I&EC research
Industrial & Engineering Chemistry Research

Research Note

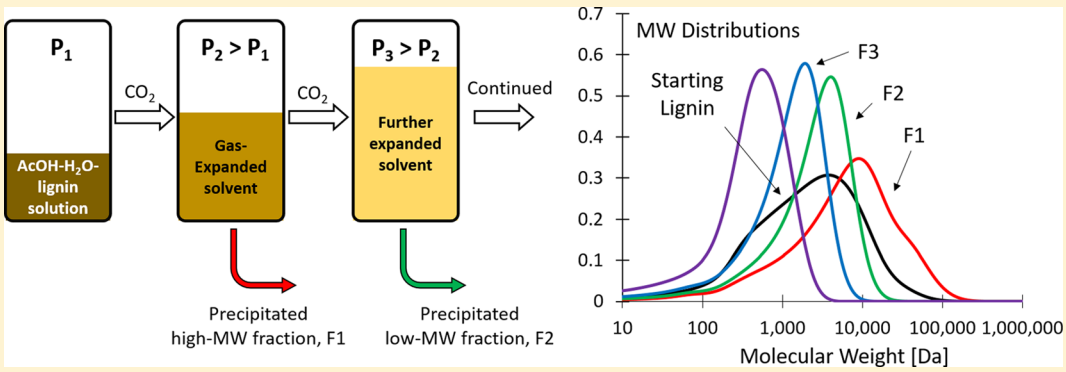
pubs.acs.org/IECR

# Benign Fractionation of Lignin with $CO_2$-Expanded Solvents of Acetic Acid + Water

Adam S. Klett,[†] A. Mark Payne,[†] Thanaphong Phongpreecha,[‡] David B. Hodge,[‡] and Mark C. Thies*[,†]

[†]Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, South Carolina 29634, United States
[‡]Department of Chemical Engineering & Materials Science, Michigan State University, East Lansing, Michigan 48824, United States

Supporting Information




**ABSTRACT:** Kraft lignin was fractionated by molecular weight (MW), using $CO_2$-expanded solutions of acetic acid/water in a 90/10 wt/wt ratio. In particular, as $CO_2$ pressures were increased from 7 bar to 48 bar, expanding the liquid-solvent phase and reducing its dielectric strength, lignin fractions decreasing in MW from 15 000 to 1250, with polydispersity index (PDI) values decreasing from 3.7 to 1.6, were obtained. The recovered lignin fractions were similar, in terms of chemical functionality. With the use of gas-expanded liquids (GXL), only one solvent composition is required, and recovery and reuse of the biorenewable $CO_2$ + acetic acid−water solution is facilitated through pressure release and recompression. The process was demonstrated for the recovery of seven lignin fractions to demonstrate its versatility and effectiveness, but simpler operation with recovery of just a low MW lignin fraction and a high MW lignin fraction is more consistent with anticipated applications.

## 1. INTRODUCTION

Lignin, which comprises 20%−30% of woody biomass on a dry basis, is the only abundant natural polymer with aromaticity, making it both a potential substitute for petroleum-derived aromatics and a unique material in its own right. Today, one of the most accessible sources of lignin is black liquor, which is the highly alkaline byproduct stream obtained from the Kraft process for making paper. Typically, black liquor is simply burned for its fuel value;[1] however, the situation is starting to change, with commercial processes for recovering "Kraft" lignin as a renewable, low-ash (1−4 wt %) biomaterial under development and coming online.[2−4]

As with any polymer, the separation of lignin into fractions having different molecular weights (MWs) will be necessary to tailor lignins for specific applications. Thus, low-MW lignin fractions are being investigated for vinyl ester resins, coatings, and adhesives.[5,6] On the other hand, high-MW fractions have recently been used to make carbon fibers with promising properties.[7] Clearly, then, the fractionation of lignin will be an important facet of the valorization of these abundant materials. The conventional laboratory method for lignin fractionation is mixed-solvent extraction, using either a series of multiple solvents or various ratios of two solvents.[8,9] Although lignins of various molecular weights can be isolated, recovery of the mixed solvents for reuse can be complex and energy-intensive.

Gas-expanded liquids (GXLs) have been proposed as solvents for performing specialty reactions and separations.[10,11] In brief, a GXL is formed by dissolving a compressible gas (e.g., $CO_2$) in an organic solvent; by increasing/decreasing the pressure to dissolve more/less $CO_2$ in the solvent, significant changes in the solubility of solutes in the solvent can be effected. Thus, multicomponent separations can be performed. Recovery of the organic solvent is effected simply by decreasing the pressure until the solubility of the $CO_2$ is minimal. Unlike supercritical fluids that typically require 100+ bar, only tens of bars are required for GXL processing.

Concentrated aqueous acetic acid (AcOH) has been used to fractionate lignins. For example, Kubo et al.[12] used concentrated AcOH/$H_2O$ mixtures ranging from 70/30 to 56/44 to generate insoluble lignin fractions for carbon fibers; recently, Klett et al.[13] used similar AcOH/$H_2O$ concentrations at

**Received:** June 1, 2017
**Revised:** July 21, 2017
**Accepted:** August 9, 2017
**Published:** August 15, 2017

ACS Publications © 2017 American Chemical Society



DOI: 10.1021/acs.iecr.7b02272
Ind. Eng. Chem. Res. 2017, 56, 9778−9782

elevated temperatures to simultaneously purify, fractionate, and solvate lignins. Biomass-derived acetic acid can potentially be generated renewably at a paper mill from wood-pulping liquors, as hardwoods are 3%−7% acetate.

If $CO_2$ could be incorporated into such AcOH/$H_2O$ systems to create an effective GXL, only one AcOH−$H_2O$ concentration might be required, simplifying the overall process and potentially reducing energy costs. Thus, this study was undertaken to determine what range of pressures would be required to dissolve sufficient amounts of $CO_2$ into AcOH−$H_2O$ solutions, such that an effective fractionation of the lignin would be obtained. In particular, a concern was that the presence of water in the AcOH would require significantly higher pressures to dissolve significant amounts of $CO_2$ into the solvent system, compared to typical, organic-only GXLs.

To our knowledge, only the group of Eckert et al.[10] has previously investigated GXLs for lignin recovery. In particular, they studied $CO_2$-expanded solutions of methanol for recovering monomers (e.g., vanillin) from lignin; however, the solubility of lignin in methanol is low at 25 °C (∼10 wt %), and no information on the precipitated lignin was reported, because the focus of the work was on monomer recovery.

## 2. METHODS

**2.1. Materials.** Glacial acetic acid was obtained from VWR Scientific. Compressed carbon dioxide (Coleman grade, 99.99% min) was obtained from Airgas USA. A softwood Kraft (alkali) lignin produced via the SLRP process and containing 1.2% ash (i.e., "SLRP" lignin) was provided by Lignin Enterprises, LLC. The lignin was then vacuum-dried under ∼10 mmHg at ambient temperatures down to a water content of 6%. For lignin acetylation, $^1$H nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC) experiments, all reagents were obtained from VWR Scientific. Poly(ethylene glycol) (PEG) standards for GPC (Cat. No. PL2080-0101) were obtained from Agilent Technologies. For $^{13}$C NMR, deuterated dimethyl sulfoxide was obtained from Cambridge Isotope Laboratories, and chromium(III) acetylacetonate was obtained from Sigma−Aldrich.

**2.2. Fractionation of Kraft Lignin.** Initial GXL screening experiments were carried out in a constant-volume, Jerguson-gauge-type view cell[14] with a volume of ∼14 mL. The cell was charged with concentrated mixtures of AcOH + $H_2O$ (i.e., 90%−95% AcOH) into which lignin had been dissolved at ambient temperatures; then, $CO_2$ was charged to the cell and the pressure was varied from 10 bar to 55 bar. Significant precipitation of the lignin from solution was observed with increasing $CO_2$ pressure, and the volume of the liquid phase was observed to more than double over the course of the experiments, thus motivating the quantitative experiments described below. At no time was more than one liquid phase observed in the view cell, which is consistent with the ternary phase behavior proposed by Maurer and co-workers[15] for higher AcOH/$H_2O$ ratios in the AcOH−$H_2O$−$CO_2$ system.

The GXL apparatus used for lignin fractionation (Figure 1) consisted of a 50 mL Parr reactor, modified to have a conical bottom with a port. Initially, a homogeneous AcOH−$H_2O$−lignin solution was charged to the vessel. $CO_2$ then was charged, with a portion of the $CO_2$ dissolving into and expanding the solution to form a GXL, effecting precipitation of a fraction of the dissolved lignin. After collection of the precipitated solids, additional increments of $CO_2$ were subsequently added, further expanding the solution and

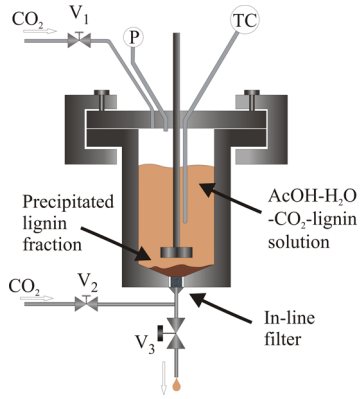



**Figure 1.** Schematic of fractionation apparatus consisting of a 50 mL Parr reactor with inlet valves for $CO_2$ at the top ($V_1$) and bottom ($V_2$) of the reactor, an exit valve ($V_3$) for the solution, and an in-line filter to prevent the loss of precipitated lignin solids.

reducing its solvent power to precipitate out additional fractions of the lignin. Experiments were conducted at ambient temperatures (i.e., 21 ± 1 °C), near the critical temperature of $CO_2$ ($T_c$ = 31 °C). Here, $CO_2$ is highly compressible and thus undergoes large changes in density (and as a result large changes in solubility) in the AcOH−$H_2O$ solutions.

In preliminary experiments, AcOH−$H_2O$ solutions containing 65−95 wt % acetic acid were evaluated for their ability both to dissolve lignin and to precipitate out the lignin when the solution was contacted with $CO_2$ to form a GXL. A $CO_2$ pressure of ∼57 bar (i.e., liquid-like densities) was used to estimate the maximum possible precipitation for that solvent composition. Results (see Figure S1 in the Supporting Information) indicated that 85−90 wt % AcOH would be a desirable operating range, so all fractionation experiments in this study were carried out using a solvent composition of 90/10 wt/wt AcOH/$H_2O$.

For a typical fractionation experiment, ∼40 g of acetic acid + water were combined with ∼5 g of SLRP lignin (containing ∼6% water) to make a 90/10 wt/wt AcOH/$H_2O$ solution with lignin (dry basis). This mixture was added to a 50 mL centrifuge vial, mixed with a vortex mixer for 5 min, centrifuged for 10 min at 6000 rpm, and decanted. Thirty milliliters (30 mL) of the decanted solution were then charged to the Parr reactor. This vessel was pressurized to 100 psi (6.9 bar) via the addition of $CO_2$ through valve $V_2$ (with valves $V_1$ and $V_3$ closed), so that the incoming $CO_2$ would bubble through and saturate the solution, forming a GXL. Valve $V_2$ was then closed, and the contents of the vessel were stirred for 30 min, to allow any lignin precipitation to occur and the system to reach equilibrium.

To collect any lignin that had precipitated from the GXL solution, the vessel was drained of the AcOH−$H_2O$−lignin solution through valve $V_3$ (with valve $V_2$ closed), with an in-line, 60-$\mu$m, sintered filter (Swagelok Part No. SS-2F-K4-60) sealed within the vessel exit port being used to capture the solid, precipitated lignin. During the draining process, the vessel pressure was held constant (i.e., to within 5 psi (0.34 bar) of the set point) by feeding in $CO_2$ through valve $V_1$. Once the solution had been completely drained from the vessel, $CO_2$ flow through $V_1$ was discontinued, and the vessel was allowed to reach ambient pressure and opened. The lignin solids that had precipitated were collected from the vessel; note that these solids had been dried because of the flow of dry $CO_2$ thru valve


DOI: 10.1021/acs.iecr.7b02272
Ind. Eng. Chem. Res. 2017, 56, 9778−9782

$V_3$ during pressure letdown. Finally, the filtered AcOH−$H_2O$ solution containing the still-soluble lignin was recharged to the reactor for the next fractionation step. The above process was repeated at sequentially higher $CO_2$ pressures in 100 psi (6.9-bar) increments up to 55 bar; no precipitation was observed at pressures above 48 bar.

**2.3. Molecular Weight Analysis by Gel Permeation Chromatography (GPC).** Molecular weights of the starting SLRP lignin, the precipitated fractions, and the portion of the lignin that remained unprecipitated at 55 bar were determined by GPC (Alliance GPCV 2000). In brief, a Waters Styragel HT5 column was used, followed by an Agilent PolarGel-L column with a mobile phase of 0.05 M lithium bromide in *N,N*-dimethylformamide at a flow rate of 1 mL/min. Poly(ethylene glycol) calibration standards were used for determination of the number-average molecular weight ($M_n$). Samples were dissolved in the mobile phase at a concentration of 1 mg/mL and detected by UV−vis with a Waters 2487 detector at 280 nm.

**2.4. $^1$H and $^{13}$C Nuclear Magnetic Resonance Spectroscopy.** Lignin samples were first acetylated for $^1$H NMR analysis, following procedures previously reported.[16] $^1$H NMR was performed with a Bruker Avance 300 MHz NMR spectrometer that was equipped with a 5 mm quadruple-nucleus probe. Samples could then be dissolved at a concentration of 50 mg/mL in deuterated chloroform. $^{13}$C NMR spectra were acquired on a 500 MHz NMR spectrometer (Varian, Inova) that was equipped with a double-resonance broadband probe. The sample (100 mg) was dissolved in 0.6 mL of DMSO-$d_6$. Additional NMR details are given in the Supporting Information.

## 3. RESULTS AND DISCUSSION

A composition of 90/10 wt/wt AcOH/water was chosen as the solvent system for this work, because it was found to be a solvent mixture capable of both dissolving a significant portion of the lignin, and then having most of that lignin precipitate out in the form of a GXL. In this work, 58% of the starting SLRP lignin dissolved in the starting AcOH−water solution. Furthermore, the solubility of $CO_2$ in binary AcOH−water mixtures increases as the acetic acid concentration increases,[17] so $CO_2$ would be expected to be a more effective antisolvent in concentrated AcOH solutions.

The cumulative percentage of dissolved lignin that precipitated out after each increment of $CO_2$ pressure is given in Figure 2. Surprisingly, more than 25% of the dissolved lignin precipitated at a $CO_2$ pressure of only 7 bar (100 psig); furthermore, at a $CO_2$ pressure of only 14 bar, 50% of the dissolved lignin had precipitated from solution. These are encouraging numbers, because they show that the combination of $CO_2$ with concentrated AcOH−water solutions forms a highly efficient gas-expanded liquid (GXL), with only modest $CO_2$ pressures (i.e., far below the critical pressure of $CO_2$ of 72.8 bar) being required to fractionate a large percentage of the lignin. As shown in Figure 2, little additional precipitation occurs above $CO_2$ pressures of 35 bar (~500 psig), with the maximum useful $CO_2$ pressure being no more than ~45 bar.

The MW distributions for each fraction, as well as for the starting SLRP lignin and for the unprecipitated lignin that remained in solution at 48 bar and above, are presented in Figure 3a; the number-average molecular weight ($M_n$) and polydispersity index (PDI) information for these fractions are given in Figure 3b. Lignin fractions encompassing a wide range

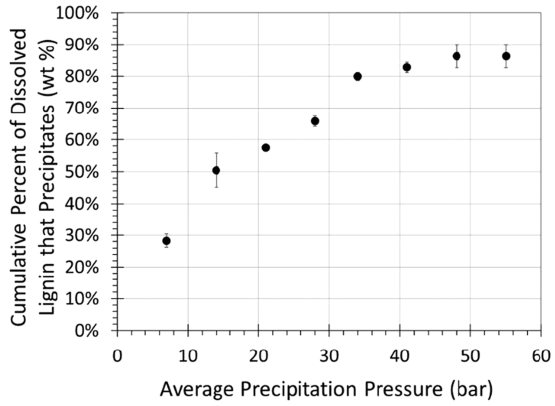



**Figure 2.** Cumulative percentage of dissolved lignin that precipitated at each pressure.

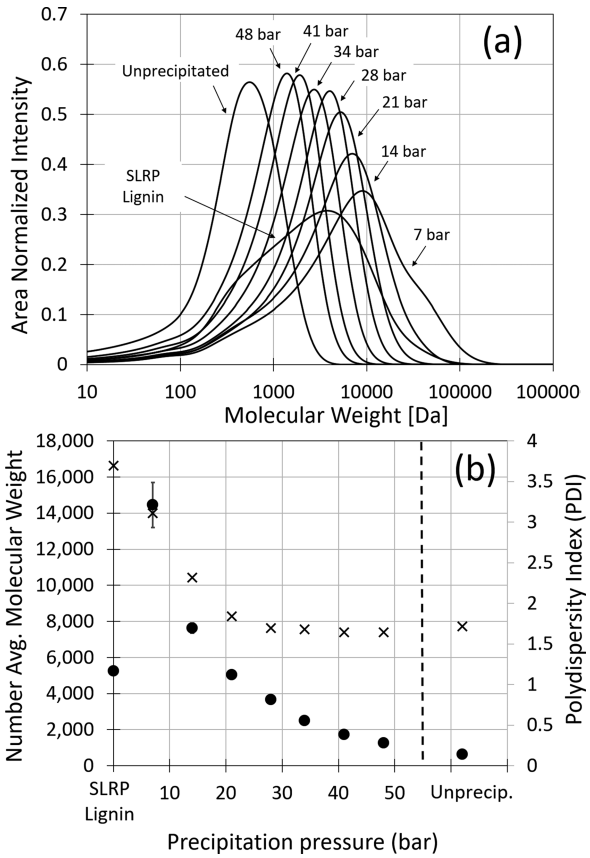



**Figure 3.** Molecular weight (MW) analysis of lignin fractions: (a) MW distributions via GPC and (b) number-average molecular weight ($M_n$), as a function of $CO_2$ pressure. Error bars for fractions 2−7 are smaller than the data points. Polydispersity is represented by cross symbols (×).

of MWs were obtained, from a low of 1250 at 48 bar to a high of almost 15 000 at 7 bar, with the PDIs being equal to or lower than those obtained with mixed-solvent fractionation.[8,9] (The unprecipitated lignin had a MW of 625.) The fact that the lignin species precipitate from solution, in terms of decreasing molecular weight as the $CO_2$ pressure is increased (and the $CO_2$ dissolved in solution increases), can be explained in terms of the balance between dispersion and electrostatic forces in the solution, as discussed by Norgren et al.[18] In particular, addition of the nonsolvent $CO_2$ to the solution reduces the electrostatic


DOI: 10.1021/acs.iecr.7b02272
Ind. Eng. Chem. Res. 2017, 56, 9778−9782

attraction between the lignin and solution, making aggregation (and thus precipitation) of the lignin more favorable, with the more lipophilic, higher MW fractions, where dispersion forces are more dominant, precipitating first. Alternatively, the precipitation of the lignin in terms of MW can be explained in terms of Flory–Huggins theory[19] if the acetic acid–water mixture is considered to be an ideal solvent for the lignin (with an ideal entropy of mixing and zero enthalpy of mixing), and with the $CO_2$ being a nonsolvent for the lignin.

The chemical functionality of the lignin fractions was determined via $^1$H NMR and $^{13}$C NMR (see Figure 4). Little

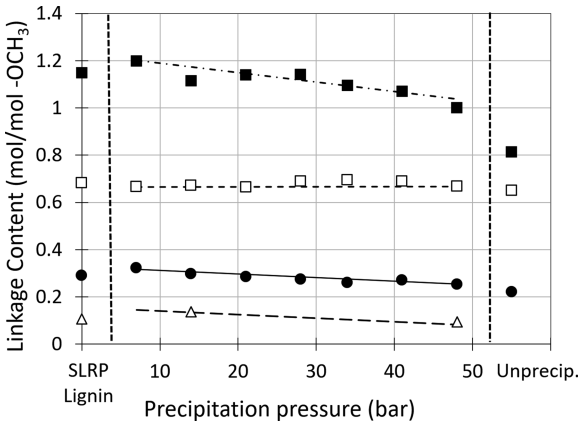



**Figure 4.** (□) Aromatic −OH, (■) aliphatic −OH, and (●) $\beta$-O-4 content of the fractions determined by $^1$H NMR, including the starting material (left) and the unprecipitated lignin (right). $\beta$-O-4 content determined by $^{13}$C NMR of specific fractions (denoted by open triangle symbols (△)) also shown for comparison. Lines are provided only to show trends.

change in aromatic −OH content was observed between fractions, but the aliphatic content did undergo a slight decrease with decreasing molecular weight. The $\beta$-O-4 content decreased with increasing $CO_2$ pressure, which is consistent with the fact that lower MW lignin species will have a lower content of these common linkages between lignin monomer units. Acid-catalyzed condensation reactions can occur in AcOH/$H_2O$ solutions at elevated temperatures,[20,21] but little evidence of such was observed at the ambient temperatures of this work.

A schematic of our envisioned GXL process for recovering a low-MW lignin fraction and a high-MW lignin fraction (e.g., for resins and for carbon fibers, respectively) is shown as Figure 5. Note that only one solution composition of acetic acid, water, and lignin is required, with compressed $CO_2$ at increasing pressures being added to expand the solvent phase (solution) and precipitate out the two desired lignin fractions. Recovery of the $CO_2$ and of the AcOH–water solution is effected by pressure release, recycle, and recompression. A purge stream[22] is also required to prevent buildup of that portion of the lignin that never precipitates out of the AcOH/$H_2O$ solution and thus is inadvertently recycled along with the solvent for the next lignin fractionation step. Compression costs dominate the economics of GXL processes,[23] so the fact that $CO_2$ pressures of no more than 35 bar would be required is an encouraging indication of the economic feasibility of the proposed application.

## 4. CONCLUSIONS

The fractionation of Kraft lignin by molecular weight (MW) is an important step in the valorization of this abundant material for applications ranging from coatings to carbon fibers. A $CO_2$-expanded solvent of 90/10 wt/wt acetic acid/water was used to separate a softwood Kraft lignin into fractions of decreasing MW, ranging from ∼15 000 to 1250, using $CO_2$ pressures increasing from 7 bar to 48 bar. Although seven fractions were generated in this study, ongoing materials work indicates that recovery of just a low- and high-MW lignin fraction would be adequate for many applications, facilitating the economics of scaleup.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b02272.

Plot of the amount of lignin dissolved in acetic acid/water solutions at ambient temperatures and the amount of lignin precipitated from GXLs at a maximum $CO_2$ pressure of ∼57 bar (Figure S1); description of $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy (PDF)

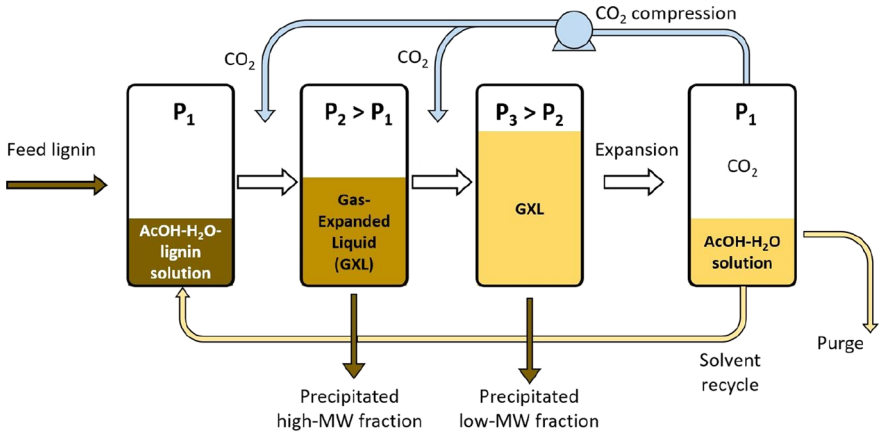



**Figure 5.** Gas-expanded liquid (GXL) process for the recovery of low- and high-MW lignin fractions.


DOI: 10.1021/acs.iecr.7b02272
Ind. Eng. Chem. Res. 2017, 56, 9778−9782

## AUTHOR INFORMATION


### Corresponding Author

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

### ORCID

Adam S. Klett: 0000-0002-3365-644X

Mark C. Thies: 0000-0002-2833-485X


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (NSF), under Grant No. CBET-1403873, and also made use of ERC Shared Facilities supported by NSF, under Award No. EEC-9731680.

## REFERENCES


(1) Gosselink, R. J. A.; de Jong, E.; Guran, B.; Abächerli, A. Co-ordination network for lignin—Standardisation, production and applications adapted to market requirements. *Ind. Crops Prod.* **2004**, *20* (2), 121−129.

(2) Tomani, P. The Lignoboost Process. *Cellul. Chem. Technol.* **2010**, *44* (1−3), 53−58.

(3) Kouisni, L.; Holt-Hindle, P.; Maki, K.; Paleologou, M. The Lignoforce System: A new process for the production of high-quality lignin from black liquor. *J. For.* **2012**, *2* (4), 6−10.

(4) Lake, M. A.; Blackburn, J. C. *Process for recovering lignin*. U.S. Patent 9,260,464, Feb. 16, 2016.

(5) Stanzione, J. F., III; Giangiulio, P. A.; Sadler, J. M.; La Scala, J. J.; Wool, R. P. Lignin-based bio-oil mimic as biobased resin for composite applications. *ACS Sustainable Chem. Eng.* **2013**, *1*, 419−426.

(6) Griffini, G.; Passoni, V.; Suriano, R.; Levi, M.; Turri, S. Polyurethane coatings based on chemically unmodified fractionated lignin. *ACS Sustainable Chem. Eng.* **2015**, *3*, 1145−154.

(7) Jin, J.; Klett, A. S.; Ding, J.; Thies, M. C.; Ogale, A. Carbon Fibers Derived from Fractionated-Solvated Lignin. In *2017 AIChE Annual Meeting Proceedings*, Minneapolis, MN, Oct. 2017.

(8) Boeriu, C. G.; Fiţigău, F. I.; Gosselink, R. J. A.; Frissen, A. E.; Stoutjesdijk, J.; Peter, F. Fractionation of five technical lignins by selective extraction in green solvents and characterisation of isolated fractions. *Ind. Crops Prod.* **2014**, *62*, 481−490.

(9) Li, M. F.; Sun, S. N.; Xu, F.; Sun, R. C. Sequential solvent fractionation of heterogeneous bamboo organosolv lignin for value-added application. *Sep. Purif. Technol.* **2012**, *101*, 18−25.

(10) Eckert, C.; Liotta, C.; Ragauskas, A.; Hallett, J.; Kitchens, C.; Hill, E.; Draucker, L. Tunable solvents for fine chemicals from the biorefinery. *Green Chem.* **2007**, *9*, 545−548.

(11) Scurto, A. M.; Hutchenson, K.; Subramaniam, B. In *Gas-Expanded Liquids and Near-Critical Media*; Scurto, A. M., Hutchenson, K., Subramaniam, B., Eds.; ACS Symposium Series No. 1006; American Chemical Society: Washington, DC, 2009; pp 3−37.

(12) Kubo, S.; Uraki, K.; Sano, Y. Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping. *Carbon* **1998**, *36* (7−8), 1119−1124.

(13) Klett, A. S.; Chappell, P. V.; Thies, M. C. Recovering ultraclean lignins of controlled molecular weight from Kraft black-liquor lignins. *Chem. Commun.* **2015**, *51*, 12855−12858.

(14) Mena, S. E.; Cervo, E. G.; Crosthwaite, J. M.; Thies, M. C. Phase equilibrium measurements for the $I_2$−$H_2O$ and $I_2$−HI−$H_2O$ systems of the sulfur−iodine cycle using a continuous-flow apparatus. *Int. J. Hydrogen Energy* **2010**, *35*, 3347−3357.

(15) Bamberger, A.; Sieder, G.; Maurer, G. High-pressure phase equilibrium of the ternary system carbon dioxide + water + acetic acid at temperatures from 313 to 353 K. *J. Supercrit. Fluids* **2004**, *32*, 15−25.

(16) 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.

(17) Briones, J. A.; Mullins, J. C.; Thies, M. C.; Kim, B. U. Ternary phase equilibria for acetic acid−water mixtures with supercritical carbon dioxide. *Fluid Phase Equilib.* **1987**, *36*, 235.

(18) Norgren, M.; Edlund, H.; Wagberg, L.; Lindstrom, B.; Annergren, G. Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: Phase behavior. *Colloids Surf., A* **2001**, *194*, 85−96.

(19) Flory, P. J. Phase Equilibria in Polymer Systems. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter XIII, pp 546−554.

(20) Li, J.; Henriksson, G.; Gellerstedt, G. Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion. *Bioresour. Technol.* **2007**, *98*, 3061−3068.

(21) Klett, A. S.; Payne, A. M.; Thies, M. C. Continuous-Flow Process for the Purification and Fractionation of Alkali and Organosolv Lignins. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6689−6694.

(22) Felder, R. M.; Rousseau, R. W. *Elementary Principles of Chemical Processes*, 3rd Edition; John Wiley & Sons, Inc.: Hoboken, NJ, 2005; Chapter 4.7g.

(23) Siougkrou, E.; Galindo, A.; Adjiman, C. S. On the optimal design of gas-expanded liquids based on process performance. *Chem. Eng. Sci.* **2014**, *115*, 19−30.




DOI: 10.1021/acs.iecr.7b02272
*Ind. Eng. Chem. Res.* 2017, 56, 9778−9782