

Solvent Fractionation of Technical Lignin Materials with Industrially Relevant Solvents

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Abstract

Lignin fractionation aims at dividing the original lignin material into more uniform fractions that have the qualities desired for further processing of the material. Solvent fractionation is a versatile method that produces a soluble and an insoluble fraction with varying compositions, including molecular weight distribution, polydispersity (PDI), and phenolic hydroxyl (OH_{ph}) content. These properties are key factors in the further downstream applicability of lignin. Kraft, organosolv, and hydrolysis lignins were fractionated using multiple solvents and their water solutions with a single-stage fractionation protocol. The produced fractions were analyzed for their molecular size distribution and OH_{ph} content. Soluble fractions were discovered with desirable qualities, including a narrow size distribution (lowest PDI 1.4) and accumulation of OH_{ph} groups (up to $3.05 \text{ mmol}_{\text{OH}}/\text{g}_{\text{lignin}}$). Three fractionation solvents, i.e., pure isopropanol, pure ethanol, and 30% γ -valerolactone, were found to produce solvent-specific soluble fractions that had relatively identical characteristic M_w , M_n , and PDI values regardless of the initial lignin material. This is crucially important new data that is beneficial for robust lignin applicability at industrial scale. Other important observations were made regarding water-alcohol solutions, as the increase in initial solid content resulted in changes in the composition of the fractions produced. Further applicability of the obtained fractions is examined in this paper. Patterns as well as differences between the three lignin materials were observed in their dissolution and the resulting compositions of the soluble fractions. This wide comparable dataset of industrially relevant solvents and lignin materials provides significant insight into the possibilities of lignin downstream processing.

Keywords

kraft lignin, organosolv lignin, hydrolysis lignin, phenolic hydroxyl, size distribution

1 Introduction

Lignin is one of the most abundant natural polymers and the dominant aromatic polymer found in nature [1, 2]. It is biodegradable and exhibits numerous advantages, including its aromatic and antioxidant nature. Lignin is present in and can be extracted from various plant-based sources, especially lignocellulosic biomass, e.g., wood. Therefore, lignin can be and usually is extracted from raw materials that do not compete with food sources [3]. These factors make lignin an attractive alternative for a variety of applications including substitutes for phenolics, thermoplastics [4], and polyols [1]. However, the extraction process has proven to be a challenge since lignin naturally resists degradation [3]. The extraction process alters the composition and the properties of the extracted technical lignin, which affects its applicability [1, 5–7]. The poor solubility of lignin is the main hindrance in the way of comprehensive

utilization [8]. Therefore, research into the properties of various technical lignins is required.

Fractionation is a technique which aims to separate lignin molecules based on their physico-chemical characteristics. Separating lignin into fractions with narrow polydispersity (PDI) regions, well-defined molecular-weight compositions, and desirable active groups would further assist downstream processing into higher value products and applications [1, 3, 6]. High and low molecular weight (MW) lignin fractions have different advantages in further processing and applicability. High MW lignin fractions are more hydrophobic, which enhances the strength of the nanoparticles. In polymer blend applications, low MW lignin is better suited, because it disperses more evenly in the matrix. Lower MW lignin and higher hydroxyl groups content is also beneficial when preparing lignin-based

polyurethane elastomers [9, 10]. In addition, low MW lignin generally has a higher phenolic hydroxyl group (OH_{ph}) content, which supplies its biological activity (e.g., antimicrobial and antioxidant properties, promising for medical applications) [2]. The two main lignin fractionation methods are solvent and membrane fractionation. Solvent fractionation is a straightforward and diverse method for dividing and extracting lignin fractions of differing molecular sizes. Solvent fractionation can be applied in multiple ways, for example single solvent [11–13], sequential [14–18], or mixed solvent-fractionation [19, 20]. The solvent mixture composition has an effect on the lignin solubility. Thus, the lignin fractions desired for further processing can be extracted by altering the solvent mixture [1, 3]. Ideally, fractionation provides an efficient single-stage pre-treatment method which allows for the original lignin structure to be utilized without harsh modification. Development of lignin fractionation via non-toxic organic solvents and water solutions is crucial for the success of large-scale lignin utilization [2, 6].

Most of the lignin side stream produced in the paper and pulp industry is burned for energy, despite its potential for higher value applications [4, 5, 21]. In general, pulping processes are designed to valorize the cellulose from the biomass and thus eliminate the lignin. Therefore, traditionally the attention has been on the cellulose fibers rather than lignin, which has been considered a side stream [1]. Naturally lignin has a very complex structure, which is dependent on its source and also affected by its isolation process. Kraft lignin is obtained via alkaline sulfate pulping, which is the traditional method for separating lignin from lignocellulose. The treatment of native lignin during kraft pulping increases the degree of heterogeneity of the material, which is undesirable in terms of the industrial applications of lignin [12]. Organosolv lignin is extracted from biomass with organic solvents at elevated temperatures. Unlike Kraft, organosolv lignin does not contain any sulfur and the non-toxic organic solvents used can be recovered after the process. The organosolv process is better suited for non-wood raw materials like straw or bamboo [3, 22]. Hydrolysis lignin is produced as a by-product in cellulosic bio-ethanol production. Hydrolysis lignin is known to contain more cross-linking than Kraft lignin and its structure is more condensed, making it harder to valorize. In addition, hydrolysis lignin contains larger amounts of cellulose than Kraft and organosolv lignin. The cellulose content in hydrolysis lignin may be up to 50% [23]. Due to the challenging and varying

compositions of different technical lignins, a fractionation method that works well for one technical lignin might not work for another [8]. One aim of fractionation is to limit the heterogeneity of the lignin material and thus broaden its applicability in technical utilization [6, 12, 21].

The objective of this study is to evaluate multiple industrially relevant solvents for their ability to fractionate lignins from different sources. Three different technical lignins (kraft, organosolv, and hydrolysis) were studied (1) to obtain a comprehensive view of the functionalities of the solvents, and (2) to gain perspective on how different lignins behave in the fractionations. In addition, a set of experiments with greater amounts of lignin was carried out on the alcohol-water fractionations to evaluate the effect of possible solubility limits on fractionation. The soluble and insoluble fractions of the lignins were studied for their molecular size distributions and OH_{ph} content. Special interest was taken in soluble fractions with low PDI, narrow size distribution, and high OH_{ph} content. These features are significant when considering the practical applicability of fractionated lignin in down-stream processing.

This study provides a wide and coherent set of comparable data on lignin solvent fractionation. The extent and consistency of the data set makes it novel and industrially significant in terms of the downstream processing of lignin.

2 Materials and methods

2.1 Chemicals and technical lignins

The following chemicals were used: dimethyl sulfoxide ($\geq 99.7\%$, Fisher BioReagents), dimethylformamide (99.9%, VWR), ethanol (100%, VWR), isopropanol (100%, VWR), γ -valerolactone ($\geq 99\%$, Sigma-Aldrich), sulfolane (99%, Alfa Aesar), sulfuric acid (Merck), bovine serum albumin (Bio-Rad), ninhydrin monohydrate ($\geq 99\%$, VWR), acetic anhydride (99.7%, VWR), pyridine ($\geq 99\%$, Acros Organics), sodium hydroxide (98.5%, VWR), lithium bromide (99%, Acros Organics), and potassium dihydrogen phosphate ($\geq 99.5\%$, Merck).

In addition to the pure solvents, some aqueous solutions were utilized. The solutions were prepared as mass fractions. Ultrapure water (Milli-Q) was used in all of the experiments. The chosen solvents were all organic solvents, including alcohols and green solvents. The solvents have a wide range of Hansen (dispersive δ_D , polar δ_P , and hydrogen bonding δ_H) and Hildebrand solubility parameter (HSP) values [24, 25] (Table 1) and the variability was also increased by utilizing water solutions (Table 2). The following water solutions were used: 50% isopropanol (IPA),

Table 1 Hansen solubility parameters (δ_D , δ_P and δ_H , [MPa^{1/2}]) [24] and calculated HSP [MPa^{1/2}] values of the pure solvents used

Solvent	δ_D	δ_P	δ_H	HSP
DMF (reference)	17.4	13.7	11.3	24.9
Water	15.5	16	42.3	47.8
DMSO	18.4	16.4	10.2	26.7
Sulfolane	20.3	18.2	10.9	29.4
GVL [32]	16.7	14	8	23.2
IPA	15.8	6.1	16.4	23.6
EtOH	15.8	8.8	19.4	26.5

Table 2 Calculated Hildebrand solubility values (HSP_{mix}, [MPa^{1/2}]) of the water solutions used

Solution	HSP _{mix}
90% SF	31.6
30% GVL	40.7
70% GVL	30.9
50% IPA	34.2
30% EtOH	40.3
70% EtOH	31.9

30% ethanol (EtOH), 70% EtOH, 30% γ -valerolactone (GVL), 70% GVL, and 90% sulfolane (SF). Sulfolane is solid at room temperature, thus it was only used as a 90% aqueous solution instead of pure solvent.

Three kinds of technical lignins were used: softwood Kraft lignin (KL) Indulin AT from MeadWestvaco (Richmond, VA, USA), non-wood organosolv lignin (OL), and softwood hydrolysis lignin (HL) from St1 Ltd (Helsinki, Finland).

2.2 Lignin characterization

Before experimentation, the lignin materials were air-dried overnight (20–24 h) in a fume cupboard at ambient room temperature. The dry solids content of the materials was then determined by oven drying a small batch at 105 °C overnight. The amounts of cellulose and hemicellulose oligomers and monomers were determined following the NREL standard method [26]. Monomeric sugars and other compounds were extracted from the lignin with water and measured. The oligomers in the water solutions were first broken down into monomers via total hydrolysis and then measured similarly, using high performance liquid chromatography (HPLC) (Agilent Technologies 1200 Series, Santa Clara, CA, USA) equipped with RID and DAD detectors. An ICsep ICE-Coregel 87H3 organic acids column (300 × 7.8 mm) (Transgenomic, Omaha, NE, USA) was utilized with a 0.005 M H₂SO₄ mobile phase at a 0.8 mL/min

flow rate at an operating temperature of 60 °C and injection volume of 10 μ L. The pH values of the water-soluble lignins were measured to evaluate the acidity of the lignin materials.

The protein content of the lignins was determined using the ninhydrin assay with alkaline hydrolysis, modified from Haven and Jørgensen [27]. Bovine serum albumin was used to determine the standard curve of protein concentrations. The 2% ninhydrin reagent solution was prepared by dissolving 2 g of ninhydrin monohydrate into 100 mL of absolute ethanol. The water and dimethyl sulfoxide (DMSO) soluble lignin samples were treated as described by Haven and Jørgensen [27] and then analyzed in 1 cm path length cuvettes using a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan).

The total hydroxyl group content (OH_{total}) of the lignin materials was determined following the standard test method using acetic anhydride acetylation [28]. Briefly, the method is based on the acetylation of the OH groups by acetic anhydride, after which the excess acetylation reagent reacts further into acetic acid. The amount of acetic acid formed is then determined via titration. Sodium hydroxide was used as the titrant. The titrant consumption was determined at pH 9. The OH_{total} concentration (mmol/g) was calculated based on the experimental data according to Eq. (1):

$$\text{OH}_{\text{total}} = \frac{(A - B)c}{m}, \quad (1)$$

where A and B refer to the consumption of the titrant in the titration of the blank and lignin sample, respectively, c is the concentration of the titrant solution, and m is the mass of the lignin sample.

2.3 Lignin fractionation

Single-stage solvent fractionation with pure organic solvents and their water solutions was carried out using a straightforward protocol Fig. 1. The air-dried lignin was weighed (0.1 g) into a 50 mL Erlenmeyer flask and 10 mL of a solvent solution was added, resulting in an initial solid concentration of 10 g/L. To keep the solid material mobile and thus maximize dissolution the flask was shaken at 100 rpm on a Digital orbital shaker (Heathrow Scientific, Vernon Hills, IL, USA) at the ambient room temperature (20–22 °C) overnight (20–24 h). The soluble and insoluble fractions were separated via filtration. The solution was vacuum filtered through a 1.2 μ m glass microfiber filter (Whatman, Maidstone, UK). The insoluble fraction was washed with ultrapure water.

The effect of a higher initial lignin concentration on the composition of the resulting fractions was examined

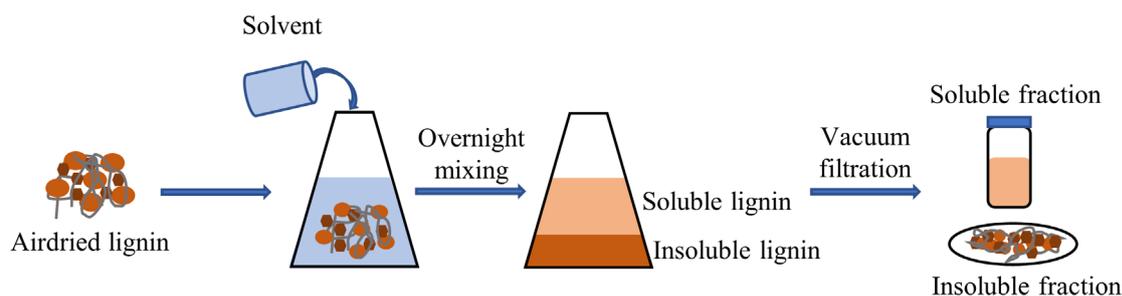


Fig. 1 Illustration of the lignin fractionation protocol

for chosen solvent solutions. A similar set of fractionations with a higher lignin content of 1.5 g was carried out with the alcohol-water solutions, resulting in an initial solid concentration of 150 g/L.

Each fractionation was carried out in duplicate to obtain one sample for the mass balance determination and one for the molecular size distribution analysis. The insoluble materials of the mass balance samples were dried overnight at 105 °C before weighing to determine the absolute dry solids content of the insoluble fraction. The insoluble materials of the molecular size distribution samples were air-dried overnight at the ambient room temperature to avoid polymerization of the lignin material caused by heat. The mass balance was determined by comparing the initial amount of dry lignin with the amount of undissolved lignin. The results are presented as mass percentages of dissolved lignin.

DMF was chosen as the reference solvent for the fractionation experiments as it is generally considered to dissolve lignin the most effectively. The reference fractionation with DMF was carried out similarly to the method described earlier. The resulting data of lignin dissolution in DMF was utilized as the reference for the overall composition of the lignin materials.

2.4 Molecular size distribution - GPC analysis

The molecular size distributions of the fractionated lignin samples were analyzed using gel permeation chromatography (GPC). The chromatography equipment used was the Agilent Technologies 1260 series (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with three Phenomenex Phenogel 5 μm columns (104 Å, 103 Å and 50 Å) (Phenomenex Inc., Torrance, CA, USA). The mobile phase consisted of dimethylformamide (DMF) with 0.05% LiBr. A VWD detector set at a wavelength of 280 nm was used for detection. The flow rate of the mobile phase was 0.5 mL/min, the operating temperature of the columns was 35 °C, and the injection volume of the sample 50 μl. Polyethylene oxide/glycol (PEO/PEG) standards (Agilent EasiVial) from 106 Da to 1 522 000 Da were used for the calibration of the

method via RID detection. Based on the retention times of the standards, the molar masses of the samples were estimated within the range of 120–500 000 Da.

When necessary, the samples were diluted with the mobile phase (DMF with 0.05% LiBr). The insoluble lignin fractions were dissolved into the mobile phase solution at a concentration of 1 g/L and analyzed in the same way as the soluble samples. The data obtained on the retention times was used to calculate the number average molar mass (M_n), weight average molar mass (M_w), and PDI, and to analyze the molecular size distribution of the samples. The parameters were calculated according to Eqs. (2)–(4):

$$M_n = \frac{\sum_i AU_i}{\sum_i AU_i / M_i} \quad (2)$$

$$M_w = \frac{\sum_i AU_i M_i}{\sum_i AU_i} \quad (3)$$

$$PDI = M_w / M_n, \quad (4)$$

where AU_i is the absorbance unit of a specific measurement point and M_i is the molar mass of that specific measurement point.

To illustrate the molecular size distributions, the absorbance units were normalized to 100 according to the maximum value. Thus, all the size distribution curves have the maximum value of 100 when the absorption is expressed in relative absorbance units (RAU) according to Eq. (5):

$$RAU_i = (100 / AU_{\max}) AU_i, \quad (5)$$

where AU_{\max} is the maximum absorbance of the size distribution curve.

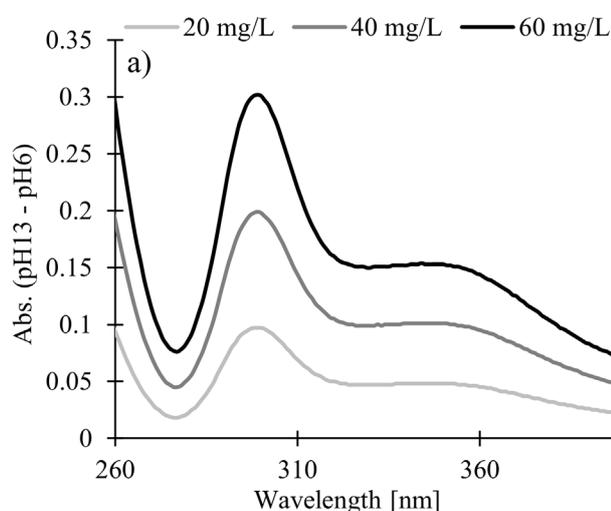
2.5 Phenolic hydroxyl group content - Δε-IDUS analysis

To estimate the phenolic hydroxyl (OH_{ph}) content of the fractionated lignin samples, the modified Δε-IDUS method was used [29]. Buffer solutions of pH 6 and pH 13 were prepared as described by Zakis [30]. Dilutions of the various soluble lignin fractionation samples were prepared using

DMSO to reach a concentration of approximately 1 g/L. The measurements using a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) were carried out as described by Goldmann Valdés [29]. Only the second ionization level (pH 13) was measured to determine the total OH_{ph} . The difference in the absorbance between the samples at pH 6 and pH 13 was measured for three concentrations of the soluble lignin samples (20 mg/L, 40 mg/L, and 60 mg/L) Fig. 2(a). The peak absorbance values of approximately 300 nm and 360 nm were determined to fit a curve of the difference absorbance as a function of concentration with zero intercept Fig. 2(b). The slopes of the curves (the difference absorptivity Δa [L/g \times cm]) were used to calculate the total OH_{ph} concentration according to Eq. (6):

$$\text{OH}_{\text{ph total}} = 0.250\Delta a^{300} + 0.107\Delta a^{360} \quad (6)$$

The calculated results were expressed in $\text{mmol}_{\text{OH}}/\text{g}_{\text{lignin}}$. A more extensive version of the method and calculations described by Goldmann Valdés [29] would result in more information on the structure of the phenolic components. In the scope of this research, determination of the total OH_{ph} concentration was considered sufficient. The $\Delta\epsilon$ -IDUS method is considered a semi-quantitative assay as it slightly underestimates the OH_{ph} content of the lignin compared with other methods, e.g., NMR spectroscopy [29]. However, this underestimation is considered systematic, and thus the method is appropriate for assessment between samples.



3 Results and discussion

3.1 Properties of the technical lignins

The characterized properties of the three technical lignin materials are presented in Table 3. The dry mass content of the lignins was determined as follows: Kraft lignin 97%, organosolv lignin 97%, and hydrolysis lignin 98%. All calculations were corrected using these dry mass content values to exclude moisture from the calculations. In addition, following the NREL total hydrolysis protocol [26], HL was found to contain approximately 28% cellulose based on the total glucose content. This was also taken into account in the calculations by subtracting the amount of cellulose from the initial mass to assess the lignin material alone. OL and KL had only negligible amounts of residual cellulose and hemicellulose. The other trace residues detected included acetic acid, furfural, and hydroxymethylfurfural. In addition, OL contained trace residues of formic acid. The presence of formic acid explained the noticeably deviant acidic pH (3.6) of the water-soluble OL. The KL and HL water solutions had neutral pH values.

Table 3 Properties of the original lignin materials: pH, protein concentration, cellulose content, and total hydroxyl group content. Solutions in a water and/or DMSO matrix specified in parentheses

	Kraft lignin	Organosolv lignin	Hydrolysis lignin
pH (H ₂ O)	6.7	3.6	6.7
mg _{protein} /g _{lignin} (H ₂ O)	3.6	0.3	2.1
mg _{protein} /g _{lignin} (DMSO)	16.4	37.6	12.3
Cellulose % (NREL)	<2.0	2.9	28.3
OH _{total} mmol/g	6.2	4.3	4.7

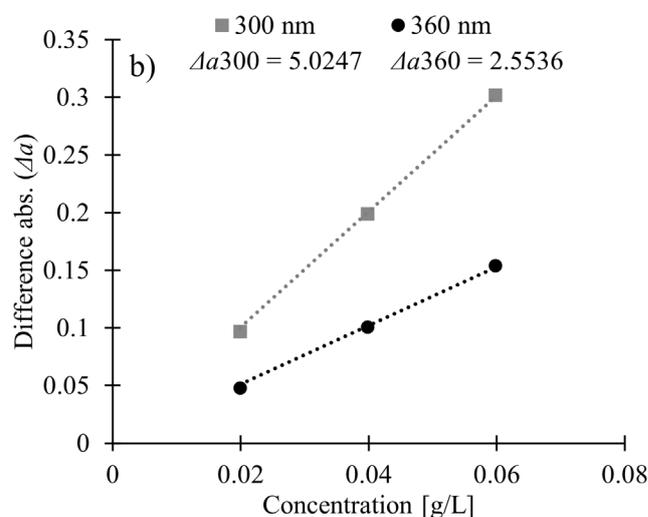


Fig. 2 (a) Difference absorption spectra (pH13 – pH6) of the lignin samples with three concentrations, (b) difference absorbance values of 300 nm and 360 nm peaks as a function of concentration with zero intercept

The protein concentration of the lignin materials was determined from the lignin samples in the water and DMSO matrices (Table 3). The protein content was greater in the DMSO solution than in the water solution. This could indicate that the proteins were hindered within the lignin 3D structure, being released once the lignin had dissolved, which it did more readily into DMSO than into water. The total hydroxyl group content (OH_{total}) of the lignin materials was determined via the standard method based on acetic anhydride acetylation (Table 3).

The overall composition of the soluble lignin materials was evaluated based on the DMF soluble samples as reference (see supplement materials). DMF is known to solubilize most lignin materials [12] and, as the matrix of the GPC analytics used, it was the clear choice for the reference solvent. Only HL showed notably low dissolution (32 wt%) in DMF, which was expected based on the known solubility issues.

3.2 Solvent selection and lignin fractionation

Selection of the solvent plays a central role in the development of the industrial process considering environment, economy, and safety issues [18, 31]. The chosen organic solvents (DMSO, SF, GVL, IPA, and EtOH) are known not to dissolve cellulose. Thus, the fractionation acted as an additional purification step for the lignin materials. Especially for HL, which contained a significant amount of residual cellulose (28%). In addition, the chosen solvents have low toxicity and reasonable chemical cost.

Solubility parameters can be used to interpret the properties involved in solubility. They reflect the behavior of the solvents and solutes in a solution [25]. The Hansen solubility parameters consist of three components: the dispersive (δ_D), polar (δ_P), and hydrogen bonding (δ_H) solubility parameters [24]. The Hildebrand solubility parameter (a.k.a. total Hansen solubility parameter, HSP) incorporates all three Hansen solubility parameters. The HSP values of pure solvents can be calculated according to Eq. (7) [32]:

$$\text{HSP} = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (7)$$

The HSP values of the water solutions utilized (HSP_{mix}) were determined using Eq. (8), derived from Lê et al. [20]:

$$\text{HSP}_{\text{mix}} = \frac{V_{\text{H}_2\text{O}} \times \text{HSP}_{\text{H}_2\text{O}} + V_{\text{solv.}} \times \text{HSP}_{\text{solv.}}}{V_{\text{tot}}}, \quad (8)$$

where $V_{\text{H}_2\text{O}}$ and $V_{\text{solv.}}$ are the volumes of water and solvent in the mixture, V_{tot} is the total volume of the solvent mixture, and $\text{HSP}_{\text{H}_2\text{O}}$ and $\text{HSP}_{\text{solv.}}$ are the HSP values of water and

the pure solvent used in the mixture, respectively. These solubility parameters were calculated for all the solvents used and their water solutions (Tables 1 and 2).

The solubility parameters provide a calculated estimation of the solvent properties. Thus, there is variation between the reported values depending on the method used for the estimation. In particular, the Hansen parameters of GVL varied significantly [32]. The presented values (Table 1) have been reported to be the most precise estimation according to Kerkel et al. [32]. Utilizing solutions with a wide range of HSP values enables a comprehensive view of lignin solubility and fractionation.

Fractionation was carried out as a single-stage process with single solvents and their water solutions. Every experiment was reproduced 2–3 times, and the average relative error was measured to be typically <2% and at the most <6%. Each fractionation resulted in a soluble and an insoluble fraction. The fractions were then analyzed for their properties to gain insight into the differences and similarities between the lignins and the fractionation solvents used. Special attention was paid to finding fractions with desirable qualities, e.g., OH_{ph} content. Based on these properties, the industrial applicability of the fractions was examined.

3.2.1 Kraft lignin fractionation

Kraft lignin has been widely studied and is known to have relatively good overall solubility. This was also observed in the experiments as KL was highly soluble in DMSO, 70% GVL, and 90% SF. The highest dissolution of KL (99 wt%) was measured in DMSO and 70% GVL. The molecular size distribution of KL was in a wide range with the peak at approximately 1500 Da, according to the DMSO soluble fraction Fig. 3(a).

The alcohol soluble fractions of IPA and EtOH had similar size distributions Figs. 3(c, d). The size distributions of the soluble fractions displayed a distinctive dip at approximately 200–250 Da, indicating less soluble lignin molecules in that particular MW area. Very similar size distributions were also found among the 90% sulfolane (SF) and 70% GVL soluble fractions Figs. 3(a, b). The characteristic M_w , M_n , and PDI values as well as the OH_{ph} concentrations of the soluble fractions were also in the same range as each other (see supplement materials). These features indicate that the solvent pairs studied produced similar fractions of soluble lignin.

However, the determined characteristic values (M_w , M_n , and PDI) of the 90% SF and 70% GVL soluble fractions differed from those of the DMSO soluble fraction (see supplement materials). In addition, the OH_{ph} content of these fractions was higher than that of the DMF soluble reference

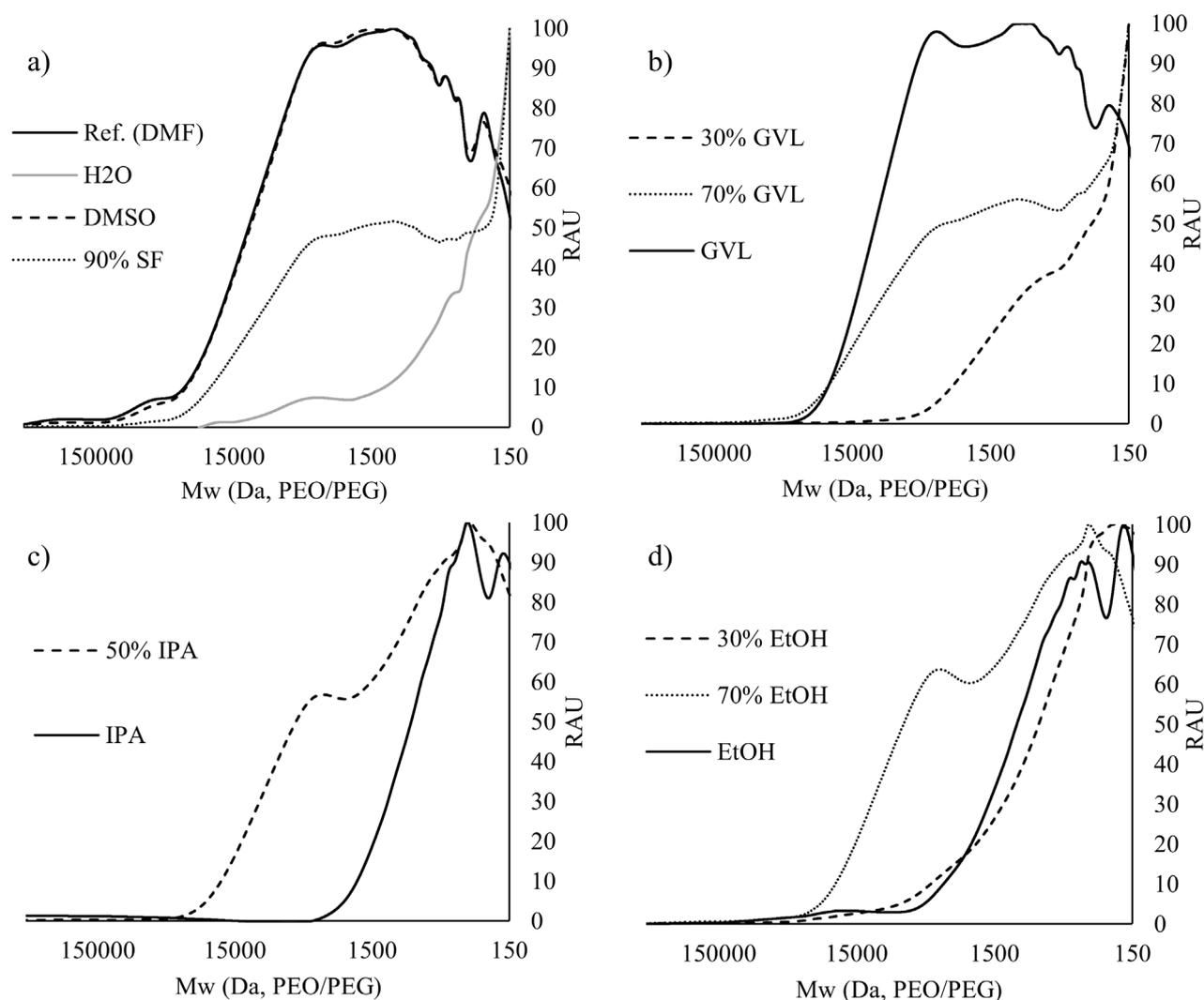


Fig. 3 Kraft lignin normalized size distributions of soluble fractions: (a) reference (DMF), water, DMSO, and 90% sulfolane (SF) soluble fractions, (b) 30%, 70%, and pure GVL soluble fractions, (c) 50% and pure IPA soluble fractions, and (d) 30%, 70%, and pure EtOH soluble fractions. Initial solid concentration 10 g/L

(2.51 mmol/g), indicating the accumulation of OH_{ph} groups. A high OH_{ph} content in the lignin fraction is favorable in certain applications when physical interaction and chemical modification of the material are required [22].

Fig. 4(a) illustrates the dissolution and phenolic hydroxyl group concentration of the soluble KL fractions. The measured OH_{ph} concentration of the DMSO soluble KL (2.55 mmol/g) was in the same range as previous measurements by Goldmann et al. [33]. Comparing the fractionations with the initial solid content of 10 g/L, the highest accumulation of OH_{ph} was observed in the 30% EtOH soluble fraction (3.05 mmol/g). A slight OH_{ph} accumulation was also observed in the 30% GVL (2.64 mmol/g), 70% GVL (2.78 mmol/g), 90% SF (2.67 mmol/g), 50% IPA (2.67 mmol/g), 70% EtOH (2.81 mmol/g), and pure EtOH (2.58 mmol/g) soluble fractions. Thus, the OH_{ph} content

rose with a slight addition of water to the solvents (IPA, EtOH, and GVL), similarly to the increase in dissolution. In general, addition of water probably increases the hydrogen bond formation [11] and polarity [16], which are beneficial for the solubility of lignin. The lowest OH_{ph} content was found in the pure IPA soluble fraction (1.17 mmol/g), where the lowest PDI (1.4) was also achieved, indicating that the fraction had a narrow size distribution. Similarly, Goldmann et al. [19] reported that the lowest PDI values for EtOH-water soluble Indulin AT lignin were reached when the EtOH content of the solution was above 80%.

3.2.2 Organosolv lignin fractionation

The highest dissolution (97 wt%) of organosolv lignin was achieved with DMSO Fig. 4(b). The size distribution of DMSO soluble OL showed a distinct peak at approximately

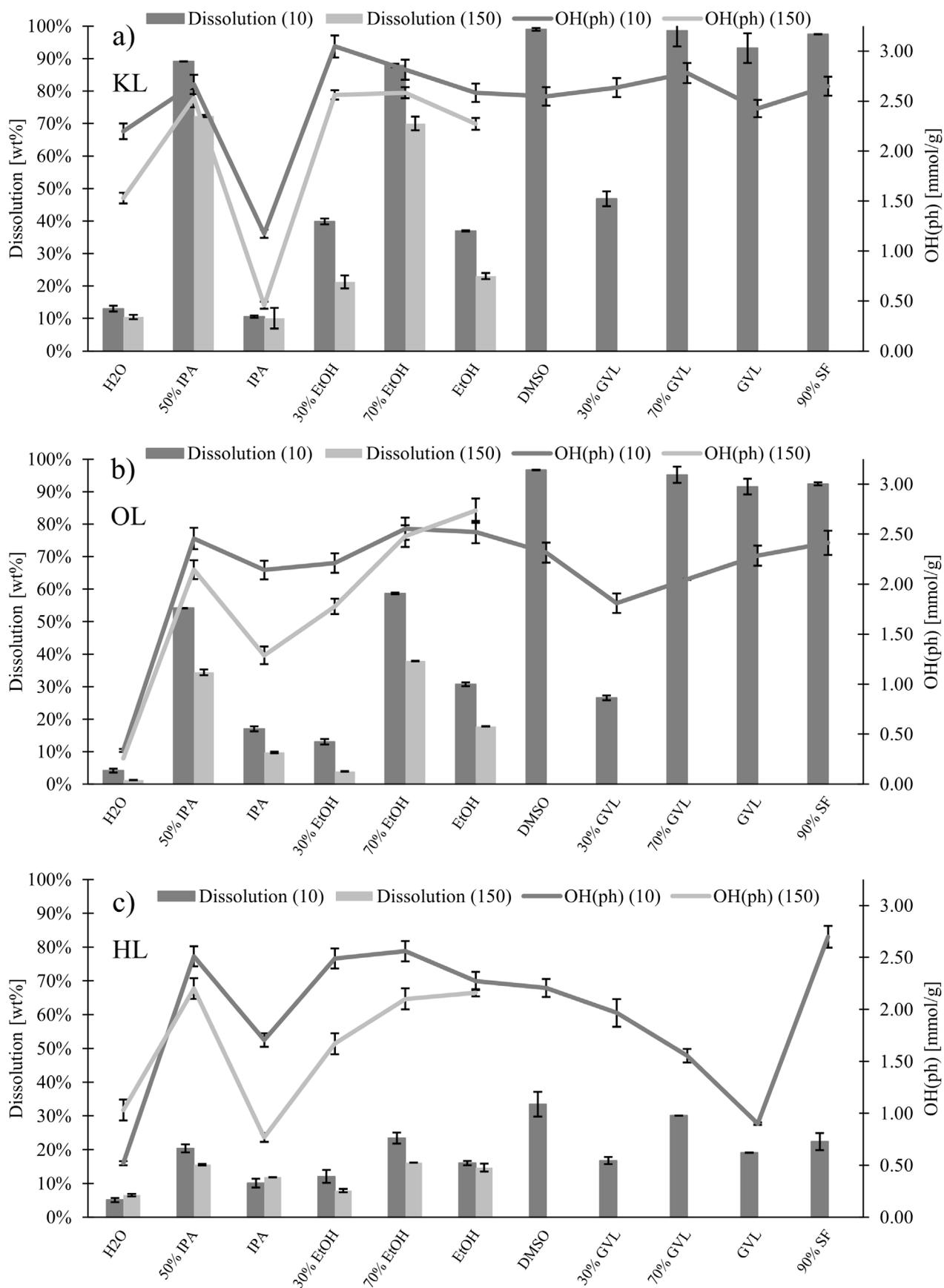


Fig. 4 Dissolution and the OH_{ph} content of the soluble lignin fractions: (a) Kraft lignin, (b) organosolv lignin, and (c) hydrolysis lignin. Initial solid concentrations 10 g/L and 150 g/L

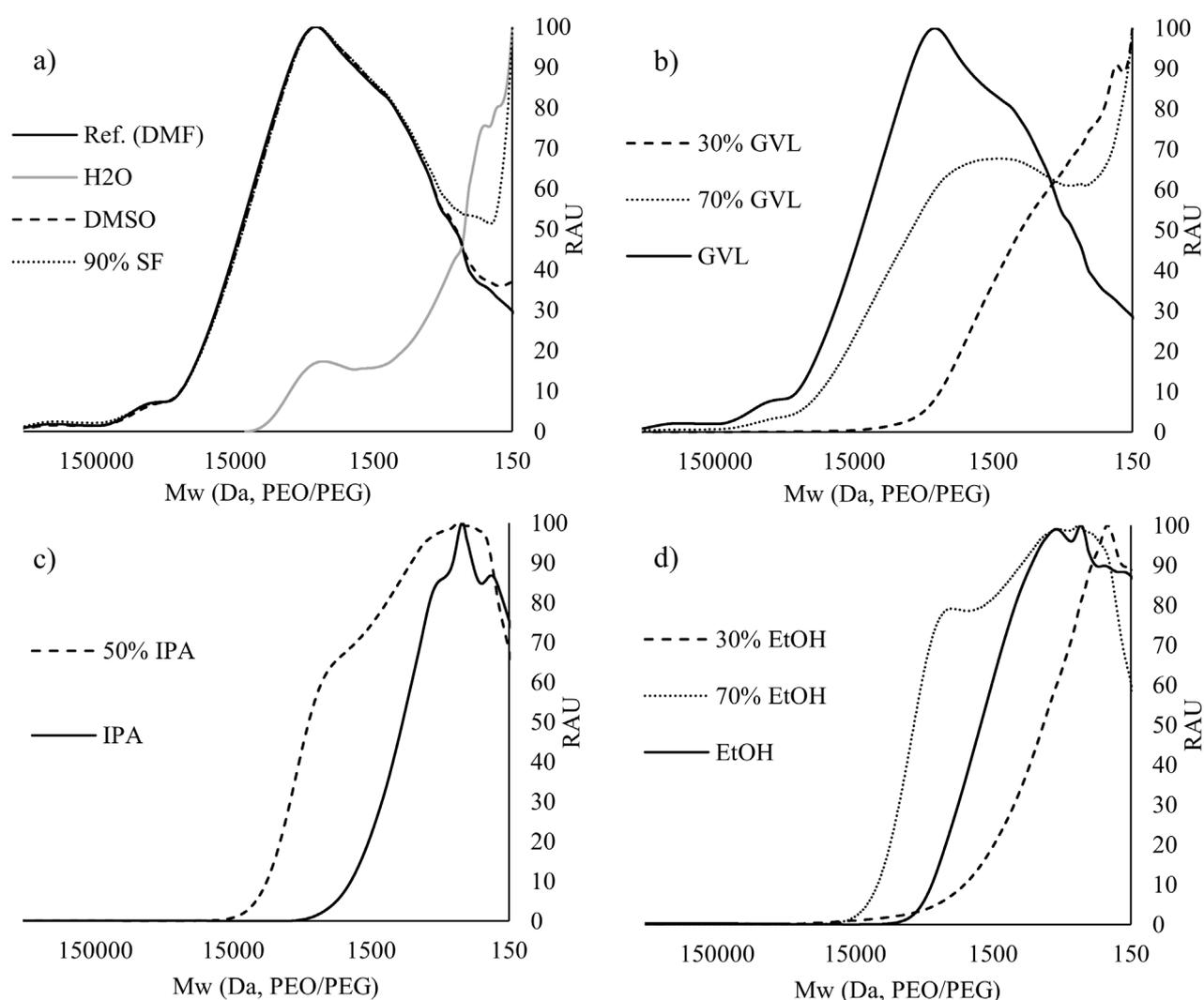


Fig. 5 Organosolv lignin normalized size distributions of the soluble fractions: (a) reference (DMF), water, DMSO, and 90% sulfolane (SF) soluble fractions, (b) 30%, 70%, and pure GVL soluble fractions, (c) 50% and pure IPA soluble fractions and (d) 30%, 70%, and pure EtOH soluble fractions. Initial solid concentration 10 g/L

3600 Da in Fig. 5(a). The pure EtOH soluble fraction of OL had a wider size distribution and a greater amount of larger molecules, whereas the pure IPA soluble fraction had a narrower size distribution in the region of smaller molecules.

The dissolution and the phenolic hydroxyl group concentration of the soluble OL fractions are illustrated in Fig. 4(b). The total soluble OH_{ph} content was estimated as 2.30 mmol/g based on the DMF reference. Higher OH_{ph} values were found in the DMSO (2.32 mmol/g), pure EtOH (2.52 mmol/g), 50% IPA (2.46 mmol/g), and 90% SF (2.41 mmol/g) soluble fractions, the highest being 70% EtOH (2.55 mmol/g). It was notable that the pure EtOH soluble fraction had relatively low M_w , M_n , and PDI values (930 Da, 510 Da, and 1.8, respectively) with a high OH_{ph} content. These characteristics of the EtOH soluble fraction became even more obvious when the lignin

content rose (see supplement materials). This soluble fraction possessed desirable qualities for various applications where narrow size distribution and high OH_{ph} content are beneficial (e.g., bio-based plasticizers [14]). The lowest OH_{ph} content was measured in the water-soluble fraction (0.34 mmol/g). A fraction with low OH_{ph} content and high MW could be utilized, for example, in composite materials as reinforcement fillers [14].

3.2.3 Hydrolysis lignin fractionation

The overall dissolution of the hydrolysis lignin was very low, as expected. The highest dissolution (33 wt%) was achieved with DMSO Fig. 4(c). The size distribution of the DMSO soluble HL peaked at approximately 800 Da Fig. 6(a), thus being the lowest peak value of the three lignin materials studied. However, the dissolution of HL is

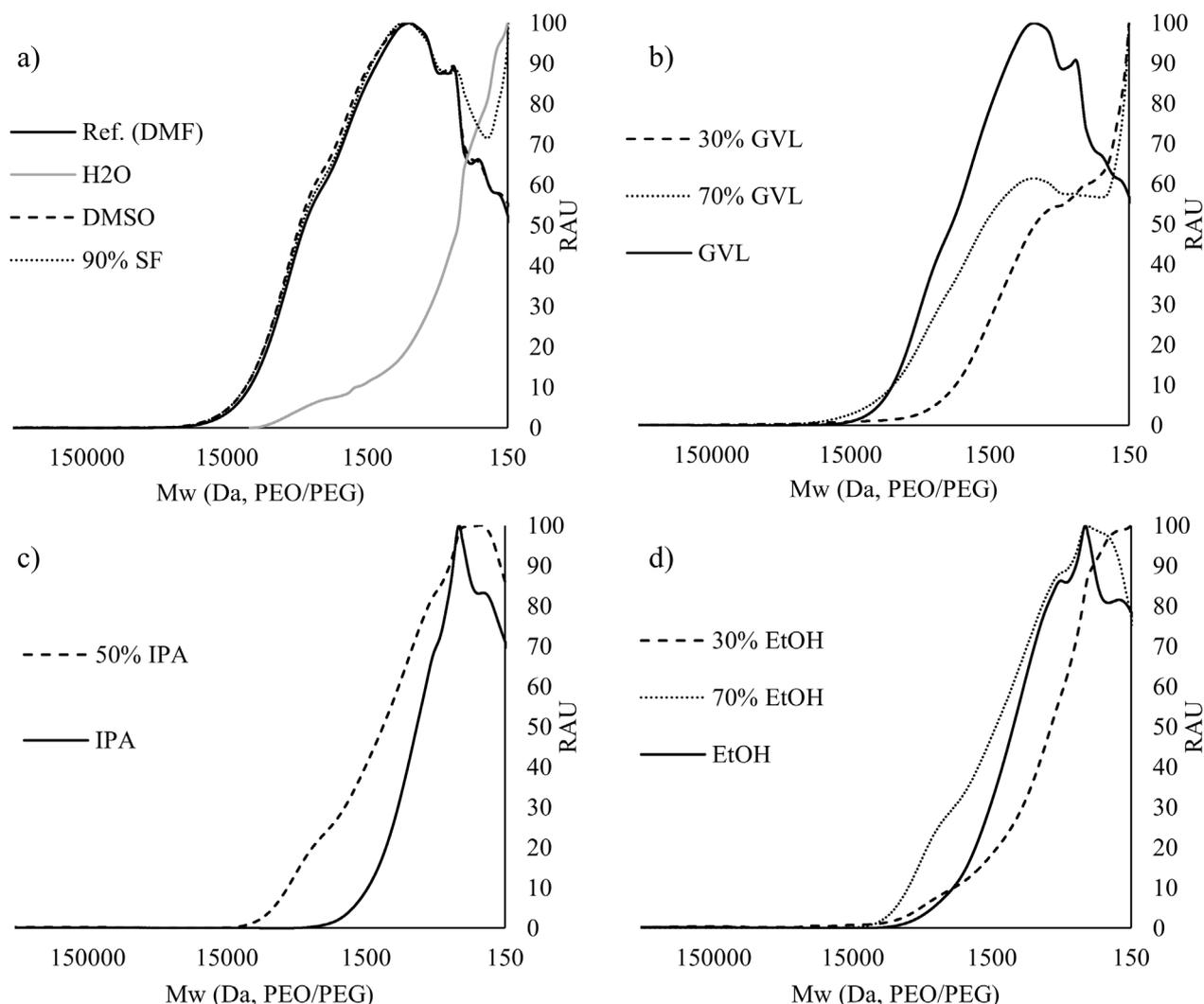


Fig. 6 Hydrolysis lignin normalized size distributions of the soluble fractions: (a) reference (DMF), water, DMSO, and 90% sulfolane (SF) soluble fractions, (b) 30%, 70%, and pure GVL soluble fractions, (c) 50% and pure IPA soluble fractions and (d) 30%, 70%, and pure EtOH soluble fractions. Initial solid concentration 10 g/L

relatively low when larger molecules can be found in the insoluble fraction. Unfortunately, the molecular size distribution of the original HL cannot be measured by GPC because of the low dissolution of HL in any solvent applicable as the mobile phase. The pure alcohols produced similar size distributions with low PDI values and a distinct peak at approximately 300 Da Figs. 6(c,d). In general, the size distributions of the alcohol-water soluble fractions resembled each other among the IPA and EtOH solutions.

Fig. 4(c) illustrates the dissolution and phenolic hydroxyl group concentration of the soluble HL fractions. The total soluble OH_{ph} of the DMF reference was measured as 1.95 mmol/g. The highest OH_{ph} concentration was measured in the 90% SF soluble fraction (2.70 mmol/g). Other notable OH_{ph} accumulations were observed in the alcohol-water soluble fractions: 50% IPA (2.51 mmol/g), 30% EtOH

(2.49 mmol/g) and 70% EtOH (2.56 mmol/g). Thus, the OH_{ph} content of the soluble fractions increased with a slight addition of water into the solution. In the case of GVL, the solution with the lowest GVL content (30%) had the highest OH_{ph} concentration (1.97 mmol/g). The lowest OH_{ph} concentration of HL was achieved with the water-soluble fraction (0.52 mmol/g). Overall, the PDI values of the soluble HL fractions were lower than those of KL and OL.

3.3 Comparison of lignin fractions

Based on the DMF reference samples, the widest molecular size distribution was found in KL, whereas OL and HL spread out more towards the larger and smaller MW, respectively Fig. 7. The experimental dissolution data showed that the most effective fractionation solvents were DMSO and GVL, as well as the reference solvent DMF. DMSO

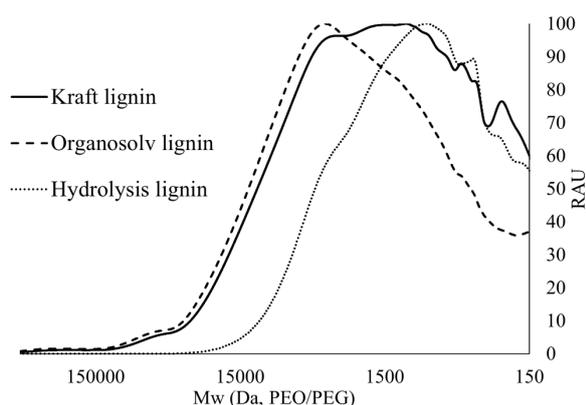


Fig. 7 Normalized size distributions of the DMF soluble reference fractions of the technical lignins

and DMF are polar aprotic solvents, which are known to be effective solvents for lignin [5, 12]. GVL is considered a mild and efficient green solvent and can be produced from carbohydrate-based biomass, e.g., cellulose [8]. High dissolution values were achieved with 90% sulfolane (SF) as well, which is also a green polar aprotic solvent [34].

Three fractionation solvents: pure IPA, pure EtOH, and 30% GVL, were found to produce almost identical solvent-specific soluble fractions regardless of the initial lignin material. The measured characteristic values of the soluble fractions revealed only a negligible variation between the three lignin materials: $M_w < 200$ Da, $M_n < 100$ Da, and $PDI < 0.5$ (see supplement materials). This observation applied to both the 10 g/L and 150 g/L experiments of the alcohol fractionations, the only exception being the 10 g/L KL EtOH soluble fraction. Of these solvents, IPA produced the smallest soluble fractions (360-410 Da) and EtOH the largest (440-510 Da), based on the number average molar masses of the soluble fractions (see supplement materials). Thus, based on the size distributions, these solvents produced similar soluble fractions regardless of the initial lignin material. This suggests that these fractionation solvents have potential for use in efficient and robust industrial fractionation processes that produce uniform soluble fractions from lignins of various origins. Significant differences between the lignins were detected only in the OH_{ph} values of the solvent-specific soluble lignin fractions. When the solvent content of the fractionation solution was changed, more deviation in the measured parameters was observed between the lignin materials. Binary similarities in the size distributions were found between KL and OL with 70% GVL as well as between OL and HL with 30% EtOH.

The PDI values of the pure IPA and EtOH soluble fractions were generally low (< 2.0), indicating a relatively narrow size distribution. In addition, the low PDI expressed

that the dissolution was more selective since the soluble fraction had less variability. Similarly, Goldmann et al. [19] reported that the lowest PDI values for the EtOH-water soluble Indulin AT lignin were achieved when the EtOH content of the solution was above 80%. When comparing the pure IPA and EtOH soluble fractions, the M_w , M_n , PDI, and OH_{ph} values of the EtOH soluble fractions were higher for all the lignins than the corresponding values of the IPA soluble fractions (see supplement materials). Similar patterns have been reported by Duval et al. [12] for Kraft lignin. Although the HSP values of the pure alcohols were generally close to those of the green solvents (Table 1), lignin dissolution into the pure alcohols was significantly lower.

Water resulted in the lowest degrees of dissolution. The calculated HSP values of the solvent mixtures increased with the addition of water (Table 2). However, the addition of water to the alcohol (IPA, EtOH) fractionation solutions increased the dissolution of the lignin materials. Regarding Kraft lignin fractionation using EtOH-water solutions, this is supported by Goldmann et al. [19] and Jääskeläinen et al. [14], who concluded that the maximum solubilities of Indulin AT were achieved when using 60% EtOH (93% solubility) and 80% EtOH (68% solubility) solutions, respectively. The same effect was observed with GVL: the highest dissolution values were obtained when utilizing 70% GVL. Thus, solutions with an HSP over 40 resulted in significantly low degrees of dissolution. When the solvent solution contained less water, and thus had a lower HSP (30–35 $MPa^{1/2}$), the dissolution of the lignins increased. However, the differences in dissolution with GVL solutions were not as significant as with the alcohols. This observation is supported by Xue et al. [8] regarding Kraft and organosolv lignin. In the present research, these findings were also discovered to apply to hydrolysis lignin. Xue et al. [8] concluded that the addition of a cosolvent (e.g., water) to a GVL solvent mixture was beneficial in breaking the hydrogen bonding in lignin. They discussed the effect of solvent mixture viscosity on lignin solubility, concluding that higher viscosity hinders lignin mobility in the solvent and thus might slow down the dissolution. In addition, when the water content in the GVL solution is higher than 50%, the GVL and water molecules interact more with each other and less with the lignin molecules, thus resulting in lower lignin solubility [8].

The structure of lignin has many aromatic building blocks, including phenolics. The phenolic hydroxyl groups (OH_{ph}) are a characteristic that makes lignin an interesting raw material and a substitute in various applications [1, 5]. The OH_{ph} content of the soluble lignin fractions was determined using

the $\Delta\epsilon$ -IDUS method, which is considered a semi-quantitative method to be used for comparison between lignin samples [33]. The overall OH_{ph} content of HL (1.95 mmol/g) was slightly less than that of KL (2.51 mmol/g) and OL (2.30 mmol/g), based on the DMF references. In addition, the accumulation of OH_{ph} followed differing patterns depending on the initial lignin. In general, the presence of water in moderate amounts increased the OH_{ph} content of the soluble fractions. For all three lignins, the pure IPA and EtOH soluble fractions exhibited low MW, although significant differences in the OH_{ph} content of these fractions were observed. In general, the EtOH soluble fractions had a significantly higher OH_{ph} content than the IPA soluble fractions.

The insoluble fractions were analyzed for their molecular size distribution for samples that had suitable amounts of insoluble material available from filtration and that were soluble in the DMF mobile phase (see supplement materials). For all the lignin materials with fractionations containing IPA and EtOH, the insoluble fractions generally had higher average molar masses (M_w and M_n) and PDI values than the soluble fractions, similarly to the observations by Jääskeläinen et al. [14] for insoluble EtOH Kraft lignin fractions. In the present study, this was also discovered to apply to the GVL insoluble HL fractions. The experimental data demonstrated that the soluble fractions more specifically contained low MW lignin and the compositions of the samples showed less deviation than the insoluble fractions. Low PDI in lignin fractions offers better control for further processing [2, 5]. Therefore, solvent fractionation can be considered as a very promising technology for applications requiring lignin fractions with enhanced homogeneity.

3.4 Effect of initial solid concentration in alcohol-water fractionations

For alcohol-water fractionations two initial solid concentrations (10 g/L and 150 g/L) were examined. Similarly to the results reported by Goldmann et al. [19] reported for Indulin AT in EtOH-water solutions, increasing the initial solid content of the fractionation solutions lowered the relative dissolution of all three lignin materials Fig. 4. Changes in the composition of the resulting soluble fractions were also detected. In particular, the OH_{ph} content of the alcohol-water soluble lignin fractions was higher with smaller lignin amounts. Thus, there was a clear difference in the dissolution of lignin materials into alcohol-water solutions in terms of the phenolic activity of the lignins.

It has been found that the smaller lignin molecules contain more OH_{ph} groups [1]. Thus, based on the differences in the OH_{ph} concentrations, it can be concluded that, for all the lignin materials studied, the smaller lignin molecules achieved maximum solubility between the two lignin concentrations, 10 g/L and 150 g/L (see supplement materials). Two exceptions were noticed: OL EtOH soluble and HL water-soluble fractions. In these fractions the larger lignin amounts resulted in a noticeable rise in OH_{ph} content.

The pure IPA soluble fractions showed the most significant differences in OH_{ph} content between the 150 g/L and 10 g/L fractionation samples: lower amounts of lignin resulted in notably elevated OH_{ph} content for all three lignin materials. Otherwise, the compositions of the soluble fractions were fairly identical between the two lignin concentrations, including the relative dissolution. Thus, the solubility of the small OH_{ph} bearing molecules of lignin reaches its maximum and has a close to null effect on the percentual dissolution due to their small mass. In addition, the PDI of the IPA soluble fractions was particularly low (<1.5), indicating the uniformity of the fractions. For EtOH solutions, the relative dissolutions changed more drastically than the OH_{ph} content of the soluble fractions. Of these, the biggest changes in OH_{ph} content were measured for the 30% EtOH soluble fractions, whereas the most notable changes in dissolution occurred in the 70% EtOH soluble fractions. With larger initial solid amounts (150 g/L), the 50% IPA and 70% EtOH soluble fractions presented very similar characteristic values for each lignin; however, no resemblance was detected between the lignin materials, only individually for each lignin (see supplement materials).

Comparing the insoluble samples of OL and HL, a clear difference between the 10 g/L and 150 g/L fractionation samples was observed (see supplement materials). The size distributions of insoluble samples from the 10 g/L fractionations leaned more toward larger lignin molecules, and samples from the 150 g/L fractionations toward smaller MW. For KL the effect was more subtle. This supports the claim that the smaller lignin molecules reach their maximum solubility at initial solid concentration of somewhere between 10 g/L and 150 g/L, since the insoluble samples from the 150 g/L fractionations have clearly greater amounts of smaller molecules. Based on these experiments, there are variations in the solubility limits of the lignin materials into alcohol-water solutions on the molecular level as well as between the different lignin materials.

4 Conclusions

This study provides a wide range of comparable and coherent data about industrially relevant solvents and their water solutions in lignin fractionation. In addition to DMSO, 70% GVL was also found to be very efficient at dissolving lignin (99 wt% KL, 95 wt% OL, and 30 wt% HL). In general, moderate additions of water to the fractionation solvents were found to be advantageous for the dissolution of lignin materials and accumulation of OH_{ph} . The highest accumulations of OH_{ph} were found in the 30% ethanol soluble fraction of Kraft lignin (3.05 mmol/g), the 70% ethanol soluble fraction of organosolv lignin (2.55 mmol/g), and the 90% sulfolane soluble fraction of hydrolysis lignin (2.70 mmol/g). Based on the characteristic values (M_w , M_n , and PDI), three fractionation solvents were found to produce similar solvent-specific soluble fractions regardless of the initial lignin material: pure isopropanol, pure ethanol, and 30% γ -valerolactone. This is highly beneficial for the development of robust industrial downstream processing of lignin since variation in the feedstock material would have an insignificant effect on the resulting fractions. Smaller lignin molecules were found to reach their maximum solubility at a lower initial solid content than

larger molecules. This reduces the OH_{ph} content of the soluble fractions with higher lignin concentrations, since smaller lignin molecules have generally more OH_{ph} activity. Based on the composition of the fractions produced, many possible downstream applications were found in the literature. The fractionation patterns identified in this study will promote the development of lignin fractionation technologies to enhance the applicability of technical lignins in the production of biobased materials.

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Supplement data

E-supplement data relating to this work can be found in the online version of the paper.

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