Pretreatment Efficacy and Lignin Solubility of Organic Solvents on Juvenile Slash Pine Chips for Lignin Value Prior to Pulping

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Organic solvent treatment of wood chips can be a key to converting pulp mills into pulp-producing biorefineries. Choosing an optimal solvent requires screening of numerous industrially relevant solvents. This work considers the delignification efficacy of several aqueous organic solvents for juvenile slash pine chips and correlates this efficacy to the lignin solubility. No correlation was shown between the pretreatment efficacy and solubility of ethanol-extracted lignin in organic solvents. At least 10% (v/v) water and 10% (v/v) organic solvent are required for effective delignification, and the different solvent delignification profiles for aqueous mixtures of 1,6 hexamethylene diamine, ethanol, 1-methylimidazole, tetrahydrofuran, and ethylene glycol were determined experimentally. No correlations were found between lignin solubility, Hansen solubility parameters, and delignification. Therefore, solubility measurements should not be a screen for lignin value prior to pulping. However, a 50% (v/v) organic solvent pretreatment at 200 °C for 2 h is a valuable screen to rank the delignification efficacy of organic solvents for further optimization.

Keywords: Lignin; Solubility; Delignification; LVPP; Pretreatment; Pulping; Organosolv

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INTRODUCTION

Lignin is a valuable commodity as a natural aromatic building-block for high-value products, including low-cost carbon fiber, engineering plastics and thermoplastic elastomers, polymeric foams and membranes, and a variety of fuels and chemicals that are currently sourced from petroleum (Ragauskas *et al.* 2014). Delignification of biomass removes the physical barrier around cellulose that restricts the breakdown of cellulose to fuels and fiber bonding for paper applications. As new pathways from lignin to chemicals are formed, the isolation of a lignin-rich stream is increasingly important.

The prevailing strategy to isolate lignin from biomass is from the black liquor in a kraft pulping system. Black liquor is traditionally burned for energy. Commercial technologies have emerged to extract lignin from black liquor using acids or carbon dioxide (Tomani 2010), and a variety of ultrafiltration techniques have been published (Wallberg *et al.* 2003; Kevlich *et al.* 2017). Removing lignin from a pulp mill is economically attractive because it reduces the lignin load on the recovery boiler and creates a new revenue stream. However, high severity kraft cooking leads to condensed lignin with a high sulfur load (Hu *et al.* 2016). An alternative to kraft lignin is the isolation of lignin by organic solvents. Processing with an organic solvent method can lead to a variety of different lignin types, many of which retain a majority of native β-ether linkages (Holladay *et al.* 2007). There are several counter-examples to this generalization, specifically with the addition of acids and high temperatures, and it is important to characterize the lignin produced in each organic solvent process (Rinaldi *et al.* 2016).

Several pulping processes of interest utilize organic solvents, typically alcohols, to solubilize lignin and hemicellulose (Klein-Marcuschamer *et al.* 2011). This process yields a purified lignin stream that has been commercialized. Other delignification techniques include using supercritical water to extract lignin (Kadam *et al.* 2014), the combination of 2-methyl tetrahydrofuran and water to fractionate lignin through partitioning (vom Stein *et al.* 2011), and using strong delignifying solvents, such as 1-methylimidazole (1-MI) (Kang *et al.* 2015) and γ-valerolactone (Petrus and Petrus-Hoogenbosch 2006), to separate lignin from the biomass fraction. These solvents and others have demonstrated efficacy in delignification, but their ability to produce quality pulp is limited because of acid and high severity requirements. Therefore, one technique produces a low-quality kraft lignin with pulp mill improvements and the other technique produces a high-quality organic solvent lignin with a low-quality pulp. A new pulping process, lignin value prior to pulping (LVPP), attempts to bridge this divide by performing moderate organic solvent lignin removal, followed by modified kraft cooking (Kwok *et al.* 2017). A partial delignification step produces a high-quality lignin stream, and the modified kraft cook maintains a strong pulp stream. Lignin has a high burning value ~28 MJ/kg, but the cost of replacing that energy with natural gas amounts to ~$80/ton. LVPP seeks to extract a high-quality lignin that can be processed into chemicals and materials that sell for >$1000/ton. This process depends on a solvent that enables selective delignification and is easily recycled. However, without a robust understanding of both the delignification mechanism and final form of lignin, predictive capabilities for delignification efficacy have not been developed.

Delignification methods all involve the cleavage of linkages holding various monolignols together (Gellerstedt and Lindfors 1984). In kraft pulping, an aqueous alkali solution cleaves these linkages and produces phenolic hydroxyl groups that enhance the lignin solubility (Chakar and Ragauskas 2004). Easily hydrolysable α-ether linkages are broken in acidic systems, and the β-aryl ether bonds are broken under different conditions (McDonough 1993). All organic solvent pulping processes rely on the chemical breakdown of lignin before it is dissolved, and typically the catalyst is an acid. Under certain conditions, the solvent or water may deacetylate the hemicellulose (Ferrini and Rinaldi 2014) and decrease the solution pH enough to autocatalyze the chemical breakdown of the lignin (Santos *et al.* 2013). While organic solvents, such as formaldehyde, are known to interact with lignin and reduce condensation (Shuai *et al.* 2016), the main functions of the organic solvent are to impregnate the plant tissue and solubilize the fragmented lignin (Rinaldi *et al.* 2016). Solubilization of lignin has been explored and modeled with a variety of different lignin samples. Since the 1950s, studies have looked at the solubility of extracted lignin in hundreds of solvents and solvent mixtures (Schuerch 1952). Correlations have been established between the lignin solubility in organic solvents and thermodynamic properties, such as the Hildebrand parameter (Balogh *et al.* 1992) and Hansen solubility (Hansen 2002), or linear free energy relationships, such as the Kamlet-Taft parameters (Parviainen *et al.* 2013). These correlations are able to explain the solubility of certain lignin types, but there is little empirical data that explores the connection between the solubility and pretreatment of biomass. These thermodynamic studies are frequently referenced to both predict lignin solubilization in organic solvents and increase the delignification of biomass (Ye *et al.* 2014; Quesada-Medina *et al.* 2010).

This work focused on solvent-water mixtures with no acid or alkali catalysts. Dilute acid is frequently coupled with organosolv pretreatment, but the downstream alkali consumption and salt formation in a two-step LVPP process should be avoided. Despite this constraint, biomass pretreatments may be performed at a variety of different temperatures (140 °C to 220 °C), cooking durations (30 min to 6 h), liquor-to-wood ratios (4:1 to 10:1), solvent loadings (0% to 100%), and chip sizes (sawdust to chips). With so many variables, it is difficult to compare solvents comprehensively. Herein, one pretreatment strategy was analyzed that was optimized for the greatest delignification separation of juvenile slash pine chips screened between 4-mm and 8-mm roll-screens. Using a moderately severe treatment, solvents were rank-ordered based on their delignification efficacy and selectivity. The solubility analysis utilized a standard source of industrial lignin, namely ethanol-extracted lignin, which can be easily obtained or produced internally. This study explored the use of a simple solubility experiment to screen solvents for LVPP and investigated the relationship between the lignin solubility and slash pine delignification. Correlation data was presented between the ability of an organic solvent to solubilize ethanol-extracted lignin and its ability to delignify slash pine chips. This data was utilized for rank-ordering a subset of solvents for LVPP.

EXPERIMENTAL

Materials

Lignin samples were donated by American Process Inc. (Thomaston, GA, USA). Mixed hardwood was treated with a mixture of sulfur dioxide, ethanol, and water at 150 °C. The resulting liquor was distilled to remove ethanol and sulfur dioxide, which resulted in lignin precipitation. The precipitate was separated by centrifugation and then washed with water. For all of the solubility experiments, the lignin was sieved to a size fraction of 75 µm to 150 µm and oven-dried at 50 °C. For the characterization experiments, the lignin was sieved to a size fraction of 300 µm to 200 µm. Juvenile slash pine wood chips were provided by Georgia Pacific (Memphis, TN, USA) from a source in Foley, Florida, USA. All of the wood chips used in the experiments were screened through 4-mm to 8-mm roll screens. The organic solvents ethanol (EtOH), 1-MI, ethylene glycol (EG), tetrahydrofuran (THF), and 1,6 hexamethylenediamine (HMDA) were all purchased from VWR International (Radnor, USA).

Methods

Solubility tests

Three hundred milligrams of lignin were weighed into 50-mL centrifuge vials. Ten milliliters of organic solvent/water mixture were added, and the solution was mixed for 4.5 h on a rotating mixer at 23 °C. The undissolved lignin was recovered by vacuum filtering the solution through Whatman 934-AH glass microfiber filters in oven-dried crucibles. The crucibles were weighed after drying for 2 d at 50 °C to determine the mass of the undissolved lignin. The solubility factor (SF) was calculated using Eq. 1,

$$SF = RL / RO \quad (1)$$

where RL is the recovered lignin (mg), and RO is the originally added oven-dried lignin (mg).

Pretreatment

Wood chips were air-dried in a fume hood for 2 d, which reduced their moisture content to approximately 7%. Six grams of wood chips and 10 mL of organic solvent/water mixture were added to a 600-mL benchtop reactor (Series 4563, Parr Instrument Company, Moline, IL, USA) with temperature control. The solution was treated at 200 °C for 2 h, not including a 20-min to 30-min warmup time. The resulting mixture was screened to recover the wood chips, which were subsequently washed in excess water for 18 h. The washed wood chips were reweighed after drying in a fume hood for 2 d. The order of the treatments was randomized before starting.

Klason Lignin Determination

The Klason lignin content was determined with a modified version of the method by Sluiter *et al.* (2008). Dry and milled (0.84-mm screen) samples (0.175 g ± 0.005 g) were weighed in flat-bottomed tubes, and 1.5 mL of 72% (v/v) sulfuric acid (VWR International, Radnor, USA) were subsequently added. The tubes were placed into a Digiblock digital block heater (Sigma-Aldrich, St. Louis, USA) to maintain the temperature at 30 °C and stirred every 3 min to 5 min for 1 h. Each sample was diluted to 42 mL, autoclaved for 2 h at 121 °C, and cooled to room temperature. The samples were filtered by G8 glass filters, and the remaining solids (Klason lignin) were dried at 105 °C to determine the Klason lignin content. The Klason lignin content was determined as a gravimetric fraction of the initial biomass.

RESULTS AND DISCUSSION

For a viable screen of LVPP solvents, a technical lignin sample was selected and characterized. This ethanol-extracted lignin had a ratio of syringyl (S) and guiacyl (G) units of 2.29 (Fig. S1A) and a relative β-O-4/β-β ratio of 0.86. This lignin had a standard attenuated total reflection-infrared profile with clear aromatic and C-O stretching (Fig. S1C), and had been partially delignified with an average molecular weight of 1080 g/mol (Fig. S1D). This hardwood lignin maintained similar linkages to native lignin, was reproducibly available, and it may be considered an industry standard.

Table 1. Hansen Solubility Parameters

Target	Dispersion [MPa$^{1/2}$]	Polar [MPa$^{1/2}$]	Hydrogen Bonding [MPa$^{1/2}$]	Interaction Radius
Lignin (Vebber *et al.* 2014)	21.9	14.1	16.9	13.7
Solvent	Dispersion [MPa$^{1/2}$]	Polar [MPa$^{1/2}$]	Hydrogen Bonding [MPa$^{1/2}$]	Relative Energy Diff.
HMDA (SpecialChem 2019)	16.8	9.6	5.3	1.17
1-MI (Hansen 2002)	19.7	15.6	11.2	0.54
THF (Hansen 2002)	16.8	5.7	8.0	1.16
EtOH (Hansen 2002)	15.8	8.8	19.4	0.99
EG (Hansen 2002)	17.0	11.0	26.0	1.00
Water (Hansen 2002)	15.6	16.0	42.3	2.07

To determine the relationship between the technical lignin solubility and wood chip delignification, five organic solvents (EtOH, 1-MI, EG, THF, and HMDA) were studied at five different organic solvent fractions (0.1, 0.3, 0.5, 0.7, and 0.9) in water. Hansen solubility parameters for each solvent were compared against the published organosolv lignin parameters. The individual parameters used are listed in Table 1, and the parameters for each aqueous organic solvent mixture were calculated as the geometric mean between the solvent and water parameters (Abbott and Hansen 2013).

The relative energy differences were calculated for all aqueous organic solvent mixtures and lignin, but no correlation was found with the measured solubility within this solvent set nor an expanded solvent set. For a potential screen for Lignin Value Prior to Pulping, the solubility must be experimentally measured. Figure 1 depicts the lignin solubility fraction of each aqueous solvent mixture.

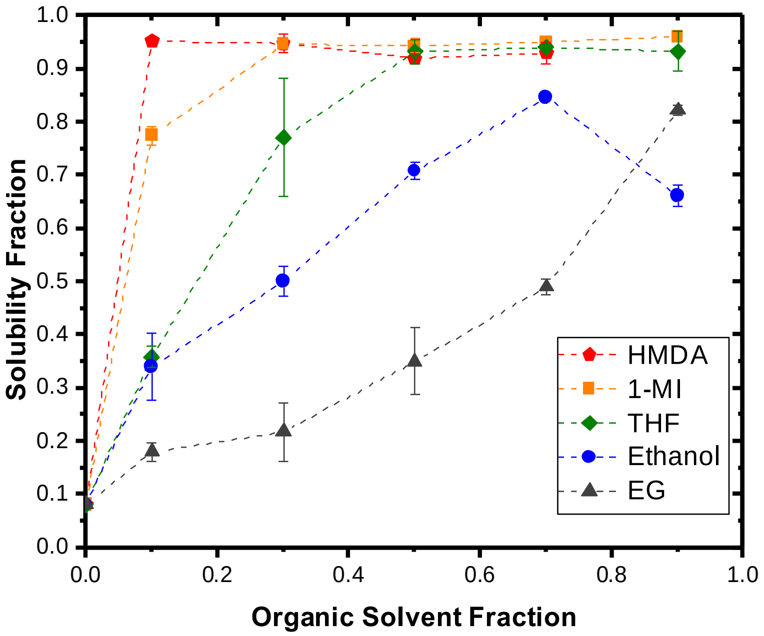

Fig. 1. Room temperature lignin solubility fractions of five organic solvents at various organic solvent fractions; the error bars indicate the standard deviation; and the lines connecting the data points are visual aids and do not indicate measured data

It was noted that HMDA and 1-MI solubilized the greatest fraction of lignin across the five organic solvent fractions, followed by THF, EtOH, and EG. Each solvent demonstrated a unique lignin solubility profile, but several patterns emerged. The solubility fraction of all of the solvent mixtures decreased as the organic solvent fraction approached zero. Ethylene glycol was the only solvent to have a solubility fraction below 0.9 at an organic solvent fraction of 0.7, and it was the only solvent where the solubility continued to increase at higher solubility fractions. The difference in solubility fractions between the solvents was greatest for the 0.1 and 0.3 solvent fractions. The solubility for the EtOH mixtures exhibited the shape pattern reported in the literature (Ni and Hu 1995). The large difference in the solubility for the 0.3 solvent fraction provided a straightforward choice for rank-ordering the organic solvents.

Rank-ordering the organic solvents did not correlate with the trends of slash pine delignification after treatment at 200 °C for 2 h (Fig. 2). This extreme temperature is used as a screening condition and is an upper bound for an LVPP treatment. The actual LVPP treatment will be less severe than 200 °C for 2 h, but this condition is used as a solvent screen to determine potential efficacy. Any ineffective treatment at these conditions will not be suitable for LVPP. The residual lignin content and the degree of delignification of wood chips were compared with the technical lignin solubility, and Fig. 2 shows a wide delignification efficacy range (11% to 88%) at solubility fractions above 0.7. There was a smaller delignification efficacy range (0% to 28%) below a 0.7 solubility for all of the solvents, except EG. Ethylene glycol, a solvent used in the pulping of alternative feedstocks (Jiménez *et al*. 2008), was an outlier and confirmed that a low solubility cannot screen out organic solvents without risking the loss of a promising solvent. From this data, it was noted that the lignin solubility in organic solvent mixtures cannot predict the delignification efficacy of pine wood chips.

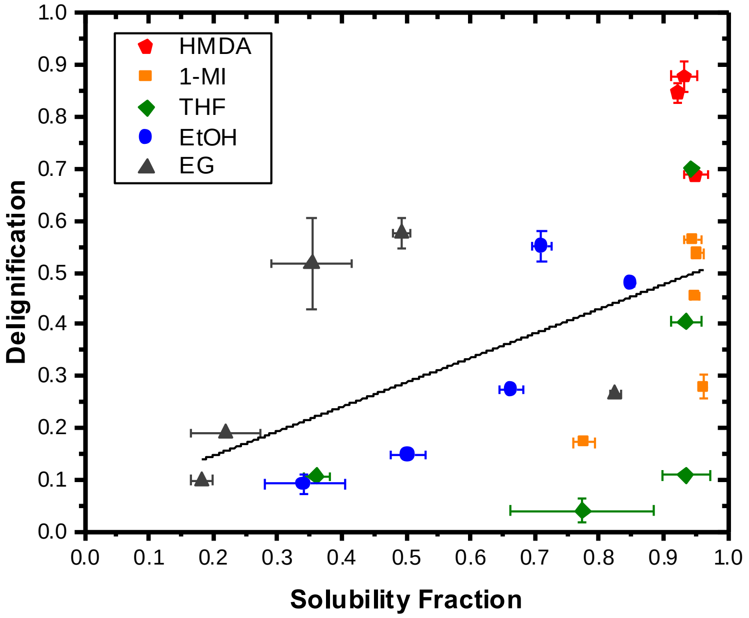

Fig. 2. Comparison between the room temperature lignin solubility fraction and wood chip treatment delignification (200 °C and 2 h); the error bars indicate the standard deviation; and the points without vertical error bars were not repeated for delignification

Another finding from this work was the requirement of the presence of a volume fraction of at least 0.1 each for solvent and water. Figure 3 shows that for both the low (0.1) and high (0.9) organic solvent fractions, delignification was low regardless of the solubility. At high solvent fractions greater than 0.9, the rate and extent of delignification likely suffered from a shortage of water, which catalyzes lignin depolymerization reactions (Rinaldi *et al.* 2016). This feature partly explained the wide range of delignification percentages at high solubility fractions. Figure 3 also shows that there was a maximum delignification achieved by each of the organic solvent mixtures with water. The EtOH maximum delignification at the 0.5 organic solvent fraction matched the published acid-free organosolv results (Yáñez-S *et al.* 2014). Similarly, the maximum EG delignification at the 0.7 organic solvent fraction was close to that of the 0.8 fraction used for alternative feedstock pulping (Alriols *et al.* 2009). This finding suggested that the primary organic solvent fraction range of interest for LVPP is between 0.5 and 0.7. Because the 0.5 fraction allowed for a lower solvent purity compared with the 0.7 fraction and because of economic constraints on separations, the use of a 0.5 screen was proposed for LVPP. Given an incoming biomass stream at 50% solids and a 4:1 liquor-to-wood ratio, a treatment stream at 67% solvent purity was required for a final solvent concentration of 0.5. In contrast, the treatment stream would require a 93% solvent purity to obtain a final solvent concentration of 0.7. Additionally, a wood chip moisture content of 55% would include too much water to reach a 0.7 final solvent treatment regardless of the solvent purity. For high-boiling point solvents, the economic benefits of removing less water are remarkable (Chrisandina *et al.* 2019). At 200 °C and 2 h, the pretreatment severity provided a wide delignification efficacy range and was more severe than standard kraft cooking. Any greater severity would be impractical within an LVPP framework. Another finding of note was the connection between a high solubility and wider range of organic solvent fractions that could effectively delignify wood chips. Solvents such as HMDA and 1-MI with broad solubility profiles had small decreases in the delignification between the 0.7 and 0.3 solubility fractions. This finding could be explored with a larger set of solvents.

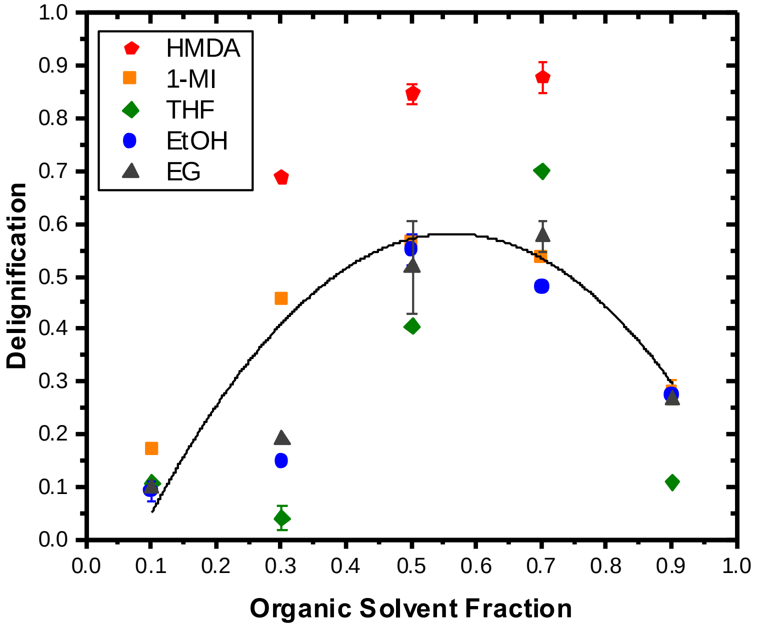

Fig. 3. Comparison between the organic solvent fraction and wood chip treatment delignification (200 °C and 2 h) with fitted 2nd order polynomial; the error bars indicate the standard deviation; and the points without vertical error bars were not repeated for delignification

To quantify the predictive power of the solubility and organic solvent fraction for the delignification efficacy, a multilinear regression model from Figs. 2 and 3 was fit. The coefficient of determination (R^2) of this model was 0.57, and a separate Spearman's rank correlation coefficient between the mixture solubility and delignification ranks was 0.49, which corresponded to a *p*-value of 0.32. These results showed that there was a weak positive correlation, but no predictive power. Whereas solubility would predict 1-MI to have the highest delignification and EG to have the lowest, it was clearly observed that delignification measurements are required.

While the room temperature solubility fraction of a solvent mixture to predict the extent of delignification is of limited use, this study highlighted five solvents for LVPP and provided delignification data on aqueous solvent mixtures for pine chips. Quick solubility measurements may provide an estimate of the delignification efficacy and hint at the diminished efficacy of the solvent at lower solvent fractions. However, wood chip treatments at 50% to 70% aqueous organic solvent mixtures are required to rank-order solvents for LVPP. When the delignification is higher at severe conditions, the LVPP pretreatment conditions required are lower for partial delignification of wood chips prior to pulping. If the treatment does not yield a delignification of greater than 60% at these severe conditions, the solvent should be precluded from future studies. The best solvents will delignify greater than 80% at 200 °C and 2 h, and the organic solvents may be ranked into quartiles based on the removal of lignin from pine chips. Together, this pretreatment and quick solubility measurement enables the efficient determination of the capacity of a solvent to delignify wood chips for downstream applications.

CONCLUSIONS

1. The existence of outliers precludes the use of industrial lignin solubility in organic solvents as a negative screen for organic solvent pretreatment for delignification.
2. For all of the tested solvents, at least 10% (v/v) water and organic solvent was required for delignification efficacy.
3. Solvents with a higher solubility tend to have a broader delignification efficacy. Solubility screening at a 30% solvent loading may differentiate similar solvents for lignin value prior to pulping (LVPP).
4. For a process such as LVPP, which seeks to maximize the solvent recovery and can tolerate minimum solvent purity requirements, a pretreatment screen with a 50:50 organic solvent:water ratio was found to be appropriate.

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DOI: 10.15376/biores.14.3.5988-6003

APPENDIX

Supplemental Methods for Lignin Characterization

Gel Permeation Chromatography (GPC)

The weight-average (M_w) and number-average (M_n) molecular weights of the ethanol extracted lignin were determined on two PL-gel 10 mm Mixed-B 7.5 mm i.d. columns. A 5 mg samples was dissolved in 2 mL of tetrahydrofuran and passed through a 0.2 µm syringe filter. A 15 µL sample was injected and the column was operated at 30 ˚C with stabilized THF as the mobile phase at a flow rate of 1.0 mL/min. Monodisperse polystyrene was used as the standard for molecular weight calculations.

2D Heteronuclear single quantum coherence spectroscopy (2D HSQC NMR)

2D HSQC NMR were recorded on a Bruker AVIII 400 MHz spectrometer at 25˚C in DMSO-d6. Lignin in DMSO-d6 at a concentration of ~100 mg/mL was measured with spectral widths of 5000 and 20000 Hz for the 1 H and 13C dimensions, respectively. The number of collected complex points was 1024 for the 1 H dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 individual time increments were recorded in the 13C dimension. The 1 JCH used was 145 Hz. Prior to Fourier transformation, the data matrices were zero filled to 1024 points in the 13C dimension. Data processing was performed using standard Bruker Topspin-NMR software. The central solvent (DMSO) peak was used as an internal chemical shift reference point (δC/δH 39.5/2.49).

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

Samples were ground and sieved to a particle size of 40 to 80 mesh and placed into a vacuum desiccator at room temperature overnight to dry. The dry lignin was analyzed using a Thermo Scientific Nicolet 8700 infrared spectrometer equipped with a Smart iTR (ZnSe crystal) sample port and an MCT detector. Spectra were taken at 4 cm^{-1} resolution and averaged over sixty-four individual scans.

Supplemental Data

The characterization of the selected technical lignin sample is presented in Supplemental Fig. 1 (Fig. S1A). Figure S1A shows the S aromatic signals ($S_{2/6}$) along with the G aromatic signals (G2, G5, and G6). An S/G ratio of 2.29 is calculated. Figure S1B shows the prevalence of methoxyl, β-O-4 and β-β linkages with a relative β-O-4/β-β ratio 0.86. Figure S1C exhibits an ATR-IR profile with strong aromatic and C-O stretching. In Fig. S1D, the molecular weight profile is mapped to demonstrate an average molecular weight of 1080 g/mol.

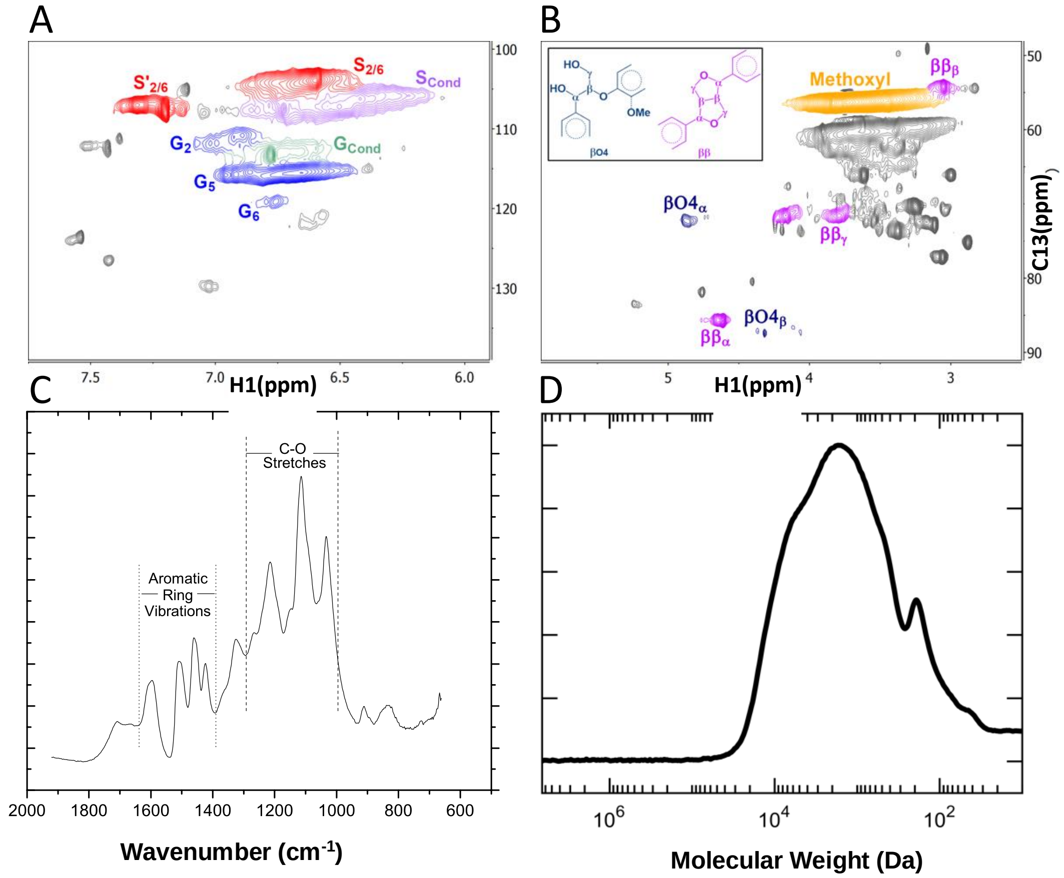

Fig. S1. Ethanol extracted lignin, characterized by 2D HSQC NMR (A and B), FTIR-ATR(C), and Gel Permeation Chromatography (D)

The compositional analysis of raw biomass and 50% solvent treated biomass is presented in Supplemental Table 1. The raw data for delignification and solubility of all solvent treatments is presented in Supplemental Table 2. This data are discussed in the body of the text and presented as Figs. 1 to 3.

Table S1. Compositional Analysis of Selected Treated and Untreated Biomass

Treatment 50% v/v 200 °C - 2h	**Arabinan**	**Galactan**	**Glucan**	**Xylan**	**Mannan**	**Klason Lignin**	**Ash**	**Total Solids**
Untreated (n=2)	1%	3%	37%	6%	9%	29%	< 1%	86%
Ethanol (n=3)	< 1%	< 1%	69%	3%	2%	24%	< 1%	98%
1-MI (n=1)	< 1%	< 1%	68%	2%	5%	23%	< 1%	98%
THF (n=1)	< 1%	< 1%	66%	1%	< 1%	31%	< 1%	98%
HMDA (n=3)	1%	1%	65%	6%	14%	8%	< 1%	95%
EG (n=1)	< 1%	< 1%	61%	3%	2%	27%	< 1%	93%
Water (n=1)	< 1%	< 1%	55%	1%	< 1%	43%	< 1%	99%

For lignin value prior to pulping, the residual sugars are important to predict a solvent's ability to selectively remove lignin while maintaining pulp yields and quality. This work utilized multiple screens in the solvent selection criteria, one of which is a hemicellulose removal screen. The Klason lignin content is the only measurement employed in calculations for this study. The residual sugar contents are for comprehensive benefit only. As such, only the 50% v/v solvent treatment results are presented.

Table S2: Delignification and Solubility Fraction Data for the Aqueous Organic Solvent Treatments in this Study

Solvent	Vol% Solvent	Delignification[1]	Solubility Fraction
1-MI	10	17%	0.78 ± .02
1-MI	30	46%	0.95 ± .01
1-MI	50	57%	0.95 ± .01
1-MI	70	54%	0.95 ± .01
1-MI	90	28% ± 2%	0.96 ± .01
EG	10	10%	0.18 ± .02
EG	30	19%	0.22 ± .05
EG	50	52% ± 9%	0.35 ± .06
EG	70	58% ± 3%	0.49 ± .01
EG	90	27%	0.82 ± .01
EtOH	10	9% ± 2%	0.34 ± .06
EtOH	30	15%	0.50 ± .03
EtOH	50	55% ± 3%	0.70 ± .02
EtOH	70	48%	0.85 ± .01
EtOH	90	28%	0.66 ± .02
HMDA	10	<20%[1]	0.95 ± .01
HMDA	30	69%	0.95 ± .02
HMDA	50	85% ± 2%	0.92 ± .01
HMDA	70	88% ± 3%	0.93 ± .02
THF	10	11%	0.36 ± .02
THF	30	4% ± 2%	0.77 ± .11
THF	50	41%	0.93 ± .02
THF	70	70%	0.94 ± .01
THF	90	11%	0.90 ± .04

Note: Standard deviation provided where applicable (n≥3).

[1]:Delignification based on a measured Klason lignin content of untreated chips of 30.1%

[2]:Unable to complete mass balance for delignification by HMDA 10% solvent fraction

The Hansen solubility parameters were compiled and correlated to the experimental solubility we measured in this study. These numbers are presented in Supplemental Table 3 and compared in Supplemental Fig. 2. No correlation was found, suggesting a need to measure the solubility experimentally.

Table S3. Hansen Solubility Parameters and Measured Solubility Fraction for Aqueous Solutions and 20 Additional Solvents at a 30% solvent Fraction

Target	Dispersion [MPa$^{1/2}$]	Polar [MPa$^{1/2}$]	H - Bonding [MPa$^{1/2}$]	Interaction Radius	Solubility Fraction
Lignin (Vebber *et al.* 2014)	21.9	14.1	16.9	13.7	N/A
Solvent (Hansen 2002)	Dispersion [MPa$^{1/2}$]	Polar [MPa$^{1/2}$]	H - Bonding [MPa$^{1/2}$]	Relative Energy Diff.	Solubility Fraction
Water	15.6	16.0	42.3	2.07	0.08
10% EtOH	15.6	15.3	40.0	1.92	0.34
30% EtOH	15.7	13.8	35.4	1.63	0.5
50% EtOH	15.7	12.4	30.9	1.37	0.7
70% EtOH	15.7	11.0	26.3	1.15	0.85
90% EtOH	15.8	9.5	21.7	1.02	0.66
10% THF	15.7	15.0	38.9	1.84	0.36
30% THF	16.0	12.9	32.0	1.41	0.77
50% THF	16.2	10.9	25.2	1.05	0.93
70% THF	16.4	8.8	18.3	0.89	0.94
90%THF	16.7	6.7	11.4	1.01	0.90
10% EG	15.7	15.5	40.7	1.96	0.18
30% EG	16.0	14.5	37.4	1.73	0.22
50% EG	16.3	13.5	34.2	1.50	0.35
70% EG	16.6	12.5	30.9	1.29	0.49
90% EG	16.9	11.5	27.6	1.09	0.82
10% HMDA	15.7	15.4	38.6	1.83	0.95
30% HMDA	16.0	14.1	31.2	1.36	0.95
50% HMDA	16.2	12.8	23.8	0.98	0.92
70% HMDA	16.4	11.5	16.4	0.82	0.93
10% 1-MI	16.0	16.0	39.2	1.85	0.78
30% 1-MI	16.8	15.9	33.0	1.39	0.95
50% 1-MI	17.7	15.8	26.8	0.96	0.95
70% 1-MI	18.5	15.7	20.5	0.58	0.95
90% 1-MI	19.3	15.6	14.3	0.43	0.96
30% 1,4-Dioxane	17.5	1.8	9.0	1.41	0.86
30% 2-methyl furan	17.3	2.8	7.4	1.39	0.19
30% 2-methyl thf	16.9	5.0	4.3	1.34	0.49
30% Acetone	15.5	10.4	7.0	1.42	0.63
30% Diethanolamine	17.2	10.8	21.2	1.63	0.95
30% Dimethyl sulfoxide	18.4	16.4	10.2	1.41	0.35
30% Ethylamine	15.0	5.6	10.7	1.50	0.98
30% Ethylene carbonate	19.4	21.7	5.1	1.31	0.74
30% Gamma butyrolactone	19.0	16.6	7.4	1.34	0.89
30% Methanol	14.7	12.3	22.3	1.71	0.18
30% Morpholine	18.8	4.9	9.2	1.38	0.97
30% N-methyl pyrrolidine	17.0	2.8	6.9	1.39	0.97
30% N-methyl 2-pyrrolidone	18.0	12.3	7.2	1.36	0.79
30% Piperidine	17.6	4.5	8.9	1.40	0.97
30% Propylene Carbonate	20.0	18.0	4.1	1.26	0.78
30% Propylene glycol	16.8	9.4	23.3	1.68	0.13
30% Pyridine	19.0	8.8	5.9	1.31	0.95
30% Pyrrolidine	17.9	6.5	7.4	1.36	0.97
30% Sulfolane	20.3	18.2	10.9	1.38	0.80
30% Triethanolamine	17.3	22.4	23.3	1.69	0.85

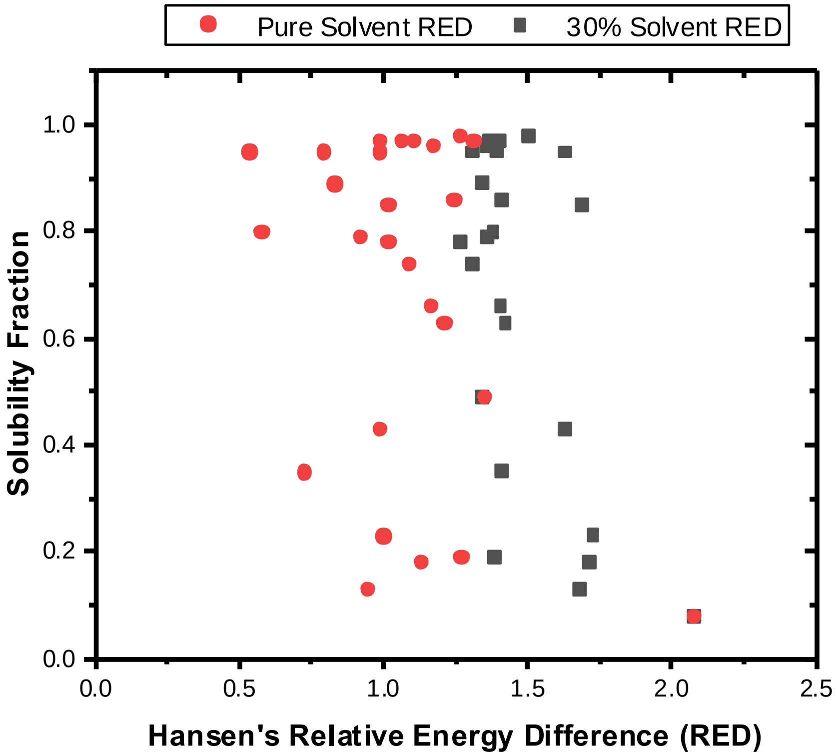

Fig. S2. Hansen's solubility - relative energy difference (RED) for solvents and aqueous solvents with lignin