

Effect of Process Parameters in Pilot Scale Operation on Properties of Organosolv Lignin

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One of the major challenges in transforming from fossil to bio-based materials is the production of biomass-derived intermediates in a well-described, reproducible manner at a relevant scale. Lignin, as the only renewable aromatic resource, will play an important role in the future bioeconomy. Various grades of lignin were produced at Fraunhofer CBP's pilot plant by variations of the following parameters: raw material (beech wood, spruce wood, and wheat straw), H-factor (combining the effect of temperature and time), addition of sulfuric acid $\omega(\text{H}_2\text{SO}_4)$, and the precipitation procedure. During the optimization of the process conditions for lignin production an in-depth analytical characterization was done by acid hydrolysis with subsequent anion-exchange chromatography (AEC), elementary analysis, ³¹P-nuclear magnetic resonance spectroscopy (NMR), size-exclusion chromatography (SEC), and differential scanning calorimetry (DSC) to monitor changes in structure and selected properties.

Keywords: Lignin; Organosolv; Beech; Spruce; Straw

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INTRODUCTION

Substituting fossil fuels with renewable resources is a recent growing trend in politics, research, and industry. The main determining factors for this development are price developments and regional availability in the markets for fossil fuels as well as greater awareness of sustainability and climate protection (BMELV *et al.* 2012).

Compared with the energetic use of renewable resources, its material use carries a high innovation potential and can contribute to achieving climate protection goals by the fixation of carbon into long-life products. For example, several building materials, such as resins, foams, and carbon fibers are currently dependent on fossil-based chemicals. Potential substitutes on a renewable basis can be produced within a biorefinery based on the separation of abundant lignocellulosic biomass, such as wood and straw, into its constituent cellulose, hemicelluloses, and lignin. Fractionation is a prerequisite for making use of these biopolymers in dedicated applications.

One method of fractionation is the organosolv process, which is based on the delignification of biomass with hot (aqueous) aliphatic alcohols (Kleinert and v. Tayenthal 1931). Significant efforts have been made to increase the economic and ecologic viability of this technology. These include the variation of solvents, expanding the original terminology of organosolv to other organic solvents such as acetone (Smit and Huijgen 2017), aqueous formic and acetic acids, and their corresponding peroxyacids (Sundquist and Poppius-Levlin 1992; Dapía *et al.* 2000; Snelders *et al.* 2014). The addition of acids or alkali accelerates the organosolv process (Sahin 2003; Constant *et al.* 2015; Rinaldi *et*

al. 2016), and in combination with water based pretreatments, there is enhanced impregnation and/or hemicellulose removal (Huijgen *et al.* 2012; Moniz *et al.* 2015). Laure *et al.* (2014) assessed a biorefinery concept based on the organosolv process pointing out its ecologic and economic feasibility provided the valorization of all the obtained fractions cellulose-rich pulp, hemicelluloses, and lignin, the latter being in the focus of this study.

Lignin, an aromatic macromolecule, is primarily derived from methoxylated hydroxycinnamyl alcohol building blocks *via* enzymatically generated radicals; it comprises up to 30% of lignocellulosic biomass (Ralph *et al.* 2004). In contrast to cellulose, which has a well described and defined structure, lignin is characterized by a variety of distinct and chemically different linkages and structural motifs such as β -aryl ether, phenylcoumaran, and resinol with varying occurrences depending on the type of biomass (Rinaldi *et al.* 2016). However, through to its higher carbon and lower oxygen content it is an attractive and unique feedstock for the production of bio-based materials and chemicals. Furthermore, the high purity of lignin obtained by an organosolv process in general, and the absence of sulfur in particular, is an additional promising advantage.

The precipitation and separation of lignin dissolved in organosolv or kraft spent liquors is a crucial step influencing heavily the lignin properties as well as the process recycling of process chemicals and the process economics. For kraft lignin, the LignoBoost process and the LignoForce process became state of the art and have been implemented on industrial scale (Tomani 2010; Appita 2013; Kouisni *et al.* 2014; Hubbe *et al.* 2019). In contrast to those aqueous, alkaline processes, where lignin is precipitated by neutralization with CO₂ and mineral acids, lignin is usually precipitated from organosolv liquors by dilution with water to lower the solvent concentration and thus the solubility of the lignin. As the addition of water into the organosolv spent liquors is unfavorable from an energetic point of view, the direct evaporation of ethanol seems the better solution. Problems with the formation of sticky lignin precipitates occurring during solvent evaporation have recently been solved at the laboratory bench scale (Schulze *et al.* 2016), and are now being considered at the pilot scale.

Other issues with the processing of organosolv spent liquors are related to the particle size of the precipitated lignin, its filterability and with the precipitation of lignin during cooling and storage of the spent liquors. The separation of different molecular weight fractions from organosolv spent liquors has been described by Hallberg *et al.* (2012) in the patent US8227004. In this paper, a high molecular weight fraction separated from the organosolv spent liquor by cooling is described.

Beside the technical questions, the challenge for the successful implementation of an organosolv process lies within the utilization of all fractions and in convincing industry to change to new feedstocks, such as organosolv lignin. This implies showing the possibility of obtaining lignin in a reproducible well-characterized way in an industry-relevant scale on the one hand and benchmarking its characteristics to commercial kraft lignin as another lignin quality on the other hand.

EXPERIMENTAL

Materials

The composition of various materials was determined according to Sluiter *et al.* (2008), as follows: beech (43.2% cellulose, 20.6% hemicellulose, 24.5% lignin), spruce

(46.0% cellulose, 21.2% hemicellulose, 28.9% lignin), and wheat straw (35.2% cellulose, 21.1% hemicellulose, 24.2% lignin). Lignin was obtained by organosolv-pulping in a digester with a capacity of 400 L within an integrated pilot plant, as depicted in Fig. 1. The H-factor was used to express the pulping severity in terms of pulping temperature and time based on an activation energy of 125.6 kJ/mol (Sixta *et al.* 2013). The process parameters varied according to the feedstock and are summarized in Table.

Table 1. Pulping Process Parameters

Feedstock	$\omega(\text{EtOH})$ (%)	T_{\max}	time t at T_{\max} (min)	$\omega(\text{H}_2\text{SO}_4)$ (%)
Beech	50	170/180	80/180	0.5/1.0
Spruce	65	170	80	1.0
Wheat straw	50	190	40	2.9

Lignin was precipitated by dilution with two volumes of water in one step, in two steps, or by evaporation (Leschinsky *et al.* 2017). Furthermore, lignin that readily precipitates after the cooling of black liquor but before precipitation by dilution with water (spontaneous precipitation) was collected. For comparison, P1000 (soda; GreenValue, Media, USA) and BioChoice (kraft pine lignin, LignoBoost, Domtar, Plymouth, MA, USA) lignins were used as commercial lignin qualities.

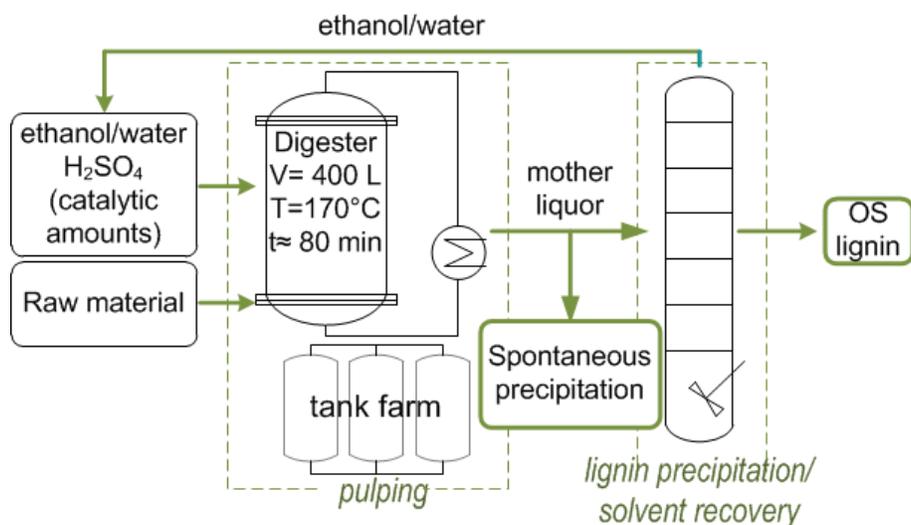


Fig. 1. Simplified process scheme of lignin production by the organosolv (OS) pulping in pilot scale

Methods

Composition

The lignin content and carbohydrate composition of the lignin were measured after a two-step hydrolysis with H₂SO₄. After filtration of the hydrolyzate, the lignin content (hydrolysis residue) was determined gravimetrically and the water soluble monosaccharides were detected by borate complex anion-exchange chromatography (Lorenz *et al.* 2016).

The ash contents of the lignin samples were determined according to TAPPI T413 om-06 (2010) by combustion at 525 °C in a muffle furnace and the subsequent gravimetric detection of the resulting residue.

³¹P-NMR

The aliphatic and aromatic hydroxyl group quantification was performed by ³¹P-NMR spectroscopy using a Bruker Avance III HD 400 MHz spectrometer (Rheinstetten, Germany) according to the method of Granata and Argyropoulos (1995). The lignin samples were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and cholesterol was used as internal standard. During acquisition, 264 scans were accumulated at 25 °C with a pulse angle of 45° and a relaxation delay of 20 s.

Elementary analysis

The elemental composition (CHNS) of the lignin was analyzed with a Elementar vario EL cube (Langensfeld, Germany). C, H, N, and S were measured in duplicate and the remaining percentage was attributed to oxygen.

Size-exclusion chromatography (SEC)

The separation was performed by two C PolarGel-M columns (300 × 7.5 mm; Santa Clara, CA, USA) in series and a PolarGel-M guard column (50 × 7.5 mm). Dimethyl sulfoxide (DMSO) with 0.1% LiBr was used as eluent. Before injection, samples and solvent were filtered using regenerated cellulose (Chromafil RC-45, Macherey-Nagel, Düren, Germany, 0.45 μm). The columns were calibrated with glucose and polyethylene glycol (180 to 82,250 g/mol, Agilent, Santa Clara, CA, USA) as standards using an RI detector. Lignin analyses were performed by ultraviolet (UV) detection at 280 nm, and phenol red was used to match detectors. The data was recorded and evaluated using WinGPC Unichrom V8.10 software (polymer standard service; Mainz, Germany).

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of lignin was determined by DSC using a Mettler Toledo DSC821e (Giessen, Germany). Approximately 5 mg of the lignin sample was placed in an aluminum crucible. A 5-step temperature profile was applied with the following heating and cooling phases:

- heating from 25 °C to 105 °C including a 20 min isothermic phase for drying,
- cooling phase to -60 °C,
- first heating phase from -60 °C to 200 °C for lignin stabilization,
- cooling phase to -60 °C,
- second heating phase from -60 °C to 200 °C to measure T_g .

Heating and cooling rates were set to 10 °C min⁻¹ for all steps. The glass transition temperature was determined from the midpoint of the turning point in the DSC curves of the second heating phase. For further details, please refer to Abarro *et al.* (2016).

RESULTS AND DISCUSSION

Lignin was obtained by the organosolv process using various raw materials and process parameters.

Reproducibility of Lignin Production

The reproducibility of lignin production was evaluated based on three trials in Fraunhofer's integrated pilot plant using beech as raw material and the following pulping

parameters: $c(\text{EtOH}) = 50\%$, $H\text{-factor} = 1000$, and $\omega(\text{H}_2\text{SO}_4) = 1\%$ on wood, precipitation by dilution. The studied characteristics are listed in Table 2. High values ($> 10\%$) for the relative deviation are generally due to extremely low mean values (*e.g.*, in case of carbohydrate content). According to the presented data, lignin was obtained in a reproducible way with regard to purity, elementary composition, functional group content, and molar mass. The deviation in yield, lignin content, and elemental analysis was very low. The deviation of ^{31}P -NMR data for aliphatic and phenolic moieties (3 to 5%) and the molar mass data (5%) were within an excellent range for these methods. Only components present in small amounts, such as carbohydrates, ash, and carboxyl groups, showed higher deviations, which was attributed to the higher analytical uncertainties for the analysis of minor components. Thus, the considerably high standard deviation obtained for the glass transition temperature is proposed to be rather due to analytical difficulties in the determination of T_g of lignin than due to lignin heterogeneity. This issue has been addressed previously (Sjöholm *et al.* 2013).

Table 2. Characteristics of Lignin Produced from Beech Wood by a Pilot Scale Organosolv Process ($n = 3$, DS = Dry Substance)

Characteristic	Mean Value	Standard Deviation	Relative Deviation (%)
Yield (Relative to Dry Wood) (%)	12.9	0.5	3.8
Composition (% DS)			
Lignin Content	94.2	0.8	0.8
Carbohydrate Content	0.2	< 0.1	10.5
Ash Content	0.2	0.1	29.4
Elementary Composition (% DS)			
Carbon	65.6	0.1	0.1
Oxygen	28.2	< 0.1	0.1
Hydrogen	5.9	< 0.1	0.3
Functional Groups ($\text{mmol}\cdot\text{g}^{-1}$ DS)			
Aliphatic Hydroxyl	1.3	< 0.1	3.0
Phenolic Hydroxyl	3.1	0.1	4.6
Carboxyl	0.1	0.1	38.5
Molar Mass			
Weight-average M_w ($\text{g}\cdot\text{mol}^{-1}$ DS)	2600	100	4.9
Number-average M_n ($\text{g}\cdot\text{mol}^{-1}$ DS)	1000	50	4.9
Polydispersity	2.6	0.1	1.9
Glass Transition Temperature T_g ($^{\circ}\text{C}$)	124	11.4	9.2

Effect of Raw Material

A variety of lignins was obtained from different raw materials including hardwood (beech), softwood (spruce), and herbaceous plants (straw). Organosolv lignin from spruce was a novel quality provided in this scale, as successful organosolv fractionation of softwoods has rarely been reported beforehand. The purity of lignin is a crucial parameter for several lignin applications, such as carbon fibers (Ragauskas *et al.* 2014). Table 3 lists the lignin, carbohydrate, and ash content of the samples with regard to commercially available references. Lignins of high purity having an acid-insoluble lignin content of more than 94% were obtained from the organosolv pulping independent of the raw material (optimized conditions). In this regard, all of the produced lignins were of higher quality than the studied commercial ones.

Table 3. Composition of Organosolv Pulping Lignin (OS) Obtained from Different Raw Materials and Commercially Available Lignins (based on dry substance)

Sample	Lignin (%)	Carbohydrate (%)	Ash (%)
OS-beech ¹	94.2	0.19	0.17
OS-spruce ¹	96.0	0.39	0.10
OS-straw	95.4	0.23	0.35
Soda (Protobind 1000)	86.7	2.53	1.48
Kraft (Domtar)	88.1	2.04	2.97

¹Mixture of lignin obtained from three different pulping trials using optimized parameters

Elementary analysis was used to measure the oxygen, carbon, hydrogen, nitrogen, and sulfur contents (Table 4). Lignins obtained by the organosolv process were free of sulfur, which in contrast is still present in the kraft lignin even when obtained by the Lignoboost process. This has also been recently reported by Abdelaziz and Hultberg (2017). Minor proportions of nitrogen of less than 0.7% were found in all lignin samples. Only organosolv lignin obtained from straw contains a larger amount being 1.36%. Nitrogen contents in lignins of herbaceous origins have also been reported previously *e.g.* by Strassberger *et al.* (2015) who determined a nitrogen content of 1.0% in Protobind 1000.

Table 4. Elementary Composition of Organosolv Pulping Lignin (OS) Obtained from Different Raw Materials and Commercially Available Lignins based on Dry Substance

Sample	C (%)	H (%)	O (%)	N (%)	S (%)
OS-beech ¹	65.64	5.94	28.17	0.26	0.00
OS-spruce ¹	67.98	5.96	25.90	0.16	0.00
OS-straw	67.20	6.41	25.03	1.36	0.00
Soda (Protobind 1000)	64.02	5.92	28.65	0.79	0.62
Kraft (Domtar)	64.03	5.84	27.94	0.25	1.94

¹Mixture of lignin obtained from three different pulping trials using optimized parameters

The molar ratio of hydrogen to carbon can be used as an indicator for the degree of aromaticity, and the molar ratio of oxygen to carbon as an indicator for the degree of oxygenation, as illustrated in Fig. 2 as a van-Krevelen diagram.

In general, lignins produced from the organosolv pulping using various feedstock and parameters exhibit a wide range of H/C and O/C ratios. It is worth noting that it was possible to produce lignin with a comparatively low degree of oxidation and a high degree of aromaticity and hence, high carbon contents by organosolv pulping. This is desirable for some applications, *e.g.*, the production of carbon fibers and could be advantageous compared with commercial soda and kraft lignin, which are frequently used for carbon fiber development after purification or chemical modification.

In addition, lignin with a promising composition in this regard (low H/C and low O/C ratio) was obtained by using spruce as feedstock. This is especially interesting, as softwood such as spruce is also used as raw material for kraft pulping, but the obtained kraft lignin had a noticeably lower carbon content compared with the organosolv lignin. Thus, organosolv technology is flexible with regard to feedstock, and it is able to produce unique lignin qualities.

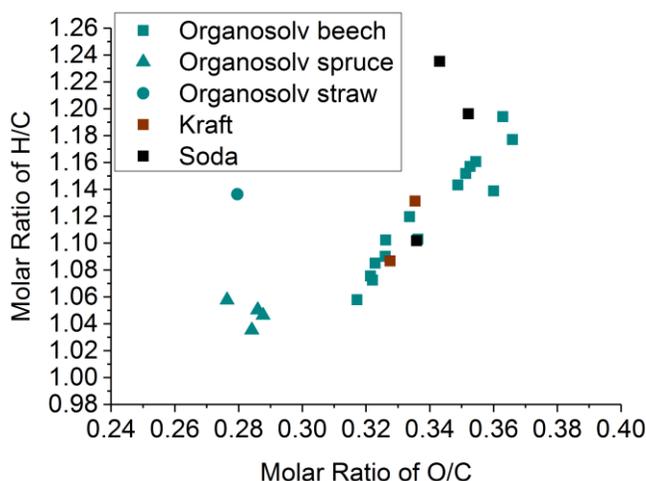


Fig. 2. Van-Krevelen diagram of soda and kraft (commercial) lignin and organosolv pulping lignin from various raw materials (indicated) and a wide range of process parameters (based on dry substance)

The content of hydroxyl groups plays a key role in lignin chemistry and its subsequent applications, as they influence its solubility, miscibility, and act as reactive sites. Figure 3 illustrates the aromatic *versus* the aliphatic hydroxyl content with regard to different raw materials in comparison to commercial lignins. Phenolic hydroxyl groups are formed during pulping due to the cleavage of aryl-ether-cleavages. The highest content is found in kraft lignin, as the active species in this pulping method HS^- is a strong nucleophile and results in cleavage of β -ether linkages in non-phenolic and phenolic units, the latter being a major depolymerisation pathway *via* a quinone methide intermediate. In contrast, the quinone methide formed during soda pulping is more frequently transformed *via* the scission of $\text{C}_\beta\text{-C}_\gamma$ bonds and the liberation of formaldehyde (Rinaldi *et al.* 2016). These aspects result in generally lower amounts of both aliphatic and phenolic hydroxyl group contents compared with kraft lignin.

Delignification during acid- or auto-catalyzed organosolv pulping is based on the acidity of the liquor as well as its function as an organic solvent, enabling both the degradation and dissolution of lignin. Further, lignin may undergo the cleavage of β -O-4 linkages starting from both phenolic and non-phenolic units under acidic conditions. However, a rather high stability of the linkage has been described for the latter under organosolv conditions without an acid catalyst (Schrems *et al.* 2012). By this, the content of phenolic hydroxyl is generally lower compared to kraft lignins but can be tuned by various amounts of acidic catalyst (*cf.* 3.3). The content of aliphatic hydroxyl groups is also strongly dependent on pH during organosolv pulping. The increase in the acidity of the liquor results in the elimination of the γ -substituent, resulting in the formation of formaldehyde and hence a loss of aliphatic hydroxyl groups (*cf.* 3.3) (Sturgeon *et al.* 2014; Rinaldi *et al.* 2016). In addition, Schrems *et al.* (2012) showed in model compound studies the derivatization of aliphatic hydroxyl groups to ethoxyl groups followed by the elimination of ethanol at temperatures above 160 °C and hence the loss of aliphatic hydroxyl groups.

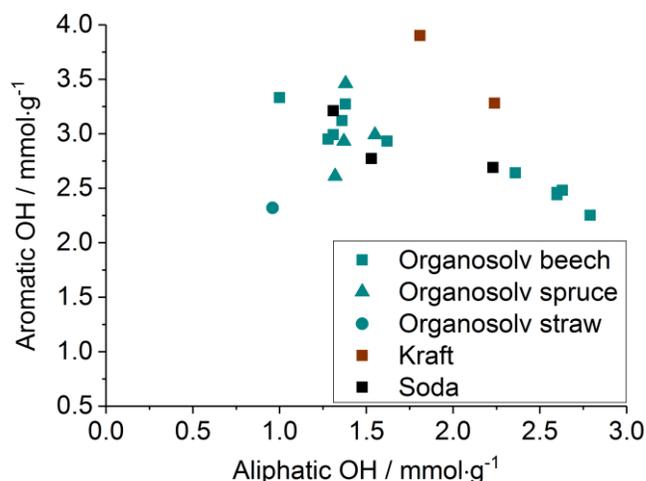


Fig. 3. Content of aromatic and aliphatic hydroxyl groups of soda and kraft (commercial) lignins and organosolv lignin from various raw materials (indicated) and a wide range of process parameters (based on dry substance)

In addition, the choice of raw material has an impact on the content of hydroxyl groups in the lignin fraction. Though the differences between spruce and beech were not as clearly dependent on the process parameters, lignin obtained from straw distinguished itself by its low content of hydroxyl groups.

The molar mass and the glass transition temperature of lignin were investigated as key properties influencing subsequent applications involving thermal processing, such as the melt-spinning of lignin fibers. The analysis is shown in Fig. 4.

The molar masses of organosolv lignin are generally lower compared to lignin obtained by soda and especially kraft pulping (Constant *et al.* 2016). However, when spruce is used as feedstock, lignin with a high weight-average molar mass and a high polydispersity was obtained. This result corroborated the slightly higher glass transition temperature, as noted previously (Li and McDonald 2014). However, this effect was by far less than expected.

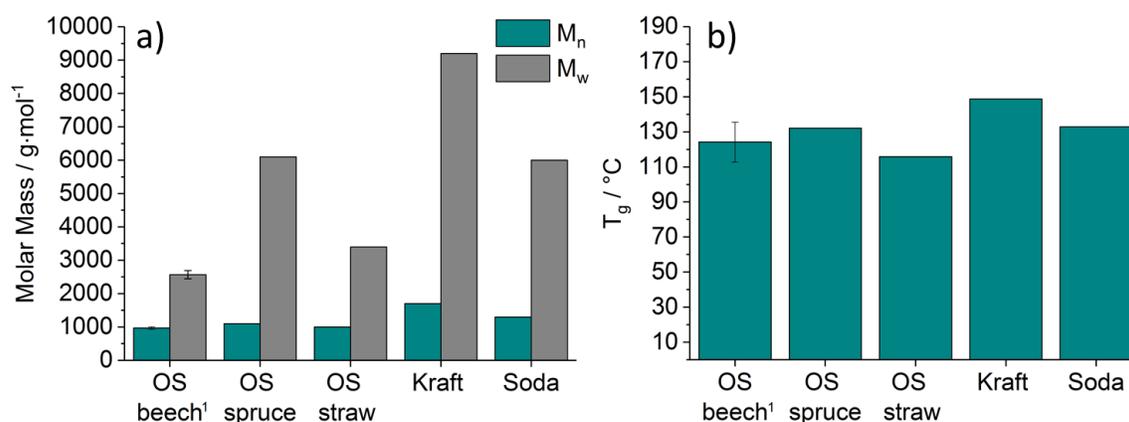


Fig. 4 a) Molar mass (number-average M_n and weight-average M_w) and **b)** glass transition temperature T_g of lignin obtained by of soda and kraft (commercial) lignin and organosolv lignin (¹ mean of three trials)

Effect of Pulping Parameters during Organosolv Pulping

The effect of pulping parameters was studied in terms of the dosage of sulfuric acid and of the H-factor. The composition of the obtained lignin is listed in Table 5. Severe pulping conditions in terms of H-factor as well as the sulfuric acid addition enhanced carbohydrate degradation and increased lignin purity. However, this is not solely explainable based on the loss of carbohydrates, but also constitutes an indicator for lignin condensation reactions.

Table 5. Composition of Beech Organosolv Pulping Lignin (OS) (Based on Dry Substance)

Variation of	Lignin Content / %	Carbohydrate Content / %	Ash Content / %
H-factor ($\omega(\text{H}_2\text{SO}_4) = 1.0\%$)			
H-factor = 1000	93.59 ▲	1.52 ▼	0.13
H-factor = 4200	97.41 ▲	0.11 ▼	0.13
Sulfuric Acid on Wood (H-factor=1000)			
$\omega(\text{H}_2\text{SO}_4) = 0.5\%$	91.93 ▲	1.93 ▼	0.03
$\omega(\text{H}_2\text{SO}_4) = 1.0\%$	93.59 ▲	1.52 ▼	0.13

The effect of different pulping parameters on the elemental composition of lignin is illustrated as a van-Krevelen diagram in Fig. 5. For some applications, such as the production of carbon fibers, low molar ratios of H/C and O/C are desirable. This can be achieved by using severe pulping conditions in terms of the H-factor as well as the concentration of sulfuric acid. The latter results in a remarkable decrease in the molar H/C ratio close to 1.0, indicating a higher lignin purity and hence, a lower content of carbohydrates (Table 5). Severe pulping conditions expressed in long reaction times, high temperatures and high acid dosages can lead to condensation reactions and therefore increased carbon content in the lignin. However, the organosolv lignins characterized in this paper showed no negative effects of condensation reactions in terms of solubility and color.

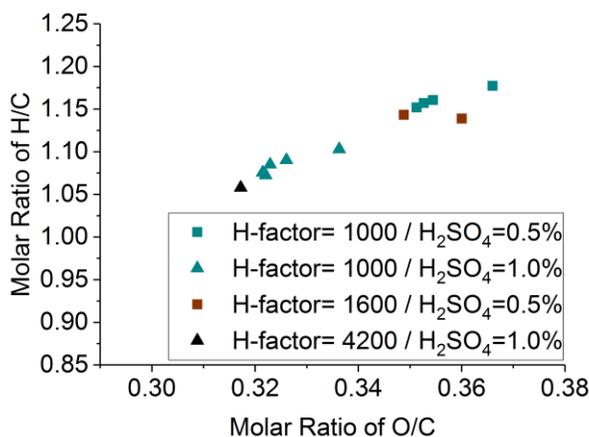


Fig. 5. Van-Krevelen diagram of lignin obtained by the organosolv pulping of beech under variation of the H-factor and concentration of sulfuric acid given in % on wood. Lignins were precipitated by dilution (one/two-step). Note that the same H-factor may imply various parameter (T , t) combinations (based on dry substance)

The content of aliphatic and aromatic hydroxyl groups is illustrated in Fig. 6. Both an increase in the H-factor as well as in the concentration of sulfuric acid resulted in an

increase in phenolic hydroxyl and a decrease in aliphatic hydroxyl groups as the more severe pulping conditions promoted the reactions already described. Thus, by using specific process parameters it was possible to adjust the ratio of aromatic and aliphatic hydroxyl groups in the product.

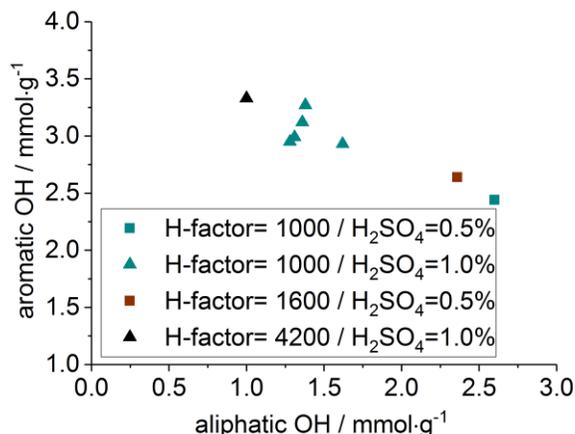
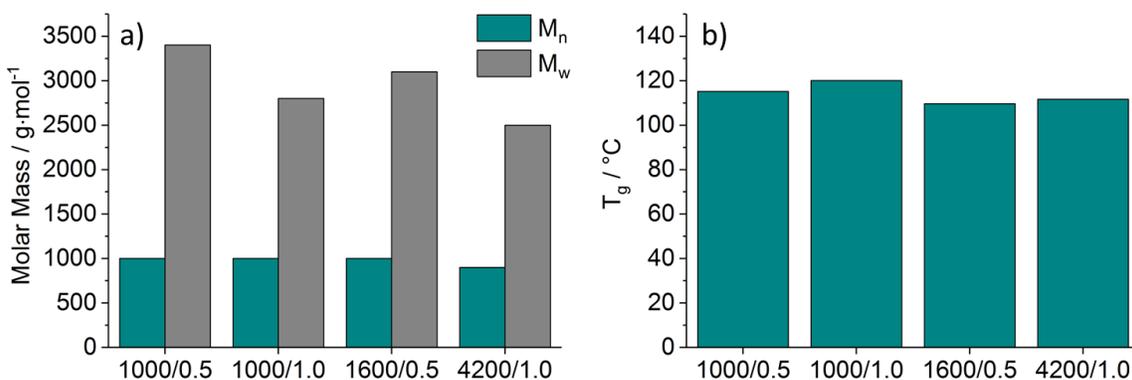


Fig. 6. Content of aromatic and aliphatic hydroxyl groups lignin obtained by organosolv pulping of beech under variation of the H-factor and concentration of sulfuric acid given in % on wood. Lignins were precipitated by dilution (one/two-step). Note that the same H-factor may imply various parameter (T , t) combinations.

The effects of pulping parameters on lignin properties in terms of molar mass and glass transition temperature are shown in Fig. 7. Whereas the effect on the number-average weight was insignificant, the weight-average molecular weight was decreased by both an increase in H-factor and in sulfuric acid concentration resulting in a decrease in the lignin polydispersity. In contrast, the effect on the glass transition temperature T_g was not as clear, especially considering that it was more of a glass transition range than an exact temperature.



Pulping conditions (H-factor/ ω (H₂SO₄) in % on wood) Pulping conditions (H-factor/ ω (H₂SO₄) in % on wood)

Fig. 7 a) Molar mass (number-average M_n and weight-average M_w) and **b)** glass transition temperature T_g of lignin obtained by the organosolv pulping of beech under variation of the H-factor and concentration of sulfuric acid. Lignins were precipitated by one-step dilution.

From the obtained data it was postulated that an increase in sulfuric acid concentration results in an increase in T_g and that an increase in the H-factor has the opposite effect. However, these are assumptions that need to be supported by additional

process experience. In addition, it needs to be clarified whether a variation of T_g within this narrow range would have a substantial effect on the performance of lignin. In contrast to the data discussed for different raw materials, no indication for a correlation between molar mass and glass transition temperature was found, possibly due to the comparatively small range that was covered.

Effect of Precipitation Parameters

Different precipitation procedures have a remarkable influence on lignin's processability. The procedures used in this study were spontaneous precipitation by the cooling of black liquor to room temperature (*cf.* Fig. 1), dilution with water in one step, dilution with water in two steps, and thermal precipitation by evaporation of ethanol.

Table 6. Composition of Lignin Obtained by the Organosolv Process from Beech Using Different Precipitation Procedures (based on dry substance)

Precipitation	Comment	Lignin (%)	Carbohydrate (%)	Ash (%)
Spontaneous	various cooks	96.50	0.30	0.36
One-step-dilution	H-factor= 1000	91.40	1.52	0.13
Two-step-Dilution¹	$\omega(\text{H}_2\text{SO}_4)=$ 1.0%	94.17	0.19	0.17
One-step-dilution	H-factor= 1000	90.00	1.93	0.03
Evaporation¹	$\omega(\text{H}_2\text{SO}_4)=$ 0.5%	89.05	1.46	0.05

¹Mean obtained from several cooks with same parameters

Table 6 lists the compositions of the obtained lignin. Lignin from spontaneous precipitation, before additional “active” precipitation by dilution or evaporation, was of high purity having a lignin content of approximately 96.5%. When comparing precipitation by dilution, stepwise dilution of the black liquor increased the purity of the precipitated lignin and was hence favorable compared with precipitation by one-step dilution. Whereas precipitation by evaporation of the ethanol is of economic interest, as ethanol can be readily recovered and the amount of water needed for the process is decreased, it does not have a particular impact on lignin purity compared to precipitation by dilution. However, in order to avoid the formation of sticky particles, a specific protocol needs to be followed (Leschinsky *et al.* 2016). The samples characterized here were obtained in fed-batch process at a process temperature of 51 °C.

The effect of different precipitation methods on the elemental composition of lignin is illustrated as a van-Krevelen diagram in Fig. 8. Precipitation by evaporation and by two-step-dilution resulted in a shift towards the low molar ratios of H/C and O/C compared with one-step dilution, which ought to be desirable for some applications, such as carbon fiber production. Whereas chemical changes might occur during thermal evaporation, the difference between precipitations by dilution in one or two steps was unexpected. It might be explained by the slightly different purity in terms of carbohydrate content.

The content of the aromatic and aliphatic hydroxyl groups with regard to the used precipitation methods is shown in Fig. 9. Lignin that is available in comparatively small yields from spontaneous precipitation had a low content of both functional groups. It had higher hydrophobicity and was less soluble in the pulping liquor. Lignins obtained by two-step dilution had a slightly lower amount of aliphatic and a higher content of aromatic hydroxyl groups compared with one step dilution. This results from the higher lignin content discussed before.

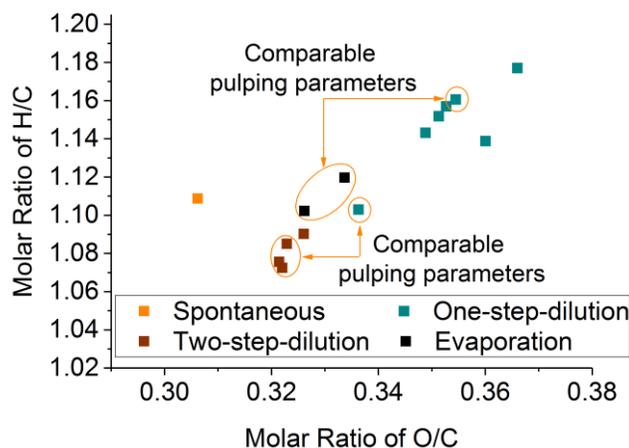


Fig. 8. Van-Krevelen diagram of lignin obtained by organosolv pulping of beech under variation of the precipitation method based on dry substance. Lignin specimens were obtained under various pulping conditions (H -factor=1000 or 1500; $\omega(\text{H}_2\text{SO}_4) = 0.5\%$ or 1.0%). Note that the same H -factor may imply various parameter (T , t) combinations. Comparable parameters are indicated.

Though these are only minor differences and data scatters especially for the content of aromatic hydroxyl, this underlines that lignin obtained by two-step-dilution is different compared with precipitation by one-step-dilution. In contrast, lignin obtained by evaporation contained similar amounts of aliphatic and aromatic hydroxyl groups, despite the structural differences revealed by elementary analysis (see above).

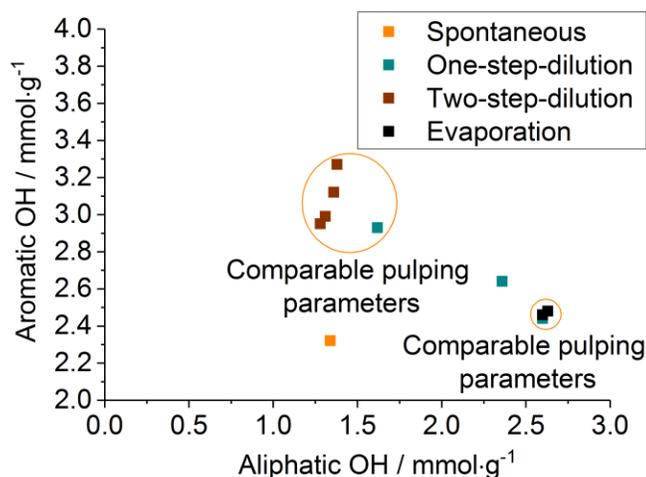


Fig. 9. Content of hydroxyl groups of lignin obtained by organosolv pulping of beech under variation of the precipitation method based on dry substance. Lignin were obtained under various pulping conditions (H -factor = 1000 or 1500; $\omega(\text{H}_2\text{SO}_4) = 0.5\%$ or 1.0%). Note that the same H -factor may imply various parameter (T , t) combinations. Comparable parameters are indicated.

The influence of different precipitation procedures on molar mass and glass transition temperature is illustrated in Fig. 10. Lignin with a high molar mass was precipitated by the cooling of black liquor (spontaneous precipitation) to room temperature after pulping. This fraction of lignin represents only a minor fraction of lignin that is soluble in the pulping solvent under pulping conditions and forms deposits in the tanks where the black liquor is stored. Beside its extremely high polydispersity of 8.6, it also has a high molar mass, which may make it a promising starting material for applications where this is

of advantage. Despite the high molar mass, the glass transition temperature was comparatively low. This is relevant, as this lignin could still be thermally workable. It further shows that the glass transition temperature is not simply dependent on the molar mass, despite previously mentioned indications and a report by Li and McDonald (2014). For the other precipitation methods, no major effect on either molar mass or glass transition temperature was found.

In summary, unique lignin qualities can be obtained by variation of feedstock and process parameters. The revealed effects of different parameters on lignin structure and properties are shown in Table 7.

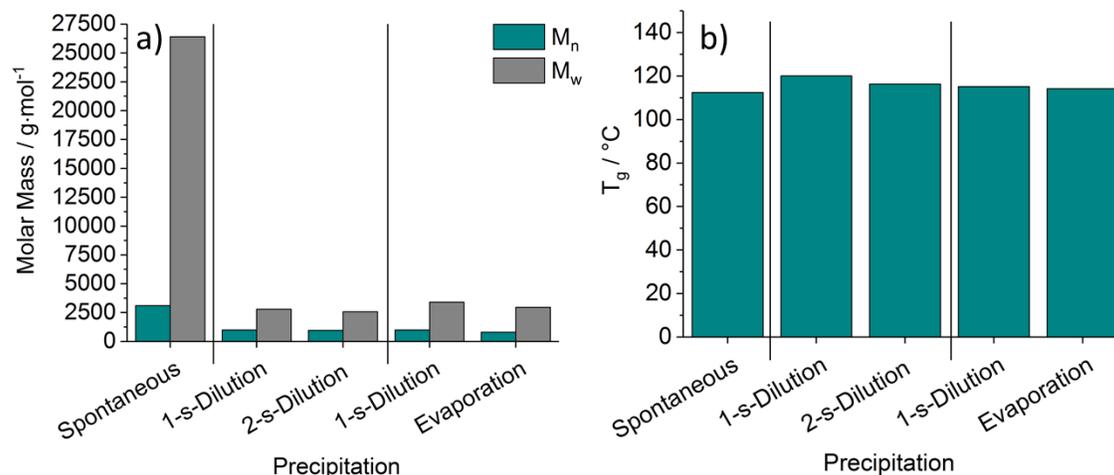


Fig. 10 a) Molar mass (number-average M_n and weight-average M_w) and **b)** glass transition temperature T_g of lignin obtained by the organosolv pulping of beech under variation of the precipitation method. Comparable parameters are grouped.

Table 7. Summary of Varied Parameters and Their Effect on Lignin Structure and Properties

Effect on Variation of	Lignin Purity	H/C Ratio	O/C Ratio	OH _{aromatic}	OH _{aliphatic}	M_n	M_w	T_g
Raw Material¹								
Spruce	-	↘	↓	↗	-	↑	↑	-
Wheat Straw	-	-	↓	-	↘	-	↑	-
Pulping Parameters								
H-factor ↑	↑	↓	↘	↗	↓	-	↓	↘
Sulfuric Acid ↑	↑	↓	↓	↑	↓	-	↓	↗
Precipitation²								
Spontaneous	↑	-	↓	↓	↓	↑	↑	-
2-step-dilution	↑	↓	↓	↗	↓	-	-	-
Evaporation	-	↓	↓	-	-	-	-	-

¹ With regard to beech wood

² With regard to one-step-dilution

Understanding the presented relationships allows the production of lignin with optimized properties for several applications including but not limited to the production of resins, biocomposites, or carbon fibers. However, other factors also need to be taken into account when specifying pulping and precipitation parameters. This includes the yield and

quality of other products, such as pulp, or economic and ecological factors, such as the advantage of lignin precipitation by the evaporation of ethanol, which decreases the water load of the process and allows the simultaneous recovery of the pulping chemical.

CONCLUSIONS

1. The organosolv technology was shown to be feedstock flexible and to produce lignin in a reproducible quality in an industry-relevant environment.
2. It was possible to obtain lignin with unique properties within the experimental setup.
3. Various lignin samples were obtained in pilot scale by the variation of raw material (beech, spruce, straw), pulping parameters (H-factor, concentration of sulfuric acid), and precipitation methods (spontaneous, one-step dilution, two-step dilution, and evaporation). They were thoroughly characterized by acid hydrolysis with subsequent AEC, incineration, elementary analysis, ³¹P-NMR, SEC, and DSC. Relationships between process variables and lignin properties were established where possible.

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