Preparation and Characterization of a Water-Soluble Kraft Lignin

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1. Introduction

Lignin as the most abundant aromatic biopolymer worldwide is generated in vast amounts in the course of pulp production, where it is usually burned in the recovery boiler for regeneration of process chemicals and power.[14] As a readily available biopolymer, Kraft lignin is an interesting material to be used in biofuels and for the production of bulk chemicals or high end products like vanillin.

Kraft lignin can be extracted from black liquor generated during wood digestion. At present, water soluble Kraft lignin is prepared chemically. Here, a method for the preparation of a purified form of CO₂-precipitated softwood Kraft lignin, which forms a stable aqueous solution at a pH value of 8.9 is described. The lignin samples are characterized by thermogravimetric analysis, IR spectroscopy, nuclear magnetic resonance spectroscopy, and gel permeation chromatography. The comparison of water-washed lignin with reference samples of unwashed- and acid-washed lignin shows that the water-washed lignin has a higher molecular weight compared to the reference samples, while the content of hydroxyl and methoxyl groups is similar. Solubility studies show that drying of washed lignin has a significant effect on its dissolution in water. Charge titration and dynamic light scattering experiments show that water-washed lignin forms a stable colloid in aqueous solution.

Each year, 55 Mt of lignin are dissolved worldwide[2] in the course of Kraft pulping, which renders the generated black liquor (BL) a promising process stream for lignin isolation. Because of the lower production capacity, spent liquor from sulfite pulping is of less importance.[3] State of the art Kraft lignin extraction processes like the LignoBoost[4–6] and the LignoForce[7–9] system use CO₂ as acidifying agent to precipitate lignin from BL at a pH value between 9 and 10. In these processes, the resulting lignin product is separated by filtration and then further acidified with sulfuric acid to a final pH value of about 2. This yields a Kraft lignin with an ash content of 0.5–1%, which is typically used on site as fuel in the lime kiln.[10]

Despite innumerable efforts to develop value added applications for Kraft lignin, only a few processes are close to industrial implementation.[10] One approach is to convert lignin or lignocellulosic biomass of varying quality to fuels or fuel intermediates, as was proposed by Cheng and Brewster[12] or Schwaiger, et al.[13] However, most potential applications require lignin in a defined high quality. Lignin quality differs not only from plant to plant, but each isolation process leads to lignin with different properties.[14] Lignin derived from Kraft pulping is generally insoluble in water in the neutral and acidic pH range.[15] While many scientific approaches aim to develop applications for this type of water insoluble lignin, a second approach is to solubilize lignin, for example, by chemical modification, and generate a water soluble product.

Applications for water insoluble Kraft lignin range from the replacement of phenol to the utilization as raw material for vanillin production or precursor in the carbon fiber production. Chemical modifications are performed to improve the reactivity of water insoluble lignin for the replacement of phenol in phenol-formaldehyde resins.[16–20] For plywood production, 30% of phenol for PF resins can be replaced by lignin without major changes in the properties of plywood.[16,21]

A high-end application for lignin would be the use as precursor in the carbon fiber production.[22–24] However, the production of carbon fibers requires a lignin of exceptionally high purity, which is hard to achieve for lignin originating from chemical pulping processes.[25]

A wide range of potential lignin-based materials are reported, but production thereof is difficult and suffers from low yields. Therefore, lignin-derived alternatives are usually not able to compete with the products already on the market.

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Lignosulfonates, which are soluble in water, are already widely used, for example, as emulsifiers or dispersing agents in concrete admixtures. An approach to open the lignosulfonate market to Kraft lignin is to introduce sulfonate groups after its isolation and thus render it soluble in water also at lower pH values. However, sulfonation usually requires complex chemical modifications of Kraft lignin involving, for example, oxidation and sulfonylation reactions that often require formaldehyde which poses serious risks for workers and the environment.

Savy et al. investigated the preparation of water soluble lignin from non-food bioenergy crops by alkaline oxidative hydrolysis. The isolated lignin is soluble in water down to a pH value of 5.5. A further decrease of pH led to lignin precipitation. Another approach to generate water soluble lignin is its copolymerization with acrylic acid. By using optimized process conditions, the solubility of Kraft lignin was increased from 1.8 to 100 g L$^{-1}$ at neutral pH value. Water solubility of Kraft lignin was also achieved by epoxidation with epichlorohydrin followed by a reaction with polyethylene glycol. Solubilized lignin prepared by this process showed potential for the application as emulsifier, detergent, or dispersant.

The present work addresses the sustainable development goal number 12, namely, “ensure sustainable consumption and production patterns”, by not using complex or costly chemical modifications to solubilize the purified lignin, but by using water as solvent.

This paper shows an approach to generate a purified fraction of CO$_2$ precipitated Kraft lignin forming a stable aqueous sol. For reasons of clarity, the terms “solution” and “solubility” of lignin are used throughout the text. However, Kraft lignin is known to form ultratine suspensions down to single molecules which are in the size range of few nanometers hydrodynamic radius.

Characterization of the lignin product as well as solubility experiments correlated the lignin properties to its solubility in water at a final pH value of 8.9. The aim of the present study was to find a Kraft lignin preparation method which leads to a large fraction with high solubility in water.

### 2. Experimental Section

#### 2.1. Chemicals

All lignin samples were based on a single lignin filter cake provided by a local pulp and paper mill. The lignin was precipitated from intermediate softwood Kraft BL with CO$_2$ at 65 °C to a pH of 8.9 at room temperature (RT), and was thereafter filtered in a filter press. The resulting lignin filter cake had a total dry solids content of 69% and was denoted unwashed lignin filter cake. This cake was the starting material for preparation of water-washed and acid-washed lignin samples.

As solvents chloroform (99.3% from VWR Chemicals, Radnor, USA), tetrahydrofuran (99%), pyridine (99% both from Carl Roth GmbH, Karlsruhe, Germany), deuterated chloroform, and dimethylsulfoxide (both from Cambridge Isotope Laboratories Inc., Cambridge, GB) were used. Additionally, acetic anhydride (≥99% from Sigma-Aldrich, St. Louis, USA), and hydrochloric acid (37% from VWR Chemicals), were used for the acetylation procedure. Pentfluorobenzaldehyde (98% from Alfa Aesar, Haverhill, USA) was purchased for the quantitative nuclear magnetic resonance (NMR) analysis. For adjusting pH, sulfuric acid (95%) and sodium hydroxide (37%, both from VWR Chemicals) were used. For the charge titration, poly-diallyldimethylammonium chloride (pDADMAC) was purchased from BTG (Batch: 77 937).

#### 2.2. Preparation of Water-Washed Lignin

An aliquot of 50–200 g of wet, unwashed lignin filter cake was re-suspended in five times the mass of deionized water and mixed for 2 min, before the water was filtered using a filtration set-up consisting of Buchner funnel, filtration flask, and vacuum pump. The filtrate was discarded and the filter cake was again suspended in the same amount of fresh water (five times the original weight). The resulting suspension was thereafter filtered again and the cake was dried in a drying oven at 60 °C for 48 h, unless stated otherwise. Subsequently, it was ground in a mortar and stored in a desiccator prior to dissolution experiments.

#### 2.3. Preparation of Acid-Washed Lignin

An aliquot of 50–200 g of wet filter cake was re-suspended in an aqueous solution of sulfuric acid. This solution contained 50 g L$^{-1}$ sulfuric acid and was pre-heated to 50 °C. Again, the mass of liquid was five times the initial mass of filter cake. Following this first re-suspension step, the suspension was filtered as described above for the preparation of water-washed lignin. The filtrate was discarded and the cake was again re-suspended in a dilute solution of H$_2$SO$_4$ with a pH of 1. After the second filtration, the resulting acid washed filter cake was dried and stored in the same way as the water-washed lignin.

#### 2.4. Characterization of Lignins

##### 2.4.1. Ash Content

The lignin filter cake was transferred to Al$_2$O$_3$ crucibles and dried to constant weight at 105 °C. The dry sample was then burned at 600 °C until it was completely ashed and no black char remained. The sample was cooled to RT in a desiccator and the weight of residual ash was determined. The resulting ash content was related to the dry sample mass.

##### 2.4.2. Thermoanalytical Characterization

The characterization was carried out by simultaneous thermal analysis, where the temperature dependency of the sample mass (thermogravimetric analysis, TGA) as well as the energy flow to- and from the sample compared to a reference (differential scanning calorimetry, DSC) were measured. The experiments were performed applying a Netzsch ST449C Jupiter apparatus (Netzsch, Selb, Germany).
The sample for the simultaneous thermal analysis (STA) was washed with water as described above. The wet filter cake was then immediately transferred to a desiccator in order to reduce its exposure to oxygen from the ambient air. The desiccator was flushed with pure nitrogen and thereafter evacuated and closed. The sample was dried in the desiccator over silica gel under exclusion of air for two weeks, prior to STA measurements.

For the measurement, clean Al₂O₃ sample containers were used, one was filled with ≈35 mg of dry sample and the other one remained empty as a reference. The applied temperature was ≈35 °C, with a heating rate of 1 K min⁻¹. The sample chamber was flushed with 170 mL min⁻¹ pure nitrogen gas.

2.4.3. Attenuated Total Reflection Infrared Spectroscopy

For attenuated total reflection infrared spectroscopy (ATR-IR) experiments the unmodified and the acetylated samples were analyzed with an ALPHA FT-IR spectrometer (BRUKER; MA, USA). For the measurement, a platinum ATR single reflection diamond module was used with 48 scans at a resolution of 4 cm⁻¹ and a scan range between 4000 and 400 cm⁻¹. The data were analyzed with OPUS 4.0 software.

2.4.4. Molar Mass Determination

The lignin samples were dried at 60 °C in a drying oven for one day. Of each sample, 50 mg were then dissolved in 5 mL acetic anhydride:pyridine 1:1 v:v and heated for 1 min up to 150 °C in an Anton Paar Monowave 50 (Anton Paar, Graz, Austria).[34] The mixture was allowed to cool down to RT before precipitation of the acetylated product by addition of 5 mL 0.1 M HCl. 10 mg of the products were then dissolved in 3 mL THF and investigated with a WGE SEC by Dr. Bures (WGE Dr Bures, Dallgow-Doeberitz, Germany). For the separation, two 5 µm MZgel-SDplus linear columns by MZ Analysetechnik equipped with a refractive index and a UV detector were used. The analysis was carried out with a flow rate of 1 mL min⁻¹, and the calibration was performed using PS standards.[35]

2.4.5. Nuclear Magnetic Resonance Spectroscopy

Quantitative ¹H-NMR spectra of acetylated lignin samples were obtained using a Bruker NMR with 300 MHz with 2 s delay time. The results were averaged over 16 scans. For the measurements, 20 mg of lignin were dissolved in 0.8 mL of CDCl₃ containing tetramethylsilane and 2.2 mg of pentafluorobenzaldehyde were added as internal standard. All NMR spectra were processed and analyzed with a TopSpin software from Bruker.

2.4.6. Particle Size Determination

The unwashed as well as the acid-washed sample were dissolved in 0.1 M NaOH with the help of a VWR ultrasonic cleaner with 60 Hz for 10 min. The solutions were filtered through a Chromafil PTFE-45/13 syringe filter. The water soluble sample was dissolved in deionized water, the pH-value was set as 1, 7, and 11, respectively, using 0.1 M sulfuric acid and 0.1 M sodium hydroxide before the dynamic light scattering (DLS) measurements. An Anton Paar LitesizerTM 500 with an Anton Paar Kalliope software was used for the determination of the particle sizes. The measurements were carried out in PS cuvettes at 23 °C using the side scattering mode at a wavelength of 658 nm. All experiments were carried out at least in triplicates.

2.4.7. Charge Titration

100 mg of the dried, water soluble lignin fraction were dissolved in deionized water, 0.1 M NaOH, and 0.1 M H₂SO₄ respectively. The solutions were autotitratred adding 0.001 n PDADMAC consequently measuring the zeta potential of the particles with the Stabino (Particle Metrix, Stabino, Meerbusch, Germany).

2.5. Solubility Experiments

The standard dissolution experiment, denoted base case, was performed with water-washed lignin, dried at 60 °C. The dissolution was carried out at RT applying 174 g L⁻¹ pulverized lignin in deionized water with a total volume of 10 mL. Table 1 summarizes the different dissolution experiments that were performed in comparison to the base case. In general, all dissolution samples were incubated on a magnetic stirrer at 700 rpm for 24 h. For determination of dissolved lignin concentration, aliquots of 500 µL were withdrawn throughout the experiment and centrifuged at 8832 rcf in a Heraeus Sepatech (Hanau, Germany) Biofuge 17RS centrifuge. The resulting supernatant was withdrawn for measurement of lignin concentration by UV–vis spectrophotometry.

2.5.1. Lignin Concentration

The lignin content of the liquid samples was estimated using UV–vis spectrophotometry. Prior to measurements, the samples were diluted with 0.1 M NaOH to assure a consistent pH of the measured solutions. The measurement was performed at RT in UV-cuvettes with 10 mm transmitted path length, using a Shimadzu UV-1800 Spectrophotometer (Shimadzu, Kyoto, Japan). Absorbance was measured at 280 nm. An absorption coefficient of 22.1 L (g cm)⁻¹ was used to calculate the UV-lignin content. The absorption coefficient was determined by calibration with purified lignin.

3. Results and Discussion

For the present work, CO₂-precipitated Kraft lignin was washed with water, dried, and then characterized and subjected to solubility experiments. The lignin washing and drying conditions were varied for the solubility trials, but the characterization measurements were performed only with the water-washed
3.1. Characterization of Lignin

3.1.1. Ash Content

The ash content of a sample of lignin filter cake is a measure for its purity and determines the suitability for various applications.\cite{25} The inorganic constituents that form ash originate on the one hand from residual lignin lean black liquor in the filter cake and on the other hand from sodium counter ions on the charged hydroxylate- and carboxylate groups of lignin itself. If the lignin is acidified below a pH value of 1–2, the counter ions are replaced by hydrogen ions and the ash content can approach zero. Water-washed lignin has a pH value of 8.9 and hence the carboxyl groups and a significant fraction of the phenolic hydroxyl groups are deprotonated. Sodium ions are bound as counter-ions to the negatively charged groups and therefore the inorganics content of such lignins cannot be decreased below a certain level by washing with pure water.

The ash content of the initial, unwashed lignin sample was 24%, while acid wash yielded a lignin product with 0.9% ash content. Water wash in the same solid to liquid ratio resulted in 9% ash. This amount can be attributed to the inevitable sodium content of the not-acidified lignin.

3.1.2. Molecular Weight Distribution

In the course of the acidic washing procedure, only a small fraction of the initial lignin is dissolved and discarded together with the filtrate fraction. Compared to that, 30–60% of the initially supplied lignin is dissolved in the wash water and hence lost throughout the water washing procedure. In order to determine the molecular mass of lignin the samples have to be acetylated to be soluble in THF for the GPC. The acetylation of lignin for analytical purposes using mixtures of pyridine and acetic anhydride is a common procedure.\cite{13} Lately, microwave-assisted procedures treating lignin in acetic anhydride at 130 °C for 10 min have been described for the acetylation of lignin.\cite{14} Only minor differences between acetylated samples using the conventional procedure, stirring for 24 h at RT followed by the addition of ethanol and consequent evaporation of the solvents and acetic acid, were reported. We used ATR-IR spectroscopy to follow the acetylation process (see Figure S1, Supporting Information). As the treatment with pure anhydrides did not yield fully acetylated products, we added pyridine as solvent and catalyst which gave fully acetylated products after 1 min.

Molecular mass data (Table 2) show that acetic washing extracts some of the smaller lignin fractions, leading to a slightly higher molecular mass of acetic washed lignin compared to the original unwashed sample. The $M_n$ and $M_w$ increase from 1.802 and 5.744 kDa for the unwashed lignin to 1.885 and 6.873 kDa for the acid-washed sample, respectively. Washing with water has a more distinct influence on the molar mass of the resulting lignin, the $M_n$ and $M_w$ increase to 2.108 and 8.602 kDa, respectively. Hence, the lignin dissolved in the course of the water washing procedure represents the smaller fraction, which has higher water solubility. This is in accordance with published results that indicate that the solubility of lignin increases with decreasing molecular weight, as is typical for polymers.\cite{36}

Table 2. Molecular mass moments of characterized lignin samples.

| Lignin sample               | $M_n$ [kDa] | $M_w$ [kDa] | $M_n/M_w$ |
|----------------------------|-------------|-------------|-----------|
| Unwashed lignin            | 1.80        | 5.74        | 3.19      |
| Acid-washed lignin         | 1.89        | 6.87        | 3.65      |
| Water-washed lignin        | 2.11        | 8.60        | 4.08      |

Table 1. Summary of preparation and dissolution conditions for lignin solubility experiments.

| Varied parameter         | Lignin sample | Dry lignin added [g L⁻¹] | Lignin drying temperature [°C] | Dissolution temperature [°C] |
|--------------------------|---------------|--------------------------|-------------------------------|-----------------------------|
| Base case                | Ww⁺           | 174                      | 60                            | 25                          |
| Lignin content           | Ww⁺           | 135                      | 60                            | 25                          |
|                          | Ww⁺           | 245                      | 60                            | 25                          |
| Drying                   | Ww⁺           | 174                      | 50                            | 25                          |
|                          | Ww⁺           | 174                      | 70                            | 25                          |
|                          | Ww⁺           | 174                      | 90                            | 25                          |
|                          | Ww⁺           | 174                      | Not dried                     | 25                          |
| Dissolution temperature  | Ww⁺           | 174                      | 60                            | 60                          |
| Lignin sample            | Aw⁻           | 93                       | 60                            | 25                          |
|                          | Aw⁻           | 200                      | 60                            | 25                          |
|                          | Nw⁻           | 174                      | 60                            | 25                          |
| Initial lignin content of solvent | Ww⁺ | 174                      | 60                            | 25                          |

⁺water-washed;⁻acid-washed;⁻not washed.
3.1.3. NMR Spectroscopy

Unwashed, acid-washed, and water-washed lignin samples, and the water soluble fraction of the water-washed lignin, were structurally analyzed. In order to compare the different lignin fractions, $^1$H NMR spectroscopic measurements were carried out after acetylation of the lignins (Figure 1). Abreu and Freire found that $^1$H NMR provides a simple method for the determination of the methoxyl content of acetylated lignins.[37,38] There is a partial demethylation of samples and the overlap with side-chain protons, thus, we decided to forego exact quantification and used pentafluoro benzaldehyde as standard for the normalization of the spectra.[39] (Figure 1). To prove the full acetylation, ATR-IR spectroscopy was carried out. Unwashed, water-washed, and acid-washed samples are comparable, showing a low amount of impurities in the $^1$H NMR spectra and a ratio of aliphatic:aromatic OH groups of approximately 1.6:1. Water soluble lignin features a lower number of methoxyl groups, most likely due to demethoxylation during the cooking process.[40] Consequently, the signal corresponding to the amount of phenolic OH in this sample is increased while the amount of methoxyl groups decreases. Curiously, in contrast to the other samples, the water soluble sample does not contain significant amounts of formyl groups.

As described by Estigneev et al., the ratio of aliphatic:aromatic hydroxyl groups is the main factor determining the solubility of lignins in alkaline aqueous solutions. They concluded that the amount of OH groups per aromatic ring is the most important factor influencing the solubility of lignin in aqueous solvents.[36] By demethoxylation of guaiacol an additional hydroxyl group is inserted leading to an o-hydrobenzoquinoniod structural motif which exhibit lower $p_K_a$ values and a better solubility in water and under alkaline conditions than the methylated form.[43]

DLS is a convenient tool to determine the size of agglomerates in solution or dispersion. This method provides important insight into solutions and (micro-) emulsions. This is one of the key parameters in order to provide suitable lignin-based products. Agglomerates have a lower availability, thus the possibilities for chemical modifications are more limited. In addition, for several applications as coating binder or filler, the homogeneous distribution of the material is important to, that is, provide good mechanical stability.

For the measurement, the intensity fluctuation of scattered light is monitored in a certain angle to the incident light. Thus, only the intensity weighted size distribution is measured and eventually transferred into a z-averaged distribution if additional information regarding the refractive index of the macro-molecule and the solvent viscosity is available. In Figure 2, the intensity weighed size distribution is depicted; in this depiction, the size of agglomerates influences the intensity by the power of 6. Thus, the larger lignin agglomerates appear to be more pronounced.

Single processed lignin molecules exhibit diameters of gyration in the range of a few nm radius as determined by X-ray or neutron scattering studies.[28] In contrast, DLS yields information about the hydrodynamic diameters which are slightly higher. Thus, the signals at low hydrodynamic diameters are in the size range of individual lignin molecules. At pH 11 all samples can be described as solutions starrng a certain amount of agglomerated nano- to microparticles. The "water soluble" sample shows low hydrodynamic diameters down to pH 7, although also here slight agglomeration behavior can be observed.

It is well known that lignin forms agglomerates in the size of single molecules, subunits, or building blocks[42] in organic and aqueous (alkaline) solutions. This has been found to be a reversible phenomenon in aqueous alkaline solutions indicating that no covalent bonds between the individual lignin molecules are formed.[43]

The hydrodynamic diameters of agglomerates present in unwashed, water-washed, and acid-washed samples were investigated at pH 11. While the unwashed and acid-washed samples, both form agglomerates with average hydrodynamic diameters of 190 nm, the water-washed sample is significantly smaller, having a mean hydrodynamic radius of 157 nm (see Figure 2). The precise values, including standard deviations, as well as graphs where the smaller diameter regions in linear scale are depicted in the Supporting Information.

At high pH values, carboxyl as well as aromatic hydroxyl groups are deprotonated, thus there are repulsive Coulomb forces present leading to a good solubility of lignin at high pH values. High salt concentrations can lead to screening of the negative charges and can consequently increase agglomeration tendencies.[46] Close to neutral pH, only the carboxyl groups are deprotonated, thus the solubility decreases strongly.

Besides coulomb interactions, main driving forces of the agglomeration of lignin are intermolecular hydrogen bonds and π–π interactions. Aliphatic hydroxyl groups are able to form stronger hydrogen bonds than aromatic hydroxyls, thus the agglomeration behavior has been found to increase with
increasing aliphatic hydroxyl content. In addition, the \( \pi-\pi \) stacking effects have been proved to increase in the order of hydroxyphenyl–guaiacyl–sinapyl as well as with increasing number of methoxyl groups. Those interactions are of hydrophobic nature and thus entropy driven by expelling water from the interaction area. The water washed sample is partially demethylated, thus there is a higher amount of polar aromatic hydroxyl groups which, in contrast to methoxyl groups, hinder the \( \pi-\pi \) stacking and limit the agglomeration.

The role of the carbohydrate contaminations is not fully understood. There are covalently bound lignin-carbohydrate complexes in wood, which are often not fully cleaved during Kraft pulping. In addition, it has been found that the alkaline pulping conditions can lead to covalent bonds between small lignin fractions and partially hydrolyzed carbohydrates. Small carbohydrate fragments in combination with small lignin fractions might lead to increased solubility in water at low degrees of cross-linking.

3.1.5. Charge Titration

Information about the charge of dispersed material in a continuous phase of another medium is important for a variety of industrial processes. The zeta potential provides information about electrostatic repulsive forces and thus the stability of solutions, emulsions, and dispersions. Typically the regions of \( \pm 0-10 \), \( \pm 10-20 \), and \( \pm 20-30 \) mV and greater than \( \pm 30 \) mV are considered as unstable, relatively stable, moderately stable, and highly stable, respectively. However, it does not provide insight into attractive van der Waals forces which might also play an essential role in colloid stability. Knowing the zeta potential is crucial when it comes to applications where the interaction at interfaces are investigated. Exemplarily, the sizing of paper (board) with lignin highly depends on the surface charges of the components. Consequently, the water-soluble lignin sample is investigated with charge titration experiments using pDADMAC as positively charged polyelectrolyte to investigate whether the system is stable or tends to undergo further agglomeration. In the presence of cations, lignins tend to stabilize as colloidal aggregates. Thereby, cations can neutralize negative surface charges reducing the repulsion between lignin molecules. A similar effect can be observed upon addition of pDADMAC; negative charges present at lignin are screened, ultimately leading to its precipitation. As shown in Figure 3, the surface charge of the smallest aggregates is close to \(-70 \) mV, it changes with the addition of pDADMAC and becomes neutral after adding 1.6 wt% of pDADMAC.

Adapting the pH significantly affects the zeta potential of the system, which is still negative under alkaline conditions (\(-10 \) mV). Acidification promotes agglomeration, further decreasing surface charge. The pDADMAC consumption increases with decreasing particle size due to a higher specific surface. Upon acidification the lignin precipitates, thus a zeta potential of zero was measured.

The most stable system is formed under neutral conditions at low ionic strength due to the repelling effects of negative charges. For maintaining a sufficient amount of anionic groups, the carboxyl plays the most prominent role.

3.2. Solubility Experiments

3.2.1. Base Case Experiment

The solubility of water-washed lignin was investigated in dependence on the initial lignin concentration, the dissolution temperature, and on the drying conditions during sample preparation. Table 1 summarizes the different dissolution experiments.

The water-washed lignin used for the experiments in this work was precipitated at a pH of 8.9 and 65 \(^\circ\)C, and it is thus not soluble in the aqueous BL. However, in pure water the...
lignin solubility is expected to be considerably higher, because of the low ionic strength.[51]

The lignin solubility versus time was determined over 24 h for the base case dissolution experiment, the result is shown in Figure 4a. From this course and preliminary experiments it can be deduced that the fraction of dissolved lignin does not increase significantly after 24 h of incubation. Thus, the amount of lignin dissolved after 24 h is considered to present the equilibrium concentration of dissolved lignin for all the solubility experiments.

The suspension of water-washed lignin in deionized water at RT led to partial dissolution of lignin. Because of the partial deprotonation of aromatic OH groups, lignin acts as a buffer, resulting in a suspension with a pH of 8.9. This corresponds to the precipitation pH of the initial lignin.

For the base case, the final concentration of solubilized lignin was 136 ± 2 g L⁻¹. Correspondingly, 79% of the initial lignin was dissolved.

3.2.2. Effect of Lignin Content

Experiments with different initial concentrations of dry, water-washed lignin showed that the final concentration of 136 g L⁻¹ found in the base case was not the solubility limit for water-washed lignin. In two additional experiments, 135 and 245 g L⁻¹ of lignin were added to deionized water. The final dissolved lignin concentrations after 24 h were 107 ± 1 and 231 ± 9 g L⁻¹, respectively. This corresponds to dissolution of 79% for the lower initial concentration and 94% for the highest concentration. Hence, the dissolution of water-washed lignin depends on the initial amount of lignin added to the solvent.

This indicates that the lignin is fractionated upon dissolution in water. Kraft lignin, as a natural polymer, is not a homogeneous compound but a mixture of lignin molecules and derivatives exhibiting a rather wide range of molecular mass and functional group distribution.[14] Water washing already extracts the smallest and thus more soluble lignin fraction, as can be deduced from the molecular mass data shown in Table 2. A further fractionation can be observed by prolonged dissolution of water-washed lignin in water. Characterization of the dissolved lignin from the base case experiment showed that the molecular mass and the functional groups distinguished the dissolved fraction from the starting material. Compared to the initial water-washed lignin, the dissolved sample had a much lower molar mass, the $M_n$ was 1.490 kDa and the $M_w$ was 4.801 kDa. The most remarkable difference lies in the lignin functional groups. As already mentioned, the lignin fraction with lower...
methoxyl- and consequently higher aromatic-OH content was preferably dissolved in water. Thus, a selective enrichment of this lignin fraction is achieved by preparation of water-washed lignin, and fractionated dissolution thereof in water. These results are consistent with experimental results published by Stoklosa and co-workers. They characterized lignin fractions precipitated from BL in several steps between pH 12.8 and 9.5. A clear correlation between the aromatic OH group content as well as lignin molecular weight and precipitation pH was observed. The fractions with a higher water solubility that were recovered at lower pH values typically exhibited a lower molecular mass and a higher aromatic OH content.\textsuperscript{[52]}

3.2.3. Effect of Initial Lignin Content of Solvent

A further dissolution experiment was performed to investigate the fractionation for very high lignin concentrations. The supernatant of the base case experiment, containing 136 g L\textsuperscript{−1} of dissolved lignin, was used as solvent in a further dissolution experiment, where again 174 g L\textsuperscript{−1} water-washed, dried lignin were added. After 1 h and 3 h of incubation, part of the freshly added lignin could still be separated by centrifugation (see Figure 4). But after 24 h, all of the lignin added was found in the supernatant, the concentration measured was 311 ± 3 g L\textsuperscript{−1}. The resulting samples were highly viscous due to the high lignin content, which hindered separation of any remaining lignin particles. This experiment showed that a stable lignin sol with very high concentration can be prepared from the water-washed lignin and that the stabilization of the lignin colloidal is not limited by concentration in the considered range. This effect also explains the results of the experiments described above, where 245 g L\textsuperscript{−1} of dry lignin were added to fresh water. The stabilization of the formed colloidal led to an apparent dissolution of 94% of lignin compared to only 79% in the cases of lower suspended lignin concentrations.

3.2.4. Effect of Lignin Sample Preparation

To investigate the effect of the water washing procedure on the lignin solubility, dissolution experiments with two other lignin samples were performed. One was an unwashed sample of the initial lignin filter cake and the other was the acido-washed lignin, both were dried and handled in the same way as the water-washed sample. The dissolution of the unwashed lignin sample led to a lignin concentration of 128 ± 1 g L\textsuperscript{−1} after 24 h. The unwashed sample had an ash content of 24% based on dry solids. Because of the high ash content, the unwashed lignin sample contained less lignin than the washed sample but still the amount of dissolved lignin was similar. Therefore, the solubility of pure unwashed lignin is comparably higher than that of the water-washed lignin. Throughout the water washing procedure, the more easily dissolvable lignin fraction is extracted, while a higher proportion of the insoluble and more slowly dissolving fractions is retained. Hence, it is to be expected that unwashed lignin is more soluble than the water-washed sample.

Acidic washing of lignin yields a product which, upon suspension in water, does not dissolve.\textsuperscript{[53]} A corresponding dissolution experiment where 93 g L\textsuperscript{−1} acid-washed lignin were suspended in water yielded a dissolved lignin concentration of 0.6 g L\textsuperscript{−1}, which can be considered negligible. However, since very little lignin is lost during the acido washing procedure, the solubility of acid-washed lignin at a defined pH value is supposedly similar to that of unwashed lignin. The water-washed lignin solution had a pH of 8.9, thus comparative experiments with acid-washed lignin need to be performed at the same pH value. In preliminary experiments, the amount of base, in this case NaOH, that was necessary to increase the solution’s pH to 8.9 at equilibrium was determined. For 1 g of dry acid-washed lignin, 0.0019 mole of NaOH were needed to increase the solution’s pH to 8.9 at equilibrium. Hence, 200 g L\textsuperscript{−1} of acid-washed lignin were dissolved in a 0.38 m NaOH solution and the experiment was performed in the same way as the dissolution experiments with water-washed lignin. The resulting plot of the dissolved lignin concentration over time is shown in Figure 4c. Interestingly, the acid-washed lignin dissolves faster than the water-washed sample, and the final concentration of dissolved lignin is with 180 ± 2 g L\textsuperscript{−1} much higher than the dissolved fraction of water-washed lignin. This again supports the theory that the more easily dissolvable lignin fraction is partially lost in the course of the water washing procedure and mainly retained during acidic washing.

3.2.5. Effect of Dissolution Temperature

Evstigneev and co-workers showed that the lignin solubility increases with increasing temperature.\textsuperscript{[36]} To verify the applicability of this rule also for the water-washed lignin, a dissolution experiment at 60 °C instead of RT was performed. The resulting lignin concentration in solution after 24 h was 171 ± 2 g L\textsuperscript{−1} and thus considerably higher than the 136 g L\textsuperscript{−1} found after the same incubation time at RT. Furthermore, the equilibrium concentration was reached faster when the dissolution temperature was 60 °C, as can be seen in Figure 4d.

3.2.6. Effect of Lignin Drying Temperature

In all the previously described experiments dried lignin was used for the solubility determination. In order to rule out a possible effect of the drying procedure, which was carried out over two days under availability of oxygen from air at 60 °C, dissolution experiments with not-dried lignin were performed. Interestingly, the lignin directly after filtration, with a water content of 41%, was not as soluble as the dried lignin. After 3 and 24 h of incubation, 83 ± 1 and 103 ± 2 g L\textsuperscript{−1} had dissolved, respectively. This is in both cases about 25% less than the amount that was solubilized in experiments where dried lignin was used. The drying obviously had a distinct and positive effect on the lignin solubility in water. In a subsequent step, different drying temperatures of the water-washed lignin were investigated. The results are shown in Figure 5. Clearly, higher drying temperatures promote the dissolution of lignin. Within the investigated
conditions, the optimal drying temperature is 70 °C. Compared to that, it makes no difference if lignin is dried at 50 or 60 °C, which indicates that at temperatures above 60 °C some additional modification of lignin takes place. This effect was further investigated by STA experiments.

3.3. Thermoanalytical Characterization

Dissolution experiments showed that the solubility of water-washed lignin was influenced by the drying temperature. To elucidate the underlying mechanism, the differential heat flow (DSC) and the change of weight (TGA) throughout heating were investigated; the results are shown in Figure 6. Interestingly, the simultaneous thermal analysis shows two distinct endothermal peaks in the range of 50 and 75 °C. Further, both peaks are associated with a slight but significant mass loss that is clearly corresponding to the respective endothermal event. It is likely that these reactions or transitions influence the solubility of the water-washed lignin. The transition represented by the first endothermal peak might lead to the higher solubility of lignin dried at 50 and 60 °C compared to undried lignin. The further increased solubility of lignin dried at 70 and 90 °C can then be attributed to the second thermal event detected at 70–80 °C. In the literature, both thermal events are usually attributed to loss of surface- and bonded moisture.[54,55] However, a simple water loss of up to 5% would not explain an increase in solubility of 25%. The peaks in differential heat flow can, for example, be caused by loss of bound water or by thermal relaxation events that occur close to the $T_g$ of lignin, which is typically in the range of 90–140 °C for the relevant molecular weight range. To determine the actual reasons for the thermal events, further experiments will be necessary. Analysis of the degradation products as well as temperature cycling experiments can facilitate the identification of the transformations that take place. Even though it is still speculation, a link between the observed thermal events and the increase in solubility seems likely.

4. Conclusions

Based on dissolution experiments with a CO$_2$-precipitated and water-washed Kraft lignin we could show that it is possible to dissolve a very large fraction of the lignin in pure water. No complex chemical modifications are necessary, only a washing step with water and drying of the resulting washed lignin at a temperature of 70 °C. The resulting lignin solution had a pH of 8.9 and contained up to about 300 g L$^{-1}$ of lignin. The water washing procedure yielded a lignin of higher molar mass compared to the original sample, although the active groups were similar. Compared to that, the dissolved fraction had a considerably lower molar mass and a lower ratio of aliphatic to aromatic OH groups, explaining its dissolution in water. The water soluble lignin had a lower hydrodynamic diameter in water, which increased with decreasing pH due to further agglomeration. Charge titration yielded a zeta potential in the range of $-60$ mV, proving again that the lignin formed a stable colloidal structure in water.

Although the preparation is still demanding with respect to water consumption and reduced yield, the water-washed Kraft lignin has a very high potential for use in aqueous lignin solutions for various applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords
kraft lignin, lignin, lignin characterization, lignin processing, water soluble lignin

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