Fractionation of three different lignins by thermal separation techniques—A comparative study

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1 INTRODUCTION

As the demand for fossil oil has increased in recent decades and tends to continue this way, the demand for alternative and renewable resources has also increased with regard to substitute limited fossil resources (International Energy Agency, 2013; Laurichesse & Avérous, 2014). A
sustainable substitution for this fossil resources in chemical applications might be lignin due to its phenolic basic structure as bio-based building block for value-added products like epoxy resins or polyurethane foams (Asada, Basnet, Otsuka, Sasaki, & Nakamura, 2015; Wysocka, Szymona, McDonald, & Mamiński, 2016).

Lignin is a three-dimensional polymer and as part of the lignocellulosic biomass the second most abundant natural polymer next to cellulose. The lignin structure consists of three phenolic monomer building blocks p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) which are linked irregular through ether and carbon-carbon bonds resulting in heterogenic and hydrophobic macromolecules (Dorrestijn, Laarhoven, Arends, & Mulder, 2000; Sjöström, 1993). The structure of lignin as well as the amount of the three monomer units depends on the origin and type of the lignocellulosic biomass. Softwood lignin is almost exclusively built of G units, hardwood contains S and G units while grass lignin consists of an almost equal H/G/S mixture (Gellerstedt & Henriksson, 2008).

To separate lignin from the lignocellulose compound, intermolecular linkages are broken during the pulping process. Molecular weight as well as the composition of several functional group (hydroxy, methoxy, carboxyl) bearing moieties are affected by the choice of separation process (del Rio et al., 2012; Toledano, García, Mondragon, & Labidi, 2010).

The most widely available lignin is produced as a byproduct in the pulp and paper industry during the Kraft process and is usually burnt for energy production and recovery of pulping chemicals. Due to the application of sodium sulfide in the Kraft process, sulfur is incorporated in the form of aliphatic thiol groups into the lignin structure (Azadi, Inderwildi, Farnood, & King, 2013). In addition to the sulfur content, Kraft lignin has further drawbacks with regard to subsequent processes or applications as for example its low reactivity (Doherty, Mousavioun, & Fellows, 2011). Furthermore, new C-C bonds (5′–5′) are formed in condensation processes especially in softwood lignin, leading to an increase in the molecular weight (Duval, Vilaplana, Crestini, & Lawoko, 2015).

The percentage of lignin used in the production of commercial applications is about 5% of the more than 70 million tons of lignin produced annually. These applications include binders, dispersants, additives, and surfactants. Next to the industrial production of vanillin and dimethylsulfoxide (DMSO), the development of lignin-based polyols as precursors for polymer synthesis has been advanced (Laurichesse & Avérous, 2014). Furthermore, a thermoplastic polymer from lignin and natural fibers called Arboform® can be injection-molded, was produced and launched by Tecnaro (Germany; Inone-Kauffmann, 2009). Further developments were lignin-based carbon fibers (Norgren & Edlund, 2014), carbon nanoparticles (Kamegawa et al., 2016) and polyolefine-based composites containing amounts of lignin (Schorr, Diouf, & Stevanovic, 2014).

Chemical applications of lignin require well defined polydispersity, functionality, reactivity, and homogeneity which can be improved by fractionation of the lignin. The number of functional groups in lignin is connected to the molecular weight distribution; therefore, it can be expected that the thermal and mechanical properties of possible lignin-based polymer applications can be influenced by the choice of the lignin fraction used (Yoshida, Mörck, Kringstad, & Hatakeyama, 1990) as it was already proven for copolymers of lignin with highly branched prepolymer (Li, Sivasankarpillai, & McDonald, 2014).

Commonly applied fractionation techniques are solvent extraction, pH-depended successive precipitation of black liquor and membrane filtration, which have already been investigated in many studies, in particular for the fractionation of Kraft lignin (Duval et al., 2015; Li & McDonald, 2014). Although some studies on the fractionation of Organosolv (OS) lignin already exist, these are primarily limited to the solvent fractionation using water to precipitate lignin fractions from organic solvents (Domínguez-Robles et al., 2018; Sadeghifar et al., 2016). However, aqueous waste streams are always a problem of disposal and sample drying. Therefore, it seems more economical to focus on the use of organic solvents, which can be easily recovered by distillation. Furthermore membrane filtration and selective precipitation of OS lignin are poorly uninvestigated.

The fractionation of Kraft lignin by successive extraction using organic solvents with varying polarity was first described by Mörck, Yoshida, and Kringstad (1986). The authors used dichloromethane, n-propanol, methanol, and methanol/dichloromethane mixtures. Investigations on the applicability of low boiling organic solvents like diethyl ether and acetone (Ropponen et al., 2011), diethyl ether and methanol (Thring, Vanderlaan, & Griffin, 1996) and several others (Wang, Xu, & Sun, 2010) followed. Ionic liquids and organic solvents as fractionation reagents of soda lignin were compared by (Lauberts et al., 2017).

For selective precipitation the lignin fractions can be isolated directly from the black liquor by stepwise reduction of the pH value (Toledano, Serrano, García, Mondragon, & Labidi, 2010). In a different approach, the solid lignin is first dissolved in an organic solvent and subsequently precipitated by adding nonpolar or aqueous solvents. (Cui, Sun, & Argyropoulos, 2014) demonstrated a selective precipitation method for several softwood Kraft lignins by adding hexane to an acetone-lignin solution.

Membrane technology was used in ultrafiltration, applying membranes with differing cutoffs for the free-reagent
fractionation of various black liquors (Costa, Pinto, & Rodrigues, 2018; Toledano, García, et al., 2010; Toledano, Serrano, et al., 2010). As membranes of various material compositions are available, ceramic membranes were found to be the most suitable option for lignin fractionation due to their temperature and pH resistance (Jönsson & Wallberg, 2009).

So far, there is no study available comparing the application of three different fractionation methods on the same feedstocks, particularly considering the functionality of the product fractions obtained. Therefore, two OS lignins from short rotation poplar with bark and Miscanthus × gigantheus as well as a softwood Kraft lignin (Indulin AT) were fractionated into low (LMW), medium (MMW), and high molecular weight (HMW) fractions by means of three different thermal separation techniques: solvent extraction, successive precipitation, and membrane filtration. Suitable solvent mixtures for each lignin and fractionation method were determined. Indulin AT is used as reference to compare the investigated hardwood and grass lignins with an industrial lignin. The obtained lignin fractions were investigated regarding mass yield, structural (molecular weight distribution, elemental composition) and functional (OH group number) features. Finally, the use of the lignin fractions as bio-based building blocks for the generation of polyfunctional intermediates and other applications will be discussed.

2 | MATERIALS AND METHODS

2.1 | Materials

Indulin AT was purchased from Westrock Company (Atlanta, USA), delivered by Interchem Austria (Woergl, Austria) and used without further purification.

Both OS lignins (short rotation poplar with bark, “Poplar” and Miscanthus × gigantheus, “Misc”) were produced in an acid-catalyzed ethanol-water Organosolv process, performed in a 13 L batch reactor. The process parameters were set to 190°C, 205 min reaction time, 59 wt.% ethanol content, solid/liquid ratio as 1:7 for poplar and 190°C, 180-min reaction time, 40 wt.% ethanol content with a solid/liquid ratio of 1:8 for miscanthus, respectively. Sulfuric acid (0.5 wt.% of dry biomass) was used as catalyst. Lignin precipitation was performed by evaporation of the ethanol at 35°C and reduced pressure. The received lignin was washed several times with demineralized water (approx. 10 L for 200 g lignin) to remove sugars and all samples were air-dried.

All chemical reagents in this study were purchased from VWR, Sigma-Aldrich or deuterated solvents from Deutero GmbH and used as received without further purification.

2.2 | Fractionation methods

2.2.1 | Solvent extraction

Ten grams of Kraft lignin was first dissolved in 100 ml of various organic solvents by stirring for one hour. The insoluble lignin fraction was filtered off, dried in a vacuum oven over night at 30°C, and subsequently dispersed in 50 ml of another organic solvent. After stirring again for one hour, the precipitate was separated by filtration. The dissolved lignin fraction was obtained by evaporating the organic solvent at reduced pressure and dried in a vacuum oven at 30°C.

Following the same protocol, the OS lignins were fractionated using different organic solvents.

2.2.2 | Successive precipitation

Ten grams Indulin AT were dissolved in a 100-ml methanol/ dichloromethane solution (3:2). The insoluble lignin fraction was filtered off and dried at reduced pressure at 30°C. The liquid phase was precipitated twice by adding 50 ml several organic solvents successively. Each precipitate was filtered, the soluble fraction as received by evaporation of solvents at reduced pressure and all samples were dried in a vacuum oven at 30°C.

Ten grams of the two OS lignin samples was dissolved in 100 ml acetone. The fractions were processed by adding organic solvents as described above.

2.2.3 | Membrane filtration

Membrane filtration was performed using ceramic membranes (ZrO₂) supplied by TAMI Industries (Nyons, France). Multichannel and tubular membranes (2.5 mm length) with 1, 15, 50 and 150 kDa cutoffs, with an hydraulic diameter of 2.0 mm and a surface of 133.3 cm² were used. Ultrafiltration was performed in a cross flow mode, filtering the lignin solutions successively through two membranes with decreasing cutoffs.

The lignin samples were dissolved in acetone/water (5:1) with a concentration of 10 g/L. The dissolved lignin samples were first filtered through a membrane with bigger cutoff producing a concentrate and a permeate fraction. The obtained permeates were subsequently filtered again through a smaller cutoff membrane. The resulting three lignin fractions were precipitated by solvent evaporation and dried in a vacuum oven at a temperature of 30°C.

2.3 | Analytical characterization of lignin fractions

Elemental analysis of Organosolv (CHON) and Kraft lignin (CHONS) was performed using an Electron Flash EA 1112 device by Thermo Fisher Scientific (Karlsruhe, Germany).
The lignin samples were additionally analyzed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) after acetylation with pyridine and acetic anhydride (2:1) with a concentration of 2–3 g/L to determine $M_n$ (molar average molecular weight) and $M_w$ (number average molecular weight) (Glasser, Davé, & Frazier, 1993). The measurements were performed on a HPLC series 1100 device by Agilent Technologies (Germany) with a PSS SDV precolumn, 3 PSS SDV columns (100 Å, 1,000 Å, 5 µm) and a Diode Array Detector. Tetrahydrofuran (THF) was used as mobile phase with a flow rate of 1 ml/min. The column temperature was 35°C and polystyrene (THF) was used as mobile phase with a flow rate of 1 ml/min. The measurement standard deviation was 5 mmol/L and the OH group content of the internal standard cyclohexanol in mmol/g. Integration regions based on adjusted data published by (Pu, Cao, & Ragauskas, 2011) were used (see Supporting Information Table S2).

3 | RESULTS

The three investigated lignins were successfully fractionated into low (LMW), medium (MWW) and high molecular weight (HMW) fractions by solvent extraction, successive precipitation and membrane filtration. Several organic solvents and mixtures were investigated using a nonpolar or a low-polar solvent for the first fractionation step of solvent extraction followed by an organic solvent with higher polarity. As the native lignin samples already differ in elemental composition as well as in molecular weight distribution, different organic solvents were necessary for the fractionation processes.

3.1 | Kraft lignin

Investigations for solvent extraction of Indulin AT with THF and different methanol/dichloromethane mixtures (2:8, 4:6, 6:4, 7:3, and 8:2 v/v) were carried out. Extractions with these solvents or mixtures resulted in large amounts (>51%) of undissolved lignin (THF, methanol/dichloromethane 2:8 v/v), thus a too large HMW fraction, or an insufficient distribution of the molar mass between the fractions (methanol/dichloromethane 4:6, 6:4, 3:7, 8:2 v/v), respectively. The best fractionation results generated by solvent extraction of Indulin AT were reached using acetone followed by methanol.

The methanol/dichloromethane 6:4 mixture was then used for successive precipitation due to the good solubility properties. The resulting solid residue was considered as a fourth and additional HMW fraction. To compare the results with those of the OS lignins, weight percentages are indicated as proportion of the dissolved lignin. For successful precipitation isopropanol, diethyl ether and ethanol were emerged as suitable solvents, still, successive precipitation with ethyl acetate provided the best fractionation results regarding, molecular weight and polydispersity of fractions. Ultrafiltration of Indulin AT with 50 kDa membranes yielded too high amounts of concentrate (70%). The filtration of 150 kDa followed by an 8 kDa membrane resulted in only 7% LMW lignin.

According to the high initial molecular weight of Indulin AT, ceramic membranes with 150 and 50 kDa cutoffs were needed for uniform separation regarding mass distribution of the three generated fractions.

3.2 | Poplar lignin

Investigations on solvent extraction of Poplar lignin demonstrated suitable fractionation results using ethanol,
whereas diethyl ether and hexane extracted only 8% or no proportion of lignin, respectively. Acetone dissolved the raw lignin sample and was therefore used as dissolving agent for selective precipitation. In this case, hexane as precipitation solvent led to a heterogeneous mass distribution and was therefore unsuitable. Ultrafiltration, performed in an ethanol-water solution by means of a 150 kDa ceramic membrane, resulted in high amounts (71%) of concentrate. Appropriate results were reached by filtration of lignin dissolved in acetone/water (5:1) using a 50 kDa followed by 1 kDa cutoff membrane. For Poplar lignin isopropanol and methanol turned out to be the most suitable solvents for the generation of fractions with different molecular weight distributions and decreased polydispersity. For the precipitation of Poplar lignin out of an acetone solution, diethyl ether as a nonpolar organic solvent was suited.

3.3 | Miscanthus lignin

Ultrafiltration of Misc lignin in an ethanol-water solvent mixture using membranes of 150 kDa cutoff lead to a successful fractionation regarding mass distribution, but no fractionation in molecular weight.

The lignin solubility in acetone, ethanol, tetrahydrofuran, and methanol was too high (93%–100%) to be used as extraction solvents, whereas diethyl ether dissolved only 11% of substance. Isopropanol did not generate well-separated fractions regarding molecular weight. The combination of dichloromethane followed by ethanol extraction resulted in small amounts of LMW lignin. Precipitation of Misc lignin by adding ethyl acetate to an acetone solution generated a LMW fraction with more than 90% of the original mass.

Regarding solvent extraction, Misc lignin was most successfully fractionated by diethyl ether and ethyl acetate. Hexane was well suited for the precipitation of the Misc lignin out of an acetone solution. For ultrafiltration of Misc lignin out of an acetone solution, 50 and 1 kDa cutoff membranes gave the best results, equal to Poplar lignin.

In the following section, only the best fractionation results are shown and discussed.

For the evaluation of type and average number of OH groups, all generated lignin fractions and unfractionated lignin samples were analyzed by $^{31}$P-NMR after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP). The OH-group numbers were attributed to aliphatic, phenolic and carboxylic OH-groups. The number of phenolic OH-groups of Poplar and Misc lignin summarizes the groups associated to S, G, and H units. As Indulin AT contains no S units, groups substituted at the C5-carbon were attributed to G and H units (Figure 1).

The results concerning $^{31}$P-NMR of LMW, MMW, and HMW lignin fractions as well as the unfractionated samples of Indulin AT, Poplar and Misc lignin are shown in Figure 2.

4 | DISCUSSION

The objective of this study was the examination of technical options for the molecular sorting of several lignin types (soft wood Kraft lignin, hard wood and grass OS lignin) into LMW, MMW and HMW fractions with respect to their yield (mass distribution) and additional structural features (polydispersity, type, and amount of functional OH-groups, elemental composition) by three different thermal separation techniques. However, significant differences in properties of the resulting lignin samples were observed, due to the lignin origin and the separation techniques applied.

4.1 | Elemental composition

The three investigated lignins show only little differences in elemental composition except for the sulfur content as presented in Table 1. The OS lignins contain no sulfur, whereas Indulin AT has a sulfur content of 1.4%. The sulfur content found in Indulin AT samples was not enriched in any fraction, except for the methanol/dichloromethane insoluble lignin generated by successive precipitation. The remaining sulfur is distributed evenly among the three fractions. With solvent extraction, sulfur content decreases from HMW to LMW fractions and using membrane filtration the highest percentage of sulfur is found in the LMW fraction.

The relative carbon content of the lignin samples increased from HMW to LMW lignin. The increasing carbon content is accompanied for the most part by enhanced hydrogen content and, accordingly, a decrease in the oxygen content. This is related to the distribution of OH-groups within the fractions. In addition, a higher share of available and intact ether bonds in the HMW lignin is assumed due to the lower depolymerization degree of HMW lignin fragments.

Small amounts of nitrogen were detected in the lignin samples, probably originating from cell proteins (Dominguez-Robles et al., 2018), and did not differ greatly within the fraction. The determined content varies from 0% to 1.2%.

4.2 | Molecular weight

The original lignins differed strongly regarding their molecular weight: Indulin AT had a more than three times higher and Poplar lignin an almost twice as high molecular mass than Misc lignin. Irrespective of the molar mass difference, all three lignin samples were successfully fractionated into
one fraction owning a higher or equal molecular weight than the original lignin sample, in one fraction with a significantly lower molecular weight and one fraction with a MMW. Meaning, both $M_w$ and $M_n$ decrease from HMW to LMW fraction, accompanied by a simultaneous decrease in polydispersity. Weight average, number average molecular weight, and polydispersity of the lignin samples are shown in Table 2.

The mass distribution (yield) of the generated fractions (as also presented in Table 1) generally show a tendency to higher amounts of the HMW fraction (40%–70%) followed by MMW and LMW fractions, which mostly show the lowest yields. However, there are some exceptions. From Misc lignin, only 31% of HMW are separated by solvent extraction. Regarding successive precipitation, it was found that the MMW fractions are separated with lower amounts (3%–13%) compared to those of the LMW fractions for Indulin AT and Misc with 48% and 33%, respectively.

The molecular weight distribution of lignin is an important factor for possible end use applications of lignin, as it determines solubility, viscosity or thermal stability properties (Aro & Fatehi, 2017; Asada et al., 2015). Therefore, different organic solvents had to be found to ensure successful separation regarding molar mass. For example, methanol turned out to be a suitable solvent for the extraction of MMW lignin of Poplar lignin and Indulin AT, although the unfractionated Kraft lignin. Polydispersity ($M_w/M_n$) of Indulin AT was reduced to a minimum of 1.9, whereas for Poplar and Misc lignin it was decreased to 1.6 and 1.4, respectively. In comparison with studies using pH-dependent fractionation of Kraft lignin black liquor, all three techniques applied on Indulin AT using organic solvents resulted in a lower $M_w$ (249–2,440 g/mol difference) and polydispersity (0.9–2.5 difference), with the exception of membrane filtration. Another advantage is saving the removal of residual acid or formed salts (Alekhina, Ershova, Ebert, Heikkinen, & Sixta, 2015).

The results of the molecular weight determination demonstrated the complexity of the relation between the nature of the suited solvent for fractionation and the native molar mass of the lignin. For example, methanol turned out to be a suitable solvent for the extraction of MMW lignin of Poplar lignin and Indulin AT, although the unfractionated lignin samples differed by more than 2000 g/mol. In conclusion, the polarity of the required solvent for dissolution increased with enhanced molar mass of the original lignin sample. Simultaneously, the molar mass of the dissolved portion decreases as the polarity of the organic solvent also decreases. This becomes evident, for example, when comparing successive precipitation of Poplar and Misc lignin from acetone solution: Ethyl acetate with a relative polarity value of 0.228 for poplar with a higher initial molecular weight lignin and diethyl ether with a value of 0.117 for Misc with a lower initial molecular weight lignin.
were required for the precipitation of lignin fractions (polarity values from Reichardt, 2006).

Compared with the study by Domínguez-Robles et al. (2018) on the fractionation of OS lignin with a similar initial molecular weight as Poplar (2,520 g/mol), for the HMW fraction a similar but for the LMW fraction a much lower mass was achieved. Polydispersity is approximately consistent with LMW lignin, although it increased about 1.0 for HMW lignin.

Despite good fractionation results, differences in the quality of the fractionation processes are evident, depending on the separation technique used. Indulin AT for example was successfully fractionated by membrane filtration into three fractions with optimally divided $M_w$ and $M_n$, but...
TABLE 1  Mass percentages and elemental composition of HMW, MMW, and LMW dry matter fractions of Poplar, Misc, and Kraft lignin, generated by successive solvent extraction, selective precipitation and membrane filtration

|                      | Mass (%) | Nitrogen (%) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Sulfur (%) |
|----------------------|----------|--------------|------------|--------------|------------|------------|
| Indulin AT           |          | 0.69         | 63         | 5.6          | 28         | 1.4        |
| Solvent extraction   |          |              |            |              |            |            |
| HMW                  | 66       | 0.62         | 62         | 5.4          | 29         | 1.6        |
| MMW                  | 24       | 0.88         | 65         | 5.8          | 27         | 1.3        |
| LMW                  | 13       | 0            | 68         | 6.6          | 24         | 1.0        |
| Successive precipitation |      |              |            |              |            |            |
| MeOH/DCM insoluble   | 20       | 0.86         | 55         | 5.2          | 32         | 2.4        |
| HMW                  | 40       | 0.48         | 63         | 5.7          | 28         | 0.76       |
| MMW                  | 13       | 0.53         | 63         | 5.8          | 29         | 0.89       |
| LMW                  | 48       | 0.40         | 67         | 6.5          | 25         | 0.64       |
| Membrane filtration  |          |              |            |              |            |            |
| HMW                  | 52       | 0.77         | 63         | 5.6          | 28         | 1.4        |
| MMW                  | 33       | 0.73         | 64         | 5.6          | 27         | 1.3        |
| LMW                  | 12       | 1.1          | 63         | 6.0          | 26         | 1.9        |
| Poplar               |          |              |            |              |            |            |
| Solvent extraction   |          |              |            |              |            |            |
| HMW                  | 50       | 0.87         | 64         | 5.7          | 29         | –          |
| MMW                  | 28       | 0.74         | 65         | 5.8          | 28         |            |
| LMW                  | 16       | 0.76         | 67         | 6.2          | 26         |            |
| Successive precipitation |     |              |            |              |            |            |
| HMW                  | 49       | 1.2          | 63         | 5.5          | 30         |            |
| MMW                  | 3        | 1.2          | 64         | 5.7          | 30         |            |
| LMW                  | 16       | 0.85         | 66         | 6.0          | 29         |            |
| Membrane filtration  |          |              |            |              |            |            |
| HMW                  | 50       | 0.92         | 65         | 5.9          | 28         |            |
| MMW                  | 40       | 0.87         | 67         | 7.2          | 25         |            |
| LMW                  | 6        | 0.86         | 65         | 6.3          | 27         |            |
| Misc                 |          | 0.62         | 65         | 5.5          | 27         |            |
| Solvent extraction   |          |              |            |              |            |            |
| HMW                  | 31       | 1.29         | 65         | 5.5          | 28         |            |
| MMW                  | 69       | 0            | 67         | 5.9          | 28         |            |
| LMW                  | 4        | 0            | 68         | 6.1          | 27         |            |
| Successive precipitation |     |              |            |              |            |            |
| HMW                  | 50       | 0.84         | 66         | 5.6          | 28         |            |
| MMW                  | 10       | 0.63         | 67         | 5.7          | 28         |            |
| LMW                  | 33       | 0            | 68         | 5.8          | 27         |            |
| Membrane filtration  |          |              |            |              |            |            |
| HMW                  | 43       | 0.75         | 67         | 5.8          | 27         |            |
| MMW                  | 39       | 0.77         | 67         | 5.9          | 26         |            |
| LMW                  | 13       | 0.57         | 68         | 6.4          | 26         |            |

the polydispersity was hardly decreased and has even increased for two fractions. Ultrafiltration of Misc lignin led to fractions with only slight differences in molecular weight ($M_w$ and $M_n$), but the polydispersity has significantly increased from HMW to LMW fraction. An important point in ultrafiltration, in addition to the adaption of
the membrane cutoff, is the complete dissolution of the lignin in a suitable solvent as experiments in ethanol/water mixtures for OS lignins showed.

### 4.3 Functional groups

OH- groups represent the most common functional groups in lignin and therefore have a great impact on reactivity and other properties. Moreover, the information on type and number of OH-groups constitutes an important indication for modification reactions or further synthesis to polymers (Arbenz & Avérous, 2015).

Indulin AT contains the highest number of aliphatic OH-groups (2.27 mmol/g) compared to Poplar lignin (1.92 mmol/g) and Misc lignin (1.24 mmol/g). However, a similar number of phenolic OH-groups was found in Misc lignin and Indulin AT (3.40 and 3.32 mmol/g), whereas Poplar lignin exhibited 2.94 mmol/g of phenolic OH-groups.

The results of Indulin AT regarding OH-groups comply with findings of other studies focusing on softwood Kraft lignin (Costa et al., 2018; Liitiä et al., 2014; Ropponen et al., 2011; Sadeghifar, Cui, & Argyropoulos, 2012, Cui et al., 2014).

The differences in OH-group contents originate from the applied pulping process. As part of the delignification process, α-O-4 and β-O-4 ether bonds are cleaved by hydrolysis during the acid-catalyzed Organosolv process. The acid-catalyzed cleavage of β-O-4 ether bonds is usually accompanied by the separation of aliphatic OH-groups and the formation of new phenolic OH-groups (McDonough, 1992).

The significantly lower molar mass of the Misc lignin indicates that it is a more hydrolyzed lignin compared to Poplar lignin and thus explains the different occurrence of OH-groups. The applicability of LMW Poplar lignin for different chemical processes, such as modification reactions, is further enhanced by a considerably higher number of more reactive and sterically unhindered aliphatic groups compared to Misc lignin. The number of aliphatic and phenolic OH-groups is not only an important factor for the reactivity of the lignin, but these groups also essential for subsequent reactions on the existing OH-groups in order to incorporate various functional groups into the lignin molecule (Laurichesse & Avérous, 2014).

In general, the aliphatic OH-number declines with decreasing molecular weight from the HMW to the LMW fraction. Simultaneously, the number of phenolic and carboxylic OH-groups increases, resulting in a lower aliphatic to phenolic OH-group ratio which is in line with other fractionation studies investigating Kraft lignin from *Eucalyptus globulus* (Costa et al., 2018) or technical lignins from spruce (*Picea abies*) and birch (*Betula pendula*) (Ropponen et al., 2011).
et al., 2011). In particular, for Indulin AT, this behavior was confirmed regardless of the separation method used.

Apart from this tendency, some deviations regarding the OS lignins can be observed. One exception is observed in the successive precipitation of Poplar lignin: the generated MMW fraction contains more aliphatic and less phenolic OH-groups compared to HMW and the LMW lignin. This results in an unexpected high number of aliphatic OH-groups in the MMW fraction. Furthermore, the results of ultrafiltration of Poplar and Misc lignin show discrepancies compared to the general trend. The phenolic OH-number of Poplar lignin declines from HMW to LMW fractions and the content of carboxylic OH-groups gets smaller with decreasing molecular weight of Misc lignin.

In summary, each thermal separation technique under investigation resulted in LMW, MMW, and HMW lignin fractions after specific experimental adjustments to the respective lignin. In particular, methods for the fractionation of the unstudied OS lignin from Poplar and Misc were shown. Significant differences between the evaluated techniques regarding molar mass and number of the different OH-groups in the generated fractions were observed. Indulin AT showed little difference in the distribution of the OH-groups within the fractions. However, solvent extraction and successive precipitation achieved a better separation of the molar masses and overall resulted in significantly reduced polydispersity. The most suitable separation method for OS lignin from Poplar turned out to be solvent extraction and successive precipitation for OS lignin from Misc, regarding fraction properties in terms of mass distribution, molar mass separation, polydispersity, and functionality characterized by OH-group distribution.

The fractionation of lignin is an indispensable interim step for the generation of lignin-based chemical building blocks to provide fractions of different structural and functional properties. HMW lignin, for example, provides potential use in adhesives, carbon fibers, and blends (Wells et al., 2013).

Particularly interesting for use in polymer synthesis are the generated LMW fractions, which might serve as Bisphenol A substitute in the production of epoxy resins (Asada et al., 2015). The applicability of LMW Poplar lignin is further enhanced by a considerably higher number of more reactive and sterically unhindered aliphatic groups compared to Misc lignin.

Lignin fractions with high phenolic OH-number are well suited for modification reactions, leading to the conversion of phenolic to aliphatic OH-groups under chain extension and to the formation of lignin with polyl-like character, which might act as a building block for polyurethane synthesis (Ahvazi, Wojciechowicz, Ton-That, & Hawari, 2011). Despite the area of polymer production, LMW lignin might be applicable in bioscience and medicine due to its high antioxidant properties (Calvo-Flores, Dobado, Isac-García, & Martín-Martínez, 2015).

After fractionation, strategies for the use of the OS lignins of Poplar and Misc as intermediates for lignin-based polymer synthesis and various applications can be developed based on the information regarding the molar mass and existing functional groups.

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