ACS Sustainable Chemistry & Engineering

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Research Article

Design of Organosolv Lignin Fractionation: Influence of Temperature, Antisolvent, and Source on Molecular Weight, Structure, and Functionality of Lignin Fragments

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Cite This: *ACS Sustainable Chem. Eng.* 2025, 13, 3452−3466

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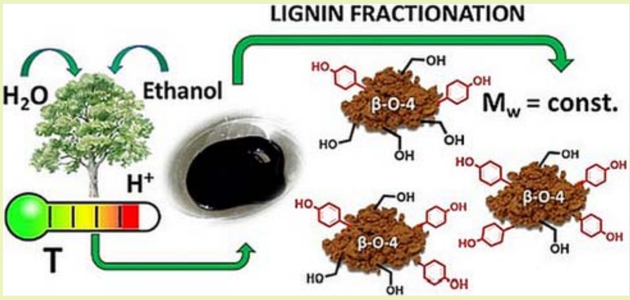
ABSTRACT: Lignin offers a sustainable alternative to fossil raw materials for chemical and material synthesis. Improving its utilization requires the production of lignin fragments with a controlled dispersity and reactivity. In this study, a sustainable protocol for direct organosolv lignin fractionation from black liquor using water as an antisolvent is developed. The approach utilizes the complementarity of the process temperature and solubility parameters to generate lignin streams with tailored properties. In particular, the protocol allows control of the structural characteristics of the lignin fractions, including OH group content, interunit bonds, and degree of ethoxylation, as demonstrated for spruce and beech lignins. The ability to adjust the ratio of aliphatic to aromatic OH groups emphasizes the potential to significantly influence the reactivity and functionality of the lignin. This water-driven fractional precipitation approach offers a sustainable way to produce well-defined lignin streams suitable for various applications, depending on the desired properties. In addition, a techno-economic assessment highlights solvent recovery and lignin value as key parameters for scaling up the process and highlights both opportunities and challenges in implementing this process on an industrial scale.



KEYWORDS: *organosolv lignin, fractionation, biomass, NMR, techno-economical assessment*

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1. INTRODUCTION

Lignin is the third most abundant biopolymer in nature and, as the largest renewable source of aromatics, attracts many researchers who seek to selectively convert it into monoaromatics aiming to replace petroleum-based ones, especially as building-blocks for polymer synthesis, or to develop new tail-made high-value applications for specific lignin-derived compounds.[1,2]

The main challenge that strongly influences the development of the high-value applications is the heterogeneity of lignin in molecular weight and chemical structure, as this macromolecule is composed of three types of phenylpropanoid units, specifically *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), randomly linked by ether (β-O-4, α-O-4, 4′-O-5) and carbon−carbon (β-β, β-5, β-1, 5-5′) bonds.[3,4] In summary, the main limitations to the direct use of isolated lignin "as is" are first, the low reactive sites content with respect to the molecular weight,[5] which limits the range of applications and requires selective catalytic depolymerization to obtain valuable lignin fragments.[6] Second, the high lignin dispersity, which undesirably affects the properties of the synthesized polymeric materials.[7] In addition, specific structural modifications are a consequence of the lignin extraction process. For example, kraft lignin and lignosulfonate produced in the pulp and paper industry contain sulfur incorporated via thiol and sulfonate groups, respectively, whereas organosolv lignin produced in bioethanol production, is a sulfur-free lignin with low ash content with partially etherified OH groups or so-called alkoxy groups.[8] Overall, the improvement of lignin valorization is absolutely critical for a sustainable development.[9]

From the chemical point of view, the organosolv process can be simplified as an aryl ether bond breakage and lignin condensation reaction system.[10] Moreover, depending on the type of solvent (alcohol, ketone, and organic acid), other reactions can be involved. Etherified hydroxyl groups or so-called alkoxy groups are formed when alcohol is used.[8] This ethylation is not observed when ketones are used.[11] Instead, esterification of hydroxyl groups is observed when organic acids are used.[12] Also the temperature has an important effect

Received: September 30, 2024
Revised: February 7, 2025
Accepted: February 14, 2025
Published: February 28, 2025

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https://doi.org/10.1021/acssuschemeng.4c08125
ACS Sustainable Chem. Eng. 2025, 13, 3452−3466

on the organosolv reaction mechanism. In fact, the increase of temperature makes the process more severe, leading to significant structural changes in the lignin in the form of depolymerization and subsequent molecular rearrangement of the lignin macromolecule.[10,13] Depending on the final target, the organosolv process conditions can be tuned. When the target is the production of bioethanol, maximum delignification has to be achieved. Therefore, high temperatures (>200 °C) and use or inorganic acids (e.g., sulfuric acid) is typically required.

Consequently, lignin undergoes to high level of condensation and cleavage reactions. At the same time, in the concept of lignin-first biorefineries, where the molecular structure of lignin must be preserved, mild organosolv process conditions, for example using ethanol and $T < 200$ °C, are applied.[14] In this case, high quality lignin, containing well preserved, thermocatalytically cleavable β-O-4 bonds, is obtained and has a high potential for further conversion into the value-added chemicals such as monoaromatics.[15] There have been numerous efforts of direct organosolv lignin depolymerization aimed at producing valuable monoaromatics/building blocks for polymer synthesis. However, the molecular structure complexity in terms of molecular weight fractions and functional groups do not allow achieving efficient processes, showing the formation of complex monoaromatics mixtures that require extensive separation procedures for their isolation.[16−18] There are several strategies to overcome the aforementioned drawbacks, thus suggesting the design of catalysts for efficient and selective C−C bond cleavage, considering the possibility of selective lignin conversion, thus reducing the complexity of the downstream processes, and stepwise, product-oriented utilization of lignin.[19] Accordingly, the application of fractionation to obtain less heterogeneous streams of organosolv lignin is one of the key steps toward selective product-oriented lignin conversion. For example, a lignin fraction with reduced dispersity, preferred alkoxylation degree, and amount of the ether linkages could be eventually used to obtain valuable monoaromatics following a stepwise modification procedure, developed by the Deuss group, to partially defunctionalize α-alkoxylated β-O-4 moieties which could be further converted into acetophenone derivatives.[20]

The ability to extract, isolate, and separate lignin to obtain lignin fragments with different molecular weights (M_w), resulting in different possible applications, increases the valorization of lignin recovered from biomass.[21,22] For example, high M_w lignin formed at lower isolation temperatures could in certain formulations induce flame-retardant properties in the final material.[21] High molecular lignin fragments (around 5000 Da) are used for the preparation of flame retardant composites. Furthermore, sulfur-free lignin (e.g., organosolv lignin) specifically could also be used in the medical sector for the drug delivery systems, as high M_w lignin cannot be absorbed by small human cells in the intestine or stomach.[23] While low M_w lignin (<1 kDa) could be used as building blocks in polymer synthesis in combination with additional (de)functionalization or further converted into the valuable monoaromatics.[24,25] For example, Asada et al. used lignin fractions with molecular weights between 1300 and 1600 Da for the production of epoxy resins.[24] Similarly, Saito et al.[26] used lignin fragments of around 1800 Da for the production of thermoplastic materials[27] and studied the influence of the molecular weight (from 800 to 10,000 Da) on the UV properties of lignin fragments and found that lower M_w offers higher sun protection factor. Pylypchuk et al.[28] obtained lignin nanoparticles (LNP) with homogeneous functional group content through a green solvent-fractionation process of kraft lignins. Such an LNP with different properties can be selected depending on the application. Furthermore, as an example of the use of valuable monoaromatics, Kaneko et al. synthesized a biopolymer with improved thermal properties and biodegradability by inserting *p*-coumaric acid-derivatives, which can be obtained from lignin.[25]

The isolation of uniform lignin fragments with the defined reactivity (functionality) would significantly accelerate the conversion of lignin into value-added products, and consequently, it would be easier to ensure the repeatability of the process; an understanding of the relationships between lignin structure and reactivity is therefore essential. Several lignin fractionation techniques have been developed, namely selective pH-dependent precipitation[29] achieved by changing the pH of the media, single step[30] or sequential solvent extraction[31] using solvents of different polarity to dissolve fractions with different characteristics, membrane ultrafiltration[32] to separate fractions of different molecular weight directly from the black liquor, and antisolvent-based technology where the gradual addition of the antisolvent to the lignin solution allows its fractional precipitation.[33]

The production of low ash (∼1.75%) sulfur-free organosolv lignin is about 12,000 tons/year, which is about 0.6% of the total lignin on the market worldwide. The availability of organosolv lignin is expected to increase in the next few years due to increasing bioethanol production (second generation biorefinery process).[9,34]

In our work, black liquor after ethanol-organosolv biomass fractionation was selected with the aim of developing a straightforward integrated lignin fractional precipitation method directly from the organosolv process effluent, using water as an antisolvent. Additionally, we investigate fractional precipitation approach to reduce the structural changes of lignin caused by acid catalysts (e.g., the evaporation of ethanol and water, usually is carried out at operating temperatures of 80−100 °C, which is considered as mild lignin depolymerization conditions).[14]

[8] Since the structure of lignin depends on the reaction conditions and the solvent used[8] (50 vol % ethanol/water, 160 °C, 1 h), the aim of the present study was to investigate lignin fractionation directly from black liquor using water as an antisolvent, focusing in particular on the preservation of lignin structure during the downstream process and the effects of the antisolvent methodology. Specifically, the aim was to reveal the influence of the organosolv process temperature on the chemical properties of lignin and to define the range within which the lignin properties can be adjusted using a simple fractional precipitation process. In order to ensure the repeatability of the process, the solubility parameter (δ MPa$^{0.5}$) is introduced to describe the ethanol/water solvent mixtures.[35] The aim of this study is also to establish the correlations between the process temperature and lignin properties and to propose a fractionation protocol that allows one to obtain defined lignin fractions for different applications based on the molecular weight, functionality, and a techno-economic analysis.

2. EXPERIMENTAL SECTION

2.1. Materials. Beech (*Fagus sylvatica*) and spruce (*Picea abies*) sawdust was provided by the local supplier. Ethanol (EtOH, absolute

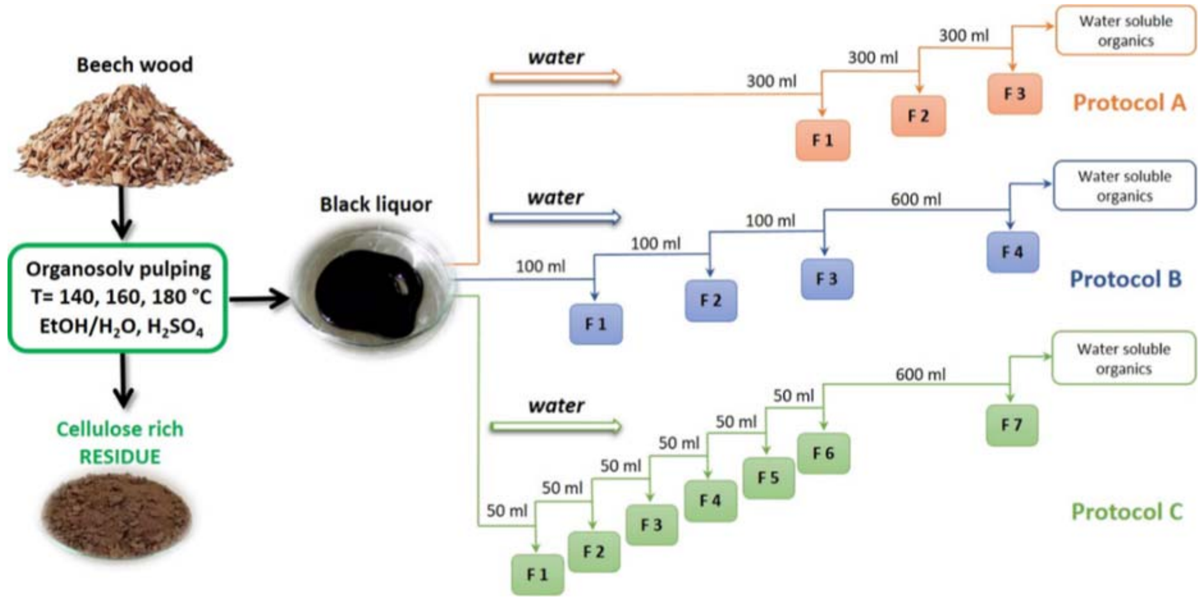

Figure 1. Schematic representation of organosolv lignin fractionation according to three different protocols directly from the black liquor using water as an antisolvent.

anhydrous, Carlo Erba Reagents SAS, CAS number 64-17-5), tetrahydrofuran (THF, ≥99%, Chromasolv plus for HPLC, Honeywell, Riedel-de Han, CAS number 109-99-9), acetic anhydride (AA, 99%, Sigma-Aldrich, CAS number 108-24-7), *N*-hydroxynaphthalimide (99%, Sigma-Aldrich, CAS number 524-38-9), chromium(III) acetylacetanoate (≥99%, Sigma-Aldrich, CAS number 21679-31-2), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%, Sigma-Aldrich, CAS number 14812-59-0), deuterated chloroform ($CDCl_3$-*d*, 99.6 atom. % D, TCI EUROPE N.V., CAS number 865-49-6), pyridine (99%, Merck, CAS number 110-86-1), hydrochloric acid (HCl, 37%, Merck, CAS number 7647-01-0), sulfuric acid (H_2SO_4, 95−97% Merck, CAS number 7664-93-9), and nitrogen (5.0, Messer) were of reagent grade and were used as received.

2.2. Lignin Extraction.

Lignin was extracted from beech (*F. sylvatica*) sawdust (25 g, 24 mesh, dried at 105 °C overnight) using 175 mL of 50 vol % ethanol/water (87.5 mL of EtOH and 87.5 mL of water) in a 1:7 (w/v) ratio and 1% H_2SO_4 (based on dry biomass) as a catalyst. Biomass fractionation was carried out in a slurry reactor (Autoclave Engineers) at 140, 160, and 180 °C for 1 h. All experiments were performed in a batch reactor at a stirring speed of 200 min^{-1}. The residual material was filtered out, carefully rinsed with the warm (~60 °C) ethanol/water mixture, and dried at 105 °C to constant weight. The detailed procedure, including yield calculation, is reported in Jasiukaitytė-Grojzdek et al.[36] Briefly, the yield of isolated lignin (%) is calculated with respect to the initial lignin content in the feedstock. To study lignin type-related effects of fractionation, black liquor from spruce (*P. abies*) was obtained following analogous procedure, only using 50 vol % ethanol/water in a 1:10 (w/v) ratio with spruce sawdust.

Fractional lignin precipitation was performed by adding antisolvent (water, H_2O) directly to the black liquor according to the three different protocols (A, B, and C) shown in Figure 1.

The recovered lignin was collected by centrifugation, washed several times with distilled water to remove residual sulfuric acid, and freeze-dried. The yields of the recovered lignin fractions (%) were determined with respect to the initial lignin content in beech wood (24.4%)[37] and in spruce (28.5%).[38]

Compositional cellulose-rich pulp analysis to determine cellulose, xylan, and lignin was performed using methods described in NREL TP:510-42618.[39] The total lignin was calculated as a sum of acid soluble (ASL) and acid insoluble lignin (AISL), and the degree of delignification was calculated from the difference between the total lignin content in the sawdust and in the cellulose-rich pulp before and after the organosolv fractionation, according to the equation

$$\text{Delignification degree (\%)} = 100 - ((\text{total lignin in cellulose-rich pulp} \times 100\%)/\text{total lignin in sawdust}) \quad (1)$$

The precipitation yield was calculated taking into account the degree of delignification achieved during the organosolv process and the amount of the recovered lignin according to the equation

$$\text{Lignin precipitation yield (\%)} = (W_{\text{recovered lignin}} \times 100 \times 100)/((W_{\text{sawdust}} \times \text{total lignin content} \times \text{delignification degree})/100) \quad (2)$$

Here, $W_{\text{recovered lignin}}$ stands for recovered lignin weight (g); W_{sawdust} stands for the initial weight of sawdust (g).

2.3. Size-Exclusion Chromatography.

Molecular weight distributions (MWDs) of lignin samples were measured by SEC (Thermo Scientific Ultimate 3000) using a Plgel 5 μm MIXED D 7.5 × 300 mm column and a UV detector set at 280 nm. Samples were analyzed at a temperature of 30 °C by using THF at a flow rate of 1 cm^3 min^{-1}. Calibration was performed using polystyrene standards, while analytical data processing was performed using PSS (Polymer Standards Service) WinGPC Unity software. Prior to analysis, lignin samples were acetylated with AA according to the exact procedure reported in our previous work.[40] It has to be noted that while PSS is often used for calibration due to its practicality, its structural and conformational differences from lignin lead to a systematic underestimation of the molecular weight. Lignin with its branched and compact structure has smaller hydrodynamic radii than linear polystyrene chains with the same molecular weight.[41] This discrepancy is well documented and leads to deviations between the actual molecular weight of lignin and the values obtained by PSS calibration. In addition, derivatization such as acetylation can alter the solubility of lignin and interactions with SEC columns, contributing to the variability of results. The challenges of using PSS calibration for lignin analysis were reported in Round Robin test carried out by the European network Eurolignin, where the use of polystyrene−divinylbenzene columns from the different manufacturers led to significant inconsistencies, even with centrally provided standards and acetylated lignin samples.[42]

The above facts are important when comparing the molecular weights of lignins given in the literature, as a direct comparison is not possible.[43] Nevertheless, the molecular weights of lignin determined under the same conditions (in the same facility) are sufficiently comparable to establish trends and to draw definitive conclusions.

2.4. Nuclear Magnetic Resonance Spectroscopy.

NMR spectra were recorded on a Bruker AVANCE NEO 600 MHz NMR spectrometer equipped with a BBFO probe according to the published protocol 44 while the spectral analysis, signal assignment, and calculations were performed according to published procedures.[45,46] Briefly, for heteronuclear single quantum coherence (HSQC) 2D NMR analysis, 85 mg of the lignin sample was dissolved in 0.6 mL of DMSO-d_6, which was also used as an internal chemical shift reference point (δ_C 39.5; δ_H 2.50 ppm). For quantitative ^{31}P NMR, approximately 30 mg of sample was dissolved in a 1:1.6 mixture of $CDCl_3$/pyridine at ambient temperature. Derivatization of *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (NHND), used as an internal standard together with lignin samples, was performed by using 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP). The average values of three parallel measurements of each sample are reported in this work. The maximum standard deviation and the maximum standard error of the reported results were 0.02 and 0.01 mmol g^{-1}, respectively.

3. RESULTS AND DISCUSSION

It is well-known that the structural properties and reactivity of lignin are strongly dependent on the reaction conditions; however, the effect of the specific parameters, such as the organosolv process temperature in combination with the solubility parameter describing the precipitation media (fractional precipitation), reveals the specific trends in the modification of lignin properties. Therefore, in order to determine the influence of the aforementioned parameters, black liquor was produced by treating beech wood (*F. sylvatica*) at three different temperatures according to the procedure described in the experimental section and shown in Figure 1. After the removal of the cellulose-rich residue, extracted lignin was fractionated by adding the antisolvent (water, H_2O) directly to the black liquor. Water was added in different but equal proportions within the same fractionation protocol to obtain a gradual change in the solubility parameter.

3.1. Development of the Fractionation Protocols.

MWDs of isolated lignin fractions were determined using SEC as shown in Figure S1 in the Supporting Information, while total lignin yield, M_w, M_n, $Đ$, and solubility parameter values are listed in Table 1.

Table 1. Yields (Total Y_{Lignin} and Y_{FR}), Weight-Average Molecular Weight (M_w), Number-Average Molecular Weight (M_n), and Dispersity ($Đ$) of Lignin Fractions Isolated in Hildebrand Solubility Parameter (δ)-Defined Aqueous Ethanol Solution[a]

FR	total Y_{Lignin}[b] [%]	Y_{FR} [%]	M_w [Da]	M_n [Da]	$Đ$	δ [MPa$^{0.5}$]
B_140_Total	31.5		5400	1600	3.3	n.d
A140_F1	30.6	72.9	8400	6100	3.0	41.5
A140_F2		20.9	5000	2100	2.8	43.7
A140_F3		6.2	4800	1700	2.9	44.8
B140_F1	30.8	35.9	9200	3500	2.6	38.2
B140_F2		38.4	6300	2400	2.6	40.2
B140_F3		15.2	4400	1800	2.4	41.5
B140_F4		10.5	3500	1400	2.5	44.8
C140_F1	24.6	7.5	11,000	9800	3.3	36.8
C140_F2		13.0	7700	6900	2.3	38.2
C140_F3		18.1	9100	6000	2.6	39.3
C140_F4		18.4	6800	3300	2.4	40.2
C140_F5		12.4	6000	2800	2.4	40.9
C140_F6		13.2	5500	2400	2.5	41.5
C140_F7		17.4	3800	1900	2.4	44.8
B_160_Total	58.3		3800	1400	2.7	n.d.
A160_F1	55.0	80.7	4400	2400	2.3	41.5
A160_F2		16.8	2000	1200	1.7	43.7
A160_F3		2.5	1900	1000	1.7	44.8
B160_F1	59.2	27.0	7300	3000	2.5	38.2
B160_F2		23.3	3800	2000	1.9	40.2
B160_F3		23.9	2700	1500	1.8	41.5
B160_F4		25.0	1800	1100	1.7	44.8
C160_F1	52.9	13.5	9200	7400	2.8	36.8
C160_F2		12.9	6400	6400	2.1	38.2
C160_F3		22.4	4300	3200	2.0	39.3
C160_F4		13.7	3400	2400	1.9	40.2
C160_F5		11.4	2800	1900	1.8	40.9
C160_F6		8.0	2500	1500	1.8	41.5
C160_F7		18.1	1900	1100	1.7	44.8
B_180_Total	71.6		2300	1100	2.0	n.d.
A180_F1	70.8	86.3	2900	1800	2.0	41.5
A180_F2		11.3	1300	1000	1.5	43.7
A180_F3		1.9	1300	1000	1.4	44.8
B180_F1	62.8	20.5	5000	200	2.3	38.2
B180_F2		28.8	2900	1700	1.7	40.2
B180_F3		25.3	1900	1300	1.5	41.5
B180_F4		25.3	1300	900	1.4	44.8
C180_F1	65.5	13.7	5600	6200	2.3	36.8
C180_F2		13.1	3800	3000	1.9	38.2
C180_F3		18.4	2700	2300	1.6	39.3
C180_F4		10.9	2100	1900	1.5	40.2
C180_F5		19.8	1700	1500	1.4	40.9
C180_F6		4.1	1600	1400	1.4	41.5
C180_F7		20.0	1200	1000	1.4	44.8

[a]Samples B_140_Total, B_160_Total, and B_180_Total represent unfractionated lignin extracted at 140, 160, and 180 °C. [b]Lignin content in beech wood was considered to be 24.4%.[37] The yield of the isolated lignin (%) is calculated with respect to the initial lignin content in the feedstock. The yield for the samples B_xxx_Total is total lignin yield, while the yield of the set of fractions, obtained from the same black liquor, represent the combined yield of the fractions.

The aim of Protocol A was to determine the limits of lignin separation by adding three equal portions (300 mL) of water to produce fractions designated A_F1, A_F2, and A_F3 at three different temperatures. Based on the results, it can be assumed that the precipitation of the larger lignin macromolecules (A_F1) was induced by the addition of the first portion of water (300 mL), while analogous oligomeric lignin fragments (A_F2, A_F3) were isolated by the subsequent two portions of antisolvent. Since most of the lignin was extracted at 180 °C, but at the same time most of the total lignin at all three temperatures was recovered within A_F1 (yield 72.9–86.3%) and in the other two fractions A_F2 and A_F3, the macromolecules showed similar M_w. It was, therefore, decided to modify the fractionation protocol in order to study and determine the fractional precipitation selectivity limits within the A_F1 fraction. Two novel protocols were developed by dividing formed A-F1 into three fractions (Protocol B, B_F1, B_F2, B_F3) and six fractions (Protocol C, C_F1, C_F2, C_F3, C_F4, C_F5, and C_F6). The fractional precipitation

Table 2. Compositional Analysis of the Cellulose-Rich Pulp Samples (B_140, B_160, and B_180) After the Beech Organosolv Fractionation at 140, 160, and 180 °C, Respectively[a]

sample	ASL [%]	AISL [%]	total lignin [%]	cellulose [%]	xylan [%]	delignification degree [%]	lignin precipitation yield [%]
B_140	1.5	9.9	11.4	58.8	11.0	53.3	57.8
B_160	0.3	4.2	4.5	78.2	8.9	81.6	72.2
B_180	0.3	5.5	5.8	85.2	2.7	76.2	83.3

[a] Determination of acid soluble lignin (ASL), acid insoluble lignin (AISL), total lignin, cellulose, and xylan. Delignification degree and the lignin precipitation yield are calculated according to the eqs 1 and 2, respectively.

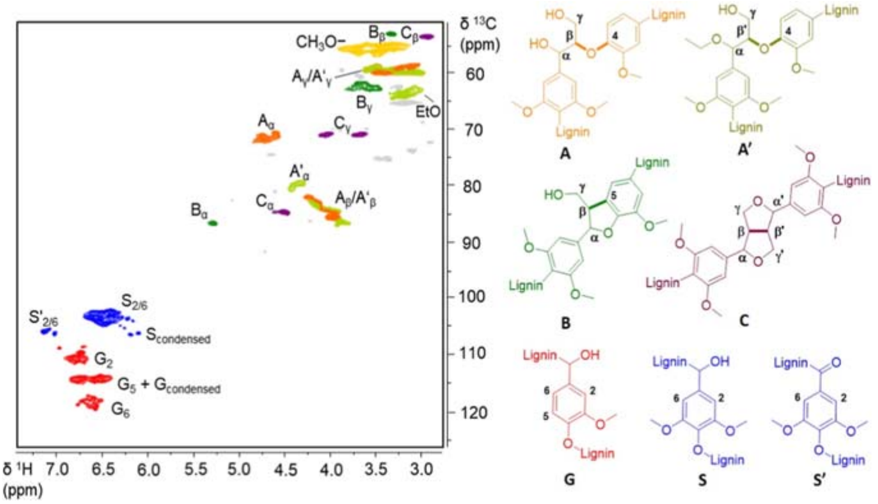

Figure 2. 2D HSQC spectrum of the main structures of lignin fraction B140_F3: A-(β-O-4) β-aryl-ether motifs; A′-(β'-O-4) α-ethoxylated β'-aryl-ether motifs; B-(β-5) phenylcoumaran motifs; C-(β-β') resinol motifs; S-syringyl units; S′-oxidized syringyl units; G-guaiacyl units.

was performed by the gradual addition of water (100 mL, Protocol B; 50 mL, Protocol C), resulting in the recovery of defined and differentiated lignin fractions, while fractions A_F2 and A_F3 were combined in protocols B and C, representing B_F4 and C_F7, respectively. Due to the different volumes of water added in each stage, the total recovered lignin was distributed differently within the fractions, depending on its structural characteristics and solubility in the precipitation media.

Data analysis revealed the possibility of tailoring the M_w as a function of the process temperature. Specifically, the higher the temperature used for the lignin isolation, the lower the M_w of the fractions were obtained. This is a consequence of the temperature-dependent degree of lignin depolymerization also reported by ref 47, whereas fractionation according to the protocols B and C with smaller antisolvent fractions successfully separated lignin macromolecules with different M_w, starting from the largest ones precipitating in the media with $\delta = 36.8$ MPa$^{0.5}$ to the smallest lignin fragments which are separated in the media with $\delta = 44.8$ MPa$^{0.5}$.

Furthermore, as shown in Figure S1 and in Table 1, fractional antisolvent precipitation allows the isolation of lignin with the M_w ranging from 11 to 1 kDa, thus increasing the possibilities for the further applications such as catalytic depolymerization, polymer synthesis, etc. Obviously, lignin solubility increases as the M_w is reduced (solvation tends to become stronger as M_w decreases); however, in the case of the complex, heterogeneous polymer, the effects of the altered structure and functionality must also be considered.

In addition, to determine the beech lignin precipitation yields, black liquor was produced at 140, 160, and 180 °C and used to recover complete lignin by adding water to achieve a precipitation media with the solubility factor of 44.8 MPa$^{0.5}$. Results of compositional analysis of the cellulose-rich pulp samples, assigned as B_140, B_160, and B_180, were obtained after the organosolv fractionation at 140, 160, and 180 °C, respectively. The results summarized in Table 2 show the tendency to recover higher yields of lignin in the case of the higher degree of delignification and consequently higher solubilized lignin concentration in the black liquor. However, to confirm this relationship, additional experiments are required. It is also difficult to exclude the effects of the molecular weight, chemical structure (e.g., level of condensation and ethoxylation), and functional groups of the total lignin in the black liquor, as lignin solubility is affected by ethanol modification and the processing conditions, which define the degree of ethoxylation.[48,49] A deeper understanding of lignin precipitation is essential, as it paves the way for new opportunities and directions in future research.

3.2. Structural and Functionality Differences within the Fractions.

The structural differences and functional group distribution between the lignin fractions were determined by NMR. To capture the trends of the structural changes within the fractions, lignins fractionated according to the Protocol B were selected for further analysis using 2D (HSQC) (Figure 2) and quantitative ^{31}P NMR in Supporting Information (Figure S2).

The fractions of Protocol B were selected because this protocol covers almost the entire range of solubility parameters (38.2−44.8 MPa$^{0.5}$, Table 1) of the solvent mixture (EtOH/H_2O) used to precipitate the lignin with antisolvent (water, H_2O). In addition, the solubility parameters for Protocol C shown in Table 1 are within the range of solubility parameters for Protocol B at all isolation temperatures, whereas the main

Table 3. 2D HSQC and Quantitative ^{31}P NMR Characterization Results of Lignin Fractions Isolated in Hildebrand Solubility Parameter (δ)-Defined Aqueous Ethanol Solution: Interunit Linkages (β-O-4, β'-O-4, β-β', β-5), Aromatic Unit and Functional Group Distribution, and the Degree of the Ethoxylation[a]

	β-O-4	β'-O-4	total β-O-4	β-β'	β-5	S/G/H	ED[b] [%]	Aliph	S	G	cond.	Ar	COOH	total
	number of linkages per 100 C9 units							OH groups [mmol g^{-1}]						
B_total_140	30	15	45	10	5	66/34/0	33.3	3.72	0.64	0.62	0.28	1.53	0.03	5.29
B140_F1	36	18	54	15	6	55/45/0	33.5	3.52	0.54	0.91	0.31	1.76	0.06	5.34
B140_F2	29	15	44	10	4	63/37/0	33.9	4.24	0.71	0.95	0.35	2.01	0.06	6.31
B140_F3	30	15	44	10	4	64/36/0	33.1	4.29	0.70	0.70	0.24	1.64	0.07	6.01
B140_F4	27	13	41	9	3	66/34/0	32.9	4.01	0.75	0.76	0.41	1.92	0.07	6.01
B_total_160	14	13	27	9	3	73/27/0	48.1	2.36	0.98	0.75	0.65	2.38	0.04	4.79
B160_F1	21	15	36	14	5	60/40/0	40.1	2.75	0.70	0.75	0.46	1.91	0.06	4.72
B160_F2	17	12	29	9	4	70/30/0	40.2	2.93	0.94	0.84	0.61	2.38	0.06	5.37
B160_F3	13	10	23	8	3	73/27/0	42.5	2.78	1.10	0.83	0.66	2.59	0.05	5.43
B160_F4	11	8	19	6	2	75/25/0	44.4	2.54	1.33	0.82	0.79	2.94	0.06	5.54
B_total_180	2	3	5	7	2	80/20/0	60.0	1.17	1.23	0.94	0.99	3.16	0.04	4.37
B180_F1	6	2	8	11	3	65/35/0	26.8	1.98	1.32	1.05	0.69	3.06	0.05	5.09
B180_F2	3	3	6	7	2	75/25/0	48.9	1.71	1.59	1.18	0.93	3.70	0.06	5.47
B180_F3	3	1	4	6	1	75/25/0	38.5	1.80	2.11	1.30	0.89	4.30	0.08	6.17
B180_F4	1	1	2	3	1	78/22/0	45.6	1.41	2.33	1.27	1.12	4.72	0.08	6.21

[a] NMR spectra of four fractions are listed in Supporting Information (Figure S3). Samples B_total_140, B_total_160, and B_total_180 represent not fractionated lignin extracted at 140, 160, and 180 °C, respectively. [b] Ethoxylation degree.

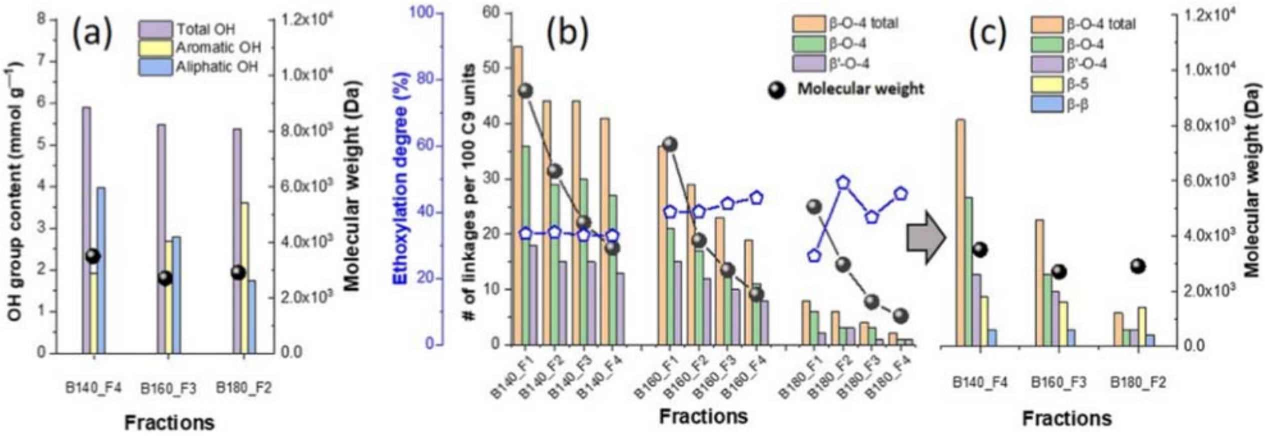

Figure 3. Structural differences between the fractions with comparable M_w, specifically B140_F4, B160_F3, B180_F2: (a) OH group distribution, (b) evolution of ethoxylation degree of fractions depending on process temperature/fraction M_w, and (c) the main lignin motifs.

objective and difference of Protocol C is to further separate the lignin macromolecules with different molecular weights based on the solubility parameter. In addition, Protocol B offers the isolation of four fractions with different molecular weights which have the potential to find different applications and enhance the process valorization.

3.3. Temperature Effect on OH Group Distribution.

Quantitative ^{31}P NMR was used to evaluate the change in aliphatic, aromatic, carboxylic, and total OH group content within the lignin fractions. From the results summarized in Table 3, several trends can be identified. In general, lignin fractions with higher aliphatic OH group content were isolated at lower process temperatures, namely 3.52−4.29 mmol g^{-1} at 140 °C, 2.54−2.93 mmol g^{-1} at 160 °C, and 1.41−1.98 mmol g^{-1} at 180 °C. The opposite was observed for the aromatic OH groups, i.e., lignin fractions with higher aromatic OH group content were obtained at elevated process temperatures, namely 1.64−2.01 mmol g^{-1} at 140 °C, 1.91−2.94 mmol g^{-1} at 160 °C, and 3.06−4.72 mmol g^{-1} at 180 °C (Table 3, Figure S2). Trends are expected as lignin depolymerization is more intense at the higher temperatures, resulting in lignin fragments with more aromatic OH groups.[50] Interestingly, the aromatic OH content increases mainly due to the appearance of new syringyl OH groups (S-OH), while the content of guaiacyl OH groups (G-OH) remains almost unchanged regardless of the fraction M_w and the process temperature, even compared to the beech milled wood lignin (S-OH 0.29 mmol g^{-1}, G-OH 0.82 mmol g^{-1}).[40] A slight increase of the G-OH content occurs only within the fractions isolated at 180 °C. Such an increase in aromatic OH groups, especially S-OH, is also in agreement with the literature, which reports an accelerated cleavage of the β-aryl ethers with syringyl moieties, especially at higher temperatures in alkaline systems.[51] The increase in the total content of aromatic OH groups in lignin fractions with process temperature is also influenced by the appearance of additional condensed OH groups, namely 0.31−0.41 mmol g^{-1} at 140 °C, 0.46−0.79 mmol g^{-1} at 160 °C, and 0.69−1.12 mmol g^{-1} at 180 °C. This indicates the presence of repolymerization phenomena in terms of molecular rearrangement as explained in our previous work.[13] During organosolv treatment, lignin undergoes a molecular rearrangement, starting with β-O-4 cleavage and followed by the formation of new C−C bonds, with both S and G units, which is in agreement with the data from HSQC spectra due to the appearance of the cross-signals corresponding to the formation of S-condensed and G-condensed units at δ_C 105−108 and δ_H 6.1−6.5 ppm and δ_C 114−117 and δ_H 6.3−6.9 ppm, respectively.

Figure 3a shows the aliphatic, aromatic, and total OH group contents of lignin fractions with comparable M_w isolated at different process temperatures, namely, B140_F4, B160_F3, and B180_F2. It is evident that by varying both the process temperature and the solubility parameter, it is possible to influence the reactivity of lignin, thus completely changing the aliphatic/aromatic OH ratio, while at the same time hardly affecting the total OH group content.

3.4. Temperature Effects on Polarity.

The polarity of lignin and, consequently, its solubility in solvents or solvent mixtures is influenced by the content of hydrophilic (aromatic and aliphatic OH groups) and hydrophobic part of the main polymer chain, which accordingly plays a role in determining the hydrophilic or hydrophobic nature of lignin.[52−55] In fact, three parameters need to be taken into account while discussing lignin polarity, which is the content of hydrophilic (aromatic and aliphatic OH groups) and hydrophobic parts, process temperature, and molecular weight, which are interconnected and can be altered. Therefore, these three parameters will be discussed with respect to lignin polarity in the subsequent paragraphs.

By investigating the literature on the lignin polarity one can find diverse and contradictory information, but mainly the polarity could be explained with the solubility of lignin in solvent or solvent mixtures, which is closely related to the ability of the hydrophilic (OH) functional groups to form various interactions with the solvent where solvent parameters for all of these interactions are captured in Hanson's solubility parameter (e.g., dispersion forces, dipole interactions, and hydrogen bonding). General fundamental principles state that aromatic OH groups present in the lignin should make it more hydrophobic, whereas aliphatic OH groups are more likely to increase the hydrophilicity of lignin due to the formation of strong hydrogen bonds with water which are one of the most important interaction discussing lignin solubility in alcohols but lignin polarity contrasts this statements.[56] Further investigating lignin polarity according to the various types of the OH group literature finds possible explanations in pK_a of both aromatic and aliphatic OH groups in combination with the different affinity to hydrogen bond formation where pK_a values are 7−11 and 14−18, respectively.[53,55,57−60] In this way, lower values would show higher or stronger affinity to hydrogen bond formation and preset aromatic OH groups in lignin as more hydrophilic. Not only do both types of OH groups in lignin play a role in the polarity and subsequent lignin solubility but the hydrophobic part of lignin also plays an important role. Furthermore, the hydrophobic part is responsible for the formation of larger lignin fragments or so-called aggregates favored by using organic solvents and is driven by van der Waals and $\pi-\pi$ interactions of the main aromatic polymer structure. In addition, this formation of larger fragments is also driven by the hydrophilic OH groups of lignin, worth noting is the formation of hydrogen bonds between the aromatic OH groups and the methoxyl groups within the lignin macromolecules making more aliphatic OH groups accessible on the surface to make more hydrogen bonds with the solvent due to less accessible aromatic OH groups in the more closed structure of the larger fragments or so-called aggregates.[53,61,62]

Overall, a small addition of water leads to the formation of lignin fragments, aggregates, or complexes with a higher molecular weight rich in aliphatic OH groups found on the aggregates surfaces due to formation of the weaker hydrogen bonds with solvent (ethanol). On the other hand, low molecular weight lignin fractions, which are rich in aromatic OH groups, require correspondingly greater changes in the solvent system due to stronger hydrogen bond formation between the lignin and solvent (ethanol) to induce precipitation with antisolvent (water) as a result of their greater solubility in less polar solvents such as ethanol and are therefore isolated with the last additions of water.[52,54,57,63−65]

Increasing the process temperature from 140 to 180 °C in combination with the water-assisted fractional precipitation changes the lignin polarity even further and leads to smaller lignin fragments with a more hydrophilic character of lignin, which changes the ratio between aliphatic and aromatic OH groups. The general change in OH group content is related to the various instant reactions during organosolv lignin isolation, such as depolymerization, mainly due to the cleavage of ether bonds (appearance of new aromatic OH groups), alkoxylation, specifically ethoxylation due to the etherification of the α-OH groups and/or the formation of new C−C bonds or the so-called molecular rearrangement at Cα position.[13,36] The ethoxylation of the aliphatic OH groups, which is favored by the temperature, additionally increases the hydrophobicity of the lignin by reducing the number of aliphatic OH groups available for hydrogen bonding with water molecules. For example, fractions B140_F3, B160_F3, B180_F3 with M_w of 4400, 2700, and 1900 Da isolated under the same conditions (δ = 41.5 MPa$^{0.5}$) show the following ratios between aliphatic and aromatic OH groups: 4.29/1.64, 2.78/2.59, and 1.80/4.30, indicating reduced polarity, but not much. Since a higher temperature favors depolymerization, which causes the appearance of lower molecular weight fragments with new aromatic OH groups, the hydrophilic character of lignin is enhanced. Furthermore, comparison of the fractions with similar M_w (3500−2700 Da) shown in Figure 3a, specifically B140_F4, B160_F3, B180_F2, provides a clearer insight into the temperature effects on the polarity of the precipitated lignin fractions as we lower the M_w-related aggregation factor. The aforementioned fractions B140_F4, B160_F3, and B180_F2 exhibit a ratio of aliphatic to aromatic OH groups of 4.01/1.92, 2.78/2.59, and 1.71/3.70, respectively. In both cases, temperature has a significant effect on the polarity of the lignins and completely changes lignin fractions, which is then driven by the water-assigned fractionation, which results in complete change of ratio between aliphatic and aromatic OH groups in final lignin fractions.

3.5. Temperature Effects on Structural Features.

3.5.1. Interunit Linkages.

The structural differences between the lignin fractions were determined by 2D HSQC NMR. The main aliphatic (β-O-4, β'-O-4, β-5, β-β') and aromatic (S-, G-units) lignin motifs were identified and evaluated (Figure 2, semiquantitative results are listed in the Table 3). In general, the content of all the interunit linkages decreases with the average M_w of the fraction especially within the lignin fractions, from the 140 and 160 °C black liquor, whereas fractions produced from the 180 °C black liquor generally have very low amounts of interunit linkages, indicating major structural changes/degradation in the lignin macromolecule. The main difference between the fractions is the content of total β-O-4 linkages, which is the highest with 54 and 41 linkages per 100 C9 units in the fractions obtained at the lowest process temperatures 140 and 160 °C, respectively, whereas for the those obtained from the 180 °C black liquor, approximately 8 to 2 β-O-4 linkages per 100 C9 units are present within the fractions. Fractions rich in β-O-4 content are of particular interest for the further depolymerization, and thus, by applying this approach of lignin fractionation directly from the black liquor (process T = 140 °C), it is possible to reduce the lignin M_w from 9200 to 3500 Da by reducing the content of β-O-4 linkages by only 23%.

3.5.2. Ethoxylation Degree. During the extraction in aqueous ethanol, lignin bearing α-ethoxylated β-O-4 motifs (designated β'-O-4 in this study) are obtained. The degree of ethoxylation increases with the temperature reaching from 32.9 up to 48.9% for B140_F4 and B180_F2 fractions, respectively. The lignin extraction temperature strongly influences the intensity of the ethoxylation reactions and simultaneously reduces the amount of the β-O-4 linkages from 54 to 2 per 100 C9 units in B140_F1 and B180_F4 fractions, respectively, thus requiring a compromise between the desired content of ether bonds, M_w, reactive and ethoxylated aliphatic OH groups (Figure 3b, Table 3). The degree of ethoxylation is one of the most important characteristics describing ethanol organosolv lignin, since in the case of further direct use it is necessary to know the amount of the reactive OH groups or, if the aim is a complete lignin ethoxylation, the amount of aliphatic OH groups left for the further ethoxylation. Additional ethoxylation of partially α-etherified lignin could be performed according to the protocol developed by the Deuss group, which combines further steps of oxidation and subsequent decarbonylation to produce defunctionalized lignin with high potential for conversion to the monoaromatic compounds such as 3,4-dimethoxyacetophenone and guaiacol.[66]

3.5.3. Aromatic Units. Contrary to the trend observed for the aliphatic interunit linkages, the content of the aromatic units increases in the lignin fractions with a lower M_w. The abundance of the S- and G-units changes within the fractions; specifically, the content of S-units increases while the amount of G-units decreases with decreasing M_w. In addition, the trend becomes more pronounced with the process temperature, while fractions with the predominant S-units are most likely produced due to the more pronounced β-O-4 bond cleavage with syringyl moieties, which is also consistent with the quantitative ^{31}P NMR data showing the increase in S-OH groups. The following implies that ethanol organosolv lignin precipitation directly from the black liquor in an ethanol/water mixture starts with the self-assembly of larger lignin macromolecules with a higher content of aliphatic OH groups and interunit linkages as well as a higher abundance of etherified G-units at δ = 36.8 MPa$^{0.5}$ and proceeds until the smallest lignin fragments rich in S-OH groups with significantly less aliphatic moieties at δ = 44.8 MPa$^{0.5}$ are recovered. Furthermore, lignin fractions with different ratios of the aliphatic/aromatic OH groups, interunit linkages, and the M_w in the range of 1 to 10 kDa could be separated using δ-controlled ethanol/water media.

Figure 3c shows the number of main aliphatic (total β-O-4, β-O-4, β'-O-4, β-5, β-β') interunit linkages in lignin fractions with comparable M_w isolated at different process temperatures, namely, B140_F4, B160_F3, and B180_F2. By comparing different fractions within the same Protocol B by adjusting the temperature, it can be observed that at the higher isolation temperature, the fraction with the selected M_w was obtained earlier (lower fraction number). However, it is possible to vary the total β-O-4 content up to 7-fold (from 6 to 41 bonds per 100 C9 units in fractions B180_F2 and B140_F4). It is also possible to influence the intensity of the ethoxylation reactions (degree of ethoxylation of fractions B140_F4, B160_F3, and B180_F2 is 32.9, 42.5, and 48.9%, respectively). With this in mind, it should be noted that the organosolv process temperature in combination with δ-controlled fractional precipitation facilitates the separation of lignin fractions with the specific structural characteristics for further applications (depolymerization, modification, polymer synthesis). Notably, the most important advantage of such lignin precipitation directly from the black liquor is the possibility of process integration, as the lignin precipitation unit could eventually be adapted to the requirements for fractional lignin precipitation, isolating lignin macromolecules with the different properties (specific lignin fraction targeted) depending on the material solubility (polarity), which is one of the key characteristics affecting further lignin valorization. Obtaining this lignin fraction through a tailored organosolv process is a promising approach that enables the valorization of the specific lignin fraction, but also the other recovered lignin fractions need to be taken into account. In this way, all the fractions produced in the sequence could be utilized effectively in some applications even though one specific fraction is targeted. For example, if the last fraction obtained using Protocol B at 160 °C (B160_F4, Table 1), which represents 25% of all lignin recovered, is targeted for use as a building block for epoxy resin formulations, with optional functionalization.[67,68] Meanwhile, the other fractions (B160_F1, B160_F2, B160_F3, Table 1), accounting for 75% of the recovered lignin in the form of fractions, could also be used via depolymerization.[69] This process produces lignin monoaromatics and lignin oligomers with even more defined functionalities and molecular weights. Moreover, these lignin oligomers could also be used in the preparation of epoxy resins as well, whereas the lignin monoaromatics, characterized by their aromatic nature, have other potential applications in polymer synthesis. One specific application of such use could be in the production of phenol—formaldehyde resins, where phenol could be substituted.[70] However, additional functionalization might be required to adapt the lignin monoaromatics for this use. Overall, linking these applications and our fractional precipitation with the economic feasibility of the organosolv fractional precipitation process, discussed later, highlights an important insight. In this way, the value of lignin fractions would vary depending on the amount of antisolvent added, making different fraction values which can be used accordingly. Fractions requiring less antisolvent would be used for less expensive applications and are more suitable for commodity applications or further functionalization and defunctionalization processes, while those needing more added antisolvent could target higher-value applications due to the higher cost associated with their precipitation.

3.6. Lignin Type-Related Effects on Fractionation. To determine the possible effects of the lignin type on fractionation, lignin was extracted from spruce sawdust (*P. abies*) and fractionated according to Protocol B. The fractions were analyzed as **S_B**. The fractions were designated as

Table 4. Characteristics (Structural Composition and OH Group Distribution) of Beech and Spruce Lignin Fractions with Similar Molecular Weight M_w (2900−3700 Da)[a]

	total β-O-4	β-β'	β-5	S/G/H	ED[b] [%]	Aliph	Ar	COOH	total	*Aliph OH/Ar OH	M_w [Da]	Đ	δ [MPa0.5]
	number of linkages per 100 C9 units					OH groups [mmol g^{-1}]							
B_B140_F4	41	9	3	66/34/0	32.9	4.01	1.92	0.07	6.01	2.1	3500	2.5	44.8
B_B160_F3	23	8	3	73/27/0	42.5	2.78	2.59	0.05	5.43	1.1	2700	1.8	41.5
B_B180_F2	6	7	2	75/25/0	48.9	1.71	3.70	0.06	5.47	0.5	2900	1.7	40.2
S_B140_F3	42	3	14	0/98/2	59.2	3.15	1.27	0.40	4.83	2.5	3700	2.5	41.5
S_B160_F2	27	4	13	0/100/0	59.4	2.63	1.70	0.28	4.60	1.5	3200	2.1	40.2
S_B180_F1	n.d.	n.d.	n.d.	n.d.	n.d.	1.38	2.35	0.12	3.85	0.6	3300	2.1	38.2

[a] Spruce and beech lignin samples are designated as S_B and B_B, respectively. *AliphOH/ArOH—ratio between aliphatic and aromatic OH group content. [b] Ethoxylation degree.

S_Bxxx_Fx: **S** as spruce lignin, **Bxxx** as black liquor produced at a temperature of **xxx** and fractionated according to Protocol B, while **Fx** is a fraction number. The experimental and analytical data are shown in Tables S1−S3 in the Supporting Information.

Comparison of the isolated spruce lignin fractions clearly shows lignin type-related effects on fractional precipitation in terms of OH group distribution, molecular weight, and structural composition. In general, there is an analogous tendency for the aromatic OH group content to increase and the aliphatic OH group content to decrease, followed by a decrease in the β-O-4 bond content as the molecular weight of the fraction is reduced. To identify lignin type-related effects, fractions of spruce lignin (softwood, samples designated as S_B) and beech lignin (hardwood, samples designated as B_B) with a similar M_w (2900−3700 Da) were compared, specifically, S_B140_F3 (3700 Da), S_B160_F2 (3200 Da), S_B180_F1 (3300 Da), B_B140_F4 (3500 Da), B_B160_F3 (2700 Da), B_B180_F2 (2900 Da) (Table 4).

For example, if the target is to produce lignin-derived fragments for the specific application with the particular M_w, in the range between 2700 and 3700 Da and with the AliphOH/ArOH = 1.0, beech wood should be used as a feedstock for the organosolv fractionation and the solubility parameter of the obtained liquor should be adjusted to the value of δ = 41.5 $MPa^{0.5}$ with water as an antisolvent. The product fitting the requirements would be the fraction B_B160_F3 (2700 Da, AliphOH/ArOH = 1.1). Data summarized in Table S1, show that, if spruce would be used as feedstock instead, lignin fraction S_B160_F3 (2300 Da, AliphOH/ArOH = 1.5) would be obtained which does not fit the range of the desired parameters. Obviously, due to the structural differences between spruce and beech lignin in terms of the interunit linkage content, guaiacyl unit content and ethoxylation degree, fractions obtained at the same conditions (process temperature of 160 °C, δ = 41.5 $MPa^{0.5}$) differ, thus to isolate fraction with the same characteristics as beech lignin, different conditions would be required.

The degree of ethoxylation (ED) of the lignin fractions is shown in Table 4. Spruce lignin fractions show a higher ED compared with the beech lignin fractions. These results are consistent with the literature and depend on the structural composition of the lignin. For example, spruce (softwood) lignin consists mainly of guaiacyl units (G), which provide more reactive sites than the syringyl units (S) of beech (hardwood) lignin.[20] The methoxyl groups in the syringyl units reduce reactivity and additionally limit ethoxylation in hardwood lignin,[20] while ethanol as a solvent suppresses lignin condensation in softwood more effectively than in hardwood lignin.[20,71] The combination of structural reactivity and reduced condensation reactions ultimately allows softwood lignins to be ethoxylated to a greater extent.The reactivity of the aliphatic and aromatic OH groups in lignin is of fundamental importance as these groups influence the behavior of lignin during chemical modification, depolymerization, and cross-linking. Understanding and controlling the reactivity of these OH groups enables the development of high-value applications in biobased materials, resins, biofuels, and chemicals, unlocking the full potential of lignin as a renewable resource.[72,73] In this study, lignin fractions with a similar M_w (2900−3700 Da), isolated from two different sources at the different organosolv process temperatures, changing the solubility parameter, have different aliphatic and aromatic OH group ratios (values are shown in Table 4). Interestingly, plotting the ratio of aliphatic and aromatic OH groups in order from the lowest to the highest value shows that the reactivity of the lignin fractions in this particular case can be tailored in the range from 0.5 to 2.5 (Figure 4.). Importantly, the adjustment of lignin reactivity, in terms of total OH group content, for spruce lignin is possible between 3.9−4.8 mmol g^{-1} and for beech lignin between 5.5−6.0 mmol g^{-1}.

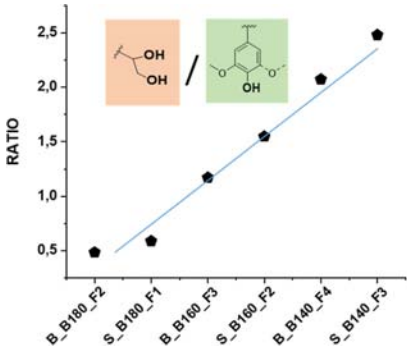

Figure 4. Aliphatic and aromatic OH group ratio in lignin fractions with similar M_w (2700−3700 Da), isolated by varying wood type (spruce or beech), process temperature, and solubility parameter.

The combination of raw materials (beech and spruce) and the fractionation allow the production of lignin fragments with M_w between 2700 and 3700 Da with the AliphOH/ArOH ratio from 0.5 to 2.5 (Figure 4). More importantly, the AliphOH/ArOH ratio could be tailored using only water, and the additional functionalization of the aromatic OH groups could be excluded. Finally, these results open up new possibilities for

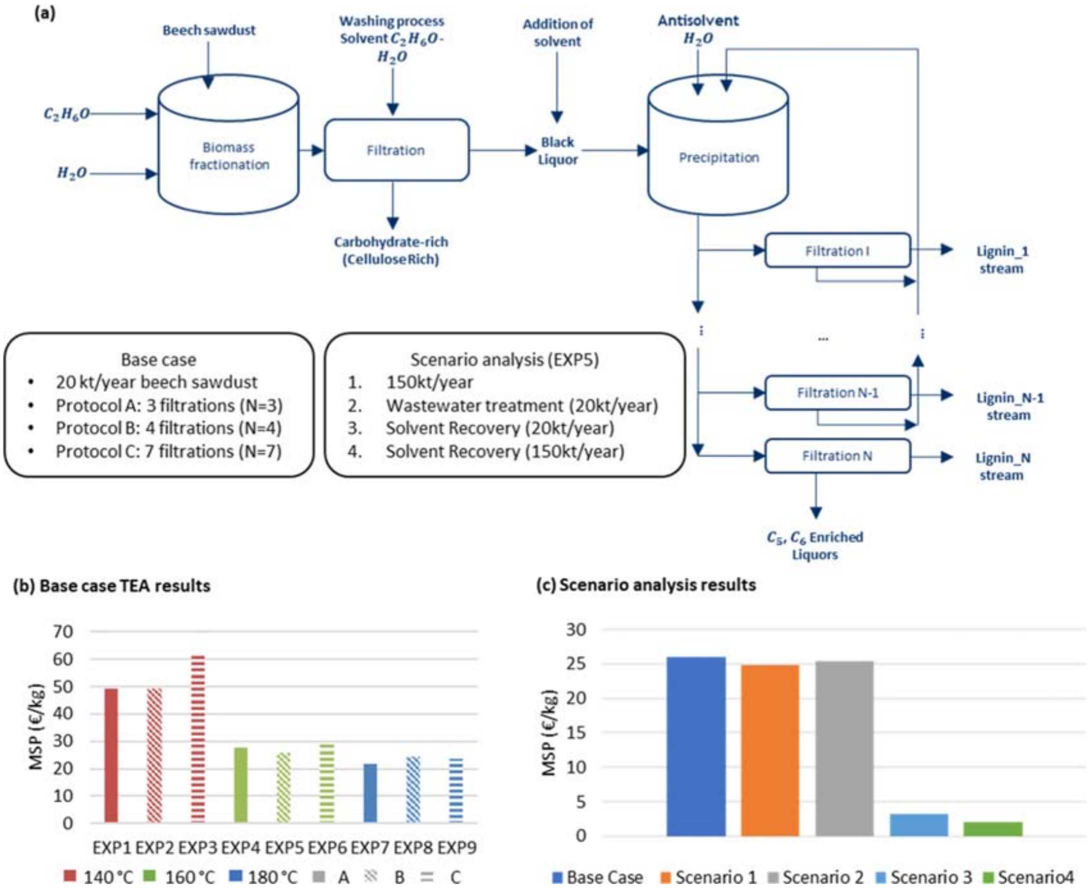

Figure 5. (a) Process flowsheet of base case of the organosolv fractionation of beech sawdust with the three protocols and 4 scenario's (b) results of the TEA representing the minimum selling price (MSP) for all the experiments in the base case, (c) results of the TEA representing the MSP for EXP5 for the 4 investigated scenario's compared to the base case.

research in the field of sustainable production of lignin fragments, including the development of models to predict the parameters required to obtain a target lignin-derived structure, ensuring process repeatability.

3.7. Techno-economic Potential of the Organosolv Process.

3.7.1. Assumptions. A full description of a techno-economic assessment is provided in the Supporting Information. Briefly, a TEA was carried out to assess the economic feasibility of organosolv fractionation of beech sawdust. As this TEA is based on laboratory scale data and many assumptions have been made, the aim is to provide a first indication of the economics of the process and to show where the key cost drivers are situated, which can be an important source of information for later technology readiness levels (TRLs). The basic process flowsheet diagram of the organosolv fractionation process is shown in Figure 5a and starts with beech sawdust, from which two product streams can be identified after fractionation: a lignin-rich stream and a cellulose-rich stream. A third stream resulting from the process is considered to be wastewater. Aspen Plus (V12.1) was used to simulate the organosolv fractionation process. This setup is chosen as the base case, because it represents the scale-up of the experimental setup studied with the currently available data. As this is not yet the optimal process in terms of waste recovery, alternative scenarios are added. For this purpose, two workup protocols have been studied: (A) wastewater treatment section and water recycling to the fractionation process and (B) recovery of the water/ethanol solvent for use in the fractionation process and the first filtration or washing step. Each of these is studied at three different fractionation temperatures (140, 160, and 180 °C) and a pressure of 2 bar, resulting in nine different simulations. A plant processing 20 kt/year of beech sawdust (see Supporting Information) is simulated. The first step of the simulation is the biomass fractionation, simulated as a reactor with the temperature (140, 160, or 180 °C) and pressure (2 bar) as input. Ethanol and water are added as solvents (atmospheric conditions) to achieve a biomass/solvent ratio of 1:7 (w/v) and a solvent composition of 50 vol % ethanol/water. In this step, the H_2SO_4 catalyst is also added at 1 wt % of the dry biomass.

As no specific region is targeted, the European average is assumed for the tax rate of the biorefinery (21.5%), shown in Table 5.[74] The project lifetime is assumed to be 20 years starting from 2021 with an annual operating time of 8000 h, a discount rate of 15% and a linear depreciation of 10 years, similar to the assumptions of Tschulkow et al.[75] and Brienza et al.[76] who both studied the economic performance of the valorization of the lignin fraction of lignocellulosic biomass. As an economic indicator, the MSP of the lignin-rich stream is calculated (i.e., the price of lignin oil product that results is a net present value of 0, given the above-mentioned assumptions). The carbohydrate-rich stream is assumed to have a value of 319 €/t (79% of the sugar price in Tschulkow et al.[75] as 79% can be recovered, Table S4) and is considered a byproduct and thus an additional revenue stream for the process. It is assumed that enzymatic hydrolysis is used to

Table 5. Techno-economic Assessment Assumptions (FCI: Fixed Capital Investment, ISBL: Inside Battery Limits)

parameter	value	reference
plant lifetime (years)	20	75, 76
base case annual biomass (kt/year)	20	assumption
cost year	2021	assumption
discount rate (%)	15	75, 76, 78
linear depreciation rate (%)	10	assumption
biorefinert tax rate (%)	21.5	74
annual operating hours (h)	8000	assumption
beech sawdust price (EUR/t)	100	79
lignin price (EUR/t)	843	[80,81] (Table S4)
byproduct price (EUR/t)	319.16	75 (Table S4)

produce the byproduct, but simulation of this is beyond the scope of this paper. Estimating the exact selling price of the carbohydrate-rich pulp is difficult due to the many factors involved enzymatic saccharification, however, Tschulkow et al.[75] examine a similar process and thus the same assumptions are made. For this purpose, the pulp byproduct selling price is included in the sensitivity analysis to assess the impact of this assumption. Details of the market study for price information, process flowsheet simulations, mass and energy balances, and process economics are provided in Supporting Information Figures S4−S11 and Tables S4−S8. The calculation of both OPEX (operating expenditures) and CAPEX (capital expenditures) are based on assumptions from the book Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design (Table S7).[77] The Aspen Process Economic Analyzer is used to determine equipment costs for the different unit operations in the simulation.

3.7.2. Base Case Results. The results of the TEA for the nine different experimental setups are shown in Figure 5b. Bars of the same color represent the same operating conditions: red (140 °C), green (160 °C), and blue (180 °C), while bars with the same pattern represent the same protocol: solid (Protocol A), diagonal stripes (Protocol B), and horizontal stripes (Protocol C). The main difference is visible among EXP1-3, EXP4-6, and EXP7-9. These three groups represent the three different operating conditions of the fractionation process, thus resulting in a different yield and MSP. As the yield of the lignin-rich fraction increases, the MSP decreases. For the processes at 140 °C the yield is between 24.6 and 30.8%, while at 160 °C the yield is 52.9−59.2%, and at 180 °C the yield is 62.8−70.8%. Within the same operating conditions, the same pattern is observed. At 140 and 160 °C the yield increases from Protocol C to A and B. However, at 180 °C the yield increases from Protocol B to C and A. A local sensitivity analysis with all the details in the appendix D (see Supporting Information, Figure S6) shows that the ethanol cost is the key influential parameter (9.2%). Based on the results observed in Figure 5b, further scenarios were investigated only for Protocol B, EXP5 (Figure 5c). The reason for choosing Protocol B operating at 160 °C is related to the MSP shown in Figure 5b, as this protocol offered the best MSP at the three temperatures examined in this work. In addition, EXP5 was preferred to experiments performed at 180 °C because the operating temperature of 160 °C offered the possibility of recovering lignin fractions with more distinct M_w. Four different scenarios are analyzed (Figure 5a) in which a larger scale is investigated and/or an extra step is added to the carbohydrates (sugars C_5 and C_6) enriched liquid. Scenario analysis is provided in the Supporting Information.

3.7.3. Economic Viability. The market study (see Supporting Information Table S4) shows the highest value of 843 €/t for high purity lignin and 584 €/t for organosolv lignin.[82] However, it is important to note that the lignin value varies drastically depending on the reference, as lignin is a complex structure that is a byproduct of many different processes. The prices quoted and selected are those most commonly found in the literature and used in economic evaluations. This price is significantly lower than the lowest MSP in this research at around 2000 €/t. In order to reduce this value, it is important to reduce the cost of ethanol. By theoretically optimizing the process to a fresh solvent requirement 14 times lower than the current one, the MSP can reach a value of 843 €/t. However, the constant linear growth of the lignin market due to increased demand in various industries, growing interest in sustainable and biobased products, research and development efforts, and finally advances in production technologies also affects the MSP. Both an increasing market volume and demand, as well as the influences of learning effects that occur as a technology matures, will lead to a reduction in costs and thus a reduction in the MSP.[83] Note that the calculated MSP is assumed to be the same for all four lignin fractions produced together and not as a single lignin.[76] Consequently, differences in the economic value of these lignin fractions are not considered. However, these may differ significantly depending on whether high added value products are targeted and could justify a higher MSP compared to lower/commodity lignin prices. As shown (see Supporting Information, Table S4), the purity of the lignin has an impact on the potential selling price. A similar effect is expected when different lignin-derived end-products. In the past, lignin was mainly obtained as a byproduct of enzymatic hydrolysis, in which the lignin was combusted for energy and thus had a value close to the current fuel prices.[84] Reports focusing on enzymatic hydrolysis consider lignin as a structure that interferes with the process and must be removed, regardless of how the lignin properties are affected,[85] again making it difficult to estimate the potential market value of lignin. Furthermore, it is also important to note that the TEA is based on laboratory scale data at a low TRL that can be scaled up to an industrial scale. It does not take into account the technological improvements associated with increasing the TRL. First, the yield of the process will increase, resulting in a more efficient process and thus having a positive impact on the economics. Current lignin yields are from the experimental data [between 24.6 and 70.8% (Table 1)], while literature shows the potential to achieve yields between 70 and 90% for larger scales.[11,86] Second, the technological advances are also associated with learning effects, where processes become more efficient, leading to a reduction in costs. These learning effects can be incorporated into the economic assessment by using learning curves, however, these learning curves are based on historical data, which limits their applicability to novel processes.[87] Vasilakou et al.[83] developed a framework to calculate the learning rate required for a process to become profitable. The calculated learning rate required to become profitable can potentially provide additional information to assess the economic potential of future processes.

4. CONCLUSIONS

Organosolv lignin fractions were directly recovered from black liquor by using water as an antisolvent. Comparison of lignin fractions from softwood (spruce) and hardwood (beech) with similar M_w isolated at different temperatures provided the opportunity to tailor lignin reactivity (functionality) by completely changing the ratio of aliphatic/aromatic OH groups with almost no change in the total amount of OH groups and by varying the amount of β-O-4 bonds by up to 7-fold. This sustainable approach increases the valorization potential of lignin. Optimizing solvent recovery, further lignin valorization, and reducing the use of antisolvents are key to profitability. Consequently, the study of other types of lignocellulosic biomass, such as agricultural crops, would allow the development of the mathematical model, explicitly taking into account the characteristics of the reaction and precipitation media, and could predict the isolation of the lignin with the properties of interest, which is beyond the scope of this research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c08125.

> SEC chromatogram profiles of the fractions isolated according Protocols A, B, and C; quantitative ^{31}P NMR spectra and aromatic OH group distribution within the fractions; 2D NMR spectra, characteristics of spruce lignin fractions; and economic feasibility of organosolv fractionation of beech sawdust (market study, process flowsheet simulations, process economics, sensitivity analysis of base case, and scenario analysis) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was founded by the Slovenian Research Agency (research core funding P2-0152, infrastructure funding I0-0039 and research project funding L2-50050). P.N. holds a FWO senior postdoctoral fellowship (grant number: 1215523N) granted by FWO Vlaanderen/Research Foundation Flanders.

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