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Continuous recovery of high-purity Kraft lignin from black liquor via simultaneous, liquid-phase acidification and purification

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ABSTRACT

A key advantage of the Sequential Liquid-Lignin Recovery and Purification (SLRP) process for the recovery of lignin from Kraft black liquor is the precipitation of a solvated, "liquid-lignin" phase (vs. the typical solid) during the CO_2 acidification step. Here, we have discovered that this lignin can also be maintained in a solvated state during the H_2SO_4 acidification step if aqueous acetic acid from the Aqueous Lignin Purification with Hot Agents (ALPHA) process is incorporated into the H_2SO_4 solution. As the liquid-lignin is converted from its salt form at pH = 9.5 to its acid form at pH = 2.5, the lignin initially solvated with water becomes solvated and thus liquefied with the acetic acid–water solution. Maintaining the lignin in a solvated liquid state has two advantages: (1) the entire SLRP + ALPHA process, from starting black liquor to final lignin product, can be operated continuously; and (2) mass transfer of metals impurities out of the liquid-lignin phase is significantly enhanced, resulting in both a cleaner Kraft lignin product (~2000 ppm Na and 0.5–1.0% ash) and reduced water washing.

1. Introduction

As a byproduct of cellulose isolation, Kraft lignin has historically been regarded as little more than furnace fuel to drive the recovery boilers. This trend is changing in recent years, however, as interest in chemical/material applications for lignin grows. As a renewable and relatively abundant biomaterial, lignin is potentially an economical substitute for petrochemicals in a range of applications. For example, lignin-based carbon fibers could sell for a fraction of the cost of carbon fibers from polyacryonitrile (PAN) (Jin et al., 2018), while polyurethane (PU) foams made from lignin could have improved microbial resistance and flame retardant properties versus conventional PU foams (Kalami et al., 2017).

Three lignin-recovery processes have been reported on in the literature and are either under development or have been commercialized: LignoBoost (Tomani, 2010), LignoForce (Kouisni et al., 2012), and SLRP (Hubbe et al., 2019; Lake and Blackburn, 2016; Velez and Thies, 2016). All three precipitate out the lignin by acidifying the black-liquor solution via CO_2 sparging, reducing the solution pH from 13.5 to 9.5. However, only with SLRP is the lignin precipitated out as what we refer to as a "liquid-lignin" phase (instead of solid lignin). In particular, at the elevated temperatures of operation (100–150 °C) and at pressures above the vapor pressure of the black liquor (5–15 bar), the lignin exists as a highly hydrated (and thus solvated) liquid phase, denser than the black-liquor solution and comprising 30–40% water by weight (Velez and Thies, 2016). Thus, this liquid-lignin can be continuously delivered to the next processing step simply by pumping. In contrast, with conventional lignin-recovery processes, a filtration step is required to separate the solid lignin from the black-liquor solution.

Whether the lignin is precipitated from the black liquor as a solid or liquid, the three recovery processes all use sulfuric acid for the 2nd acidification step. Here the pH is reduced from 9.5 to 2.5, converting the lignin from its salt (mostly sodium) to acid form – and all lignin to the solid state. This acidification results in a reduction in the sodium/ash content of the lignin from 5 wt% Na/20% ash (Velez and Thies, 2016) to ~8000 ppm Na/2–3% ash. The resultant solid is then filtered from solution, dried, and sold as Kraft (alkali) lignin.

Although these Kraft lignins can be used "as is" for a number of applications, including dispersants, specialty dyes, fillers, and binders, much cleaner lignins are required for other uses. For example, lignins suitable as precursors for carbon fibers must contain less than 200–250 ppm metals (Jin et al., 2018; Ogale et al., 2016), as these impurities create flaws in the final fibers during the carbonization process. Another example is lignin-based coatings applied via electrodeposition, where the lignin must be similarly clean. Finally, the positive effects of highly de-ashed lignins on the CO_2 adsorption of activated carbons has been

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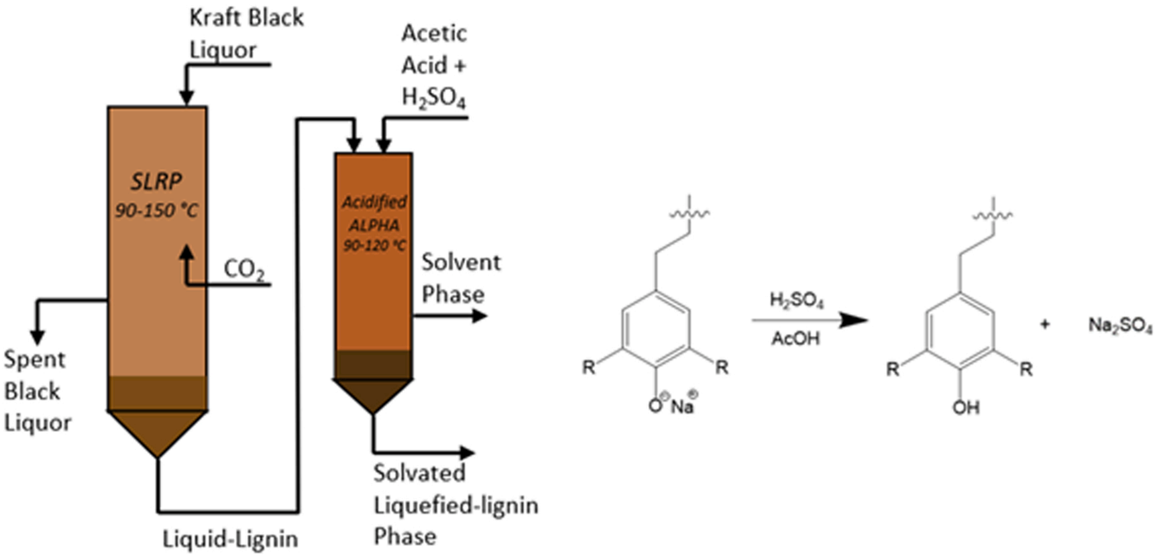

Fig. 1. Incorporating the solvation step of ALPHA into the H_2SO_4 acidification step of SLRP to produce a solvated, liquefied-lignin phase. The reaction of lignin from its sodium salt to acid form during the process is also depicted.

recently demonstrated (Puziy et al., 2018).

Thies and co-workers have developed the Aqueous Lignin Purification Using Hot Agents (ALPHA) process (Klett et al., 2015; Thies et al., 2018) for simultaneously cleaning and fractionating bulk lignins, including Kraft lignins and those recovered from biorefinery waste streams. By combining solid bulk lignin from any of the three recovery processes with *single-phase*, aqueous organic solutions at elevated temperatures, a liquid-liquid equilibrium can be formed whereby most of the lignin coalesces and precipitates out as a solvated, lignin-rich liquid phase, reduced up to tenfold in metals versus the starting Kraft lignin. (This lignin-rich liquid phase from ALPHA should not be confused with the preceding liquid-lignin phase obtained via SLRP, as discussed above.) When ALPHA is operated with 2–3 stages, very clean lignins (<50 ppm Na/0.01% ash) (Klett et al., 2015; Tindall et al., 2021) of controlled molecular weight can be produced. It is important to note that ALPHA is *not* classic liquid–liquid extraction, which requires two immiscible solvent phases. In fact, the solvent-rich and lignin-rich phase compositions are surprisingly similar in composition on a lignin-free basis. Instead, the phase split is created by differences in the properties of the lignin polymer moieties, such as molecular weight (Ding et al., 2018).

With the SLRP process producing solvated liquid-lignin from black liquor and ALPHA generating a solvated, lignin-rich liquid phase from solid bulk Kraft lignin, we hypothesized that a solvated, so-called "liquefied lignin" could be generated directly from SLRP liquid-lignin in a single step by combining the H_2SO_4 acidification step of SLRP with the solvation step of ALPHA (see Fig. 1). A key benefit to such a setup would be a continuous process for lignin recovery, purification, and fractionation starting from black liquor and continuing to the final lignin product, as all components would be present as easily processable (e.g., pumpable) liquids.

In this work, the effect of adding acetic acid (AcOH) to the H_2SO_4 acidification step of SLRP was investigated. Here the focus was on (1) determining whether operating conditions existed such that the desired solvated, liquefied lignin could be formed and (2) if such a liquefied lignin could be formed, what its yield and properties would be. In previous work, researchers (Lake and Blackburn, 2017) treated liquid-lignin from SLRP with 3.5 M acetic acid, but no liquefied lignin was reported after this acidification. In addition, the ash content of the final lignin product was relatively high, that is, greater than 5%, even after following acidification with a water wash of at least 10:1 v/v water-to-lignin. Other groups have used acetic acid–water mixtures in conjunction with either sulfuric acid (Pan and Sano, 2005; Shui et al., 2016) or hydrochloric acid (Gong et al., 2016; Shui et al., 2016) as a catalyst to extract lignin from biomass, but the lignin either completely dissolved in the solvent phase or remained in the insoluble biomass. That is, no separate, liquefied-lignin phase was reported.

2. Materials and methods

2.1. Materials

A Southeastern pine Kraft black liquor with a pH of 13.5, Kappa no. of 29, solids content of 42 wt%, total lignin content of 20 wt%, and ash content of 37 wt% was obtained from a Southeastern U.S. pulp mill. Compressed carbon dioxide (Coleman grade, 99.99% min) for acidifying the black liquor was obtained from Airgas USA. Glacial acetic acid (VWR cat. no. BDH3098–3.8LB) and 95–98% sulfuric acid (Fisher Sci. cat. no. A300–212) were obtained as indicated above. Deionized water (resistivity > 18.2 MΩ-cm) was obtained in-house from a Culligan deionization system followed by a Milli-Q reference system (Millipore Z00QSV0WW) to produce Type 1 water. 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.

2.2. Generating liquid-lignin from kraft black liquor via SLRP

First, the Kraft black liquor was diluted from the starting 42–35 wt% by the addition of water to ~1600 g of black liquor in a 2-L Parr pressure reactor (Model 4541). The reactor body had a custom-made, 45° conical bottom, and a helical ribbon impeller operating at 60 rpm was used for agitation. After mixing the water and black liquor together for 15 min, the reactor head space was purged with nitrogen. The system pressure was then maintained at 50 psig over the entire course of the experiment in order to minimize the evaporation of water into the gas phase. Next, the black liquor was heated to 120 ± 5 °C; once temperature was reached, acidification (i.e., carbonation) commenced with the addition of CO_2 via sparging into the liquor at 250 std mL/min (Brooks 5850 mass flow meter and 5878 Controller). All gases exiting the reactor were vented into a hood, as poisonous H_2S gas is generated from the acidification reaction. This carbonation step resulted in formation of liquid-lignin as the pH dropped from 13.5 to 9.5. To monitor the pH, samples were taken through a dip tube in the reactor. Once the pH reached 9.5, agitation and CO_2 feed were discontinued, and the dense, viscous, liquid-lignin phase that had formed was allowed to settle at temperature and pressure for 2 h. After obtaining a clean separation of the liquid-lignin phase from the spent black-liquor phase, the reactor was cooled to 65 °C and depressurized. The spent black liquor was then decanted off. Recovery of the liquid-lignin, which has a melting point of ~105 °C, was simplified by allowing it to cool and solidify. The solidified liquid-lignin was then removed from the reactor and collected. Additional details of the CO_2 carbonation process via SLRP are given elsewhere (Velez and Thies, 2016). In order that the overall solvent composition of the system be known, the water content of the original liquid-lignin phase was determined by Karl-Fischer titration (Ding et al., 2018).

2.3. Identifying phase-transition temperatures for liquefying solidified liquid-lignin

Acetic acid (AcOH) concentrations ranging from 0 to 80 wt% of a solvent mixture consisting of AcOH, H_2SO_4, and H_2O were evaluated in the search for temperatures at which solidified liquid-lignin would liquefy in the presence of the above solvent mixture. A given experiment was carried out in a 9.5-dram glass vial (VWR cat. no. 66012–066) containing a magnetic stir bar of appropriate size (e.g., Fisher, part no. 14–512–121, 9.5 mm o.d. x 10 mm long). The temperature of the contents of the vial were measured with a 1/16″ o.d., grounded, K-type thermocouple (Omega cat. no. CASS-116 G-12), which was inserted into the lignin–solvent mixture through a pre-pierced septum cap (VWR part no. 89042–292). The thermocouple was calibrated to within 0.2 °C accuracy using the boiling point and freezing point of water. Vials were immersed so that the mixture level was ~1/2 in. below that of the oil bath (Dow Corning 200 silicone heat transfer fluid, a poly(dimethylsiloxane)), which was heated with a 200 W quartz heater (Glo Quartz Electric, LHP200) and temperature-controlled with an OMEGA Series CN370 controller. For sample preparation, stock solutions consisting of acetic acid mixed with a 2 N H_2SO_4 solution in water were used. ~2 g of lignin were added to the vial, and solvent was added to create a 6:1 solvent-to-lignin wt/wt ratio. Because the solidified liquid-lignin consisted of 48.1 ± 0.2% water (as determined by Karl-Fischer titration), this water had to be accounted for during preparation of the stock solution. Vials were stirred continuously at ~120 rpm and heated at ~2 °C/min. As the particles began swelling, the vial was periodically removed for ~5 s from the bath to examine its contents (the solvent phase was relatively dark) and thus more precisely determine the temperature at which the lignin particles liquefied and then (within ~2–3 s) coalesced to form a separate liquid phase. (These quick looks had no discernible effect on the temperature of the contents of the vial.) The observed phase transition was from solid liquid-lignin in solvent to liquefied lignin in solvent, that is, from solid–liquid (SLE) to liquid–liquid phase equilibrium (LLE). For each phase-transition observation, experiments were performed in duplicate.

2.4. Lignin yields and properties for the liquefied-lignin and solvent phases

Once the region of LLE had been identified as described above, lignin yields and properties for both of the resultant, liquefied-lignin and solvent phases were determined. For these experiments, a 50-mL Parr reactor (Part no. 2430HC2) was used in lieu of vials, so that adequate amounts of material would be available for analysis. The pressurized reactor also enabled operation above the normal bpt (~105 °C) of the solvent mixtures. AcOH concentrations in H_2SO_4 solutions (typically 2 N) were prepared as described above, except now AcOH concentrations were limited to the discovered LLE region. For a typical experiment, ~10 g of solidified liquid-lignin was added to the reactor, along with the amounts of glacial AcOH and H_2SO_4 required to make up the desired weight fraction of acetic acid, normality of sulfuric acid, and solvent-to-lignin ratio of 6:1. The reactor was heated to temperature (i.e., 90, 105, or 120 °C) within 5–10 min under agitation at 100 rpm; then the contents were allowed to equilibrate under agitation for 15 min. Phase separation between the solvent and the liquefied-lignin phases that formed was essentially immediate after the cessation of agitation. After allowing the reactor to cool for 2–5 min to 75 °C so as to facilitate handling, the less-dense solvent phase was decanted off. The liquefied-lignin phase that had precipitated was recovered by scraping it off both the impeller and the bottom of the reactor.

2.4.1. Lignin yield and distribution

The lignin in each phase was isolated in order to determine its distribution between the phases. Lignin was recovered from the solvent phase by adding DI water to that phase in a 1:1 wt/wt water/phase ratio, thus precipitating out the lignin as a solid. The lignin was then isolated using a Buchner funnel with a cellulose filter (cat. no. 09–790–4 C). Lignin was recovered from the liquefied-lignin phase by again using a 1:1 wt/wt DI water/phase ratio. The resultant slurry was then thoroughly mixed in a blender to ensure the complete removal of sulfuric acid from the precipitated solid lignin particles. The solid lignin was then isolated via the Buchner funnel setup described above. Finally, the lignin recovered from each phase was allowed to dry overnight in a fume hood down to ~5 wt% water, with the water content of the lignin being determined via by Karl–Fischer titration. Mass balances on the initial mass of lignin vs. the sum of the amounts recovered in both the solvent and liquefied-lignin phases closed on average to better than ± 8%.

2.4.2. Metals content of recovered lignins

Metals analyses of dried lignin samples from the liquefied-lignin and solvent phases, as well as from the liquid-lignin feed, were carried out by the Agricultural Service Lab at Clemson University using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Analyses were carried out using an Ametek Spectro Scientific spectrometer, model ARCOS. Submitted samples were air-dried and then vacuum-dried to remove water as completely as possible, as any residual water would be considered part of the lignin mass. Details of the ICP method are described elsewhere (Klett et al., 2016).

2.4.3. Molecular weights of recovered lignins

Dried lignin samples from the liquefied-lignin and solvent phases were analyzed by gel permeation chromatography (GPC) to determine the extent of fractionation by molecular weight. GPC was also used to look for evidence of increases in lignin molecular weight due to acetic acid-catalyzed condensation reactions, as previously observed for mixtures of lignin with hot AcOH–water solutions (Ding et al., 2018). GPC separation was achieved using a Waters Styragel HT 5 column followed by an Agilent PolarGel-L column, using a mobile phase consisting of dimethylformamide (DMF) plus 0.05 M LiBr at a flow rate of 1 mL/min. Samples were prepared by dissolving lignin in the mobile phase at a concentration of 1 mg/mL and filtered using a 0.2 µm PTFE membrane syringe filter (VWR cat. no. 28145–291). The instrument was calibrated with polyethylene glycol (PEG) standards on a refractive index detector, and the lignin samples were detected using a Waters 996 UV–vis PDA detector at 280 nm.

2.4.4. Chemical functionality of recovered lignins by ^{31}P NMR Spectroscopy

The hydroxyl content of selected lignins and lignin fractions was determined using phosphorus nuclear magnetic resonance (^{31}P NMR) spectroscopy following previously published methods (Pu et al., 2011; Kalami et al., 2017). Three lignins were analyzed: SLRP liquid-lignin (see Section 2.2), commercial BioChoice lignin, and the liquefied-lignin phase from one-step SLRP + ALPHA having the highest yield (Section 2.4).

2.5. Effect of sulfuric acid concentration on formation of a liquefied-lignin phase

For these experiments, the AcOH concentration was held constant at

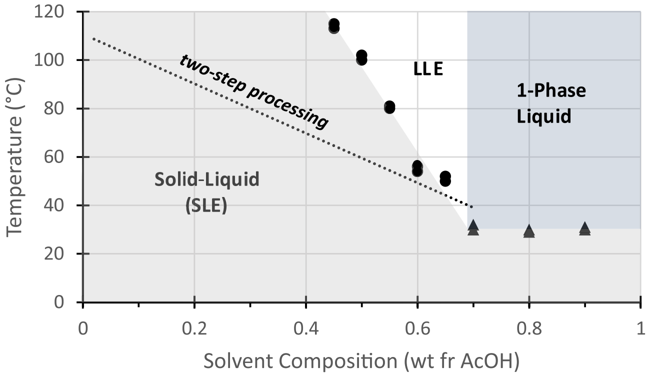

Fig. 2. SLE to LLE phase-transition temperatures with increasing acetic acid (AcOH) concentration at a 6:1 solvent-to-lignin ratio. The solvent system is AcOH dissolved in 2 N H_2SO_4. Dark circles denote the one-step phase transition of solidified liquid-lignin directly from SLE to LLE (i.e., one-step SLRP + ALPHA). The dotted line (Klett et al., 2015) denotes the conversion of (solid) SLRP lignin to liquefied lignin via ALPHA. Dark triangles denote the direct transition from SLE to a one-phase liquid, with no formation of LLE. All measured data including duplicates are shown.

55 wt% of the total solvent (at this concentration, the liquefied-lignin phase was observed over a relatively wide range of temperatures), and the effect of changes in H_2SO_4 normality on lignin yields and properties was explored. The 50-mL Parr reactor and methods described above were used. Experiments were performed at 90 °C.

3. Results and discussion

3.1. *Liquid–Liquid Equilibrium (LLE) region and yields for liquid-lignin–AcOH–H_2O–H_2SO_4 system*

The impact of partially replacing 2 N sulfuric acid, which is normally used to acidify the liquid-lignin, with acetic acid is illustrated in Fig. 2. The results confirmed our hypothesis, namely, that a solvated (i.e., liquefied) lignin phase can be generated directly from SLRP liquid-lignin by combining H_2SO_4 acidification and AcOH–water solvation into a single step. Note from the figure that when neat 2 N H_2SO_4 (i.e., 0.0 wt fr AcOH) is used, solid lignin particles precipitate out in the acid solution in solid–liquid equilibrium (SLE). This solid lignin is the conventional SLRP lignin product. Only SLE exists until the composition reaches 45 wt % AcOH, so that now 45% of the 2 N H_2SO_4 solution has been replaced with AcOH. Here at this composition and ∼115 °C we have the first appearance of liquefied lignin in LLE, as the solid lignin particles now liquefy in the presence of the AcOH-fortified solution. As the wt% AcOH in the solvent is further increased, the temperature at which the lignin liquefies decreases rapidly, ∼3.4 °C for every mol% increase in AcOH concentration. This region of LLE continues until 70 wt% AcOH, where the phase transition becomes that which typically occurs for solid/liquid mixtures: the solid lignin directly dissolves in the solvent (here, at 31 ± 1 °C), with no intermediate LLE step, to form a single liquid phase.

It is interesting to compare the above phase behavior created by one-step SLRP + ALPHA processing with that obtained when SLRP and ALPHA are conventionally employed as two separate steps; that is, the liquid-lignin is *first* converted into SLRP lignin (a solid) via 2 N H_2SO_4 acidification, and *then* the SLRP lignin is liquefied with AcOH–water mixtures to create "ALPHA" lignin. As shown in Fig. 2, two-step processing does expand the region of LLE, with aqueous AcOH concentrations as low as 10 wt% (at 100 °C) being effective for liquefying the lignin. The dependence of phase-transition temperature on AcOH concentration is also markedly less, with the temperature dropping only 1.0 °C per mol% increase in AcOH concentration. Interestingly, for both the one-step and two-step methods, the LLE region disappears at 70 wt% AcOH and is replaced with a single liquid phase.

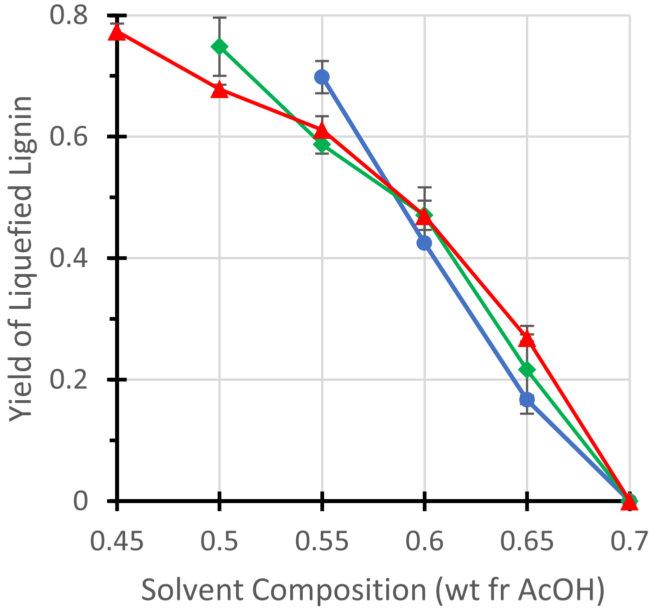

Fig. 3. Lignin yield/recovery in the liquefied-lignin phase with increasing AcOH concentration for 90 (●), 105 (◆), and 120 °C (▲). H_2SO_4 normality was held constant at 2.0. Error bars here and in Fig. 4 are for one std devn. Trendlines here and in Fig. 4 are included to guide the eye.

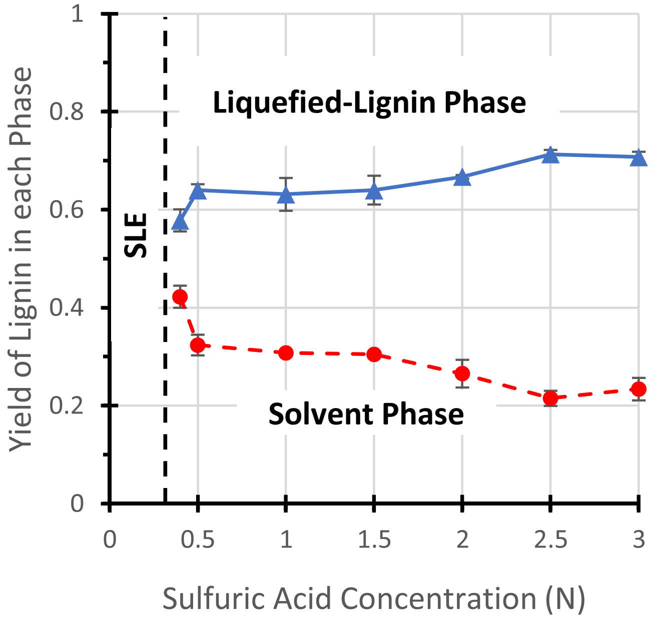

Fig. 4. Lignin recovery/yield in each LLE phase with increasing H_2SO_4 normality. AcOH was held constant at 55 wt%, the solvent-to-lignin ratio at 6:1, and the temperature at 90 °C.

The significant difference in phase behavior between the two processing methods can be explained as follows: Because the liquid-lignin being fed to one-step is precipitated directly from the black liquor with CO_2, it undergoes only a mild acid precipitation, that is, with carbonic acid. Thus, it has a relatively high Na content of 55,000 ± 2500 Na (equivalent to ∼20% ash (Velez and Thies, 2016)). Although this is much less than the 20% Na/50% ash content of the starting black liquor, a significant percentage of the hydroxyl groups are still in their Na-salt form. This excess sodium would be expected to have an impact analogous to the "salting out" effect observed with proteins (Bailey and Ollis,

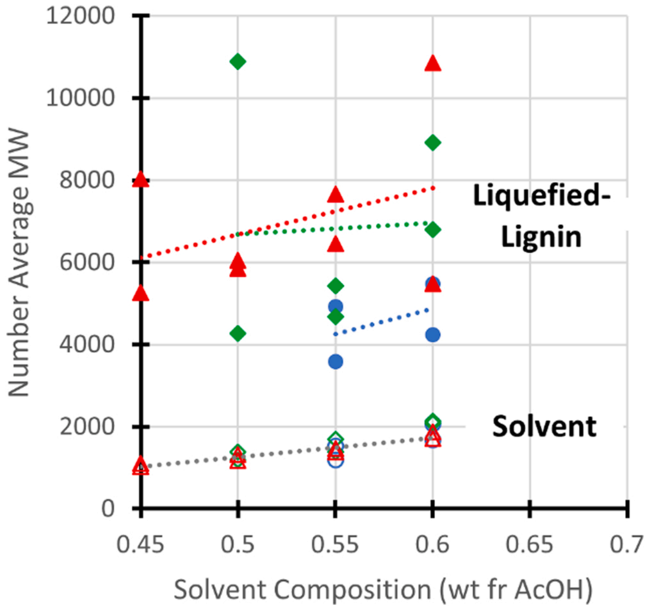

Fig. 5. Number average molecular weight (Mn) in each LLE phase with increasing AcOH concentration at 90 (●○), 105 (◆◇), and 120 °C (▲△). H_2SO_4 normality was held constant at 2.0. All data including duplicates are shown here and in Fig. 6, with linear regression being used to guide the eye.

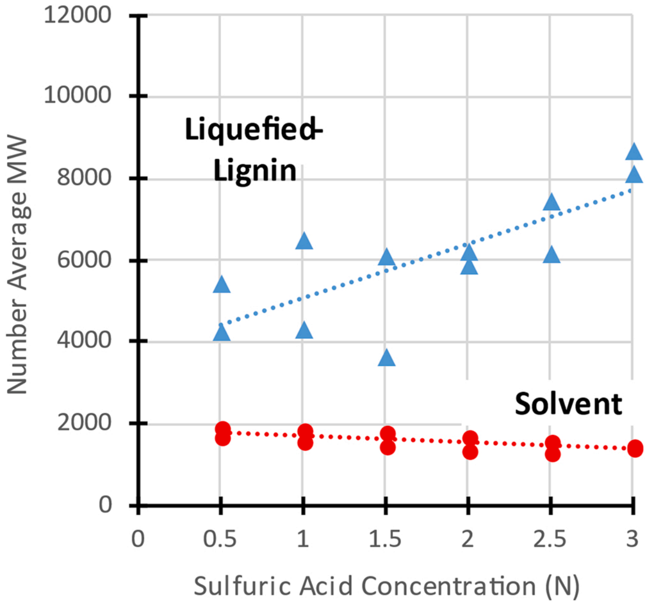

Fig. 6. Mn of lignin from each LLE phase with increasing H_2SO_4 normality. AcOH was held constant at 55 wt%, the solvent-to-lignin ratio at 6:1, and the temperature at 90 °C.

1986); thus the SLE region is much larger than the LLE region when liquid-lignin is the feed. In contrast, the SLRP lignin fed via two-step processing contains only ~8000 ppm Na, so most OH groups are in their acid form. Aggregation of the lignin, and thus formation of the liquefied-lignin phase, is therefore favored, as attractive (i.e., dispersive) forces dominate (Norgren et al., 2001; Velez and Thies, 2016). Nevertheless, having a smaller LLE region to work with is preferred if it enables the continuous processing of lignin from black liquor to a clean lignin product in a single processing step.

The fraction of lignin from the liquid-lignin feed contained within the lignin-rich, liquefied-lignin phase (i.e., yield) is shown in Fig. 3. These yields are similar to but lower than the ALPHA processing (Klett et al., 2015) of SLRP lignin with AcOH–H_2O solutions via ALPHA at 70 and 95 °C, with their yields being 0.82 at 0.50 wt fr AcOH for comparison (not shown). The effect of temperature on lignin yields in the liquefied-lignin phase was small in this work, whereas in Klett at al.'s work the effect was more pronounced.

As shown in Fig. 4, the effect of H_2SO_4 concentration on lignin yield was also investigated. Here we see that below 0.4 N H_2SO_4, insufficient Na is removed from the lignin to enable its solvation by the AcOH–H_2O solution; thus, only SLE exists. However, even at only 0.5 N, sufficient Na removal has occurred so that attractive (dispersive) forces between the lignin moieties become dominant, and the desired liquefied-lignin phase can form.

3.2. Molecular weight analysis

Number average molecular weights (M_n) for the lignin that precipitated out in the liquefied-lignin phase, versus that which remained dissolved in the solvent phase, are presented in Fig. 5. For the liquefied-lignin phase, the trend, as shown by the linear regressions plotted for each temperature, is one of increasing molecular weight, both with increasing temperature and AcOH concentration. However, the scatter in molecular weight (MW) is large. Typically, we do observe more scatter in MW measurements for lignins recovered from the lignin-rich liquid phase – whether from the liquid-lignin phase of SLRP (Velez and Thies, 2016) or the lignin-rich liquid phase of ALPHA (Tindall et al., 2020). We attribute this phenomenon to the increased tendency of the higher-MW lignin molecules to aggregate, especially when they are initially present in a phase rich (i.e., >50 wt%) in lignin polymer, so that entanglement is more likely to occur. However, the unusually large scatter in Fig. 5 indicates that this aggregation effect is more pronounced when SLRP + ALPHA are practiced simultaneously in one step – vs the conventional, two-step processing of SLRP followed by ALPHA. Ongoing experiments are being carried out to see how we might reduce aggregation before MW analysis.

The increase in molecular weight of lignin in the liquefied-lignin phase with temperature is consistent with the work of Velez and Thies with liquid-lignin from SLRP (Velez and Thies, 2015). Others (Ding et al., 2018) have reported an increase in lignin molecular weight with increasing AcOH concentration in ALPHA. Two complementary effects could be occurring here: (1) The yield of lignin in the liquefied-lignin phase decreases with increasing AcOH concentration as the solvent phase becomes more powerful. As a result, only the higher MW lignins remain undissolved in the solvent and phase-split to form a separate liquid phase. (2) Acid-catalyzed condensation reactions are favored in the lignin-dense, liquefied-lignin phase, as the lignin molecules are in intimate contact. Additionally, higher temperatures tend to accelerate these reactions (Ding et al., 2018; Sano et al., 1998; Velez and Thies, 2015). However, residence times for our one-step SLRP + ALPHA process were kept to 15 min, as the previous work cited above indicated that this would keep condensation reactions in the liquefied-lignin phase to a minimum, and thus not significantly impact MW results.

For the lignin dissolved in the solvent phase, no significant effect of temperature was seen either here in Fig. 5, or in previous work with SLRP (Velez and Thies, 2015) or ALPHA (Ding et al., 2018). Condensation reactions are minimal, as now the lower MW lignin is dissolved in (and thus surrounded by) solvent molecules. (Contrast this with the situation in the liquefied-lignin phase, where the solvent is dissolved in (i.e., plasticizes) the lignin (Sperling, 2015).) In fact, the modest increase in molecular weight with AcOH concentration observed in the solvent phase can be explained solely by the yield of lignin in the solvent phase more than tripling between 45% and 60% AcOH, as the higher MW lignin becomes increasingly soluble in the solvent phase.

The effect of H_2SO_4 concentration on the molecular weight of the lignin in each LLE phase is given in Fig. 6. Consistent with the above discussion, we see an increase in the lignin molecular weight in the

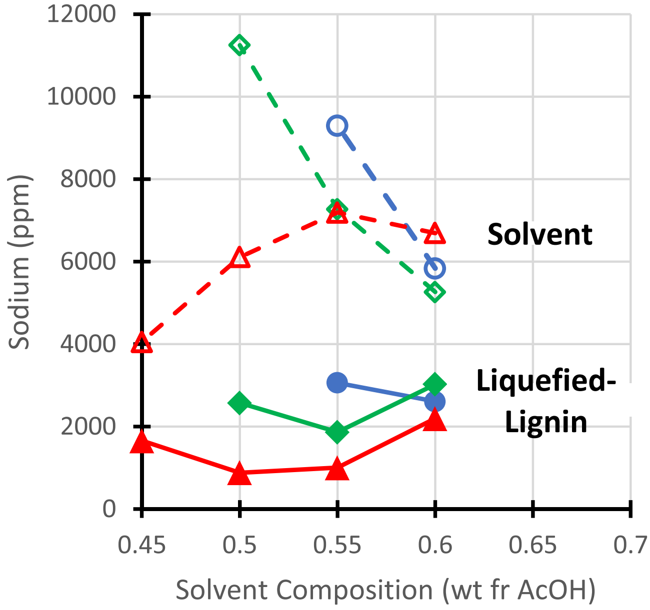

Fig. 7. Sodium content of lignin from each LLE phase with increasing AcOH concentration at 90 (●○), 105 (◆◇), and 120 °C (▲△). H_2SO_4 normality was held constant at 2.0. Trendlines connect the individual measurements here and in Fig. 8.

lignin-rich, liquefied-lignin phase, but no change in the lignin-poor, solvent phase. These results lend further credence to our hypothesis that acid-catalyzed condensation reactions are at least partially responsible for the observed increases in lignin molecular weight.

3.3. *Chemical functionality of recovered lignins by ^{31}P NMR spectroscopy*

^{31}P NMR spectroscopy indicated no significant structural differences in OH content, whether aromatic, aliphatic, or carboxylic, between the three evaluated lignins, all derived from Southeastern Southern pine black liquor: (1) a liquefied lignin recovered by one-step SLRP + ALPHA at 120 °C using 45% acetic acid in a 2 N H_2SO_4 solution (Fig. 3), (2) a SLRP liquid-lignin Control recovered per Method 2.2, and (3) a BioChoice lignin produced by Domtar. The liquefied lignin with a yield approaching 80% was chosen for comparison, as it should contain ∼80% of the same lignin molecules originally present in the "parent" SLRP liquid-lignin control, assuming no changes in the structure of individual lignin species due to chemical reactions. The above results support our hypothesis that reactions between lignin moieties to effect structural changes are relatively rare, and that the dominant effect of one-step SLRP + ALPHA is the separation of lignin species into two distinct liquid phases due to entropic and enthalpic effects, as is typical for many polymer–solvent solutions (Sperling, 2015).

3.4. *Metals analysis*

The effect of increasing AcOH concentration on the sodium content of the lignin recovered from each LLE phase is given in Fig. 7**.** For the liquefied-lignin phase, the highest temperature (120 °C) consistently resulted in lower levels of Na. At 45% AcOH, where lignin yields approach 80% (see Fig. 3), the sodium content of the dried lignin recovered from the liquefied-lignin phase was 1700 ppm Na (equivalent to ∼0.8% ash). At 50% and 55% AcOH, the sodium content in the liquefied-lignin phase was reduced to 1000 ppm (∼0.5% ash), albeit with some drop in lignin yield. Thus, a significant fraction of very clean lignin can be obtained from the starting liquid-lignin at these conditions. In particular, these Na levels represent a reduction in Na by a factor of ∼25 (i.e., from 55,000 ppm Na) over those present in the liquid-lignin phase from SLRP (or from the intermediate solid lignin phase in LIgnoBoost or LignoForce), and a reduction by 3–4 over the levels (7000–8000 ppm, Klett et al., 2016) typically present in a commercially available Kraft lignin. On the other hand, even higher AcOH levels (i.e., 60% and above) create an increasingly organic solvent phase that, in combination with lignin yields falling below 50%, effect increased sodium levels in the dried, liquefied-lignin phase. Finally, recall from Section 2.4.1 that recovering the lignin from the solvent and liquefied-lignin phases required minimal amounts of water (i.e., a 1:1 wt/wt water: phase ratio); thus, washing requirements for obtaining lignin with such low ash/metals content are much lower than the multiple (15−20) washing steps (e.g., Zhang and Ogale, 2016) required to

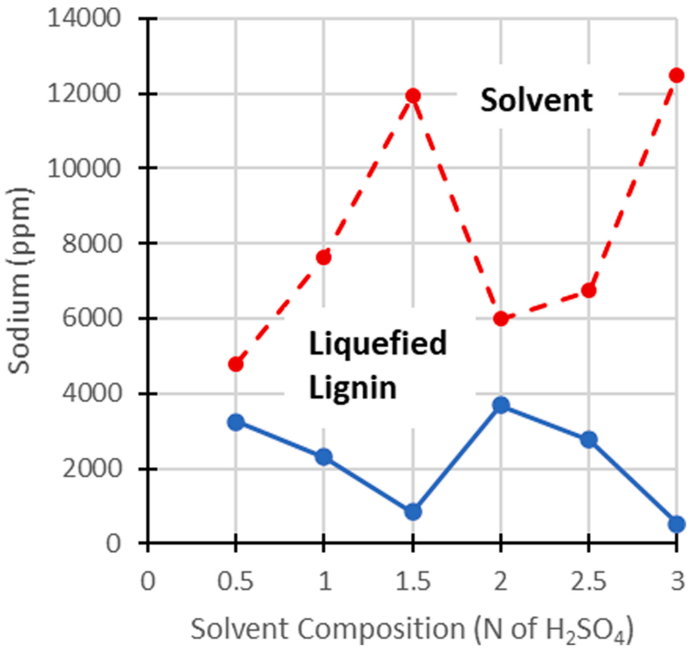

Fig. 8. Sodium (Na) content of lignin recovered from each LLE phase with increasing H_2SO_4 normality. AcOH was held constant at 55 wt%, the solvent-to-lignin ratio at 6:1, and the temperature at 90 °C.

obtain a similarly clean Kraft lignin.

With respect to the solvent phase in Fig. 7, previous studies with lignin–solvent–water systems (e.g., Tindall et al., 2020) have shown that Na results for the phase dilute in lignin (here, the solvent phase) can be in significant error vs. those derived from an overall Na balance using the Na content of the feed and liquefied-lignin phases, both of which have proven to be reliable. (Such a Na balance cannot be performed here because each phase is water-washed (see Section 2.4.1) before drying to remove the H_2SO_4, which also removes a portion of the Na.) For example, the solvent phase typically consists of 1–5 wt% lignin and thus is concentrated by a factor of 20–100 by drying, resulting in high Na numbers. As shown in Fig. 7, this combination of washing and drying results in a wide range of values for Na content. However, qualitatively the trends are correct: When the Na content goes "up" in one phase, it goes "down" in the other, and vice versa – as it must to satisfy the overall Na mass balance.

Referring to Fig. 8, the effect of H_2SO_4 concentration on the Na content in each LLE phase was also investigated. Fortunately, only moderate levels of H_2SO_4 are required to achieve low levels of Na in the liquefied-lignin phase, with 1.0–1.5 N H_2SO_4 being optimum. The surprising minimum/maximum behavior in Na content for the liquefied-lignin phase, which appears to be a case of competing effects, was reproducible (see Supplemental Information), and will be the subject of a future investigation. As in Fig. 7, the Na content of the two phases qualitatively track each other "up and down", and there are large variations in the Na content of the solvent phase due to sample-concentration effects.

4. Conclusions

A liquefied lignin reduced by a factor of 3–4 in metals/ash content vs. conventional Kraft lignin can be produced by adding hot (90–120 °C) acetic acid to the aqueous H_2SO_4 acidification step used for lignin recovery and purification from black liquor. Although this technique can be added to the back end of any of the three lignin-recovery processes currently being commercially practiced or developed, the preferred option is to apply this technique to the liquid-lignin phase of the SLRP process, thus enabling continuous processing from the black liquor to a high-purity Kraft lignin product. Furthermore, if lignin of ultrahigh purity (i.e., <0.01% ash) and controlled molecular weight is desired for higher-value applications, the liquefied-lignin product from above can be fed continuously to the ALPHA process, thus maintaining a continuous train throughout the entire multi-step sequence. Finally, it should be noted that the hot aqueous AcOH solvent phase from above can be recycled, after adjusting the AcOH/H_2O ratio and metal salts via minimal distillation, to serve as the solvent feed for ALPHA.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2022.115084.

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