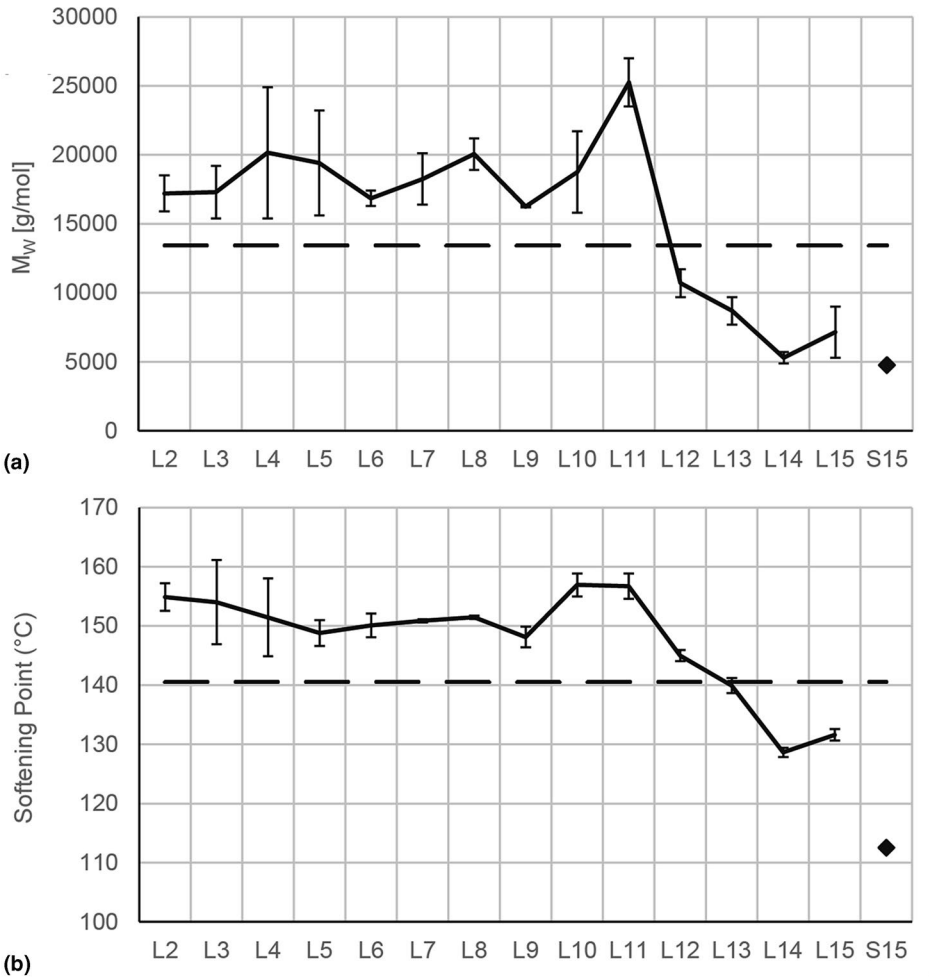

Figure 3. (a) Absolute weight average molecular weight (M_w) by MALS for dried lignin-rich phases L2–L15. Error bars are for one standard deviation. Dried solvent-rich phase S15 (error bars are miniscule) is shown as a diamond. The feed lignin value of 13,400 (±300) Da is given as a horizontal dotted line. (b) Softening points (SPts) of fractions L2–L15, with the same notes applying as given above.

the SPt measurements displayed the same general trend as the MALS M_w measurements. Although some early **Lx** samples showed high variability with one or both techniques, there is a generally flat trend for fractions L5–L9. A maximum of M_w is achieved at L11, while SPts for L10 and L11 are approximately the same, yet still significantly higher than that of L5–L9. After L11, both M_w and SPt plummet, reaching a minimum value with S15.

Discussion

As indicated by the level of ash in L1 (see Table I), the overwhelming majority of the metal salts in the feed lignin are retained in the L1 filter as insolubles. Additionally, a smaller proportion of these salts are readily soluble and end up in S15. As a result, ash is at the limits of detection in the dried, L2–L15 lignin-rich-phase fractions that precipitate as the solvent is diluted from 80 to ~35% EtOH by water addition. Although the solubility of lignin in ethanol–water solutions is seen to be strongly dependent on composition (see Fig. 2), the solubility of both the carbohydrate and metals impurities is only weakly dependent on this factor (Table I). Clearly, this difference allows for a highly effective separation of lignin from its impurities in fractions L2–L15. To our knowledge, such low impurity levels in lignin or lignin fractions as given in Table I have not been reported to date—either by the ALPHA process or by other means.

Precipitation of lignin-rich liquid phases L2–L15 is driven by reduced solubility in the EtOH–water solution as water is added and is most likely a function of both molecular weight and chemical functionality. Curiously, M_W for L2–L9 is relatively unchanged as more and more water is added to the system. Clearly, M_w is not the only factor that determines the solubility of lignin in this system.

Considering the unusual M_w data, it is encouraging that the SPt measurements qualitatively affirm the M_w results. However, the M_w and SPt measurements do not fully explain the mechanism for precipitation. To better understand the impetus for this phase behavior, characterization of hydroxyl content via ^{31}P NMR will need to be performed. This could reveal why the lignin in L8 remains soluble in EtOH–water solutions at much higher water contents versus L2, despite being marginally higher in M_w. Or why L11 (with the highest M_w of all lignin fractions except for the impure L1 fraction) does not precipitate out until the solvent composition exceeds 50% water—and when L11 does precipitate, why it comprises such a large percentage (20%) of the recovered lignin. Depending on the intended use for the lignin fractions, it may make more sense economically to add only enough water to precipitate the maximum M_w, hitting the inflection point on the yield curve.

Using the information collected in this study, a practical ALPHA process of 3–5 stages is proposed for the fractionation of hybrid poplar lignin. The first stage is a simple, hot filtration step with a green solvent, an ethanol–water solution, well below its azeotropic composition. Here, virtually all carbohydrate and salts impurities are removed from the lignin. The recovery of this highly enriched stream could have a positive impact on the overall techno-economic analysis (TEA) of an ethanol biorefinery. However, the most promising fractions would be the very high purity, high M_w fractions generated by some combination of L2–L11. For example, as an already solvated material with no more than trace of impurities, the highest M_w fractions would be prime candidates for dry spinning into lignin fibers, followed by conversion into carbon fibers. Hardwood lignins are traditionally melt-spun,[25] but this poses a challenge, as preventing the fusion of the final fibers during stabilization is notoriously difficult. Dry spinning in combination with ALPHA allows for higher M_w fractions that soften at temperatures above those necessary for the reactions involved in stabilization.

In addition to the high M_w, high-purity fractions, two low M_w fractions would exist: L12–L15 and S15. These fractions could be diverted to a process that values low M_w and/or highly soluble lignin fractions, such as for coatings applications. Furthermore, the lower M_w are likely to coincide with an increased hydroxyl content that would make these fractions more valuable than the feed for applications, such as a substitute for the polyols in PU foams, that require this chemical functionality.

In summary, while further experiments are needed to elucidate the effects of changing temperature, starting ethanol composition, and solvent-to-lignin ratio, the reported results document that this version of the ALPHA process can be leveraged to completely remove insoluble impurities from hybrid poplar lignin, while also generating fractions of controlled molecular weight.

Acknowledgments

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Data availability

Supplemental tables have been provided that contain the relevant collected data for the experiments of this work.

Declarations

Conflict of interest

The authors of this work have no conflicts of interests to declare that are relevant to the content of this article.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1557/s43579-021-00090-4.

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