ACS Sustainable Chemistry & Engineering

Research Article

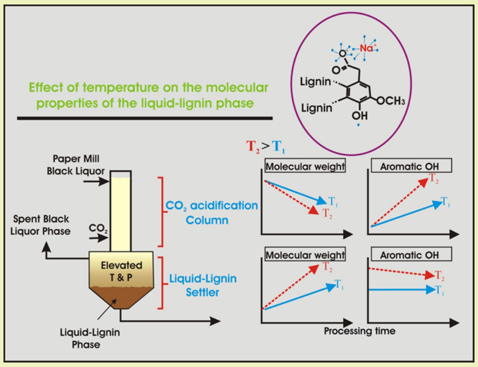
pubs.acs.org/journal/ascecg

Temperature Effects on the Molecular Properties of Liquid Lignin Recovered from Kraft Black Liquor

Julian Velez and Mark C. Thies*

Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634-0909, United States

Supporting Information



ABSTRACT: The effect of temperature on the molecular properties of a "liquid-lignin" phase recovered from Kraft black liquor via CO_2 acidification at elevated temperatures was investigated. For softwood black liquors, up to a 4-fold increase in the molecular weight (mol wt) of the recovered liquid-lignin phase was observed as the acidification temperature was increased from 100 to 150 °C. Thus, experiments were carried out in which the CO_2-acidification steps of preheating, acidification, and phase separation were decoupled from each other in order to elucidate the mechanisms for the observed changes in molecular weight. Results indicate that some lignin cleavage and a corresponding decrease in molecular weight occur during the black-liquor preheating step. However, a significant net increase in molecular weight occurs after the lignin has phase-separated from the black liquor in the form of a new, denser liquid phase, pointing to condensation reactions as the most likely cause. Minimal changes in lignin aromatic content were observed in the new liquid-lignin phase. Because elevated-temperature, CO_2 acidification can be carried out continuously via the SLRP process, adjusting residence times in the black liquor—liquid lignin phase separator would be an effective method for controlling the molecular weight of the recovered lignin for a given product application.

KEYWORDS: *Black liquor, Liquid—liquid equilibrium, Molecular weight, Lignin condensation, Lignin hydration, Lignin precipitation*

■ INTRODUCTION

Processes for recovering and purifying lignin from paper-mill black liquors have been developed in which lignin is precipitated by acidifying the black liquor.[1−3] The recovered lignin is envisioned as a clean-burning biofuel,[4,5] as well as a renewable precursor and substitute for petroleum-derived polymers and other materials (e.g., polyurethane foams, thermoplastic and thermoset composites, phenolic resins, etc.).[6−9]

In recent years, three processes have been proposed for the recovery of lignin from Kraft black liquor: LignoBoost, LignoForce System, and sequential liquid-lignin recovery and purification (SLRP).[1−3] Each has its advantages and disadvantages. In two of the lignin-recovery processes (i.e., LignoBoost and LignoForce System), the lignin is recovered as a precipitated solid phase, whereas with SLRP, the lignin phase-separates out and is recovered as a new, dense liquid (a so-called "liquid-lignin") phase. The fact that the lignin is in the form of a liquid means that the SLRP process can be operated in a continuous manner (see Figure 1). Clearly, this can be a significant advantage on a commercial scale.

For the CO_2-acidification step, the temperature at which the lignin first phase-separates as a liquid (vs a solid) phase is about 100 °C. Temperatures as high as 200 °C can be employed for forming liquid lignin, as long as enough pressure is maintained on the black-liquor and liquid-lignin phases such that all components remain in the condensed state. However, the economics of operating at such elevated temperatures would be expected to be untenable.

Extensive characterization work on the molecular properties of both residual and soluble lignins, and how they change during the Kraft pulping process, has been performed over the past 20+ years by a number of groups. (Residual lignins are those that remain with the cellulose, whereas soluble lignins are those that are dissolved in the black-liquor phase.) Some of the earliest work in this area was carried out by Gellerstedt and coworkers;[10−12] in more recent years, the work of Argyropoulos' group[13−15] has been prominent. For example, it is well-known that as the pulping process proceeds (and as a result the Kappa number decreases), the molecular weight of both the residual and soluble lignins decreases primarily because of the cleavage of the β-O-4 linkages, which has also been shown to result in a corresponding increase in phenolic OH content.[15,16] However, information on the molecular-property changes that lignin undergoes when it phase-separates from the black liquor to form a new phase during lignin-recovery processes, such as those mentioned above, is scarce. Zhu et al.[17] investigated changes in molecular weight and functional-group composition for the solid lignin phase that precipitates during the CO_2 acidification step of the LignoBoost process. The focus of this

Received: November 7, 2014
Revised: April 23, 2015
Published: May 5, 2015

ACS Publications

DOI: 10.1021/sc500703m

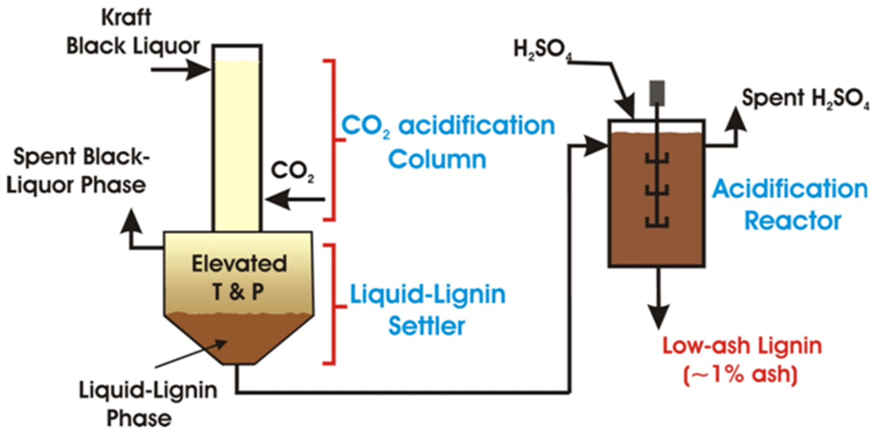


Figure 1. Sequential liquid-lignin recovery and purification (SLRP) process for the production of low-ash lignin.

Table 1. Origin, Kappa Numbers, Black-Liquor Solids Content, and CO_2 Acidification Temperatures of the Three Kraft Black Liquors Used To Produce Liquid-Lignin Phases

	origin	Kappa no.	solids content (wt %)	CO_2-acidification temperature (°C)
Kraft black liquor "A"	softwood	90	20, 30, and 40%	100, 125, and 150
Kraft black liquor "B"	softwood	25	20, 30, 42, and 50%	100, 125, and 150
Kraft black liquor "C"	hardwood	18	20, 27, and 35%	100, 125, and 150

work was on the effect of precipitation pH, ion strength, and temperature on product yield, molecular weight, and functional-group composition for the precipitated solid lignin phase. Temperature effects were minimal for the 45−75 °C range that was investigated (where solid lignin is the precipitating product), and so were not the focus of this work.

The objective of the study herein was to investigate the effect of elevated processing temperatures (i.e., 100−150 °C) on the molecular properties of the liquid-lignin phase that phase-separates from the black-liquor solution during CO_2 acidification at these conditions. No previous investigations have been performed, at least partly because only recently have researchers discovered[1,18,19] that lignin recovery from black-liquor solutions can be carried out at such temperatures.

■ EXPERIMENTAL SECTION

Materials. Three black liquors, two softwood and one hardwood, were obtained from commercial Kraft pulp mills and used to produce the liquid lignins discussed herein. High performance liquid chromatography (HPLC)-grade dimethylformamide (CAS 68-12-2, purity of 99.7%) and lithium bromide (CAS 7550-35-8, purity 99.9%), used for gel permeation chromatography (GPC) analysis, and deuterated chloroform (CAS 865-49-6) and pentafluorobenzaldehyde (CAS 653-37-2), used for NMR analysis, were all obtained from Alfa Aesar. Pyridine (CAS 110-86-1, 99.0%), acetic anhydride (CAS 108-24-7, 99.0%), chloroform (CAS 67-66-3, 99.8%), diethyl ether (CAS 60-29-7, 99.0%), and ethanol (CAS 64-17-5, 99.5%), used for the acetylation of liquid lignins, were all obtained from VWR.

Producing Liquid Lignin via CO_2 Acidification of Kraft Black Liquors. Liquid-lignin phases were produced via CO_2 acidification of three different black liquors of various solids content over a range of acidification temperatures. Briefly, black liquor with a pH of 13−14 and a given solids content was loaded into a specially modified, 2 L batch reactor (see Figure S1 in the Supporting Information), heated up with stirring at a rate of 60 rpm to the desired operating temperature, and then acidified with carbon dioxide at a flow rate of ~250 std mL/min down to a pH of 9.3 ± 0.3 in order to separate out the desired, liquid-lignin phase. Once the desired pH was achieved, the liquid-lignin phase was allowed to settle for 2 h at the operating temperature and pressure. This hydrated, lignin-rich phase was then recovered as a solid for analysis after the reactor had been cooled to 65 °C. A more detailed description of the experimental apparatus is presented elsewhere.[18] The three black liquors used in this work, selected properties, and the CO_2 acidification temperatures used are shown in Table 1.

Softening Points of Liquid Lignins. The softening points of selected liquid lignins were measured in a pressurized, water-saturated atmosphere, so that the chemical composition of the liquid-lignin phase would be unchanged from the equilibrium state formed in the 2 L batch reactor (i.e., with heating, water will evaporate from the liquid lignin under atmospheric pressure). For a given experiment, a cup-and-ball assembly from a Mettler dropping-point apparatus (model no. FP83HT) was filled with the lignin sample and then put inside a PVT cell (DB Robinson & Assoc., model no. 150-10-155). As the cell was heated up, the lignin sample would fall from the cup and block the path of a laser beam focused on a photoresistor. The temperature at which a step change in the photoresistor response was observed was reported as the softening point. This procedure is described in detail elsewhere.[18]

Acidification and Acetylation of Liquid Lignins for ^1H NMR Analysis. A solidified sample of the liquid-lignin phase of interest was obtained from the 2 L batch reactor, crushed with a mortar and pestle, and redissolved in a 0.5 N sodium hydroxide solution. This solution was then reacidified at ambient temperatures to a pH of 2 with 1 N sulfuric acid in order to reprecipitate the entire lignin sample back as a solid phase. The resulting lignin−acid slurry was vacuum-filtered to recover the lignin, which was then dried under nitrogen at 40 °C. The actual acetylation procedure, which is similar to the method of Gosselink et al.[20] except for the replacement of methanol with ethanol, is described in detail elsewhere.[19]

Gel Permeation Chromatography (GPC). The relative molecular weights of the precipitated liquid lignins were determined via GPC in a Waters Alliance GPCV 2000. Two columns were used in series: a Waters Styragel HT4 followed by an Agilent PolarGel-L column. The mobile phase consisted of dimethylformamide (DMF) with 0.05 M lithium bromide (LiBr) delivered at a flow rate of 1 mL/min. Detection was by a UV−vis spectrophotometer (Waters, model no. 2487) at a wavelength of 280 nm. The lignin samples were dissolved in the mobile phase at 1 mg/mL and filtered using a 0.2 μm, nylon membrane syringe filter (VWR, part no. 28145-487). Monodisperse poly(ethylene glycol)/poly(ethylene oxide) (PEG/PEO) standards (part no. PL2080-0101, Agilent Technologies) were used to calibrate the GPC for determination of the weight-average and number-average molecular weights of the liquid lignins.

Nuclear Magnetic Resonance (NMR). Quantitative ^{1}H NMR was performed with a 300 MHz Bruker Avance 300 spectrometer following the procedure used by Stoklosa et al.[19] Acetylated liquid-lignin samples were prepared at a concentration of 44 mg/mL in deuterated chloroform, which contained a trace amount of trimethylsilane (TMS) as a reference peak. Pentafluorobenzaldehyde (PFB) was added as an internal standard for functional-group quantification. Samples were run using a 30° pulse with a 2 s pulse delay and a total of 128 scans. Integration was performed using TopSpin 2.1 software (Bruker Corp.); integration regions were used according to Froass et al.:[16] 4.2−3.6 ppm for methoxyl groups, 2.6−2.2 ppm for acetylated aromatic hydroxyl groups, and 2.2−1.6 ppm for acetylated aliphatic hydroxyl groups.

■ RESULTS AND DISCUSSION

The lignin originally present in the three black liquors used in this study was precipitated at ambient temperature by acidifying with sulfuric acid to a pH of ~2. The aromatic hydroxyl content, number-average, and weight-average molecular weights of these solid lignins are presented in Table 2 as a basis for reference.

Table 2. Number-Average Molecular Weight, Weight-Average Molecular Weight, and Aromatic Hydroxyl Content of the Solid Lignin Precipitated at Ambient Temperatures and pH ~ 2 from the Three Kraft Black Liquors Used in This Study

black liquor (BL)	MW_n[a] (Da)	MW_w[b] (Da)	aromatic OH (mmol/g lignin)
softwood BL "A"	1900	6950	1.3
softwood BL "B"	2800	10800	1.5
hardwood BL "C"	1000	3400	1.9

[a] MW_n: Number-average molecular weight based on PEG/PEO standards. [b] MW_w: Weight-average molecular weight based on PEG/PEO standards.

Molecular Weight vs Softening Point for Liquid Lignins. The number-average molecular weight (MW_n) of the liquid-lignin phase as a function of the CO_2 acidification temperature at various black-liquor solids contents is presented in Figure 2. (The weight-average molecular weight (MW_w) and PDI are given in Tables S1−S3 in the Supporting Information.) Here we can see how MW_n for the liquid lignins derived from softwood black liquors "A" and "B" increases by up to a factor of 4 as the CO_2 acidification temperature is increased from 100 to 150 °C.

Reliable measurements of the molecular weights (mol wt) of lignin can be a challenge. GPC continues to be the method of choice, but as discussed in the literature,[21] misleading results can occur due to association effects. Thus, of interest to us was an assessment of the validity of our GPC results via an independent alternative. For that purpose, we chose the softening point, as it has been shown to have a good correlation with molecular weights for other poorly defined systems.[22] Figure 3 gives softening-point results for liquid lignins recovered from the same three black liquors as given in Figure 2, with results shown for black-liquor solids content of 30 wt %. Clearly, the trends are consistent with those obtained by GPC: softening-point increases track mol wt increases for "A" and "B", while for "C" both softening point and mol wt are essentially constant. Softening-point measurements by Velez[23] for other softwood and hardwood black liquors demonstrated a similar, well-behaved correlation of GPC mol wt with softening point. Thus, we concluded that our GPC system could be used to reliably detect mol wt changes in our lignin phases.

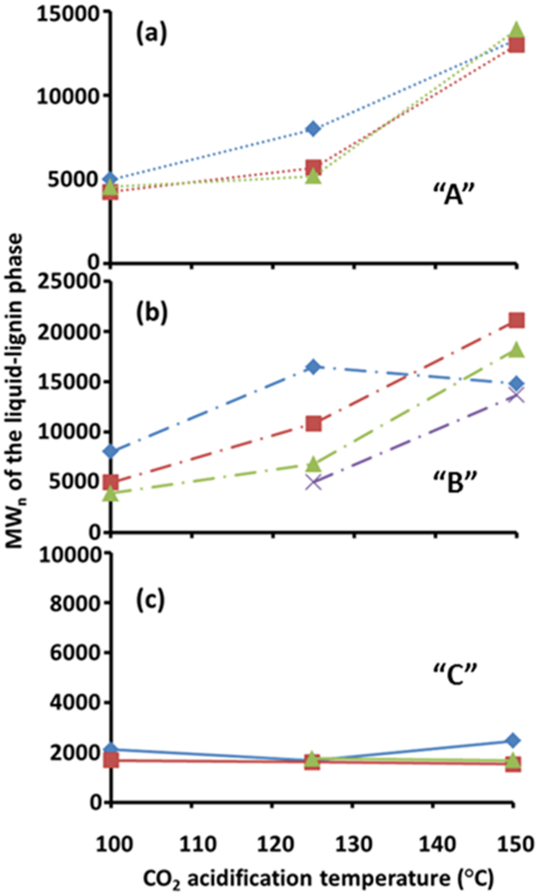


Figure 2. MW_n of the liquid-lignin phases as a function of CO_2 acidification temperature at solids contents of (blue ◆) 20, (red ■) 30, (green ▲) 40, and (purple ×) 50 wt % for softwood black liquors "A" and "B" and hardwood black liquor "C".

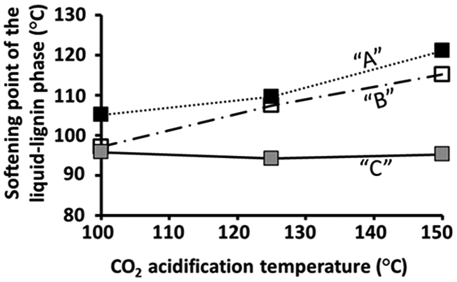


Figure 3. Softening points of the liquid-lignin phases derived from black liquors "A" (black square), "B" (white square), and "C" (gray square) as a function of the CO_2 acidification temperature, with all black liquors at a solids content of 30 wt %.

Molecular Weight of Liquid Lignins: Temperature Effects. Two possible explanations for the increases in molecular weight with CO_2 acidification temperature seen in Figure 2 for the "A" and "B" liquid lignins were considered: (1) the equilibrium distribution of lignin species between the liquid-lignin phase and the spent black-liquor phase is such that higher mol wt lignin species distribute preferentially into the

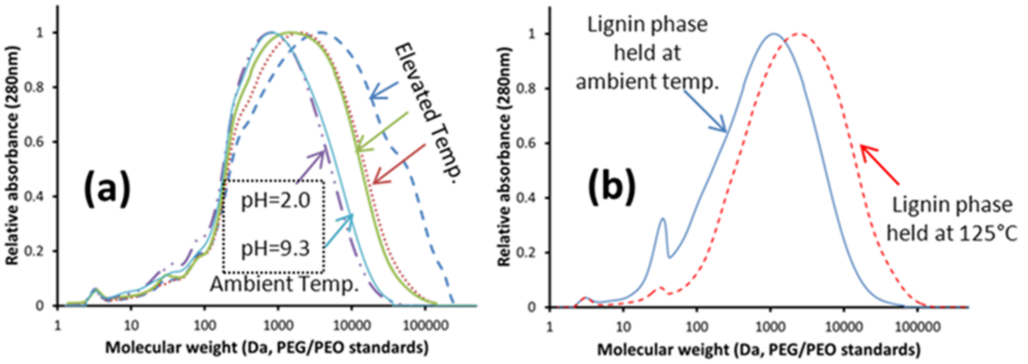


Figure 4. (a) GPC elution profiles for lignins precipitated from black liquor "B" at ambient temperatures down to pHs of 9.3 (blue) and 2.0 (purple), compared to liquid lignins precipitated at elevated temperatures (green, 100; red, 125; blue, 150 °C) down to a pH of 9.3. (b) GPC elution profiles for lignin derived from black liquor "B" heat-treated for 4 h at 125 °C: lignin phase precipitated from "B" at ambient (blue); lignin phase precipitated from "B" at ambient, heated to 125 °C, and then held there for 2 h (red).

liquid-lignin phase at higher temperatures, and (2) a reaction is causing an increase in the molecular weight of the liquid lignin.

To evaluate the above two possibilities, several elucidating experiments were carried out. First, (solid) lignin was precipitated from black liquor "B" via CO_2 acidification to a pH of ~9.3 using ambient instead of elevated temperatures. Then another ambient-temperature experiment was performed where the lignin again was precipitated as a solid phase from black liquor "B", but this time with 1N sulfuric acid down to a pH of 2.0; this experiment would be expected to precipitate out all of the acid-insoluble lignin present in the black liquor. A comparison of these two ambient-temperature precipitations with those carried out at elevated temperatures (i.e., at 100, 125, and 150 °C) down to a pH of 9.3 is given in the GPC chromatograms of Figure 4a. Clearly, the higher mol wt lignins are not initially present in the "B" black liquor, but are being generated by processing at elevated temperatures.

To determine at what point in the acidification process the higher mol wt species were being formed, an additional set of experiments was performed in which black liquor "B" was first held at 125 °C for 4 h, cooled down to ambient temperatures, and then acidified with CO_2 to precipitate a solid lignin phase. In a second experiment, black liquor "B" was again held at 125 °C for 4 h and then cooled down to ambient for CO_2 acidification. But this time, the precipitated solid lignin phase was subsequently heated to 125 °C and then held there for 2 h. As shown in Figure 4b, the molecular weight of the lignin precipitate increased significantly after it was heated in the form of a separate lignin phase, but not when it was preheat-treated as a solute within the black-liquor "solution".

The most likely cause for the observed increases in the molecular weights of the "A" and "B" liquid-lignin phases that were processed at elevated temperatures (see Figure 2) are condensation reactions similar to those that occur during the Kraft pulping process.[24,25] Although condensation reactions occur during pulping, fragmentation reactions (e.g., *β*-O-4 cleavage) typically take place at higher rates, resulting in a net decrease in molecular weight of the lignin.[15,16] Condensation reactions are minimized because the HS^- ions present in the black liquor act as external nucleophiles.[25] However, as the pH of the black liquor is decreased during CO_2 acidification, HS^- ions are reduced in concentration as they are protonated, releasing them in the form of H_2S gas.[1−3] Furthermore, any remaining HS^- will distribute preferentially into the aqueous black-liquor phase vs the more hydrophobic, liquid-lignin phase being formed. Lower HS^- concentrations in the lignin phase favor condensation reactions.

Our hypothesis that the condensation reactions that increase the molecular weight of the lignin in the liquid-lignin phase are the same as those that have been identified as occurring during pulping in the black-liquor phase is supported by the fact that a similar increase in molecular weight with temperature was not observed for the lignin phase precipitated from hardwood black liquor "C" (see Figure 2c). This is because the most common condensation reactions in pulping occur at the C5 position,[24] and this cannot occur in the syringyl-type lignin units that dominate in hardwoods, as the C5 position is occupied by a methoxyl group.

Figure 5 shows the number-average and weight-average molecular weight of lignin from black liquor "B" as a function of the time that the lignin was held at 125 °C (i.e., the "reaction time") after being precipitated via CO_2 acidification at ambient temperatures. (GPC chromatograms for the 0 h and 2 h reaction times were plotted in Figure 4b.) The observed increases in molecular weight are consistent with the occurrence of condensation reactions such as those described above.

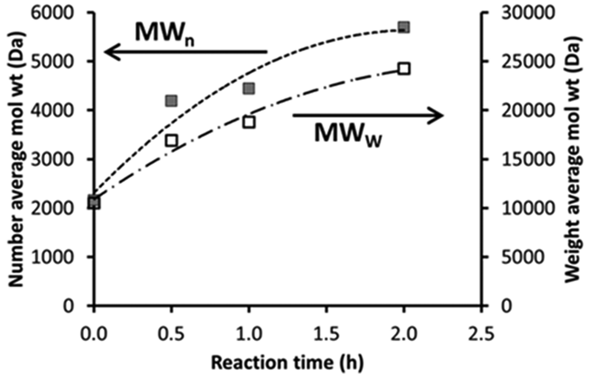


Figure 5. Number-average (gray square) and weight-average (white square) molecular weight as a function of "reaction time" at 125 °C for a lignin initially precipitated from black liquor "B" at ambient temperatures.

Hydroxyl Content of Liquid Lignins: Temperature Effects. The effect of CO_2 acidification temperature on the aromatic hydroxyl content of the liquid-lignin phase is given in Figure 6, with results being shown for a range of black-liquor

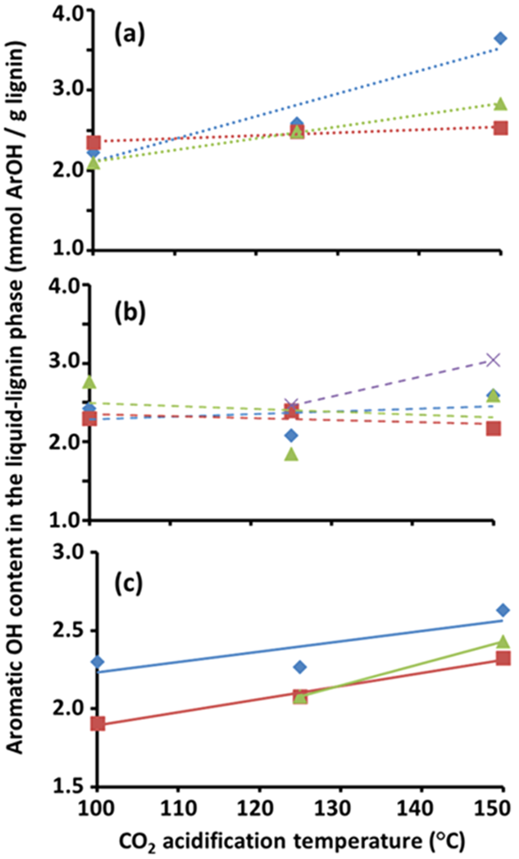


Figure 6. Aromatic OH content of the liquid-lignin phases as a function of CO_2 acidification temperature at a solids content of (blue ◆) 20, (red ■) 30, (green ▲) 40, and (purple ×) 50 wt % for (a) softwood black liquor "A", (b) softwood black liquor "B", and (c) hardwood black liquor "C".

solids contents. For the softwood black liquors "A", there is a general trend of increasing phenolic content with temperature. Recall that "A" has a high Kappa number (90). For "B" with a much lower Kappa number (25), the increase in phenolic content is minimal. The larger increase in OH content for the black liquor with the higher Kappa number ("A") was expected, as this black liquor had previously undergone less extensive Kraft pulping.[16] We would not expect the observed increases in phenolic hydroxyl content to occur because of condensation reactions, as they typically occur at the C5 position and thus do not involve the OH group.[24,25] Note that the most consistent increase in phenolic hydroxyl content also occurs for hardwood-derived "C" black liquor, which the data indicate does not undergo significant condensation reactions (see Figure 2c), providing further verification that the hydroxyl increase is unrelated to condensation reactions.

We thus hypothesized that the most likely source of the aromatic hydroxyl increase was the aryl ether cleavage reactions that occur as part of the Kraft pulping process, in particular the reaction that commonly occurs at the β-O-4 linkage and leads to the formation of an aromatic hydroxyl group.[24,25] The simultaneous occurrence of lignin fragmentation (cleavage) and condensation reactions during Kraft pulping has been reported by Ragauskas and co-workers[16] for soluble lignins and by Argyropoulos and co-workers[15] for residual lignins.

But were these reactions taking place in the black-liquor phase before lignin phase separation, or in the lignin phase after phase separation? To answer this question, we devised a set of experiments to "decouple" the black-liquor heatup, the CO_2 acidification/lignin precipitation, and the liquid-lignin settling steps from each other.

In one set of experiments, we heated black liquor "A" samples at 100 and 150 °C and held each for 2 h at temperature. Lignin was then precipitated from these black-liquor samples via CO_2 acidification at ambient temperatures down to a pH of ~9.3. A portion of these two lignin samples were first analyzed for molecular weight by GPC; then they were acetylated and analyzed for hydroxyl content via ^{1}H NMR (both analytical methods were previously described). In a second set of experiments, a portion of the lignin precipitated in the first set of experiments was divided up into two more samples, which were subsequently heated up to 100 and 150 °C, respectively, to form a liquid-lignin phase and held there for 2 h. These lignin samples were also analyzed for molecular weight and hydroxyl content.

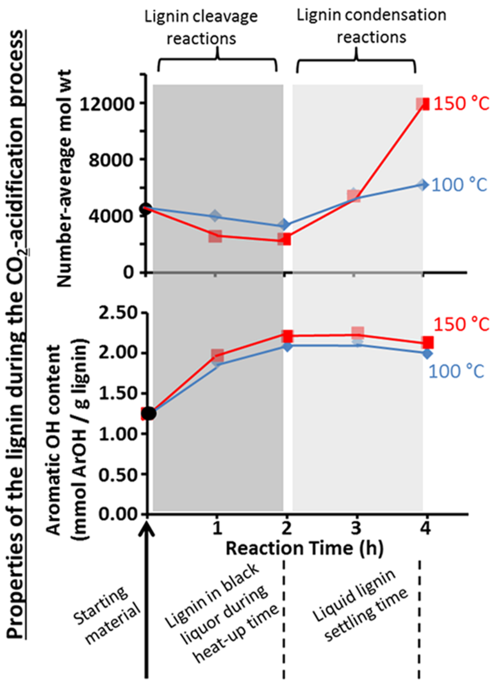


Figure 7. Molecular weight and aromatic hydroxyl content changes that occur as "A" lignin is heated for 2 h while in solution in the black-liquor phase, precipitated out with CO_2 to form a separate phase, and then heated to the liquid-lignin state and held there for 2 h.

Figure 7 illustrates the results of this work. Note how the molecular weight of the lignin when completely dissolved in the black liquor decreases as it is held at elevated temperatures; these results are consistent with higher temperatures leading to more lignin cleavage, probably primarily at the β-O-4 linkage. Furthermore, we see that this cleavage process leads to an increase in the aromatic hydroxyl content. Similar results have been been observed by others during Kraft pulping. For example, Jiang and Aryropoulos[14] observed a drop of about 1 mmol of β-O-4 ethers/g lignin, and a significant increase in the aromatic hydroxyl content of lignin monomer units, when a soluble lignin was delignified by about 70%. The behavior shown in Figure 7 is also consistent with the observations of previous researchers that as Kraft pulping proceeds, the aromatic OH content increases and the molecular weight decreases.[14−16,24]

Some of the increase in aromatic OH content may also be due to demethylation of the methoxyl group, but our results show that the trends shown in Figure 6 are similar, whether the *y*-axis denominator is in g lignin (as shown here) or in mol OCH_3 (as presented elsewhere[23]). The work of others[15,16] also indicates that the β-O-4 cleavage is the main contributor to the increase in aromatic hydroxyl content.

The CO_2-induced precipitation of the lignin from the black-liquor phase that then takes place at ambient temperatures so that no reactions occur is shown simply as a point and discontinuity in the mol wt and aromatic hydroxyl curves at a time of 2 h. Finally, we see how the mol wt and hydroxyl content change as the precipitated liquid-lignin phase is held at elevated temperatures for 2 h. Significant increases in the molecular weight of lignin occur due to condensation reactions (as previously described), but the hydroxyl content remains constant or modestly decreases at the higher temperatures (with the decrease in hydroxyl content being consistent with some type of a repolymerization involving an aromatic hydroxyl group, e.g., the α-O-4 linkage[24]).

■ CONCLUSIONS

When the recovery of high-purity lignin from Kraft black liquor entails an acidification step that is carried out at elevated temperatures (e.g., 100−150 °C), the lignin separates out as a liquid (instead of a solid) phase. As has been shown in this study, such elevated-temperature operation can be used as a tool for controlling the molecular weight of the recovered lignin. To investigate the changes in both molecular weight and chemical composition that occur during elevated-temperature CO_2 acidification, experiments were carried out in which the preheating, acidification/precipitation, and phase-settling steps were decoupled from each other. Results indicate that by controlling the time of both the preheating and settling steps, the molecular weight of the recovered lignin can either be decreased, kept unchanged, or increased. In a commercial setting, in situ control of the molecular weight of the final, high-purity lignin product could be effected by changing the residence time of the liquid-lignin phase in the settler located below the carbonation column (see Figure 1), through changes either in the feed flow rates or in the settler volume.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Batch-reactor apparatus, tables with weight-average and number-average molecular weights of the liquid-lignin phases, and a typical ^{1}H NMR spectrum of the analyzed lignin samples. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/sc500703m.

■ AUTHOR INFORMATION

Corresponding Author

*Mark C. Thies. E-mail: mcths@clemson.edu. Tel.: +1 864 656 5424. Fax: +1 864 656 0784.

Funding

This material is based upon work supported by the National Science Foundation (Award No. CBET-1236759).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (Award No. CBET-1236759). The authors thank Michael Lake, John Blackburn, and Charles Scouten (Liquid Lignin Co.) for helpful discussions and for providing the black liquor, Dan Edie for helpful discussions, and Alfredo Picado for assistance with the NMR measurements.

■ REFERENCES

(1) Lake, M. A., Blackburn, J. C. Process for recovering lignin. International Patent Application PCT/US2010/049773, 2011.

(2) Öhman, F., Theliander, H., Tomani, P., Axegard, P. A method for separating lignin from black liquor, a lignin product, and use of a lignin product for the production of fuels or materials. International Patent Application PCT/SE2008/000142, 2009.

(3) Kousini, L., Paleologou, M. Method for separating lignin from black liquor. U.S. Patent Application 2011/0297340A1, 2011.

(4) Tomani, P. The LignoBoost Process. *Cell Chem. Technol.* **2010**, *44* (1−3), 53−58.

(5) Berghel, J.; Frodeson, S.; Granstrom, K.; Renstrom, R.; Stahl, M.; Nordgren, D.; Tomani, P. The effects of Kraft lignin additives on wood fuel pellet quality, energy use and shelf life. *Fuel Process. Technol.* **2013**, *112*, 64−69.

(6) Doherty, W. O. S.; Mousavioun, P.; Fellows, C. M. Value-adding to cellulosic ethanol: Lignin polymers. *Ind. Crops Prod.* **2011**, *33*, 259−276.

(7) *Top Value Added Chemicals from Biomass. Volume II: Results of Screening for Potential Candidates from Biorefinary Lignin*; Report PNLL-16983; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 2007; www1.eere.energy.gov/bioenergy/pdfs/pnnl-16983.pdf.

(8) Lora, J. H.; Glasser, W. G. Recent industrial applications of lignin: A sustainable alternative to nonrenewable materials. *J. Polym. Environ.* **2002**, *10* (1−2), 39−48.

(9) Thakur, V. K.; Thakur, M. K.; Raghavan, P.; Kessler, M. R. Progress in green polymer composites from lignin for multifunctional applications: A review. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1072−1092.

(10) Gellerstedt, G.; Gustafsson, K. Structural changes in lignin during Kraft cooking Part 5. Analysis of dissolved lignin by oxidative degradation. *J. Wood Chem. Technol.* **1987**, *7* (1), 65−80.

(11) Gellerstedt, G.; Robert, D. Structural changes in lignin during Kraft Cooking. (7). Quantitative ^{13}C NMR analysis of kraft lignins. *Acta Chem. Scand.* **1987**, *B41* (7), 541−546.

(12) Gellerstedt, G.; Lindfors, E. Formation of enol ether structures in lignin during Kraft cooking. *Nordic Pulp Pap. Res. J.* **1987**, *2*, 71−75.

(13) Faix, O.; Argyropoulos, D.; Robert, D.; Neirinck, V. Determination of hydroxyl groups in lignins: Evaluation of ^{1}H-, ^{13}C-, ^{31}P NMR, FTIR and wet chemical methods. *Holzforschung* **1994**, *48* (5), 387−394.

(14) Jiang, Z. H.; Argyropoulos, D. The stereoselective degradation of arylglycerol-beta-aryl ethers during Kraft pulping. *J. Pulp Pap. Sci.* **1994**, *20* (7), J183−188.

(15) Koda, K.; Gaspar, A. R.; Yu, L.; Argyropoulos, D. S. Molecular weight-functional group relations in softwood residual Kraft lignins. *Holzforschung* **2005**, *59*, 612−619.

(16) Froass, P. M.; Ragauskas, A. J.; Jiang, J. E. NMR studies Part 3: Analysis of lignins from modern Kraft pulping technologies. *Holzforschung* **1998**, *52*, 385−390.

(17) Zhu, W.; Westman, G.; Theliander, H. Investigation and characterization of lignin precipitation in the LignoBoost process. *J. Wood Chem. Technol.* **2014**, *34*, 77−97.

(18) Velez, J.; Thies, M. C. Solvated liquid-lignin fractions from a Kraft black liquor. *Bioresour. Technol.* **2013**, *148*, 586−590.

(19) Stoklosa, R. J.; Velez, J.; Kelkar, S.; Saffron, C. M.; Thies, M. C.; Hodge, D. B. Correlating lignin structural features to phase partitioning behavior in a novel aqueous fractionation of softwood Kraft black liquor. *Green Chem.* **2013**, *15*, 2904−2912.

(20) Gosselink, R. J. A.; Abächerli, A.; Semke, H.; Malherbe, P.; Käuper, P.; Nadif, A.; van Dam, J. E. G. Analytical protocols for characterization of sulfur-free lignin. *Ind. Crops Prod.* **2004**, *19* (3), 271−281.

(21) Contreras, S.; Gaspar, A. R.; Guerra, A.; Lucia, L. A.; Argyropoulos, D. S. Propensity of lignin to associate: Light scattering photometry study with native lignins. *Biomacromolecules* **2009**, *9* (12), 3362−3369.

(22) Cervo, E. G.; Kulkarni, S. U.; Thies, M. C. Isolating polycyclic aromatic hydrocarbon (PAH) Oligomers via continuous, two-column supercritical extraction. *J. Supercrit. Fluids* **2012**, *66*, 120−128.

(23) Velez J. Solvated liquid lignins from Kraft black liquor: Phase behavior and molecular characterization. Ph.D. Dissertation, Clemson Univerity, Clemson, SC, 2014.

(24) Sixta, H.; Potthast, A.; Krotschek, A. W. Chemical pulping processes. In *Handbook of Pulp*; Sixta, H., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006.

(25) Gierer, J. The chemistry of delignification. *Holzforschung* **1982**, *36*, 43−51.