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Research Article

Fractionation of Poplar Wood Using a Bifunctional Aromatic Acid under Mild Conditions

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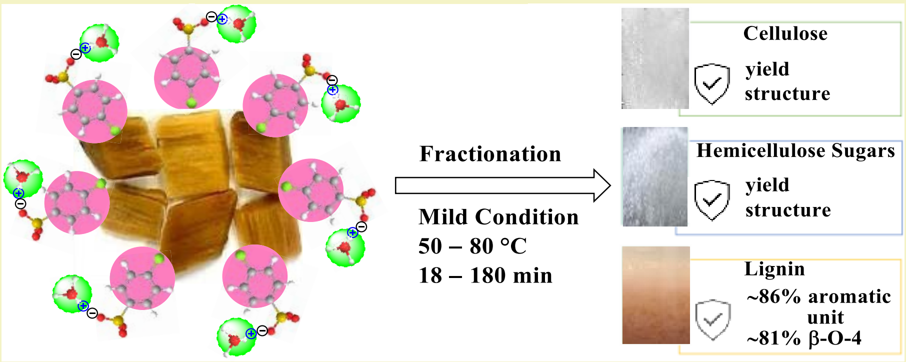

ABSTRACT: The development of an energy-efficient fractionation process as well as the preservation of the fractionated cellulose, hemicellulose sugars, and lignin are the key to the valorization of lignocellulose. This study presents a mild-condition fractionation process based on a recyclable and bifunctional 4-chlorobenzenesulfonic acid (4-Cl-BSA). The aqueous (e.g., 72%) 4-Cl-BSA solution near-completely fractionated unmilled poplar chips at 50−80 °C for 18−180 min and successively preserved the theoretical maximum yields and key structures of the fractionated cellulose, lignin, and hemicellulose sugars. Around 21.3−27.8% lignin was hydrotropically dissolved at a mesoscale level through accumulation by and complexation with 4-Cl-BSA and its aggregates. The solubilized lignin preserved about 24.7−50.7% of the 61% *β*-O-4 linkages in the native lignin and about 48.3−82% aromatic units uncondensed. About 72.2−78.7% lignin was insolubilized and quickly deposited on the surfaces of cellulose fibers. Remarkably, the deposited lignin preserved about 61.9−81.1% of the *β*-O-4 linkages in the native lignin and about 78.2−86.2% aromatic units uncondensed. Hemicellulose sugars and cellulose (millimeter-size, CrI: 71−75, DP$_v$: 910−1022) had high purity and high quality. Compared to the other selected aryl sulfonic acids whether they have or do not have substituents (dichloro, bromo, hydroxyl, and methyl) and mineral acids, 4-Cl-BSA performed better in fractionating unmilled poplar chips and preserving the *β*-O-4 linkages and aromatic units of lignin. The results indicate that both acidity and hydrophobicity of aryl sulfonic acid greatly influence its fractionation and preservation performances.

KEYWORDS: *mild-condition fractionation, mesoscale solubilization, structural preservation, aryl sulfonic acid, theoretical calculation*

INTRODUCTION

In lignocellulosic biomass, lignin (15−30%) chemically and physically holds cellulose and hemicelluloses together in the plant cell walls.[1] To fractionate lignocellulose into its three main components (cellulose, hemicelluloses, and lignin), catalysts are typically necessary to effectively cleave the linkages (e.g., ether and ester bonds) in the lignin-carbohydrate complex (LCC), lignin, and hemicelluloses.[2] Mineral acids (e.g., sulfuric and hydrochloric acids) and inorganic bases (e.g., sodium, potassium, and calcium hydroxides) have been commonly used for the fractionation of lignocellulose.[3] During fractionation, the catalytic species of mineral acids (proton) and inorganic bases (hydronium) readily contact and react with lignin, hemicelluloses, and cellulose. Consequently, depending on the fractionation conditions (such as catalyst dosage, temperature, and time), acid or base catalysts can cause unwanted structural alterations or/and losses to the fractionated lignin, hemicellulose sugars, and cellulose, which affect their yields and qualities.[4] For example, cellulose and hemicelluloses can be depolymerized into sugars under acidic conditions; however, these sugars can be further transformed to low-value humins by the condensation of sugar-derived furans under severe conditions.[5]

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Also, acids or bases can significantly cleave the β-O-4 linkages in lignin and cause the undesirable condensation of lignin, which make the subsequent lignin valorization process (e.g., depolymerization to high-value monoaromatics) difficult.[6,7]

The mild-condition fractionation is preferred to preserve the fractionated cellulose, hemicellulose sugars, and lignin. However, the fractionation of lignocellulose is often limited under mild conditions, which cannot completely or even substantially fractionate lignocellulose.[8] Practically, concentrated catalysts or/and higher temperatures (e.g., 120−220 °C) are needed to achieve the substantial or complete fractionation of lignocellulose.[4,9,10] For these reasons, the fractionation strategy of lignocellulose is usually compromised to preserve the yields and qualities of the fractionated cellulose, hemicellulose sugars, and lignin. In recent studies, aldehydes (e.g., formaldehyde and propionaldehyde)[11−14] and diols (e.g., ethylene glycol[15,16] and 1,4-butanediol[17]) have been applied to assist the substantial or even complete fractionation with the preservation of lignin and hemicellulose sugars. Depending on their types and the fractionation conditions, aldehydes and diols can react with the surface hydroxyls of cellulose, which may influence the reactivity, accessibility, and enzymatic digestibility of cellulose.[12,13] Instead of preservation, the fractionated lignin in alcohols (e.g., methanol, ethanol, and isopropanol) can be instantly depolymerized to stable monomers, dimers, and oligomers using heterogeneous redox-active catalysts (e.g., Pd/C) and hydrogen in the absence or the presence of an acid cocatalyst.[18,19] Similarly, cellulose can be decrystallized or even depolymerized through the catalytic reductive fractionation.[20] Alternatively, the fractionated lignin can be solubilized and continuously collected at the outlet during the rapid flow-through fractionation[21,22] and then separated from catalysts through the precipitation in water followed by filtration. However, the rapid flow-through fractionation requires more solvents or/and catalysts, compared with the batch fractionation. Nevertheless, low energy inputs are highly desirable to improve the economics of the fractionation of lignocellulose. With the aforementioned methods, high temperatures (e.g., 120−220 °C) and pressures (e.g., 10−50 bar) and/or the energy-intensive (e.g., 100−1000 kWh electricity/ton) size reduction (e.g., from centimeter to millimeter) of lignocellulose are still needed because the conventional acid or base catalysts are mostly insufficient to fractionate unmilled lignocellulose under mild conditions.[23−27] Thus, it is expected that high-performance catalysts can be a solution to improve the economics of the fractionation process by operating at mild conditions without an energy-intensive milling step.

Within this context, aryl sulfonic acid (also referred to as hydrotropic acid) has been introduced as an alternative to mineral acids for fractionating lignocellulose at mild temperatures.[22,28−30] Owing to the aromatic nature, the bifunctional aryl sulfonic acid is advantageous over the investigated monofunctional mineral acids and inorganic bases. First of all, aryl sulfonic acid as a small amphiphile can in situ solubilize the fractionated lignin in an aqueous environment through its aggregate to form a noncovalent complex due to the aromatic−aromatic and hydrophobic interactions or/and accumulating around lignin due to the hydrophobic effect. The in situ solubilization of lignin is believed to promote the fractionations of the remaining lignin and lignocellulose. Second, aryl sulfonic acid is able to actively interact with lignin in lignocellulose through the aromatic−aromatic and hydrophobic interactions, which likely facilitates the fractionation of lignin. In addition, aryl sulfonic acid can be easily recycled through crystallization or extraction using organic solvents such as ethanol. *p*-Toluenesulfonic acid (TsOH) was the first aryl sulfonic acid used to fractionate various milled lignocelluloses at mild temperatures.[22,28,29] In our recent study, we successfully demonstrated that the lignin-derivable phenol-4-sulfonic acid (PSA) near-completely fractionated unmilled hardwood chips (poplar and birch) at mild conditions (e.g., 50−80 °C, 0.5−3 h, atmospheric pressure) into cellulose fibers at high-quality, fermentable hemicellulose sugars and lignin in theoretical maximum yields.[30] However, PSA severely condensed the fractionated lignin and only retained the 4.9−14.7% β-O-4 linkages of lignin.

Aryl sulfonic acid can be molecularly designed and task-specifically functionalized through the aromatic ring. It can be envisioned that aryl sulfonic acid with an optimal structure (e.g., the type and the number of substituents) and properties (e.g., amphiphilicity, solubility, and acidity) could near-completely fractionate unmilled lignocellulose at mild temperatures and successively preserve the yields and qualities of the fractionated lignin, cellulose, and hemicellulose sugars. Toward achieving this goal, we herein demonstrate 4-chlorobenzenesulfonic acid (abbreviated as 4-Cl-BSA) as a superior aryl sulfonic acid to PSA. Due to the electron-withdrawing chloro group, 4-Cl-BSA is a stronger acid than PSA, which can easily realize the mild-temperature fractionation of lignocellulose. Given the hydrophobic nature of the chloro group, 4-Cl-BSA tends to aggregate easily in an aqueous environment than PSA. Owing to the limited mobility, the formed 4-Cl-BSA aggregate might not aggressively approach and not cause severe structural alterations to the deposited lignin particle on the surface of a cellulose fiber. Thus, 4-Cl-BSA is expected to perform better in fractionating lignocellulose and especially preserving the fractionated lignin than PSA. The main objectives of this study include: (1) finding mild temperatures to achieve a near-complete fractionation of poplar chips, (2) characterizing the obtained cellulose and lignin from the near-complete fractionation, (3) elucidating the mechanisms for the solubilization and preservation of lignin through theoretical calculations and experimental measurements, and (4) qualitatively analyzing the structure−-performance relationship of aryl sulfonic acid by comparing 4-Cl-BSA with other aryl sulfonic acids that have or do not have other substituents such as dichloro, bromo, hydroxyl, and methyl.

■ EXPERIMENTAL SECTION

Materials. 4-Chlorobenzenesulfonic acid (purity: 90%, also known as 4-chlorobenzene sulfonic acid or *para*-chlorobenzenesulfonic acid) (accordingly abbreviated as 4-Cl-BSA or *p*-CBSA), 4-bromobenzenesulfonic acid (4-Br-BSA, purity: 98%), toluenesulfonic acid (TsOH, purity: ≥98%), benzenesulfonic acid (BSA, purity: 98%), polystyrene standards, and guaiacylglycerol-β-guaiacyl ether (GG, purity: ≥99%) were purchased from Sigma-Aldrich. 2,5-Dichlorobenzenesulfonic acid (di-Cl-BSA, purity: 97%) was obtained from Fisher Scientific. Phenol-4-sulfonic acid (PSA or 4-OH-BSA, water: 10%, sulfate ≤2%), acetic anhydride (≥99%), pyridine (≥99%), tetrahydrofuran (THF) (anhydrous), dioxane (≥99%), ethanol (200 proof), dimethyl sulfoxide-d_6 (99.9 atom % D), cupriethylenediamine hydroxide (0.5 M), sodium hydroxide (pellets, ≥98%), hydrogen peroxide (30%), xylose (≥99%), mannose (≥99%), arabinose (≥99%), galactose (≥99%), and rhamnose (≥99%) were purchased from TCI AMERICA. All chemicals were used without further purification. The cellulolytic enzyme (CTec2) was bought from Sigma-Aldrich.

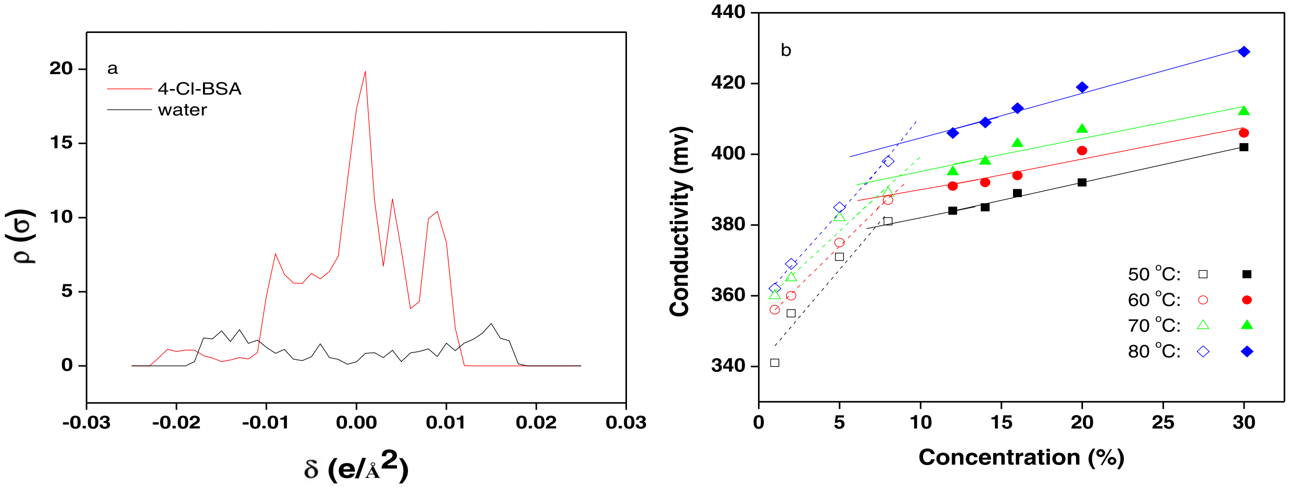

Figure 1. Calculated sigma profile (a) and measured conductivities (b) of 4-Cl-BSA under different concentrations and temperatures.

Fast-growing poplar (2−3 years) was harvested in the Michigan area and was chopped to woodchips of approximately 1−2.5 cm (length) × 0.8−1.5 cm (width) × 0.3−1 cm (height) (Figure S1). The poplar chips are composed of about 26.1% lignin, 42.5% glucan, and 20.9% hemicelluloses (xylan: 17.3%, arabinan: 0.6%, mannan: 2.5%, and galactan: 0.5%). Woodchips were soaked in water at room temperature for 24 h.

Chemical Composition Analysis. Chemical compositions of woodchips and the extracted cellulose, hemicellulose sugars, and lignin were analyzed using the NREL/TP-510-42618.[31] Monomeric sugars were determined using high-performance liquid chromatography (HPLC, Agilent Technologies 1260 Infinity) equipped with a Hi-Plex column (7.7 × 300 mm^2) and a UV and a Refractive Index Detectors.

Critical Aggregation Concentration. Critical aggregation concentrations of 4-Cl-BSA at 50−80 °C were determined by measuring the conductivities of different concentrations (2−70%) of the aqueous 4-Cl-BSA solutions.

Mesoscale Solubilization of Lignin. Lignin (M_w = 3505) isolated from poplar[30] was added to 2 mL of an aqueous 72% 4-Cl-BSA solution until no more lignin was solubilized. The obtained solution was centrifuged to remove the insolubilized lignin. The amount of solubilized lignin was calculated based on the difference between the added lignin and the insolubilized lignin.

Fractionation of Poplar. Water-soaked poplar chips (3 g, 40−60% moisture) were incubated with concentrated aqueous 4-Cl-BSA solution (40−80%, 20 mL) with stirring in a 50 mL plastic tube. The fractionation experiments were conducted at 50−80 °C for 4−60 min (Figure S2). When softened, chips were manually disintegrated into jelly-like pieces using a glass rod (end area: 0.7854 cm^2) with a pressure of about 140 g/cm^2 for around 0.5−1 min (Figure S3), and then filtered.

Lignin was collected as two fractions: solubilized and deposited fractions (Figure S2). The solubilized lignin in the filtrate (the solubilized lignin fraction) was precipitated with an excessive amount (50 mL) of water. The lignin (the deposited lignin fraction) in the lignin-containing acetone solution was recovered through the precipitation method using water. Cellulose fibers were obtained from residual solids by washing with acetone 2−3 times and then with water once. Hemicellulose sugars (mainly xylose) were recovered after the spent 4-Cl-BSA was extracted using ethanol. The lignin (or hemicelluloses) yield is calculated from the extracted lignin (or hemicelluloses) as a percentage of the theoretically available lignin (or hemicelluloses) from poplar

$$\text{lignin or hemicelluloses yield (\%)} = \frac{\text{extracted lignin or hemicelluloses (g)}}{\text{lignin or hemicelluloses in poplar (g)}} \times 100\% \quad (1)$$

The calculated lignin yield is also compared with the difference between the theoretically available lignin from poplar and the residual lignin in the obtained cellulose fiber. It turns out that the calculated lignin yield is slightly (averagely around 1.5−2.2%) overestimated due to the presence of 4-Cl-BSA.

Isolation of Untreated Lignin from Poplar. Cellulolytic enzyme lignin (CEL, named as untreated lignin) was isolated from untreated poplar. Poplar was milled using a Retsch planetary ball mill PM 100 with a stainless steel jar at 600 rpm for 2 h. The ball-milled poplar sample was treated with cellulolytic enzyme (CTec2, pH = 5) at 50 °C for 72 h. The residual solid after the enzymatic hydrolysis was extracted with 96% dioxane for 48 h. The extracted lignin was recovered after dioxane was evaporated.

Cleavage of the Lignin Dimeric Compound. Guaiacylglycerol-*β*-guaiacyl ether (GG, 10 mg) was mixed with 4-Cl-BSA (10 mg) in water (0.5 mL). The reaction was carried out at 60 °C for 30 min. Then, after water was removed by evaporation, the obtained products were analyzed using NMR spectroscopy.

Gel Permeation Chromatography (GPC) Analysis of Lignin. Molecular weights of lignin samples were analyzed using a Waters 2498 gel permeation chromatograph (GPC) equipped with three Waters Styragel columns (HR0.5, HR3, and HR4E) using tetrahydrofuran as a mobile phase and calibrated with polystyrene standards. Before analysis, about 5 mg of the lignin sample was acetylated in 5 mL of acetic anhydride/pyridine (1:1, v/v) in a dark environment for 24 h. The acetylated lignin sample was recovered using a rotary evaporator with ethanol washing.

Nuclear Magnetic Resonance Analysis of Lignin. Structural properties (composition and interunit linkage contents) of lignin samples were analyzed by two-dimensional (2D) $^{13}C-^{1}H$ heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) analysis using a Bruker AVANCE III HD 800 MHz spectrometer equipped with a TCI cryoprobe with a standard Bruker heteronuclear single-quantum coherence pulse sequence (hsqcetgpspsi2.2). About 20 mg of the lignin sample was solubilized in DMSO-d_6 (0.5 mL) and loaded into the 5 mm NMR tube. The NMR operation parameters were 12 ppm spectral width in the F2 (^{1}H) dimension with 1024 data points and 160 ppm spectral width in F1 (^{13}C) dimension with 512 data points, a 1.2 s pulse delay, and 32 scans. The relative abundance of the lignin interunit linkage and monomer compositions were calculated using volume integration of contours in HSQC spectra (e.g., C_α, $S_{2/6}$, and G_2) semiquantitatively.[31]

X-ray Diffraction (XRD) Analysis of Cellulose. XRD of cellulose samples was measured using a SmartLab X-ray diffractometer (Rigaku, Japan) with a 35 mA Cu Kα radiation source energized at 40 kV. Measurements were collected in the 2θ range from 10 to 30° at a rate of 5°/min. The measurement resolution was

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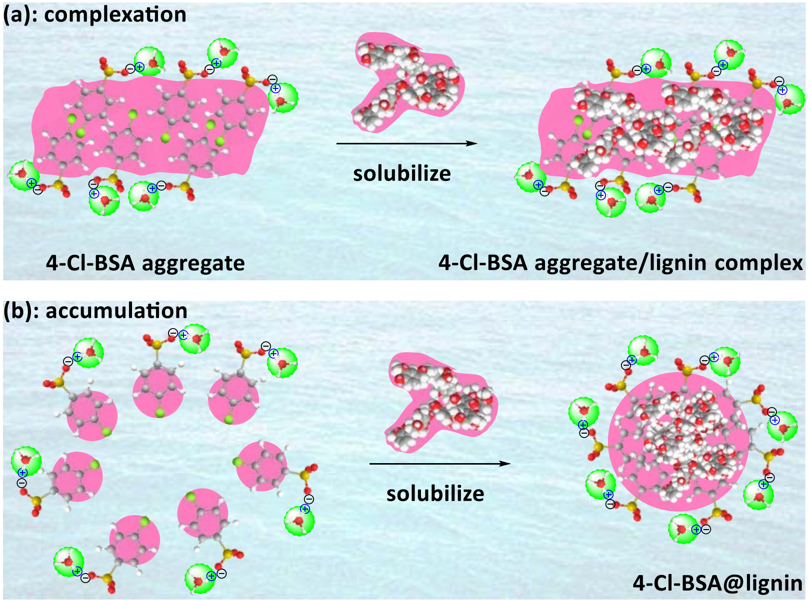

Figure 2. Proposed complexation (a) and accumulation (b) mechanisms (light blue background: water, pink: the hydrophobic domain, and green: the hydrated proton) for the solubilization of lignin (space-filling model) in water by 4-Cl-BSA (ball-and-stick model).

0.02°. Then, the results were analyzed using TOPAS software. The crystallinity index (CrI) was calculated using the Segal equation[32]

$$\mathrm{CrI} = \frac{(I_{200} - I_{\mathrm{min}}) \times 100}{I_{200}} \tag{2}$$

Degree of Polymerization (DP_v) of Cellulose. Intrinsic viscosities (η) of cellulose samples were measured with an Ubbelohde viscometer using 0.5 M cupriethylenediamine hydroxide as a solvent at 20 °C according to the ASTM D1795 method. The degree of polymerization (DP_v) was calculated using the Mark–Houwink equation[33]

$$(\mathrm{DP_v})^{0.905} = 0.75 \times [\eta] \tag{3}$$

RESULTS AND DISCUSSION

Aggregation/Clustering Behavior of 4-Cl-BSA. 4-Chlorobenzenesulfonic acid (4-Cl-BSA) is considered as a small ionizable amphiphile due to the hydrophobic chloro-substituted benzene ring and the hydrophilic sulfonic acid group. To theoretically analyze the hydrophobicity/hydrophilicity, we calculated the log D values at pH = 0−2 (log K_{ow}, a log of partition coefficient of 4-Cl-BSA between octanol and water) of 4-Cl-BSA using ChemAxon software. The calculated log D value decreases from −0.5138 to −0.617 with the increase in the pH value (Figure S4). This result indicates that 4-Cl-BSA has hydrophilic nature and exhibits higher hydrophilicity under an elevated pH value due to the ionization of the sulfonic acid group. The hydrogen-bonding and hydrophobic interaction potentials of 4-Cl-BSA were calculated through the sigma profile and sigma potential profile using the COSMO-RS method (water as a reference) (Figures 1a and S4).[34] The sigma profile and sigma potential profile confirmed that 4-Cl-BSA could have hydrophobic interactions (-0.007 e/Å^2 < σ < 0.007 e/Å^2) through the chloro-substituted benzene ring and can act as the hydrogen bond donor (δ^+H, $\sigma < -0.007$ e/Å^2) and acceptor (δ^-O, $\sigma > 0.007$ e/Å^2) through the sulfonic acid group.[35,36]

To probe the aggregation/clustering behavior in water, critical aggregation concentration (also referred to as the minimum hydrotropic concentration) values of 4-Cl-BSA at 50−80 °C were estimated through measuring the electrical conductivities under different concentrations (Figure 1b). The conductivity of the aqueous 4-Cl-BSA solution expectedly increased as the concentration and temperature increased. The estimated critical aggregation concentrations at 50, 60, 70, and 80 °C were about 7.2, 8.3, 8.6, and 8.7%, respectively. Owing to the nature of amphiphilicity, the aggregation/clustering behavior of 4-Cl-BSA in water is affected by the hydrophobic hydration of the chloro-substituted benzene ring and the hydrophilic hydration of the sulfonic acid group.[37] With an increase in temperature, the hydrophobic hydration decreases while the hydrophilic hydration increases, causing a slight increase in the critical aggregation concentration.[38] Although the measured critical aggregation concentrations indirectly verified the occurrence of the aggregation/clustering of 4-Cl-BSA in water, further studies are necessary to accurately determine the number of molecules required to form aggregate, and the type and size of the formed aggregate.[30]

Mesoscale Solubilization of Lignin by 4-Cl-BSA. To verify the hydrophobic nature of lignin, we calculated the log D values, sigma profiles, and sigma potentials of several representative lignin monomers and dimers using the same methods (Figures S5 and S6). As expected, the calculated log D values (1.2−3.8) and sigma profiles verified that lignin is highly hydrophobic and is more hydrophobic than 4-Cl-BSA. Based on the predicted aggregation/clustering behavior, the hydrogen-bonding/hydrophobic interaction potentials, and the previous studies on the mesoscale (or hydrotropic) solubilization of lignin,[22,28−30] 4-Cl-BSA is expected to solubilize the hydrophobic lignin in water through two mechanisms: complexation and accumulation (Figure 2). (i) 4-Cl-BSA can solubilize lignin through its aggregate.[22,28−30] Due to the amphiphilic property of 4-Cl-BSA, it can form the stack-type (non-micelle) aggregate in which the immobilized sulfonic acid group points outward in water.[39] When they are present in water, the 4-Cl-BSA aggregate and lignin spontaneously come together to minimize the total surface area exposed to water.[40] Then, the 4-Cl-BSA aggregate presumably forms a temporary

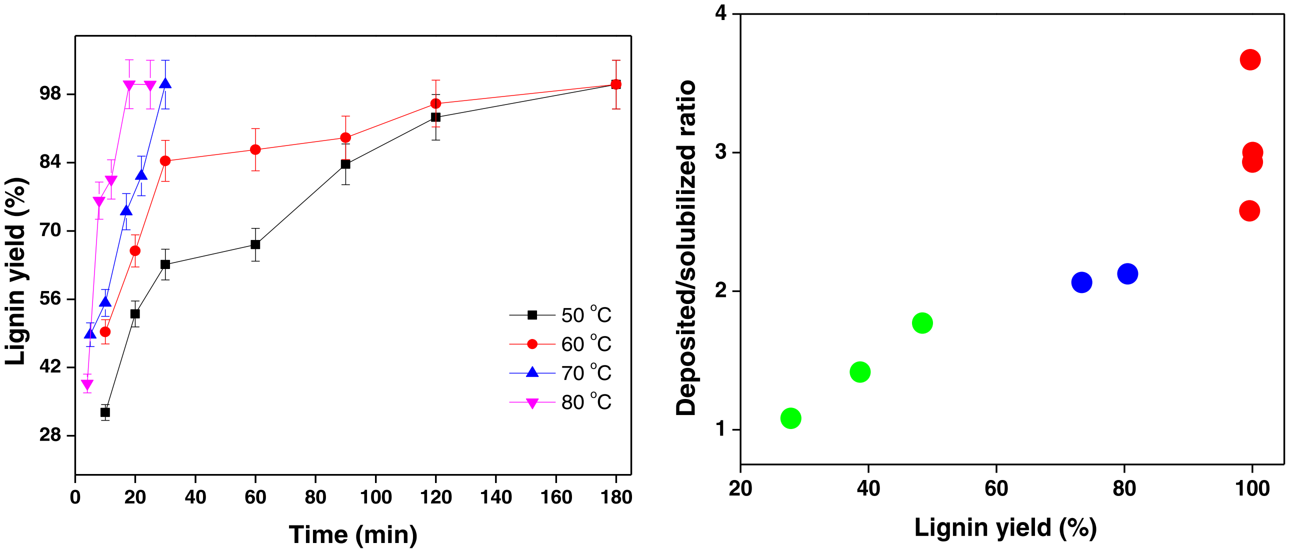

Figure 3. Lignin yield during the fractionation of poplar at varied experimental conditions and the correlation between the lignin distribution (the deposited/solubilized ratio) and the lignin yield.

complex with lignin mainly due to the aromatic−aromatic interaction and accordingly solubilizes lignin at the mesoscale level (Figure 2a).[30] (ii) The unaggregated 4-Cl-BSA can deliberately accumulate around lignin owing to the hydrophobic effect,[41] by which lignin is solubilized by 4-Cl-BSA at the mesoscale level (Figure 2b). However, further studies are needed to verify the proposed two mechanisms to elucidate which mechanism dominates the mesoscale solubilization of lignin, and the size difference of the 4-Cl-BSA aggregate before and after solubilizing lignin.

To attest the hypothesized mesoscale solubilization of lignin, the aqueous 72% 4-Cl-BSA solution was used to solubilize the isolated poplar lignin (M_w = 3505 g/mol). The result showed that 1 g of the aqueous 72% 4-Cl-BSA solution solubilized about 28 mg of lignin at 60 °C (Figure S7). To indirectly verify the roles of the hydrophobic effect and associated aggregation, the anhydrous liquid 4-Cl-BSA was used to solubilize lignin.[30] Without the hydrophobic effect and aggregation, the same amount (1 g) of anhydrous liquid 4-Cl-BSA only solubilized about 5 mg of lignin. This result also verifies the significant roles of water in triggering the aggregation of 4-Cl-BSA and assisting with the mesoscale lignin solubilization. For comparison, the commonly used lignin solvents such as ethanol, acetone, and tetrahydrofuran were also used to solubilize lignin. It turns out that the aqueous 72% 4-Cl-BSA solution is similar to the aqueous 72% ethanol but less efficient than the aqueous 72% acetone and tetrahydrofuran in solubilizing lignin (Figure S7).

Effects of Reaction Conditions on the Fractionation of Poplar by 4-Cl-BSA. Functionally, during the fractionation of poplar chip, the sulfonic acid group of 4-Cl-BSA is responsible for cleaving the lignin-carbohydrate complex and depolymerizing hemicelluloses and lignin, while the aqueous 4-Cl-BSA solution is accountable for solubilizing the fractionated lignin and hemicellulose sugars. Considering the low density (a calculated 5.19 mmol $-SO_3H$/g) of the sulfonic acid group, high concentrations are necessary for 4-Cl-BSA to ensure sufficient depolymerization and solubilization of lignin. Thus, we tested different concentrations (40−80%) and different acid/poplar ratios (4−20, oven-dry weight) at 60 °C for 2 h. The results indicate that a 72% concentration and a 20 acid/poplar weight ratio are sufficient for 4-Cl-BSA to achieve about 96% lignin yield (Figure S8). The 72% concentration and 20 acid/poplar weight ratio were thus used for the rest of the experiments. To find other experimental conditions toward achieving the near-complete fractionation of poplar, the experiments by the aqueous 72% 4-Cl-BSA solution were conducted under different temperatures (50−80 °C) and times (4−180 min).

The yields of lignin were monitored at each reaction condition and are shown in Figures 3 and S8. The near-complete lignin isolation and the resultant fractionation were achieved under each temperature at different times (80 °C: 18 min, 70 °C: 30 min, 60 °C: 180 min, and 50 °C: 180 min). The results also indicated that the deposited fraction/the solubilized fraction ratio was around between 2.6 and 3.7 when a near 100% lignin yield was achieved (Figure 3). The color of the lignin sample was light brown (Figure S9). Hemicellulose sugars obtained under the condition for the near-complete lignin isolation (80 °C and 25 min) were measured using HPLC to calculate the hemicelluloses yields (eq 1) in the fractionation process. When the lignin fractionation was completed, hemicelluloses were mostly hydrolyzed to sugars in theoretic maximum yields without the formation of furan-based products (Figure S10). After hemicelluloses and lignin were fractionated, high-purity cellulose fibers were obtained from residual solids in theoretical maximum yields.

Inefficient recycling of 4-Cl-BSA can balance against the perceived less energy consumption (the elimination of the milling process coupled with mild-condition operation) and the structural preservation of lignin benefits. More importantly, similar to chlorobenzene, 4-Cl-BSA can cause environmental issues if treated improperly.[42] After the fractionation, about 99% of 4-Cl-BSA was recycled using ethanol extraction (Figure S2). The loss of 4-Cl-BSA was partially attributable to the speculation that 4-Cl-BSA reacted with lignin (see Figure 4). The recyclability of 4-Cl-BSA can be further improved through the repeated ethanol extractions or using an adsorbent such as a hyper-cross-linked microporous polymer[43] or cross-linked poly(ethylenimine).[44] If needed, the chlorine group introduced to lignin can be catalytically converted into the hydroxyl group,[45] which avoids the generation of chlorinated aromatics

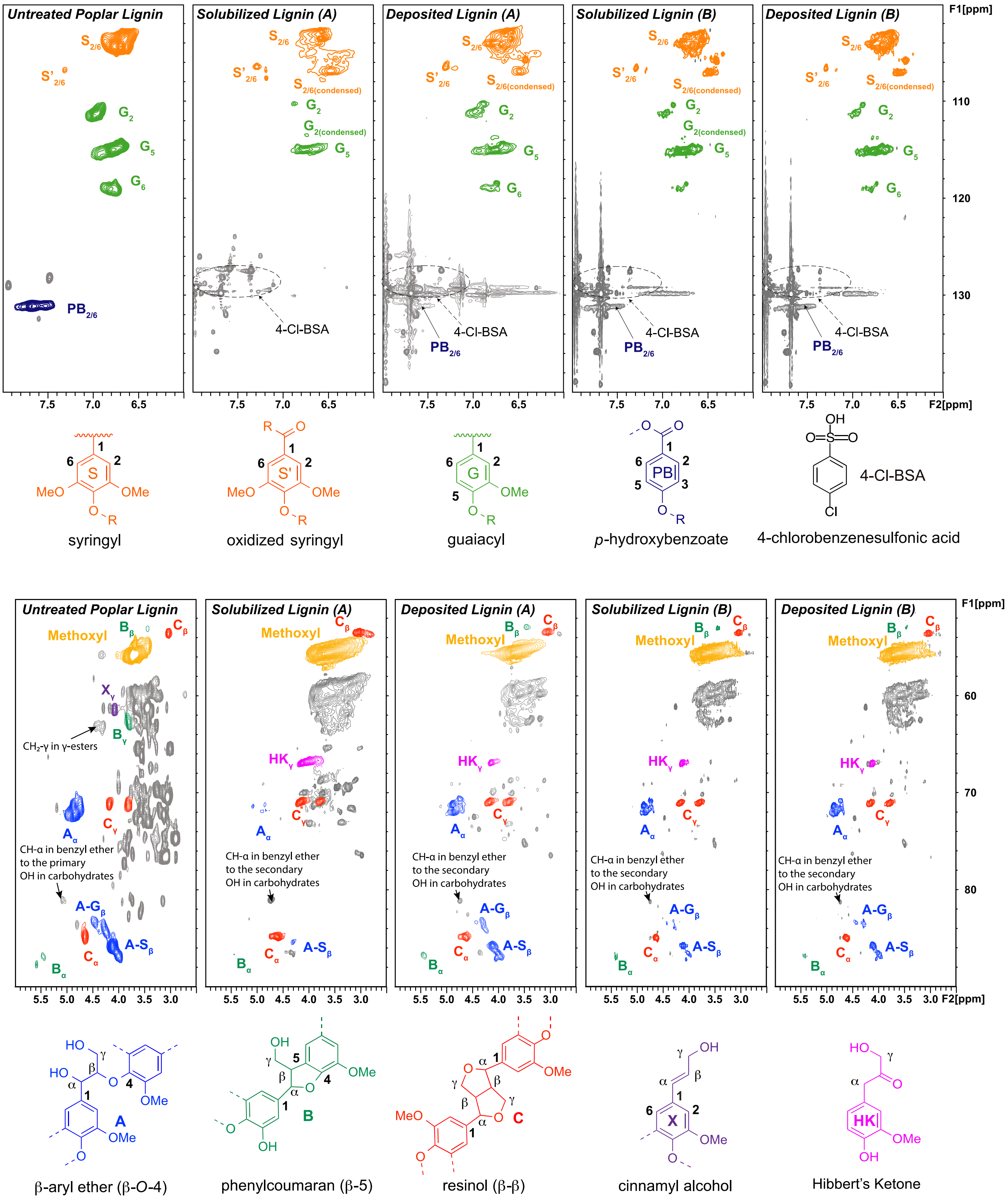

Figure 4. 2D HSQC NMR spectra of the untreated poplar lignin sample and fractionated (the solubilized and deposited fractions) poplar lignin samples from different conditions (A: 60 °C, 2 h, and B: 70 °C, 30 min).

during the subsequent lignin valorization through hydrogenation. The recycled 4-Cl-BSA (Figure S11) was diluted to a 72% aqueous solution, which was used to directly fractionate the fresh poplar chips. It turned out that the recycled 4-Cl-BSA exhibited slightly reduced performances at 2nd (93.3%) and 3rd (89.2%) runs.

4-Cl-BSA is adaptable to fractionate other unmilled hardwood. For example, the aqueous 72% 4-Cl-BSA solution near-completely isolated lignin from the birch chip at 80 °C for

Table 1. Compositions and Interunit Linkage Contents of Untreated and Fractionated Poplar Lignin Samples[a]

comp. (%)		untreated	A		B	
			solubilized	deposited	solubilized	deposited
S	total	69.8	72.0	80.0	80.1	78.5
	condensed	0.0	29.4	18.3	17.8	14.0
	uncondensed	69.8	42.7	61.7	62.3	64.5
G	total	30.2	27.9	20.0	19.9	21.5
	condensed	0.0	22.2	3.5	0.0	0.0
	uncondensed	30.2	5.7	16.5	19.9	21.5
S/G ratio		2.31	2.58	3.99	4.03	3.65
condensed/uncondensed		0.00	1.07	0.28	0.22	0.16
β-O-4		61.0	15.1	49.5	30.9	37.8
β-5		3.8	2.7	4.7	5.6	3.9
β-β		5.1	9.9	10.0	6.0	6.0

[a] A (solubilized/deposited = 1/3) and B (solubilized/deposited = 1/3.8) samples were fractionated with 100% yields from poplar chips by 72% 4-Cl-BSA aqueous solutions at 60 °C for 2 h and 70 °C for 30 min, respectively. The content (%) is expressed as a fraction of total lignin subunits (S + G).

40 min. However, like other aryl sulfonic acids,[29,30] 4-Cl-BSA at mild temperatures is less effective (around 45.7% lignin yield at 80 °C for 40 min) to unmilled softwood such as pine.

Effects of Fractionation on the Structures of Lignin and Cellulose. The structural properties of the fractionated lignin and cellulose were dependent upon the fractionation conditions. As representatives, the lignin samples (named as A with about 25% solubilized and 75% deposited fractions) isolated at 60 °C for 2 h and the lignin samples (named as B with about 21% solubilized and 79% deposited fractions) isolated at 70 °C for 30 min were analyzed in terms of the lignin-carbohydrate complex (ester and benzyl ether linkages), compositions (S and G units), interunit linkages (β-O-4, β-5, and β-β), and molecular weights using 2D HSQC NMR and GPC, respectively (Figure 4 and Tables 1 and 2). The contour for CH$_2$-γ in γ-esters at 63−64/4.15−4.2 ppm was observed in untreated poplar,[46−48] while the signals disappeared in the fractionated poplar lignin samples. The contour of CH-α in benzyl ether to the secondary hydroxyl groups of carbohydrates (mainly xylan) observed at 80−81/4.9−5.1 ppm also disappeared after the fractionation. Another contour of CH-α in benzyl ether to the primary hydroxyl groups of carbohydrates such as C6 of glucose, galactose, and mannose, and C5 of arabinose assigned at 81−80/4.7−4.5 ppm was only observed at the noise level in untreated biomass.[47−51] However, this signal became stronger after the fractionation. It indicates that the benzyl ethers connecting the CH-α of lignin to the primary hydroxyl groups of carbohydrates were relatively stable than other LCC linkages during the fractionation. The fractionated lignins had higher S/G ratios (2.58−4.03) compared to the native (untreated) lignin (2.31) (Table 1). The increase of S/G ratios after the fractionation is possibly due to the removal of the G unit and/or the condensation of the G unit, in particular, at G2 and G6 positions. A similar result was reported in the previous study.[52] In spite of the acid-labile nature of the β-O-4 linkage, the aqueous 72% 4-Cl-BSA solution remarkably retained the 61% β-O-4 linkages in the native poplar lignin. The retention of the β-O-4 linkage was defined as the β-O-4 linkages in the fractionated lignin sample as a percentage of the β-O-4 linkages in the native poplar lignin (i.e., untreated lignin). Specifically, at 60 °C for 2 h, the aqueous 72% 4-Cl-BSA solution kept about 81.1 and 24.7% of β-O-4 linkages in the deposited fraction and the solubilized fraction, respectively; at 70 °C for 30 min, the aqueous 4-Cl-BSA solution kept about 61.9 and 50.7% of β-O-4 linkages in the deposited fraction and the solubilized fraction, respectively. Regardless of the fractionation conditions, the deposited lignin fraction generally had more β-O-4 linkages. During the acidic cleavage of the β-O-4 linkage, the benzyl carbonium intermediate was generated and then caused the condensation of the aromatic unit.[12] The lignin that retained more β-O-4 linkages was likely less condensed. At 60 °C for 2 h, the aqueous 72% 4-Cl-BSA solution caused 21.8% (the deposited fraction) or 51.7% (the solubilized fraction) of condensed aromatics. In contrast, at 70 °C for 30 min, the aqueous 72% 4-Cl-BSA solution resulted in 13.8 and 18.0% of condensed aromatics in the deposited and solubilized fractions, respectively. Clearly, the deposited fractions were less condensed relative to the solubilized fractions. The results also indicated that the G unit was less condensed than the S unit.

Table 2. Molecular Weights of Untreated and Fractionated Poplar Lignin Samples[a]

sample		M_w (g/mol)	M_n (g/mol)	PDI
untreated		13 012	5267	2.47
		12 690	5143	2.47
A	solubilized	10 822	4447	2.43
		9167	4113	2.23
	deposited	8575	4359	1.97
		8983	4499	2.00
B	solubilized	7990	3188	2.51
	deposited	6440	3251	1.98

[a] A (solubilized/deposited = 1/3) and B (solubilized/deposited = 1/3.8) samples were fractionated with 100% yields from poplar chips by 72% 4-Cl-BSA aqueous solutions at 60 °C for 2 h and 70 °C for 30 min, respectively.

To verify the condensation mechanisms of lignin, 4-Cl-BSA was used to cleave guaiacylglycerol-β-guaiacyl ether (GG, a representative lignin dimeric model compound) in water at 60 °C for 30 min (Figure 5).[22] The NMR results showed that GG was cleaved and was also condensed by 4-Cl-BSA to form 4-(3-hydroxy-1-(3-hydroxy-4-methoxyphenyl)-2-(2-methoxyphenoxy) propyl)-2-methoxyphenol trimer (CD-I, 10%) and 3,3-bis(4-hydroxy-3-methoxyphenyl)propane-1,2-diol dimer (CD-II, 31%). It can be reasonably deduced that the condensation

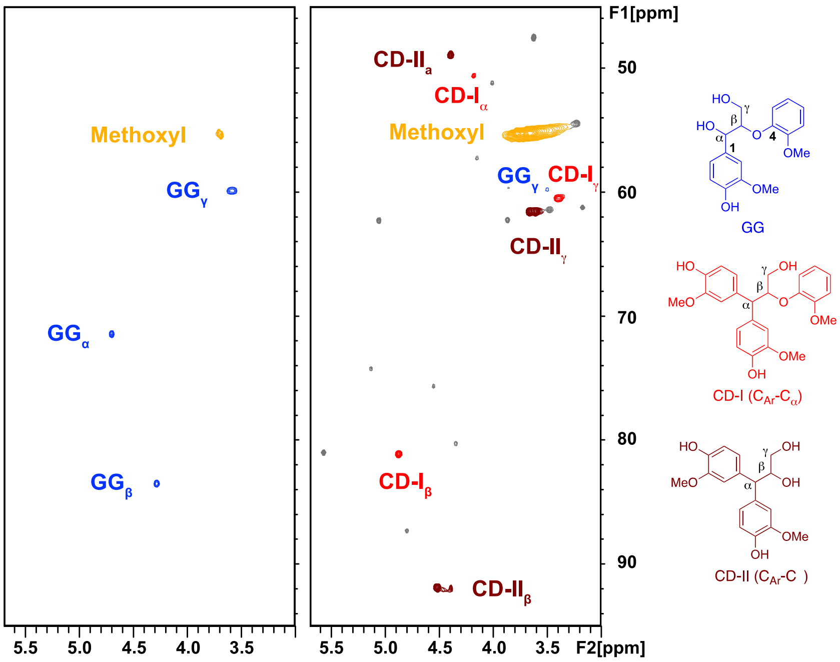

Figure 5. 2D HSQC NMR spectra of GG before and after being treated with the aqueous 4-Cl-BSA solution at 60 °C for 30 min.

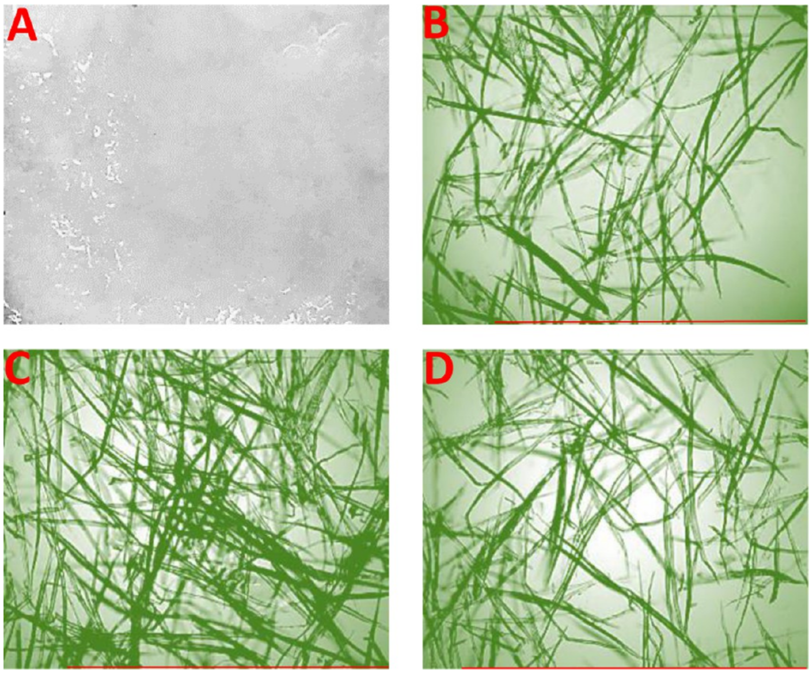

Figure 6. Image and optical microscopy images (scale bar is 1 mm) of cellulose fibers from different conditions (A and B: 60 °C, 180 min; C: 70 °C, 30 min; and D: 80 °C, 20 min).

of lignin by 4-Cl-BSA in water is initiated by the α-benzyl carbonium intermediate.[53] Due to the electron-rich aromatic ring (δC3 = δC5 = −0.277) (Figure S12), 4-Cl-BSA might compete with the lignin fragments for the α-benzyl carbonium intermediate (Figure S13). The lignin NMR results verified the presence of 4-Cl-BSA in the fractionated lignin (both the dissolved and deposited fractions), as evidenced by the presence of the 4-Cl-BSA signals in δH 7.38−7.94 ppm and δC 127−130 ppm regions (Figures 4 and S14).

Throughout the fractionation, lignin was subject to the cleavage of the β-O-4 linkage and the condensation of the aromatic unit. As a result, the cleavage of the β-O-4 linkage resulted in a smaller molecular weight, while the condensation of the aromatic unit significantly increased the molecular weight. Both the solubilized and deposited lignin fractions expectedly had lower molecular weights than untreated lignin (Table 2). Compared with the deposited lignin fraction, the solubilized lignin fraction had a larger molecular weight, which is consistent with the fact that it was more condensed.

When the fractionation and lignin isolation were completed, the obtained cellulose fibers with a creamy-white color contain small amounts of lignin (less than 0.1%) and hemicelluloses

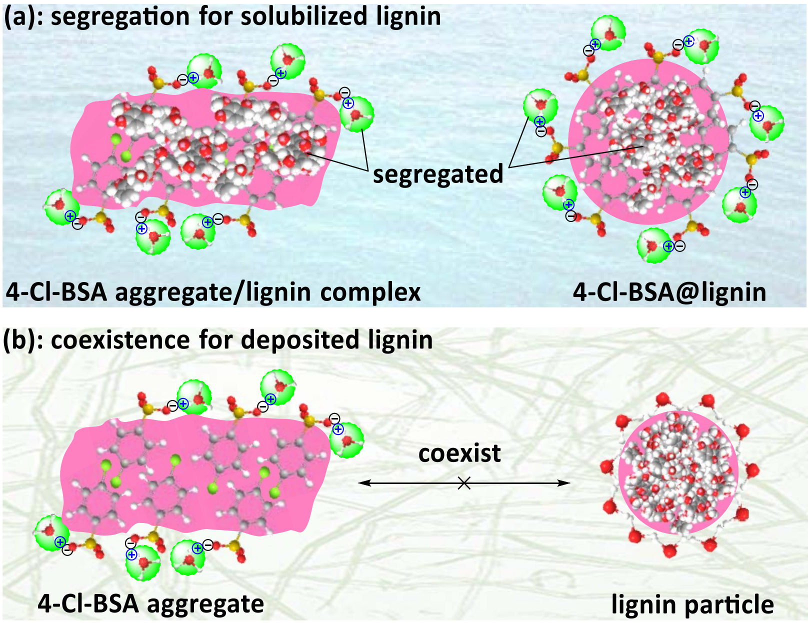

Figure 7. Proposed segregation (a) and coexistence (b) mechanisms (light blue background: water, pink: the hydrophobic domain, green: the hydrated proton, and light green background: cellulose fiber) for the preservation of lignin during fractionation.

(around 0.2%) (Figure 6A). Cellulose fibers were further analyzed in terms of the crystallinity index (eq 2 and Figure S15), degree of depolymerization (eq 3 and Figure S16), size, and morphology (Figure 6B–D), and were compared with those fractionated by the previously reported phenol-4-sulfonic acid (PSA).[30] The optical microscopy images show that the lengths of cellulose fibers were less than 1 mm, which were shorter than those (>1 mm) of cellulose fibers fractionated by PSA. However, the cellulose fibers fractionated by 4-Cl-BSA had higher molecular weights, indicated by higher (910–1022 vs 830–887) degrees of polymerization (DP_v). The crystallinity indexes (CrI) of cellulose fibers ranged from 71 to 75, which were higher than those (61–65) of cellulose fibers fractionated by PSA.

Discussion of the Structural Preservation of Lignin by 4-Cl-BSA. The above NMR results clearly indicate that both solubilized and deposited lignin fractions were preserved by the aqueous 4-Cl-BSA solution to different degrees. To explain the observed structural preservation of the fractionated lignin by 4-Cl-BSA, we proposed two preliminary mechanisms accordingly: segregation (the solubilized lignin) and coexistence (the deposited lignin) (Figure 7). The proposed two preservation mechanisms were logically deduced from the experimental results (Figure 4 and Table 1) and the previous studies on lignin[22,28−30] and other substances.[35−40] The liquid phase was composed of water, 4-Cl-BSA, the solubilized lignin, and hemicellulose sugars. At the mesoscale level, the liquid phase is divided into the hydrophobic domain and the aqueous domain.[36] Due to the hydrophobic effect, the chloro-substituted benzene ring of 4-Cl-BSA and the solubilized lignin presumably reside in the hydrophobic domain, while the sulfonate ion and the immobilized hydrated proton stay in the aqueous domain. The solubilized lignin in the hydrophobic domain is physically segregated from the hydrated proton in the aqueous domain (Figure 7a) and thus is preserved well without further structural alterations caused by the hydrated proton.[29,30] The insolubilized lignin can quickly aggregate to form a particle coated with structured water. The formed lignin particle was subsequently redeposited onto the surface of the cellulose fiber. On the other hand, the 4-Cl-BSA aggregate can also be adsorbed on the surface of the cellulose fiber. However, the 4-Cl-BSA aggregate is expected to coexist with the lignin particle rather than unfavorably disaggregate and then approach to the lignin particle (Figure 7b). Accordingly, the lignin particle (the deposited lignin) was preserved without further depolymerization/condensation by the adjacent 4-Cl-BSA aggregate. If it does not coexist, 4-Cl-BSA would further attack and cause structural alterations to the deposited lignin particle. For example, in our previous study, phenol-4-sulfonic acid was less hydrophobic and aggregated less in water; therefore, the deposited lignin particle was severely depolymerized and condensed.[30] Cellulose fibers may provide sites for the redeposition of the form lignin particle and spreading the 4-Cl-BSA aggregate along with their surfaces.

Comparison with Other Aryl Sulfonic Acids. With the attempt to qualitatively analyze the structure−performance relationship of aryl sulfonic acid, 4-Cl-BSA was compared with five carefully chosen aryl sulfonic acids including benzenesulfonic acid (BSA), phenol-4-sulfonic acid (PSA or 4-OH-BSA), toluenesulfonic acid (TsOH), 2,5-dichlorobenzenesulfonic acid (di-Cl-BSA), and bromobenzenesulfonic acid (4-Br-BSA) (Figure S17). Compared with BSA (the parent), other aryl sulfonic acids have different substituents (i.e., the hydrophobic chloro, bromo, methyl, and the hydrophilic hydroxyl). They are therefore expected to have varied structural properties such as hydrophobicity[54] and acidity[55] and to perform differently in the aggregation/clustering, the lignin solubilization, the fractionation of poplar, and the preservation of the fractionated lignin (the *β*-O-4 linkage and the aromatic unit). The selected aryl sulfonic acids were partially or fully compared in terms of the aggregation/clustering potential (the calculated $\log D$ value, sigma profile, and sigma potential profile), the critical aggregation concentration, the capability of the aqueous solution to solubilize lignin, the solubility in water, the inherent acidity (the calculated pK_a value), the acidity of the aqueous solution

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(the measured proton concentration), the fractionation of poplar, and the lignin isolation, with results presented in Figures 8 and S18, and Tables S1−S3.

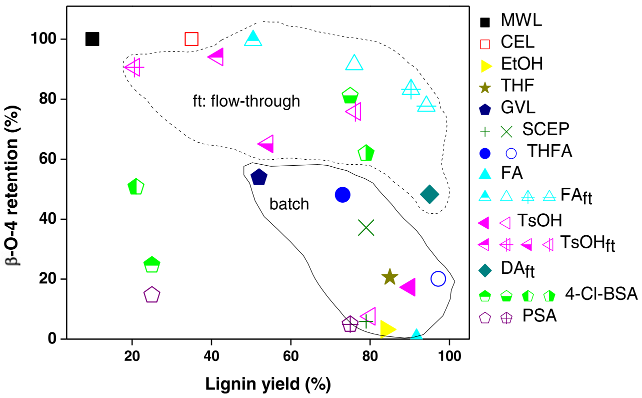

Figure 8. Poplar lignin yield and the corresponding β-O-4 linkage retention achieved by the aqueous 72% 4-Cl-BSA solution and the reported batch and flow-through fractionation systems.[21,22,29,30,56−58] For 4-Cl-BSA and PSA, the lignin yields are presented separately as the solubilized and deposited fractions.

As anticipated, the hydrophobicity follows the order: di-Cl-BSA > 4-Br-BSA > 4-Cl-BSA > TsOH > BSA > PSA. The aryl sulfonic acid with a higher hydrophobicity tends to easily aggregate/cluster in water at lower concentrations. For example, 4-Cl-BSA (as a representative of the halogen-substituted aryl sulfonic acid), TsOH, and PSA incline to aggregate/cluster at 7.2−8.2, 11.5,[29] and 16.8−18.6%,[30] respectively. The capability of the aqueous aryl sulfonic acid solution to solubilize lignin is related to the aggregation/clustering behavior of aryl sulfonic acid (Figure 2). With the same amount and concentration (e.g., 1 g of the aqueous 72% solution at 60 °C), the aqueous 4-Cl-BSA solution can solubilize slightly more lignin (28 mg) than the aqueous TsOH (21 mg), BSA (16 mg), and PSA (25 mg) solutions.[30] Despite the lower hydrophobicity, the aqueous PSA solution solubilized more lignin than the aqueous BSA solution, indicating that the hydrogen bonding also contributed to the solubilization of lignin in water except the aromatic−aromatic and hydrophobic interactions. The hydrophilic substituent increases the water solubility of aryl sulfonic acid, while the hydrophobic substituent decreases it. The calculation results prove that the water solubilities at 25 °C (mg/mL) of PSA (3429) and BSA (1266) are higher than those of TsOH (407), 4-Cl-BSA (253), 4-Br-BSA (237), and di-Cl-BSA (227).

The acidity of aryl sulfonic acid is greatly affected by the aromatic substituent. For example, the strong electron-withdrawing substituent such as halogen can stabilize the negative charge on the sulfonate anion, making a stronger aryl sulfonic acid.[55] The inherent acidity of aryl sulfonic acid can be evaluated using the pK_a value. As the pK_a value decreases, the acidity of aryl sulfonic acid increases. The calculated pK_a values for di-Cl-BSA, 4-Cl-BSA, 4-Br-BSA, PSA, BSA, and TsOH are −3.33, −2.94, −2.85, −2.59, −2.36, and −2.14, respectively. This result verifies that the halogen-substituted aryl sulfonic acids are inherently more acidic than the hydroxyl- and methyl-substituted ones. The acidity of the aqueous aryl sulfonic acid solution is affected by not only the inherent acidity of the sulfonic acid group but also the density of the sulfonic acid group. The calculated density (mmol $-SO_3H$/g) of the sulfonic acid group in BSA, TsOH, PSA, and 4-Cl-BSA are 6.32, 5.81, 5.74, and 5.19, respectively. The acidity of the aqueous 72% aryl sulfonic acid solution was measured by the proton concentration. For an aqueous 72% solution, the measured proton concentration (mol/L H^+) values at 60 °C of 4-Cl-BSA, PSA, BSA, and TsOH are 0.85, 0.62, 0.55, and 0.59, respectively. Thus, despite the lower density of the sulfonic acid group, the aqueous 4-Cl-BSA solution was stronger than the aqueous PSA solution followed by the aqueous TsOH and BSA solutions.

The stronger acidity and the better capability to solubilize lignin were favorable for the aqueous aryl sulfonic acid solution to fractionate the poplar chip.[29,30] It was thus expected that di-Cl-BSA, 4-Cl-BSA, 4-Br-BSA, and PSA could generally perform better than BSA and TsOH in fractionating poplar chips. At the same experimental conditions (e.g., the aqueous 72% solution at 60 °C for 2 h), 4-Cl-BSA and PSA[30] near-completely fractionated the unmilled poplar chips and isolated all lignins, and 4-Br-BSA isolated 83% lignin, while di-Cl-BSA, BSA, and TsOH only isolated lignin by 46, 33, and 35.8%, respectively. The di-Cl-BSA and TsOH were also tested at 80 °C for 40 min, isolating 51.2 and 39.4% lignin, respectively. By comparison, 4-Cl-BSA and PSA are the most effective aryl sulfonic acids for the fractionation of unmilled poplar chips at mild temperatures. However, 4-Cl-BSA can preserve the chemical structure (e.g., the β-O-4 linkage, the aromatic unit, and molecular weight) of the fractionated poplar lignin better than PSA,[30] BSA (Tables S1 and S2), and TsOH (with the milled poplar, Table S3)[22,29] (Figure 8). The lower density of the sulfonic acid group (4.22 mmol $-SO_3H$/g) may limit the fractionation performance of 4-Br-BSA. The higher hydrophobicity and lower density of the sulfonic acid group (4.40 mmol $-SO_3H$/g) likely resulted in the poor fractionation performance of di-Cl-BSA.

There are several speculations on these results achieved by the investigated aryl sulfonic acid with varied structural properties. Seemingly, the acidity of the aqueous aryl sulfonic acid solution directly affected the fractionation performance, with a slight difference in acidity causing the significant difference in the fractionation performance. For example, with a slightly stronger acidity (0.62 vs 0.55−0.59 mol/L H^+), the aqueous 72% PSA solution performed much better than the aqueous 72% BSA and TsOH solutions. The hydrophobicity of aryl sulfonic acid directly influences the solubilization and especially the preservation of the fractionated lignin. For example, the aqueous 4-Cl-BSA solution preserved well the fractionated lignin while the aqueous PSA solution did not. The hydrophobicity of aryl sulfonic acid also influences the water solubility, which affects the fractionation performance, in turn, evidenced by the fact that the aqueous di-Cl-BSA solution did not substantially fractionate the poplar chip. However, these speculations are needed to be further validated through comprehensively investigating structural properties and performances of a wide range of aryl sulfonic acids. Also, it is better to control the acidity when investigating the effect of hydrophobicity and vice versa. The quantitative structure−performance relationships are necessary to provide guidance for rationally and molecularly designing high-performance aryl sulfonic acids that are able to achieve the near-complete fractionation of various unmilled lignocelluloses at mild conditions while maximally preserving the β-O-4 linkages and aromatic units of fractionated lignin besides the fractionated carbohydrates.

In terms of retaining the β-O-4 linkage, the aqueous 72% 4-Cl-BSA solution was also compared with the previously reported acid-catalyzed batch fractionation systems (Figure 8 and Tables S1−S3).[21,22,29,30,56−58] To fractionate milled or unmilled popular chips, these reported batch systems need higher temperatures (e.g., 120−180 °C). They are carried out in the aqueous-organic solvents, for example, with formic acid (FA),[21] ethanol (EtOH),[56] γ-valerolactone (GVL),[56] tetrahydrofuran (THF),[56] tetrahydrofurfuryl alcohol (THFA),[57] and supercritical carbon dioxide/ethanol (SCEP).[58] Milled wood lignin (MWL) and cellulolytic enzyme lignin (CEL) have been applied as a representative structure close to the native form of lignin.[59] However, these methods have either low yield or required multiple extraction steps to obtain the lignin.[60] Also, a milling step, which can cause a certain degree of cleavage of the β-O-4 linkage is unavoidable in both methods.[61] For batch fractionation systems, the β-O-4 linkage retention greatly decreased with the increase of the lignin yield. Less than 20% of the β-O-4 linkages were retained as the lignin yield reached over 80%. The flow-through fractionation systems using acids such as FA,[21] TsOH,[22] and dilute sulfuric acid (DA)[62] can preserve more β-O-4 linkages than the batch fractionation systems.[21,22,29,30,56−58] For example, the flow-through fractionation system kept 48−99% of the β-O-4 linkages while achieving the 20−95% lignin yield. In contrast, the aqueous 72% 4-Cl-BSA solution as a batch fractionation system still retained 24.7−81.1% of β-O-4 linkages even as about 96−100% lignin yield was achieved. However, like other aryl sulfonic acid-based batch fractionation systems,[29,30] the aqueous 72% 4-Cl-BSA caused condensation of lignin to a greater extent than flow-through and other less acidic batch fractionation systems.

CONCLUSIONS

The concentrated aqueous 4-chlorobenzenesulfonic acid (4-Cl-BSA) solution can near-completely fractionate unmilled poplar chips at mild temperatures and preserve key structural properties of cellulose and lignin with the theoretical maximum yields. Cellulose was effectively preserved without severe depolymerization/decrystallization. Hemicellulose sugars were generated without unwanted dehydration. Lignin was partially solubilized through the formation of the 4-Cl-BSA aggregate/lignin temporary complex and accumulated by unaggregated 4-Cl-BSA due to its hydrophobic effect. The solubilized lignin was physically segregated from the hydrated proton, and its β-O-4 linkage and aromatic unit were preserved accordingly. The preservation of the β-O-4 linkage and the aromatic unit of the deposited lignin was explained by its coexistence with the adjacent 4-Cl-BSA aggregate. The deposited lignin was better preserved compared with the solubilized lignin. The acidity of the aqueous aryl sulfonic acid solution directly affected the fractionation performance, while the hydrophobicity influenced the fractionation, solubilization, and preservation performances. 4-Cl-BSA showed superior performances in fractionating unmilled poplar and preserving the yields and structures of the fractionated cellulose and lignin compared to other aryl sulfonic acids and inorganic acids at mild conditions. However, further studies are needed to evaluate the perceived less energy consumption and the structural preservation of lignin benefits and the potential corrosion issue and the environmental impact.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c00123.

Additional tables and figures including chemical structures; calculated log D values, the partial charge diagram, sigma profiles, and sigma potentials; the flowchart of fractionation; comparison in solubilizing lignin; disintegration and images of the poplar chip; effects of the acid concentration and dosage; images of lignin and acid; the NMR spectrum of the acid; the XRD spectrum and the degree of polymerization of cellulose; the xylose yield; and comparison with other acids (PDF)

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All of the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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