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Continuous-Flow Process for the Purification and Fractionation of Alkali and Organosolv Lignins

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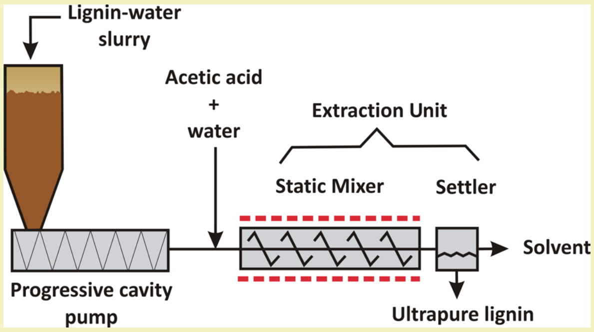
ABSTRACT: Hot acetic acid–water mixtures can be used to purify and fractionate alkali (kraft) and organosolv lignins via the Aqueous Lignin Purification with Hot Acids (ALPHA) process. However, condensation polymerization reactions can occur in the solvated, lignin-rich liquid fraction at the elevated temperatures (e.g., 60–100 °C) of operation, significantly increasing the lignin molecular weight. Thus, conversion of ALPHA to continuous-flow operation was investigated in order to determine the effect of reduced residence times on both the above reactions and on the extraction of metals from the solvated lignin to the solvent phase. All four lignins investigated could be converted to a homogeneous lignin–water slurry at ambient temperatures, facilitating continuous operation. When a static mixer is used for the mixing and equilibration device, reducing residence times to 20–30 s, condensation polymerization reactions are essentially eliminated. For example, the molecular weight of the lignin fraction remained unchanged with continuous processing but increased from 7900 to 13200 when batch processing was used for the same ALPHA conditions. Furthermore, the 10-fold reduction in metals content (e.g., sodium content reduced from 1400 to <100 ppm) was equal to or better than that obtained by single-stage batch processing. Thus, continuous ALPHA can be used to obtain an ultrapure, metals-free lignin of well-defined and controllable molecular weight.



KEYWORDS: *Acetic acid, Solvent, ALPHA, Extraction, Molecular weight, Condensation, Polymerization, Ultraclean*

INTRODUCTION

As the push for greener and more sustainable technologies is advanced, renewable feedstocks to replace those derived from petroleum are desired. Lignin is one of the world's most abundant renewable biopolymers, with 25%–30% of land biomass consisting (on a dry basis) of lignin; only cellulose is more abundant. Furthermore, it is the only abundant land biopolymer with aromaticity. A readily available source of lignin (more than 50 million tons/yr)[1] is in the alkaline liquor (also called black liquor) byproduct generated from processes for recovering cellulose from woody biomass, where the cellulose is converted either to paper or to biofuels. Today, however, most (99+%) of this lignin is not recovered but is simply burned as part of the alkaline liquor stream for its heating value. Fortunately, the situation is starting to change, as several processes have been developed in recent years for recovering lignin from the alkaline liquors, including LignoForce, LignoBoost, and Sequential Liquid Lignin Recovery and Purification (SLRP).[2−4] The lignin products (called alkali or Kraft lignin) obtained are relatively clean, "low-ash" materials, as only about 5% of the sodium originally present in the alkaline liquor remains in the lignin product, which typically contains 1500–10,000 ppm of Na and 1%–4% ash. Two significant applications that have been identified for these low-ash, alkali lignins include partial phenol replacement in phenol–formaldehyde resins[5,6] and partial polyol replacement in rigid polyurethane foams.[7,8]

For other, higher-value applications such as carbon fibers and coatings, however, the lignin has to be much cleaner; that is, it must be essentially metals-free (i.e., "ultrapure"), containing less than 100 ppm sodium (the dominant metal impurity) and lower amounts of any other metals.[9−11] Furthermore, the limited evidence available[12] suggests that control of the molecular weight of the lignin will also be important for a number of applications.

We have discovered[13,14] a renewable solvent system that can be used to simultaneously clean, fractionate, and solvate lignin. In particular, mixtures of acetic acid and water at elevated temperatures (i.e., 50–120 °C) can be used to create a system of two liquid phases with novel properties. The first phase is a less-dense, solvent-rich phase that extracts the metal salts from the lignin feed; the second is a denser, lignin-rich phase that contains a cleaned, purified lignin. Furthermore, the lignin partitions between these two phases by molecular weight (mol wt), with the lower mol wt lignin residing in the solvent-rich phase and the higher mol wt lignin in the lignin-rich phase. Such a phase split forms the basis of a liquid–liquid extraction and fractionation process that we call Aqueous Lignin Purification with Hot Acids (ALPHA).

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Although ALPHA has proven to be effective on the batch scale both for fractionating an alkali lignin by molecular weight and for reducing its metals content so that an ultrapure lignin is obtained,[13] our goal here was to determine if ALPHA could be operated such that the undesirable polymerization reactions that can occur in the batch setup (with its residence times of 20−30 min) could be minimized by reducing processing times. Thus, we investigated the viability of converting ALPHA into a continuous process. Furthermore, the effect of residence time on the extraction of the metal salts from the lignin also needed to be investigated to ensure that ultrapure (i.e., < 100 ppm sodium) lignins could still be obtained at the much lower residence times which continuous processing normally entails.

■ METHODS

Materials. A low-ash Kraft lignin was recovered from a softwood black liquor with a Kappa number of 25 and a solids content of 42 wt % by means of the SLRP process. BioChoice lignin, a softwood-derived Kraft lignin, was obtained from Domtar, and Lignol lignin, an organosolv lignin, was supplied by Lignol Innovations. Indulin AT, a softwood-derived Kraft lignin, was supplied by MeadWestvaco (now Ingevity), lot no. MA27M. The water content of the four lignins was measured and determined to be 43.1 wt % (SLRP), 33.1 wt % (BioChoice), 3.9 wt % (Lignol), and 5.9 wt % (Indulin AT). Glacial acetic acid (cat. no. MKV193-45) was supplied by VWR. Deionized water was obtained from an in-house distillation apparatus followed by a water purification unit (Millipore Milli-Q Academic). For GPC analysis, lithium bromide (cat. no. 35705-14) and HPLC grade (99.7+ %) N,N-dimethylformamide (cat. no. 22915-K7) were obtained from VWR.

Continuous Process Operation. A schematic of the continuous process for the production of ultrapure lignin via ALPHA is given in Figure 1. In brief, the process consists of combining a lignin−water slurry with a solution of acetic acid and water at elevated temperatures in a static mixer and then separating the two liquid phases that are formed in a settler. In order to carry out the separation process, the processing temperature must be maintained in the liquid−liquid region, where solvent-rich and lignin-rich liquid phases exist in equilibrium with each other (Figure 2). The lignin−water slurry, which consists of 30−45 wt % lignin in water, is prepared beforehand by mixing the ingredients in a conventional, 1.25 L kitchen blender. A homogeneous, pumpable slurry of the desired viscosity is obtained only within the range of lignin−water compositions given above.

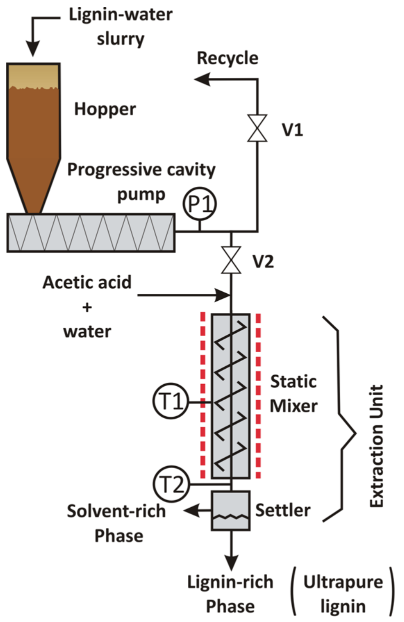

Figure 1. Schematic of the continuous process used to produce ultrapure lignin.

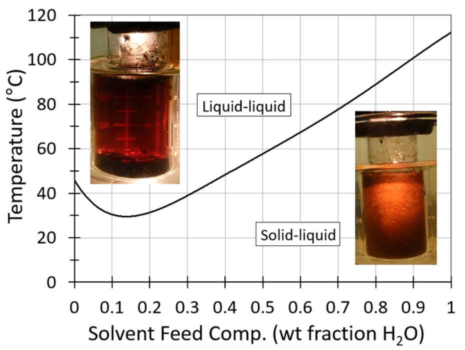

Figure 2. Phase diagram of the lignin−acetic acid−water system. Below the curve, solid lignin is in equilibrium with a solvent-rich liquid phase; above the curve, a lignin-rich liquid phase is in equilibrium with a solvent-rich liquid phase.[13,15] The curve shown is for a solvent:lignin ratio of 9:1, but only minor variation was observed over the ratios tested (i.e., from 1.8:1 to 19:1).

For a typical experiment, the lignin−water slurry was fed from the hopper into the inlet of a Seepex MD series progressive cavity pump, which was used to deliver the slurry at a pressure of 4.7−5.4 bar, as measured at the pump exit at pressure gauge P1. Initially, valve V2 was closed and valve V1 opened so that the slurry was recycled in a continuous loop. A constant flow rate of a solvent mixture of acetic acid and water was then delivered through the static mixer (Koflo Stratos, 1/4 in. tube, model no. 1/4-34, with 34 alternating right-and left-handed helical mixing elements) with an Isco Dual Syringe Pump (Model 500D). This solvent was heated to temperatures of 72 ± 3 °C, as measured at the exit of the mixer, by means of two 0.5 in. wide × 6 feet long heating tapes (BriskHeat, model no. BIH051060L) controlled via Minitrol on/off temperature controllers (model PL-312), with one tape wrapped around the solvent line and one around the mixer. When the wall temperature of the static mixer, as measured at midlength by thermocouple T1, had reached a steady-state temperature of 90 ± 5 °C, V1 was closed and V2 opened so that the hot solvent mixture and cold lignin−water slurry were simultaneously delivered to the static mixer for intimate mixing so as to achieve the desired liquid−liquid equilibrium. The Minitrol percent power setting was then increased to compensate for the addition of lignin slurry to the flow stream, so as to continue to maintain the wall temperature of the static mixer at 90 ± 5 °C. The temperature of the two-phase, liquid−liquid mixture exiting the static mixer was frequently measured by inserting a thermocouple into the end of the static mixer and was found to be 69 ± 5 °C. Upon exiting the static mixer, the two liquid phases were separated using a 60-mesh, stainless steel screen filter. The more viscous, lignin-rich phase collected on the screen, and the solvent-rich phase passed through the screen into a collection vessel. Residence times of the lignin−solvent mixture in the static mixer at temperature were ~20 s.

The solvent-rich phase contained the extracted metal salts and the lower mol wt lignin species, while the denser, more viscous lignin-rich phase contained the purified, higher mol wt lignin along with significant amounts (i.e., ~50% by weight of the lignin-rich phase) of solvent. The lignin-rich phase was dried overnight in a vacuum oven (Fischer Scientific IsoTemp, Model 280A) at ambient temperature and a pressure of 10−20 mmHg in preparation for the analyses described in the next section.

For a given experiment, the acetic acid−water ratio in the solvent feed stream was set so as to obtain the desired solvent composition and lignin-to-solvent ratio for the overall acetic acid−water−lignin system. For example, to obtain a combined feed stream to the static mixer with an overall composition of 10 wt % lignin and an overall solvent composition of 50/50 wt/wt acetic acid/water at a flow rate of 20 g/min, a lignin slurry of 30/70 wt/wt lignin (dry basis)/water was delivered at a flow rate of 6.7 g/min to the static mixer, and a solvent stream containing 67.5/32.5 wt/wt acetic acid/water was delivered at a flow rate of 13.3 g/min to the mixer. A reduced-metals, higher mol wt lignin product composed of ~50/50 wt/wt lignin/solvent (i.e., the lignin-rich phase) was then generated at a flow rate of 2 g/min, with the remainder of the lignin and solvent being contained in the solvent-rich phase.

All thermocouples used were Type K grounded thermocouples sheathed in 1/16 in. o.d. stainless steel (Omega Engineering) and were calibrated against a secondary standard RTD (Burns Engineering, Model No. 18072-A-6-30-0-A/LT60) to an accuracy of ±0.2 °C. Pressure gauge P1 (Bourdon-tube type, 0−200 psi, 2.5 in. dial) was calibrated against a Budenberg dead weight pressure tester (Model 380H) to an accuracy of ±0.5 psi (±0.035 bar).

GPC Analysis. Lignin samples from the lignin-rich and solvent-rich phases generated by the ALPHA process were analyzed by gel permeation chromatography (GPC) to determine (1) the extent to which fractionation by molecular weight had occurred and (2) whether the lignin fractions had undergone any condensation polymerization reactions, as was observed in previous batch work.[13] The fractions were analyzed using an Alliance GPCV 2000 instrument. Two columns were used in series: a Waters Styragel HT5 column (10 μm, 4.6 mm × 300 mm) followed by an Agilent PolarGel-L column (8 μm, 7.5 mm × 300 mm); the mobile phase consisted of 0.05 M lithium bromide in N,N-dimethylformamide (DMF) at a flow rate of 1 mL/min. Poly(ethylene glycol) calibration standards were used for estimation of number-average molecular weight. Samples were dissolved in the mobile phase at a concentration of 1 mg/mL and filtered using a 0.2 μm nylon membrane syringe filter (VWR, part no 28145-487). Detection of PEG standards was by refractive index using a Waters differential refractometer, and detection of lignin samples was by UV−vis with a Waters 2487 detector at 280 nm.[16] Molecular weights for a given sample were analyzed in duplicate and were generally reproducible to within ±50.

ICP Analysis. Metals content in the (dried) lignin-rich phase was determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES). Analyses were carried out using a Spectro Analytical Instruments spectrometer, model ARCOS. To prepare a typical sample for ICP-AES analysis, 0.1 g of a dried 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 hydrogen peroxide and heating to 125 °C for 60 min. Three more milliliters of hydrogen peroxide were added, and the sample was kept at 125 °C for 60 min. Finally, the sample was dried at 200 °C for 1 h. The above dried samples were diluted in 10 mL of 1.6 M nitric acid and, after cooling, in another 50 mL of deionized water. The resulting liquids were then transferred to the ICP tube for analysis and detection. Error in metals analysis was ±15 ppm and was determined by analyzing a single sample six times and determining the standard deviation of the set.

■ RESULTS AND DISCUSSION

The effect of changes in the solvent composition on the effectiveness of the continuous purification and fractionation of lignin via the ALPHA process was investigated. For these experiments, SLRP lignin was used, with the total flow rate of lignin plus solvent being 20 g/min and the solvent:lignin (S/L) ratio being held constant at 9:1 (i.e., 10 wt % lignin). Solvent compositions of 60/40, 50/50, 40/60, and 30/70 wt/wt acetic acid/water were investigated. This composition range was investigated because here most of the lignin partitions into the purified, lignin-rich phase. Batch experiments at the above feed solvent compositions and S/L ratios were performed in 20 mL sealed vials, with a stir bar at 350 rpm for mixing, as previously described.[13]

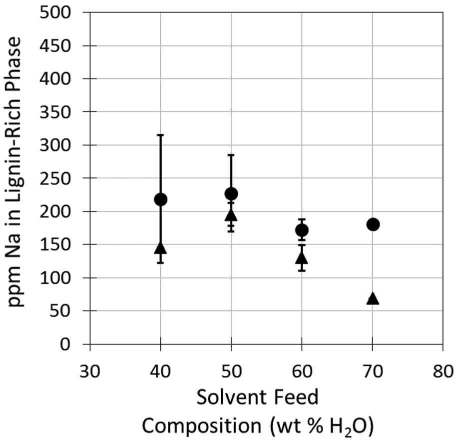

Figure 3. Effect of solvent feed composition on the sodium content of the lignin recovered in the lignin-rich phase. The circles (●) are for batch, and the triangles (▲) are for continuous ALPHA processing. Error bars are given both here and in other figures for those batch and continuous runs that were duplicated. A 9:1 solvent:lignin ratio was used both here and in all succeeding figures.

Our first concern was that the short residence times of 20 s used in continuous ALPHA might negatively impact the removal of metal salts. As shown in Figure 3, the opposite proved to be true, as sodium levels in the lignin recovered from the lignin-rich phase were always less for continuous vs single-stage, batch operation.[13] For example, with continuous ALPHA, the sodium level of lignin recovered in the lignin-rich phase was reduced from the original SLRP lignin source level of 1400 ppm to 70 ppm when using the 30/70 acetic acid/water solvent mixture, a 20-fold reduction in one mixer/settler step. Thus, excellent mass transfer rates are obtained in the static mixer, such that a residence time of even 20 s is adequate for removing the metal salts from the lignin down to the ultrapure state (total residence times in the batch setup were 20−30 min[13]). We hypothesize that the shorter times for mass transfer to occur are more than compensated for by the dramatic increase in interfacial surface area provided by the static mixing elements. Furthermore, the static mixer setup tends to "renew" the interfacial area more frequently than with batch operation, which will tend to maintain a higher concentration gradient across the interface. With these results, an investigation of the effect of residence time on the metals content of the recovered lignin was not carried out, as significantly shorter residence times would neither be warranted nor particularly practical because of equipment limitations. Solvent compositions exceeding 70% water were not investigated because the lignin-rich phase significantly increases in viscosity with such water-rich solvents, increasing the chances of clogging the static mixer.

With the effect of residence time on metal salts extraction during continuous ALPHA being resolved, we then investigated the effect of reduced residence times on minimizing the undesirable lignin condensation reactions. Results in Figure 4 indicate that a significant if not complete reduction in such reactions occurs when continuous instead of batch ALPHA processing is used. With continuous processing, we see a small but well-behaved increase in the number-average molecular weight ($\bar{M}_n$) of the lignin-rich phase as the acetic acid concentration in the solvent is increased (and the water concentration is decreased). A slight increase in $\bar{M}_n$ of the lignin-rich phase would be expected even with no reactions occurring because the solvent-rich phase becomes a more powerful solvent with increasing acetic acid concentration,

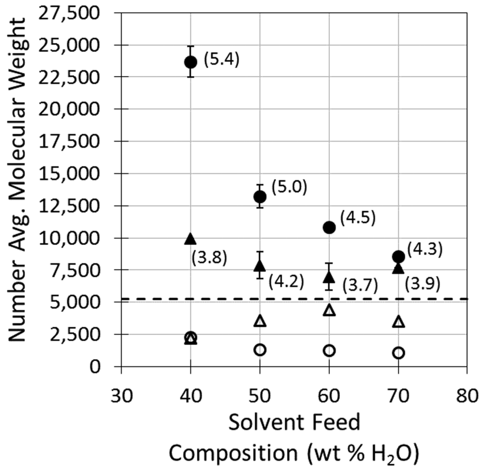

Figure 4. Effect of solvent feed composition on number-average molecular weight ($\bar{M}_n$) of the lignin recovered in the lignin-rich phase: ● = lignin-rich batch; ○ = solvent-rich batch; ▲ = lignin-rich continuous; Δ = solvent-rich continuous. The dotted line is for the SLRP feed lignin ($\bar{M}_n$ = 5250, PDI = 3.7). PDIs for the lignin-rich phase are given in parentheses.

capable of dissolving higher mol wt lignins. Thus, the molecular weight of the lignin that remains unextracted in the lignin-rich phase must increase, as is observed. In contrast, with batch operation, both $\bar{M}_n$ and the polydispersity index (PDI) of the lignin-rich phase increase significantly with increasing solvent strength, reaching almost 25,000 and a PDI of 5.4, respectively, for a 60/40 acetic acid−water solvent mixture. The GPC chromatograms of Figure 5 show how high mol wt lignin is formed in the lignin-rich phase when ALPHA is processed in a batch manner. Note the shoulder that appears in the "batch ALPHA" chromatogram, which extends to molecular weights higher than what is present in the starting material. Condensation reactions of model lignin compounds in hot acetic acid−water mixtures have been previously reported,[17−19] and the mol wt data shown here are consistent with such a polymerization reaction. In contrast, the "continuous ALPHA" chromatogram has no such high mol wt region, indicating minimal or no reactions.

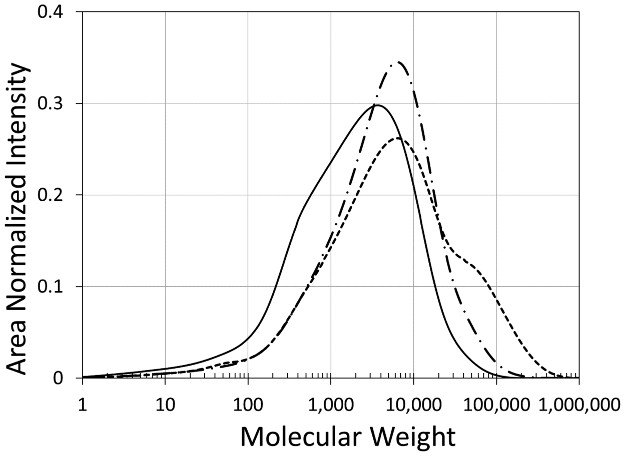

Figure 5. GPC chromatograms of the lignin recovered from the lignin-rich phase for a solvent feed composition of 60/40 wt/wt acetic acid/water: Feed SLRP lignin (—); lignin via continuous ALPHA (— • — •); lignin via batch ALPHA (---).

Evidence for similar polymerization reactions taking place in the solvent-rich phase is, however, lacking—regardless of whether batch or continuous operation is used. First, note in Figure 4 that with continuous processing the lignin species dissolved in the most powerful solvent mixture tested (i.e., 60/40 acetic acid/water) have the lowest $\bar{M}_n$. Furthermore, the trend of slightly increasing molecular weight with solvent strength observed in the solvent-rich phase with batch operation is more consistent with increasing solvent strength, not condensation reactions. Mol wt results for the solvent-rich phase under continuous operation are less conclusive, but there is certainly no consistent increase in $\bar{M}_n$ with solvent strength. We therefore hypothesize that the lignin-rich phase, where the solvent is dissolved in the lignin, is a more conducive environment for lignin condensation reactions to occur than the solvent-rich phase, where the lignin is dissolved in the solvent. In the solvent, the lower the mol wt is, the more polarizable lignin molecules tend to be shielded from each other by electrostatic forces.[20,21]

Why does the static mixer increase the mass transfer rate of metals between the phases but at the same time dramatically decrease the extent of condensation reactions? With respect to metals content, we hypothesize that the static mixer dramatically increases the interfacial area and enhances mixing of the phases, both of which promote mass transfer of metals from the lignin to the solvent phase. This increased interfacial area and mixing appears to more than compensate for the greatly reduced residence times in continuous vs batch ALPHA processing. But with respect to condensation reactions, the reduced residence times essentially eliminate these reactions in the lignin-rich phase; furthermore, the increase in interfacial area and enhanced mixing with the solvent-rich phase, where the propensity for reaction to occur is far less, can only reduce and not increase the propensity for reaction to occur.

The above experiments were all performed at a solvent-to-lignin (S/L) ratio of 9:1 (i.e., 10 wt % lignin). As would be expected from a knowledge of extraction technology,[22] changes in the S/L ratio increase/decrease the metal salts content in a relatively linear fashion (Figure 6). From a commercial feasibility standpoint, an economic optimum exists, with lower S/L ratios requiring higher capital costs (i.e., more extraction stages) but reduced operating (i.e., solvent recovery) costs and vice versa.

It was also of interest to know if other types of lignins could be purified and fractionated by continuous ALPHA processing. To this end, BioChoice, Lignol, and Indulin AT lignins were evaluated. For both BioChoice and Lignol lignins, lignin:water ratios were found such that a homogeneous lignin−water slurry could be constituted, which served as a vehicle to feed the source lignin to the progressive cavity pump (Figure 1). No conditions for making a lignin−water slurry with Indulin AT were found, so no continuous ALPHA experiments were carried out with this lignin. We hypothesized that this was a consequence of the product morphology created by the method used to produce the lignin particles, which was probably spray-drying, based on a patent that was awarded to Westvaco.[23] (In contrast, both SLRP and BioChoice lignins are precipitated from solution and filtered.) To test our hypothesis, ~10 g of Indulin AT was dissolved in a solvent so as to eliminate the original product morphology; the lignin that was precipitated

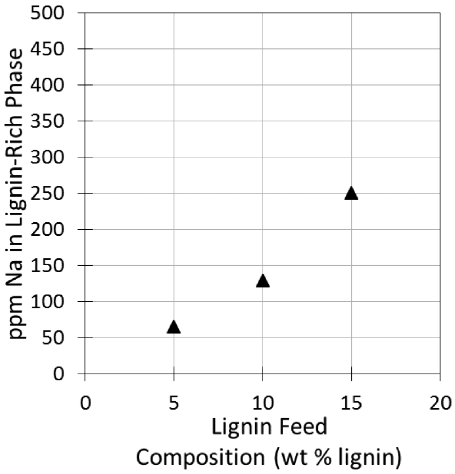

Figure 6. Effect of lignin feed composition (i.e., wt % lignin) on the sodium content of lignin recovered in the lignin-rich phase. For all of the above runs, the overall solvent feed composition was 40/60 wt/wt acetic acid—water.

from solution by adding an antisolvent could then be used to produce a stable, homogeneous slurry. However, performing such a dissolution—precipitation procedure on the large scale required to carry out continuous processing was not of interest, so no further experiments with this lignin were conducted.

ALPHA processing conditions of 50/50 acetic acid—water for the solvent composition and a solvent:lignin ratio of 9:1 were applied to BioChoice and Lignol lignins at a temperature of 69 ± 5 °C. The liquid—liquid phase separation of the feed mixture into a solvent-rich and lignin-rich liquid phase (as required for an extraction process such as ALPHA) occurred, so that continuous ALPHA could be applied. As shown in Table 1, significant metals purification of the lignins occurred, comparable to the reductions in metals content obtained with SLRP lignin. The success of these continuous runs was somewhat surprising because similar compositions and conditions were applied to both BioChoice and Lignol lignins in the batch setup, and the required liquid—liquid phase split between a lignin-rich and a solvent-rich phase simply did not occur (probably because the interphase mixing generated with a stir bar was inadequate).

Table 1. Metals Content of Lignin Recovered from Lignin-Rich Phase (e.g., "final Na") for Continuous ALPHA Processing of Three Different Source Lignins (e.g., "initial Na")[a]

lignin source	initial Na [ppm]	final Na [ppm]	initial Ca [ppm]	final Ca [ppm]	initial K [ppm]	final K [ppm]
SLRP	1400	200	340	35	310	20
BioChoice	7160	565	670	20	570	50
Lignol	<15	6	240	500	110	20

[a] Overall solvent feed composition was 50/50 wt/wt acetic acid—water and the S:L ratio was 9:1.

CONCLUSIONS

Although ultrapure lignin that is essentially devoid of metal salts can be generated by means of the ALPHA extraction process, undesirable condensation polymerization reactions can take place in the lignin-rich liquid phase, increasing the molecular weight and altering the molecular architecture of the lignin in ways that are not necessarily conducive to the various materials applications proposed for lignin. Fortunately, these reactions can be reduced to levels that are essentially undetectable by operating ALPHA as a continuous-flow process. In particular, a lignin—water slurry and an acetic acid—water mixture are combined in a mixing tee at ambient temperatures and then enter a static mixer heated to the operating temperatures (i.e., 60—100 °C) required to obtain the liquid—liquid phase split that forms the basis of the ALPHA process. Residence times in the heated mixer are no more than 20—30 s, essentially eliminating condensation reactions. Fortunately, the mass-transfer characteristics of the static-mixer setup are equally favorable for maintaining if not enhancing the extraction of metals from the lignin-rich liquid phase to the solvent-rich liquid phase, with sodium levels of 100 ppm being achievable at the proper operating conditions.

In addition, ALPHA operated as a continuous-flow process is robust, as two types of Kraft lignin and an organosolv lignin have all been successfully purified and fractionated with this method. In fact, one of these Kraft lignins could not even be processed in the batch mode during the early evaluation of the ALPHA process. Finally, continuous-flow ALPHA processing will have a decided advantage over batch processing when the time comes to generate the nontrivial quantities of ultrapure lignin required for evaluation in proposed product applications.

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Notes

The authors declare no competing financial interest.

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