



Cite this: *RSC Sustainability*, 2025, 3, 4514

Influence of the biomass-source and the extraction process on lignin properties and γ -valerolactone induced conversion of biomass towards valuable lignin monomers

Moritz Schweiger,^{ID}* Thomas Lang, Didier Touraud, Eva Müller^{ID} and Werner Kunz^{ID}

With a rising demand in fossil-based chemicals and their derived products, alternatives have to be developed from bio-based materials to meet the declining fossil resources. Lignocellulosic biomass is widely seen as a promising alternative, especially on the topic of bioplastics. However, challenges still lie in complete and efficient valorization of biomass and converting its components into suitable products. For this purpose, the tailoring of the lignin structure through extraction method and choice of biomass have to be studied extensively. The green solvent γ -valerolactone (GVL) was shown to facilitate efficient fractionation of all main components of lignocellulosic biomass in our previous study. To further build on this process of a GVL-based extraction process at mild conditions, lignin from different process conditions and biomass types was extracted, and subsequent hydrogenolysis experiments were conducted to decompose especially lignin oligomers with high ether contents into specific monomers. The structure of the products, referring to lignin oligomers and monomers, largely depends on the biomass type of origin of the lignin and the extraction process. The product characteristics from several biomass sources were analyzed using NMR spectroscopy, UV/Vis spectroscopy, and chromatography techniques. Default extracted lignin and lignin extracted with an aldehyde-assisted process led to a broad spectrum of lignin with different properties, indicating the influence of the extraction process on the extracted lignin properties. The present study examines the production of lignin oligomers and monomers with different properties from lignocellulosic biomass after two different selective extraction and decomposition processes using the green solvent GVL. These products can be used for different applications depending on their post-extraction properties that originate from its biomass source and the extraction/degradation process.

Received 5th May 2025
Accepted 15th July 2025

DOI: 10.1039/d5su00324e

rsc.li/rscsus

Sustainability spotlight

Within our green biomass fractionation process, lignin is extracted with γ -valerolactone in different structural forms depending on the process conditions. The lignin structure, such as molecular weight, hydroxy group content, methoxy group content, or ether content can be tailored by choice of biomass, process parameters, and follow-up depolymerization reactions to fit specific applications of polyaromatic or monoaromatic biobased molecules. This builds upon our process by producing tunable lignin for a large spectrum of applications under green and mild conditions to encourage a biobased chemical industry under the concept of biorefinery. Our process aligns with the UN goals in responsible consumption and production (UN SDG 12).

1 Introduction

The efficient use of lignocellulosic biomass in many fossil-based applications provides great prospects for the future replacement of fossil resources with renewable resources. The concept of lignocellulosic biorefineries as a strategy to produce high-value chemicals from lignocellulosic biomass thus stands

as a highly prioritized research topic.¹ Still, lignocellulosic biomass is currently only utilized at around 5% compared to its global annual production.^{2,3} Using the potential of its three main components, cellulose, hemicellulose, and lignin, different pathways towards replacements for fossil-based products are possible and have to be studied to finalize the concept of biorefineries, inducing a scale-up to industrial levels, and ensuring a functional competition with fossil-based products.⁴

In our previous article, we have shown a complete process of biomass fractionation into its three main components using the

Faculty of Chemistry and Pharmacy, Department of Physical Chemistry II, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany. E-mail: Moritz.Schweiger@chemie.uni-regensburg.de



green solvent γ -valerolactone (GVL) at mild conditions. All three biopolymers could be separated at high yields and high purities.⁵ This was conducted for various biomasses. For certain biomasses, like coffee silverskin, a waste-stream from the coffee industry, extractives like caffeine can be pre-separated in high quantities with a simple aqueous solution, maximizing the waste stream biomass valorization.⁶ Based on these findings, the three separated biopolymers (lignin, cellulose, hemicellulose) can be further processed now separately. While the valorization or efficient dissolution of hemicellulose and cellulose will be addressed in a future article, this work shows the production of lignin oligomers and lignin monomers with certain properties for optimized further processing from lignocellulosic biomass. The aim is to demonstrate the effects of the extraction process and the biomass' origin on the lignin properties past extraction and thus the options of valorization.

Lignin is a highly complex three-dimensional biopolymer, consisting of the three building blocks sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol, which are all modifications of *p*-hydroxy cinnamyl alcohol. These building blocks link together to form the complex biopolymer, where the alcohols form corresponding subunits called syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H), respectively.^{7–13} The overall composition of lignin entirely depends on the type of biomass source. Lignin from softwoods is mainly composed of G (90–95%) and small amounts of H (5–10%), while lignin from hardwoods is mostly composed of G (25–50%) and S (50–75%) in various parts and small amounts of H (1–5%). Lignin from grasses or other non-wood lignocellulosic biomasses contain G (25–50%), S (25–50%), and H (10–25%) in more similar parts.^{8,14} In the polymerized state, the subunits are interconnected through various linkages. The most prevalent are ether linkages, including β -O-4', 4-O-5', and α -O-4' linkages. Carbon-carbon linkages are also formed, including β - β' , β -1', and 5-5' linkages. Additionally, a combination of both carbon-carbon and carbon-oxygen linkages leads to β -5'/ α -O-4' and β - β' / α -O- γ' linkage systems, which refer to phenyl coumaran (PC) and resinol (R) structures in the lignin biopolymer structure, respectively. The most prominent linkages are β -O-4' (~60%), β - β' , and 5-5' linkages.^{7,8,10} Depending on the type of biomass source, lignin has different concentrations of functional groups attached to its main structure, which include methoxy, hydroxyl, carboxyl, and carbonyl groups.⁷ These specific groups are important for later using extracted lignin for specific applications, depending on the concentration of certain functional groups. Functional groups, linkage types, subunit structures, and general nomenclature of lignin structures for this work are shown in Fig. 1.

Lignin is only present in plant cells as lignin-carbohydrate complexes (LCC) with hemicellulose, which are formed through phenolic glycoside, ester, and ether linkages between hydroxyl groups of lignin and substituted backbone sugars of hemicellulose. These LCC function as an embedding matrix for the cellulose chains.^{7,10} During extraction, lignin will be depolymerized to a state where the linkages between the biopolymers are broken down and the intermolecular interactions between the biopolymers are weaker than the interactions between lignin and the extraction solvent. Due to its many hydroxyl

groups and ether linkages, lignin is comparatively polar, however mostly preventing swelling or chemical attacks due to strong interactions with the hemicellulose and also intermolecular interactions at mild conditions, which had to be considered in the extraction process. These properties also enable lignin to protect the polysaccharides in lignocellulosic biomass from degradation. Other functions of lignin include the regulation of cell water for nutrient transport and the formation of a mechanically stabilizing polymer network.^{7,10}

In the chemical industry, lignin is mostly produced in the form of Kraft lignin. This type of lignin is obtained *via* the Kraft pulping process, which involves the treatment of biomass with a sodium hydroxide/sodium sulfide mixture at 150–170 °C. In a precipitation step in an acidic aqueous medium, lignin can be separated from the pulp.¹⁵ Kraft lignin is typically highly soluble in alkaline solutions, contains about 1–3% of sulfur in covalent bonds with thiol groups or aromatic sulfur substituents, is highly condensed with high C–C bonding, and has a low molecular weight of ~1000–3000 g mol^{−1}. However, 98% of it is burned to recover the energy of the pulping process or produce fuel. The residual 2% are used to produce valuable bio-substitutes for petroleum-based chemicals.^{16–18} Another source for lignin is the lignosulfonate process, which is similar to the Kraft process. Here, biomass is treated with sulfite and bisulfite anions in combination with calcium, magnesium, or ammonium cations at 160 °C. The resulting lignin is about 5% rich in sulfonate groups and is generally at significantly higher molecular weights than Kraft lignin (up to 140 000 g mol^{−1} with high polydispersity¹⁹) due to the different conditions of the extraction process. Lignosulfonate lignin is highly water soluble due to the higher dispersity coming from the sulfonate groups and linked carbohydrate impurities. Lignosulfonates thus have special applications in animal feed, surfactants, pesticides and additives in different colloidal mixtures.^{7,9,20} Another type of lignin comes from the organosolv process, which uses organic solvents, mostly in combination with water, under acidic conditions and various temperatures between 80–220 °C and 0.5–24 h.²¹ Organosolv lignin typically has a low molecular mass and high condensation similar to Kraft lignin (~1000–3000 g mol^{−1}), but without sulfur impurities, leading to higher hydrophobicity and lower water solubility.¹⁰ This process was used in our previous study and was optimized to use comparably mild conditions (85 °C for 3 h) and gain lignin with high yields and purities. Using different extraction process conditions, the properties of organosolv lignin can be altered to fit certain applications, which will be elaborated on in this article. Enzymatically hydrolyzed lignin is another type of lignin gained from enzymatic hydrolysis of biomass, which uses enzymes to achieve monomeric sugars in high yields from biomass, leaving behind a high molecular weight lignin in relatively native state, with its properties depending on the biomass type and the hydrolysis conditions. It is typically less soluble in water and more hydrophobic than sulfur-containing lignin with lower molecular weight.^{22–24} Additionally, lignin can be extracted through a soda process, using basic conditions (16–18% NaOH) at 140–170 °C. This leads to lignin products similar to Kraft lignin and organosolv lignin with around 3000 g mol^{−1} and



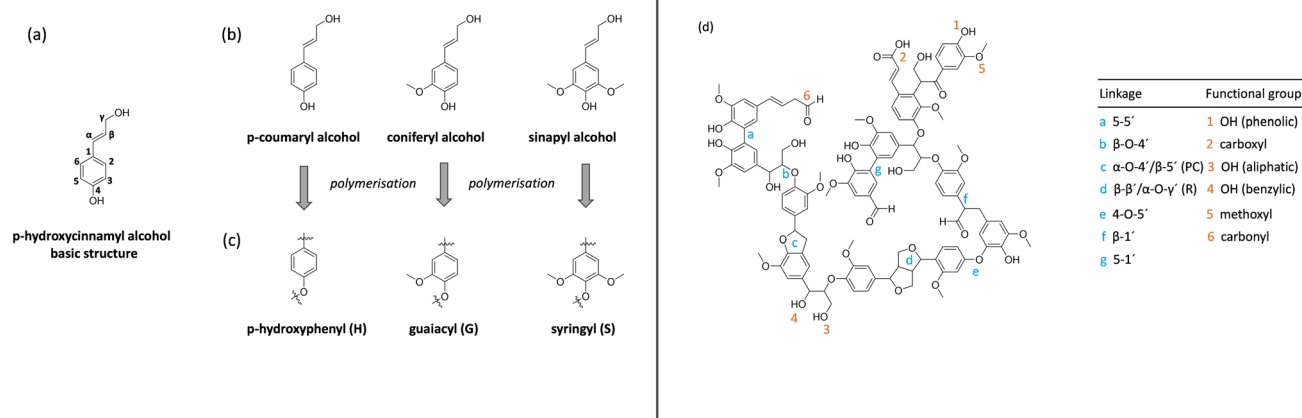


Fig. 1 Compositional description of lignin. (a) Lignin subunit *p*-hydroxy cinnamyl alcohol basic structure and common nomenclature; (b) lignin building units *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; (c) lignin subunits after the polymerization of the building units towards a 3D-structure, in which *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) are present as subunits; (d) excerpt of the 3D-structure of lignin, showing all possible linkage structures and functional groups present in the lignin structure.

high condensation.^{7,9} All different lignin types can have different applications depending on their specific properties. For the produced lignin in our process,⁵ properties can be tailored towards different applications, while being produced at mild conditions and high yields and purities.

Lignin needed to be efficiently extracted using green solvents and thoroughly analyzed across different biomass types to evaluate its properties post-extraction. Lignin extractions were carried out using previously optimized methods,⁵ a well-established default extraction process using an aqueous acidic GVL solution,^{25,26} and an aldehyde assisted extraction process first established by Lan *et al.*²⁷ The latter ensures that, compared to the default extraction process, lignin is extracted without condensation, meaning close to no formation of unbreakable C–C bonds during extraction. This enables a more efficient extraction at milder conditions with higher yields and purities, but leads to lignin oligomers with very different properties, as shown in this research. The extraction process affects linkage type composition, free phenolic hydroxy group content, and molecular weight after extraction, which are key parameters for lignin valorization.

After extraction of lignin with high ether linkage content, subsequent hydrogenolysis experiments could be established to produce valuable monoaromatic lignin monomers. This can be realized with the support of metal catalysts like Ru/C or Pd/C under high pressure hydrogen atmosphere.^{28,29} While the catalyst type and the hydrogenolysis conditions can have significant influence on the monomer yield and structure,³⁰ another important part is the structural quality of the lignin substrate. With a larger ether linkage content in lignin, the ether-linkage-selective degradation is more efficient. When speaking of selective lignin degradation, the term selective depolymerization often comes up. As lignin is not a classical biopolymer, but rather a complex heterogeneous macromolecule, selectivity on degradation is often very low. For our process, we refer to our

degradation method as an ether-linkage-specific cleavage degradation, which cleaves the ether linkages in lignin structures to produce monomers in significant quantities, but also oligomers of lignin with carbon–carbon bonds bridging multiple subunits. A larger degree of condensation and thus a higher number of C–C linkages reduces the degradation efficiency.²⁹ To achieve maximum degradation efficiency, lignin has to exhibit certain properties like high ether linkage content and no condensation, which can be obtained using the aldehyde-assisted extraction process.

Regarding lignin valorization, there are different challenges to overcome for its efficient use in the chemical industry. Industrial lignin is usually very heterogeneous in its structure, coming from Kraft-pulping or lignosulfonate-pulping. These lignins are mostly burned for energy recovery and the recycling of pulping chemicals. Its low use in chemical industry products can be explained by its complex structure, dark color, strong smell, and recalcitrance to depolymerization.³¹ Novel strategies to make use of lignin in the chemical industry thus have to include quality extraction/fractionation processes, selective degradation (linkage-selective or product-selective) methods, and specific valorization strategies. The usability of lignin for certain applications entirely depends on the desired properties of the target molecule, and how these properties can be achieved through lignin treatment processes.^{31–33} This research applies the findings of previously used extraction processes to influence the properties of extracted lignin molecules and explain the pathways towards achieving desired lignin properties for specific applications. The main factors here are the lignin biomass source and the lignin treatment processes. Achieving possible lignin applications from a biodiverse source material can lead to a deeper understanding of how to tailor lignin properties through treatment methods and thus improve the usability of lignin in the chemical industry.

2 Materials and methods

2.1 Chemicals and materials

Sulfuric acid (95–98%, CAS 7664-93-9), L-cysteine (98%, CAS 52-90-4), DMSO-d₆ (99.8%, CAS 2206-27-1), acetaldehyde (for synthesis, CAS 75-07-0), acetone (>99.5%, CAS 67-64-1), chloroform (anhydrous, CAS 67-66-3), choline chloride (>98%, CAS 67-48-1), dichloromethane (DCM) (for analysis, CAS 75-09-2), *N,N*-dimethylformamide (DMF) (for analysis, CAS 68-12-2), dimethyl sulfoxide (DMSO) (for analysis, CAS 67-68-5), 1,4-dioxane (for analysis, CAS 123-91-1), ethanol (for analysis, CAS 64-17-5), ethyl acetate (for analysis, CAS 141-78-6), ethylene glycol (for analysis, CAS 107-21-1), *para*-formaldehyde (37% in water, CAS 50-00-0), hydrochloric acid (37%, CAS 7647-01-0), methanol (for analysis, CAS 67-56-1), palladium/activated carbon (1, 5, 10%, CAS 7440-05-3), trifluoroacetic acid (TFA) (>99%, CAS 76-05-1), toluene (for analysis, CAS 108-88-3), sodium hydroxide (for analysis, CAS 1310-73-2), propionic aldehyde (>98%, CAS 123-38-6), ruthenium on carbon (5 w%, CAS 7440-18-8), perchloric acid (0.1 M, 7601-90-3), methanol (>99%, CAS 67-56-1), were purchased from Merck KGaA (Darmstadt, Germany).

Gamma-valerolactone (GVL) (anal. grade, CAS 108-29-2) was provided by KVT-Technology/Glaconchemie (Graz, Austria).

Tetrahydrofuran (THF) (anal. grade, CAS 109-99-9), *n*-hexane (>99%, CAS 110-54-3), *n*-heptane (>99%, CAS 142-82-5), methyl-tetrahydrofuran (>99%, CAS 96-47-9), were purchased from Fisher Scientific GmbH (Schwerte, Germany).

Benzyl alcohol (>99%, CAS 100-51-6), lithium chloride (>99%, CAS 7447-41-8), lithium hydroxide (>99%, CAS 1310-65-2), microcrystalline cellulose (MC) (CAS 9004-34-6), sodium hydrogen carbonate (>99.5%, CAS 144-55-8), were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany).

Millipore distilled water was cleaned in a Millipore purification system ($p > 18 \text{ M}\Omega \text{ cm}$).

Peanut shells and skin were removed from store bought peanuts; pistachio shells were removed from store bought pistachios; hazelnut shells were removed from store bought hazelnuts. Walnut shells were removed from home grown walnuts.

Coffee silverskin was provided by Rheorik Rösterei & Feinkost GmbH (Regensburg, Germany).

Birch and beech wood were provided by Schreinerei Heitzner (Traitsching, Germany).

Cashew shell powder was provided by Orpia-Innovation (Paris, France).

Almond shells were provided by Otto A. Müller Recycling GmbH (Ahrensburg, Germany).

Spruce sawdust was provided by HCR Holz Centrum Regensburg GmbH (Regensburg, Germany).

Polystyrene standards (ReadyCal-Kit for GPC, Part No. PSS-mmkitrl) was purchased from PSS Polymer Standards Service (Mainz, Germany).

2.2 Ether-linkage-selective degradation of lignin into monomeric units

Lignin was extracted efficiently from lignocellulosic biomass using the biomass fractionation process from our previous

work.⁵ Lignin was extracted in a default organosolv extraction, and additionally in an aldehyde-assisted organosolv extraction (for detailed information, see SI Chapter 1).

To selectively depolymerize protected lignin structures into different monomeric units, hydrogenolysis was performed after the lignin extraction process. 200 mg of protected lignin, 20 mL of THF (or M-THF or GVL), and 250 mg of Pd/C (1%) or 100 mg of Ru/C (5%) were added to a 100 mL Parr high-pressure reactor containing a 20 mm PTFE-coated magnetic stir bar. After a 10 min leak test using 40 bars of nitrogen, the reactor was purged with hydrogen to 40 bars three times. The reactor was placed into a heating mantle, which was coupled to a PID temperature controller. The stirring of the reactor was set to 600 rpm and the heating was started. The reaction conditions were set to 200 °C for 15 h when using Pd/C, and 250 °C for 3 h when using Ru/C. The heating time was included in the reaction time. After the reaction time, the heating was turned off, and the reactor was allowed to cool to room temperature naturally, without the use of additional cooling methods. The solution was drawn into a syringe and the catalyst was removed using a syringe filter. 1 mL of the resulting solution was mixed with 0.1 mL of internal standard (2 mg per mL decane in THF). The mixture was analyzed *via* GC-MS and quantified *via* GC-FID.

Reductive catalytic fractionation was carried out similarly. Biomass was directly subjected to hydrogenolysis without prior fractionation to compare the achieved monomer yields. The reagent amounts used were: 1 g of biomass, 200 mg of Ru/C (5%), and 20 mL of methanol.

2.3 Solvent recovery process

Solvents from all mixtures containing GVL could be recovered for solvent reusability. GVL was recovered through simple vacuum distillation at 60 °C and 10^{-3} bar. Water can be separated from GVL through rotary vacuum evaporation at 40 °C and 0.1 bar.

2.4 NMR spectroscopy

NMR experiments were conducted using an Avance III HD 400 spectrometer (400.13 MHz proton, 5 mm BBO 400 SB BB-H-D sample head with Z-gradient). Lignin samples were dissolved in DMSO-d₆ at 60 mg mL⁻¹ and transferred to NMR glass tubes after complete dissolution. For all samples, ¹H-NMR and 2D-HSQC-NMR spectra were measured to evaluate the aromatic subunit and the linkage composition of lignin from different biomass sources. SpinWorks was used to analyze the NMR spectra.

Lignin and sugar molecules were analyzed in 2D-HSQC-NMR spectra using a method established by Zijlstra *et al.*³⁴ The content of each monomeric building block and the content of each linkage type can be calculated *via* integration of the respective signals. Lignin consists of the three main building blocks guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H). Each of those show distinguishable signals in the HSQC spectrum. Similar to the monomeric units, each linkage type of lignin, mainly β-O-4', β-β', and β-5', also show distinguishable signals. Each building block and linkage unit has distinct labelling,



referring to signal ranges in the HSQC spectrum (each G,S,G (x) or linkage-type_x stands for the respective integral of the 2D-HSQC-NMR signals for the following data, see Table 1 and Fig. 2).

Via eqn (1), the total aromatic integral is calculated.

$$\text{Total aromatic} = (S(2,6) + S(\text{con})) + \frac{G(2) + G(5) + G(6) - H(2,6)}{3} + \frac{H(2,6)}{2} \quad (1)$$

With the total aromatic integral, the percentages of the G, H, and S units can be calculated via eqn (2)–(4) respectively.

$$S \text{ content} = \frac{(S(2,6) + S(\text{con}))}{\text{total aromatic}} \times 100[\%] \quad (2)$$

$$G \text{ content} = \frac{\left(\frac{G(2) + G(5) + G(6) - H(2,6)}{3} \right)}{\text{total aromatic}} \times 100[\%] \quad (3)$$

$$H \text{ content} = \frac{\left(\frac{H(2,6)}{2} \right)}{\text{total aromatic}} \times 100[\%] \quad (4)$$

Additionally, the number of linkages for every one hundred aromatic units can be calculated for each linkage type via eqn (5)–(7). Only the integrals of the α -atoms of the linkages are considered for this calculation.

$$\beta\text{-O-4}' \text{ content} = \frac{(\beta\text{-O-4}'_{\alpha})}{\text{total aromatic}} \times 100[\%] \quad (5)$$

$$\beta\text{-5}' \text{ content} = \frac{(\beta\text{-5}'_{\alpha})}{\text{total aromatic}} \times 100[\%] \quad (6)$$

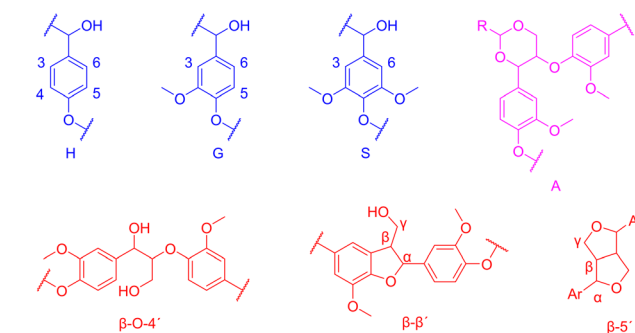


Fig. 2 Labelling of all atoms relevant for 2D-HSQC-NMR analysis and interpretation for all lignin subunit and linkage units. A = Labelling of protected lignin structures for protection rate analysis through 2D-HSQC-NMR.

$$\beta\text{-}\beta' \text{ content} = \frac{(\beta\text{-}\beta'_{\alpha})}{\text{total aromatic}} \times 100[\%] \quad (7)$$

A full compositional analysis of extracted lignin samples was possible with this method. Even acetal-protected lignin samples from hydrogenolysis could be analyzed. Since acetal-protected linkage signals have a different chemical environment, the signals shift to different ppm ranges. This makes it possible to calculate the percentage of acetal-protected (A) linkages compared to all linkages present in lignin samples. Fig. 2 also shows the labelling of acetal-protected linkage structures. The A_{α} signal was discovered at a [proton/carbon] range of [(4.0–4.2)/(74–79)]. Via eqn (8), it is possible to calculate the number of acetal-protected linkages per one hundred aromatic units in extracted lignin. Eqn (9) describes the calculation of percentage $\beta\text{-O-4}'$ linkages that are acetal-protected.

$$A \text{ content} = \frac{A_{\alpha}}{\text{total aromatic}} \times 100[\%] \quad (8)$$

$$\text{Protected percentage} = \frac{A_{\alpha}}{(A_{\alpha} + \beta\text{-O-4}'_{\alpha})} [\%] \quad (9)$$

Table 1 Signal ranges for different lignin subunit and linkage units. Labelling can be seen in Fig. 2

| Signal | Proton range [ppm] | Carbon range [ppm] |
|--------------------------------|---------------------|--------------------|
| S(2,6) | 6.48–6.90 | 104.0–109.0 |
| S(condensed) | 6.35–6.65 | 106.0–109.0 |
| G(2) | 6.78–7.14 | 111.5–116.0 |
| G(5) | 6.48–7.06 | 115.0–120.5 |
| G(6) | 6.65–6.96 | 120.5–124.5 |
| H(2,6) | 7.05–7.29 | 128.5–133.0 |
| $\beta\text{-O-4}'_{\alpha}$ | 4.76–5.10 | 73.0–77.5 |
| $\beta\text{-O-4}'_{\beta}$ | 4.03–4.48 | 85.0–90.5 |
| $\beta\text{-O-4}'_{\gamma}$ | 3.10–4.00 | 58.5–62.0 |
| $\beta\text{-5}'_{\alpha}$ | 5.42–5.63 | 88.0–92.0 |
| $\beta\text{-5}'_{\beta}$ | 3.36–3.56 | 53.0–54.5 |
| $\beta\text{-5}'_{\gamma}$ | 3.50–4.00 | 62.0–64.5 |
| $\beta\text{-}\beta'_{\alpha}$ | 4.59–4.77 | 86.5–89.5 |
| $\beta\text{-}\beta'_{\beta}$ | 2.98–3.20 | 55.5–59.0 |
| $\beta\text{-}\beta'_{\gamma}$ | 3.75–3.96/4.10–4.31 | 72.5–76.0 |

2.5 UV/vis spectroscopy

2.5.1 Spectroscopy. UV/Vis spectroscopy experiments were conducted on a double-beam UV/Vis spectrophotometer from PerkinElmer Lambda 19 UV/Vis/NIR (Dodgau, Germany). Examined samples were measured in micro-UV cuvettes with an optical path length of 1 cm from brand GmbH & Co. KG (Wertheim, Germany) against a reference sample at 25 °C in a wavelength range from 200 nm to 400 nm.

2.5.2 Ionization difference spectroscopy. The phenolic hydroxy content was determined using ionization difference spectra. The applied method was done according to Chen *et al.*³⁵ Extracted lignin (10 mg) was dissolved in 1 mL ethylene glycol. Additionally, the same solution was prepared with a concentration of NaOH of 2 mol L^{−1}. The UV/Vis spectra of both solutions were measured against a blank solution. Calculating the difference between both spectra, ionization difference spectra were formed. Taking ionization difference absorbance values at



300, 320, 350, and 370 nm, the concentration of free hydroxy groups can be calculated for extracted lignin samples using eqn (10)–(14).

$$\Delta A_{300} = (3619 \times C1) + (586 \times C2) - (6728 \times C3) - (4880 \times C4) \quad (10)$$

$$\Delta A_{320} = (3039 \times C2) - (11428 \times C3) + (391 \times C4) \quad (11)$$

$$\Delta A_{350} = (344 \times C2) + (5436 \times C3) + (24010 \times C4) \quad (12)$$

$$\Delta A_{370} = (22590 \times C3) + (10658 \times C4) \quad (13)$$

From the received values $C1$, $C2$, $C3$, and $C4$, the concentration of hydroxy groups can be calculated, shown in eqn (14).

$$c(\text{OH}) [\text{mol L}^{-1}] = C1 + C2 + C3 + C4 \quad (14)$$

Through multiplication of the hydroxy group concentration $c(\text{OH})$ with the mass concentration of the lignin sample ($\beta(\text{lignin}) = 10 \text{ g L}^{-1}$) in the sample solution, the molality $m(\text{OH}) [\text{mmol g}^{-1}]$ can be calculated.

2.6 Gel permeation chromatography

To separately analyze the molecular weight distribution of isolated lignin samples, gel permeation chromatography (GPC) was used. The GPC system employed was the Malvern Viscotek 270-03 setup with a Malvern GPC100 column (Malvern, United Kingdom). Samples chosen for GPC analysis were dissolved in tetrahydrofuran, which was used as the mobile phase, at a concentration of 1.5 mg mL^{-1} through stirring for 24 h at room temperature. The resulting solutions were filtered into screw-cap flasks with PTFE septa using a $0.2 \mu\text{m}$ syringe filter to stop larger particles from entering the column. Each sample was placed into the autosampler and $150 \mu\text{L}$ of each sample were injected into the column with a 1 : 45 split and a flow rate of 1 mL min^{-1} . A refractive index detector was used to monitor the separation. The mass average molecular mass (M_w), the number average molecular weight (M_n), and the polydispersity index (PDI) were calculated by the software based on a sample retention time, using polystyrene calibration standards provided by PSS Polymer Standards Service (Mainz, Germany).

2.7 Thermogravimetric analysis

Lignin samples were analyzed with a thermogravimetric analysis device, TGA-7 of PerkinElmer Comp., to evaluate the effectiveness of the lignin extraction process. Measurements were performed under synthetic air (80/20 nitrogen/oxygen) with a flow rate of 25 mL min^{-1} . The temperature range was between 50 and $700 \text{ }^\circ\text{C}$ with a heat rate of $10 \text{ }^\circ\text{C min}^{-1}$. A samples preparation was not necessary after lignin extraction and drying.

2.8 Gas chromatography coupled with mass spectrometry

The method used for the characterization of monomers after hydrogenolysis is based on a publication from Amiri *et al.*³⁶

Qualitative analysis was carried out using GC-MS with an Agilent 7890B GC system, fitted with a ZB-5MSplus column, and a Jeol AccuTOF GCX mass spectrometer. Samples ($1 \mu\text{L}$) were injected using an autosampler in split mode (split ratio 75 : 1) at an injection temperature of $300 \text{ }^\circ\text{C}$. The septum purge flow was maintained at 3 mL min^{-1} . The column temperature was initially set at $40 \text{ }^\circ\text{C}$ for 3 minutes, then ramped to $100 \text{ }^\circ\text{C}$ at $30 \text{ }^\circ\text{C min}^{-1}$, followed by a further increase to $300 \text{ }^\circ\text{C}$ at $40 \text{ }^\circ\text{C min}^{-1}$, where it was held for 5 minutes. Monomers were identified by comparison with the NIST MS Search 2.2 database.

2.9 Gas chromatography with flame ionization detection

Quantitative analysis of lignin hydrogenolysis products was performed on an Agilent 7820A GC system equipped with a VF-5ms column and a flame ionization detector (FID). The temperature program for the GC-FID was identical to that used in the GC-MS analysis. Sensitivity factors for the products were determined based on estimates using the effective carbon number (ECN) approach. The ECN factors used were the ones published by Amiri *et al.*³⁶

Monomer yield calculations were conducted using the peak area of the monomer and an internal standard (decane) from the GC-FID chromatogram. The specific calculation procedure was as follows, in eqn (15)–(18).

$$n_{\text{decane}} = \frac{m_{\text{decane}}}{M_{\text{decane}}} \quad (15)$$

$$n_{\text{monomer}} = \frac{A_{\text{monomer}}}{A_{\text{IS}}} \times \frac{\text{ECN}_{\text{decane}}}{\text{ECN}_{\text{monomer}}} \times n_{\text{decane}} \quad (16)$$

$$m_{\text{monomer}} = n_{\text{monomer}} \times M_{\text{monomer}} \quad (17)$$

$$\text{Monomer yield} = \frac{m_{\text{monomer}}}{m_{\text{lignin}} \times 20} \quad (18)$$

where n is the amount of substance (mol), m is the weight (g), M is the molecular weight (g mol^{-1}), and A is the FID integral area. The monomer yield (unit: weight percent) calculated with eqn (18) is corrected by the factor 20 as 1 mL of 20 mL hydrogenolysis solution was subjected to analysis.

3 Results and discussion

3.1 GVL-assisted lignin extraction and analysis

3.1.1 Lignin analysis using acidic GVL/water mixtures. All extracted lignin samples were analyzed with UV/Vis spectroscopy to determine the content of free hydroxy groups per lignin molecule, NMR spectroscopy to determine the structural composition and the binding composition for different biomasses, thermogravimetric analysis to confirm the lignin purity and overall composition, and gel permeation chromatography to determine the molecular mass of lignin samples for different biomasses. Analytical data was collected for the default extraction process of lignin from different biomasses using an acidic GVL/water solvent mixture at $120 \text{ }^\circ\text{C}$. Thermogravimetric analysis confirmed the successful extraction and



purity of lignin through its thermal behavior. Fig. 3 shows the exemplary TGA and DTG curves for spruce sawdust lignin.

The degradation of all lignin samples usually starts at temperatures of 350 °C. Before, around 5% of residual moisture evaporated at around 100 °C and 3% of residual GVL at 200 °C. Above 250 °C, 7% of the total composition of residual carbohydrates degraded. Residual 85% of the sample could be attributed to lignin, with around 30% of the sample remaining as highly condensed aromatic structures of lignin monomeric subunits.³⁷ This was due to the extraction process yielding partly condensed lignin structures, which would be unfavorable for further degradation due to complicated structural inconsistencies. This was similar for lignin from other biomasses, where only the char content was different, which correlates with the thermal stability and condensation of the lignin. Table 2 shows the experimental TGA data.

2D-HSQC-NMR spectra were recorded for extracted lignin samples from different biomasses for a deeper structural understanding of lignin from different biomasses. The aromatic region of the HSQC-spectra (6.25 to 7.55 ppm) gives information on the structural subunit composition of lignin. A quantitative evaluation can be made by integration of respective signals for different lignin subunits G, S, and H. The monomers can bond through carbon-carbon linkages, including β - β' , β -1', and 5-5', or through carbon-oxygen bonds, such as β -O-4', which can be analyzed in the aliphatic region of the HSQC-spectra (3.10 to 5.40 ppm). The aromatic and linkage compositions of extracted lignin were determined for each biomass and are depicted in ternary diagrams in Fig. 4(a and b). Fig. 4(a) shows the G/S/H composition of lignin from different biomasses.

Table 2 Experimental data from thermogravimetric analysis of GVL extracted lignin from different biomass sources. TGA provided the content of residual carbohydrates, the lignin purity, and the content of highly condensed aromatic units (char), which correlates with the thermal stability and the condensation of the lignin

| Type of biomass | Carbohydrate content [%] | Lignin purity [%] | Char content [%] |
|-------------------|--------------------------|-------------------|------------------|
| Spruce sawdust | 7 | 93 | 30 |
| Coffee silverskin | 5 | 95 | 16 |
| Walnut shell | 8 | 92 | 28 |
| Hazelnut shell | 8 | 92 | 27 |
| Peanut skin | 7 | 93 | 45 |
| Peanut shell | 9 | 91 | 43 |
| Pistachio shell | 8 | 92 | 40 |
| Almond shell | 7 | 93 | 29 |
| Cashew shell | 12 | 88 | 36 |
| Beech sawdust | 7 | 93 | 20 |
| Birch sawdust | 6 | 94 | 15 |

Overall, the G or S contents of lignin subunits are the most prevalent, with softwoods like spruce showing only G and no S content, and hardwoods and other lignocellulosic materials usually showing a wide variety of different compositions. This can be interesting in terms of specifically controlling the creation of different monomeric units from the extracted lignin structures, as for example the further degradation of spruce sawdust lignin would yield around 92% of guaiacyl monomers and 8% of hydroxyphenyl monomers, while the further degradation of walnut shell lignin would yield 32% G monomers, 66% S monomers, and 2% H monomers. Fig. 4(b) shows the linkage composition of lignin from different biomasses. This linkage composition is highly dependent on the extraction process, as different conditions influence the type of linkages that are preserved or even newly formed (condensation). All extracted lignin samples exhibit a major percentage (based on all linkages present) of ether-linkages (74–94%), depending on the biomass source. The overall ether linkage content correlates with the thermal stability of lignin from certain biomasses. A lower number of ether linkages compared to C–C linkages in the lignin structure creates a more condensed, complex, and thus more thermally stable polyphenolic structure. Depending on the properties of a desired lignin-based product, the type of lignocellulosic feedstock can be chosen through evaluating its structural composition. The GVL organosolv extraction process extracts lignin with different structural compositions with similar efficiency. The only hindrance in selectively degrading the extracted lignin is the presence of inconsistent condensation structures. The assumed condensation of lignin structures, forming different C–C linkages in the process at various points in the lignin structure, becomes evident in the merging/strong overlapping of the else distinctly visible signals for G and S in the aromatic region and in the existence of higher amounts of carbon-carbon linkage signals in the aliphatic region, which are typically only present in very few amounts. While the subunit composition only depends on the type of biomass used for extraction, the condensation depends on the conditions of the extraction process. In GVL-extracted lignin samples, the G

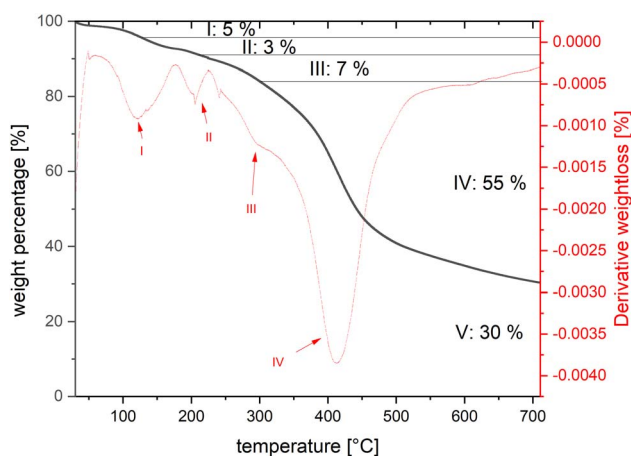


Fig. 3 Analytical data of GVL-organosolv extracted lignin from different biomasses – thermogravimetric analysis of spruce sawdust lignin. Weight percentage referring to the straight black graph correlates to the left y-axis, the derivative weight loss referring to the punctuated red graph correlates to the right y-axis. Both graphs are a function of temperature over a range of 0 °C to 700 °C. Phases I to V on both graphs show the different stages of thermal degradation in a lignin sample (I: moisture, II: organic solvent residue, III: residual carbohydrates, IV: lignin, V: lignin highly condensed aromatic residue (char)).

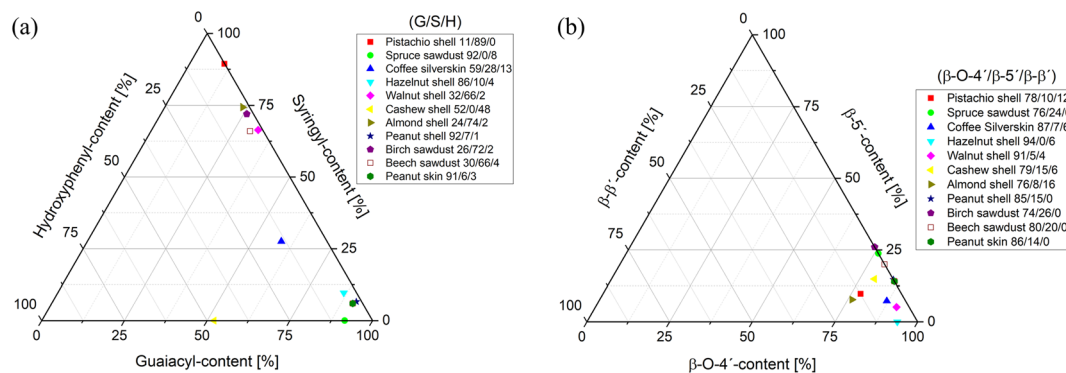


Fig. 4 Analytical data of GVL-organosolv extracted lignin from biomasses – NMR results. (a) 2D-HSQC-NMR results: aromatic lignin subunit determination for extracted lignin from different biomasses, guaiacyl (G), syringyl (S), and hydroxyphenyl (H) contents are depicted in a ternary compositional diagram. (b) 2D-HSQC-NMR results: lignin linkage composition determination for extracted lignin from different biomasses, β -O-4', β - β' , β -5' contents are depicted in a ternary compositional diagram. The signal correlation for both ternary compositional diagrams is given in the respective legend.

and S signals are distinguishable, but slightly overlap. Also, the existence of around 10–20% of carbon–carbon linkages for all biomasses confirms the presence of condensed lignin structures. However, condensation is low due to the more or less mild extraction conditions, but still significant enough to prevent efficient separation of lignin from the cellulose fibers and a selective degradation towards lignin monomers, as even slight condensation rates can significantly reduce the degradation efficiency.²⁹ However, the structural integrity of the core aromatic polymer that the extracted lignin still exhibits can lead to a use in several lignin-based applications, which is elaborated on through analysis of different necessary properties.

GPC analysis of extracted lignin samples, depicted in Fig. 5(a), determined the molecular mass values of lignin including the weight-average molecular mass distribution and the polydispersity index, and thus its residual degree of polymerization. Lignin from spruce wood showed a molecular mass distribution of 2060 g mol^{-1} with a polydispersity index of 1.59, while lignin from nut biomasses showed a higher molecular

mass distribution with a lower polydispersity index. Due to the harder surface structure of nutshells, lignin structures are extracted in higher degrees of polymerization, which can be interesting for applications of lignin where molecular mass plays a role, for example in flocculants.³⁸ To fully complete the lignin analysis, the phenolic hydroxy group content of GVL-extracted lignin was analyzed through UV/Vis spectroscopy. This can be particularly interesting for an application where such functionalities on the subunits are required, such as in antioxidant mixtures.³⁹ Ionization difference spectra of the extracted lignin were calculated from UV/Vis absorption spectra, from which the phenolic hydroxy group content in mmol g^{-1} (lignin) was determined, depicted in Fig. 5(b). Different wood lignins show the highest phenolic hydroxy group content of 0.81 to 0.91 mmol g^{-1} . Using molecular mass values, this converts to around two free phenolic hydroxy groups per extracted lignin molecule. Similar but slightly lower values were determined for several nutshell lignins (almond, cashew, pistachio, peanut). Walnut and hazelnut lignin show only 0.32

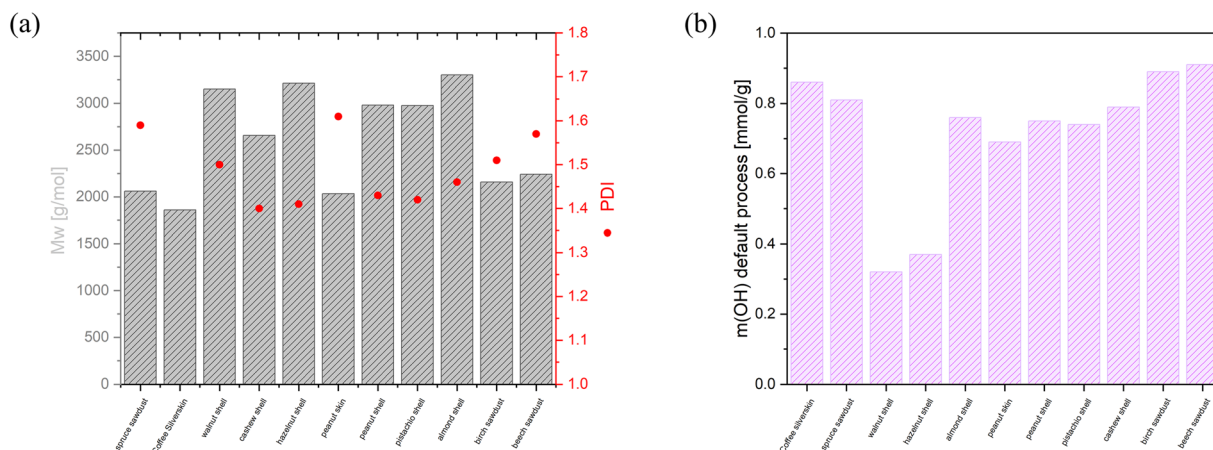


Fig. 5 Analytical data of GVL-organosolv extracted lignin from different biomasses – GPC and UV/Vis ionic difference results. (a) Biomass dependent gel permeation chromatography data of lignin. Grey columns: weight average molecular mass distribution of extracted lignin correlating to the left y-axis. Red points: polydispersity index of molecular mass distribution correlating to the right y-axis. (b) Biomass dependent free phenolic hydroxy group content of extracted lignin in mmol g^{-1} (lignin), determined through UV/Vis ionization difference spectroscopy.

and 0.37 mmol g⁻¹ of free phenolic hydroxy groups, respectively. This converts to one phenolic hydroxy group per oligomer for those biomasses regarding their molecular weight values. Also, regarding their higher molecular mass and higher β -O-4' content, the harder shells of both biomasses lead to a higher crosslinking content in lignin and more rigid and stable biomass structuring through their different lignin structures. The less linkages and molecular mass a lignin from a certain biomass shows, which correlates with decreasing rigidity of the biomass structure, the higher is the free phenolic hydroxy group content in its structure.

While the analysis of extracted lignin with an acidic GVL/water solvent at 120 °C shows the difference in lignin depending on the type of lignocellulosic feedstock, a reoccurring problem for all used biomasses is the condensation of the extracted lignin during the extraction process. To prevent condensation reactions, a different method of extraction was applied to our GVL-assisted extraction process. The aim was to produce structurally consistent lignin without condensed structures, which can be subsequently degraded into valuable lignin monomers depending on the biomass and its lignin composition. The less condensed lignin structures were predicted to show higher overall ether linkage contents, higher molecular mass and higher free phenolic hydroxy group content due to milder extraction conditions. This is further explained in the following chapter.

Still, several possibilities of lignin valorization became apparent after thoroughly analyzing the properties of different GVL-extracted lignins. While condensation leads to a loss in lignin's native structure, including parts of free phenolic hydroxy groups, ether linkages, and free aliphatic hydroxy groups, the core polyaromatic structure stays intact. Therefore, condensed lignin can be of value in different applications, which will be addressed in Chapter 3.3. However, extracting lignin in a more consistent and less condensed way can open up more possibilities of creating biomass-based applications, even using selected lignin monomers for different purposes. This will be addressed in the following chapter.

3.1.2 Aldehyde-assisted lignin extraction and analysis. For the modified lignin and hemicellulose extraction process from lignocellulosic biomass, the method of aldehyde-assisted fractionation, first established by Lan *et al.*,²⁷ was used and optimized for the green solvent GVL. This method uses aldehydes as protecting agents for the β -1,4-diol functions in lignin polymers, forming acetal-functionalities in the process. These acetals cannot be broken down in the slightly acidic environment of extraction, thus protecting the lignin structures from condensation during the extraction process. This was expected to yield more consistent lignin structures with higher ether-contents and a larger amount of phenolic hydroxy groups. These lignin structures were expected to be more suitable for subsequent hydrogenolysis towards lignin monomers, as higher overall ether-contents and less condensed aromatic structures lead to more cleavable sites between lignin subunits.

In general, 2D-HSQC-NMR analysis showed that the G/S/H ratio does not change with the modified extraction process, which is obvious as condensation only leads to a decrease in

ether-content and an increase in carbon-carbon linkage content. With the help of GPC, UV/Vis and further 2D-HSQC-NMR experiments, the improvements of the modified extraction process towards cleanly extracted lignin structures were shown, which is depicted in Fig. 6.

The qualitative analysis of lignin extracted with the modified extraction process proved the expected results. 2D-HSQC-NMR analysis showed no additional condensation in extracted lignin structures due to no more overlapping in the G/S signals, which proves the protection of the β -1,4-diol groups as well as the milder extraction conditions to be successful. The overall ether content, calculated from HSQC spectra per 100 aromatic units, greatly increased from around 15–35% (depending on the biomass source) for the default extraction process to around 30–61% for the modified extraction process. This again confirms the extraction of uncondensed, consistent lignin structures for the modified extraction process. The biodiversity of this extraction method is also shown here: it is evident that guaiacyl rich lignin from softwoods tends to have lower ether contents than syringyl rich lignin from hardwoods, which is in line with the experimental data. The extraction process completely conserves the ether content of lignin structures. Different nutshells, especially walnut shell and cashew shell show very high ether contents, which can be particularly interesting for the valorization of nutshells towards selective monomeric lignin subunits. This highlights the biodiversity of this extraction process, as all lignocellulosic biomasses can be fractionated and valorized further. Furthermore, the phenolic hydroxy group content increased from 0.3–0.9 mmol g⁻¹ lignin for the default extraction process to around 1.2–2.3 mmol g⁻¹ lignin for the modified extraction process. Additionally, GPC experiments showed that molecular mass distributions for the lignin from the modified extraction process almost doubled compared to the default extraction process. Combining these results, lignin oligomers extracted with the modified extraction process have 8–10 free phenolic hydroxy groups per molecule, which is a large increase compared to the 1–2 free phenolic hydroxy groups per molecule for lignin extracted with the default extraction process. All these results confirm the uncondensed, consistent state of extracted lignin using the aldehyde-assisted extraction method.

Generally, these extracted lignin oligomers could thus be used for subsequent hydrogenolysis experiments in a GVL solution, further expanding this process of lignocellulosic biomass fractionation towards valuable lignin monomers. However, even these acetal-protected high molecular mass lignin oligomers, which are high in ether-content and high in free phenolic hydroxy groups, can be interesting in terms of finding or improving certain applications of lignin due to their different solubility-behavior and maximized structural properties. Even through variation of the protection group, lignin could be functionalized towards different applications. There are already various ways to functionalize default lignin structures through chemical or enzymatic ways, or form crosslinking networks through polymer resins or hydrogels.⁴⁰ The functionalization through variation of the protecting agent, which can be an aldehyde or even molecules like glyoxylic acid, greatly



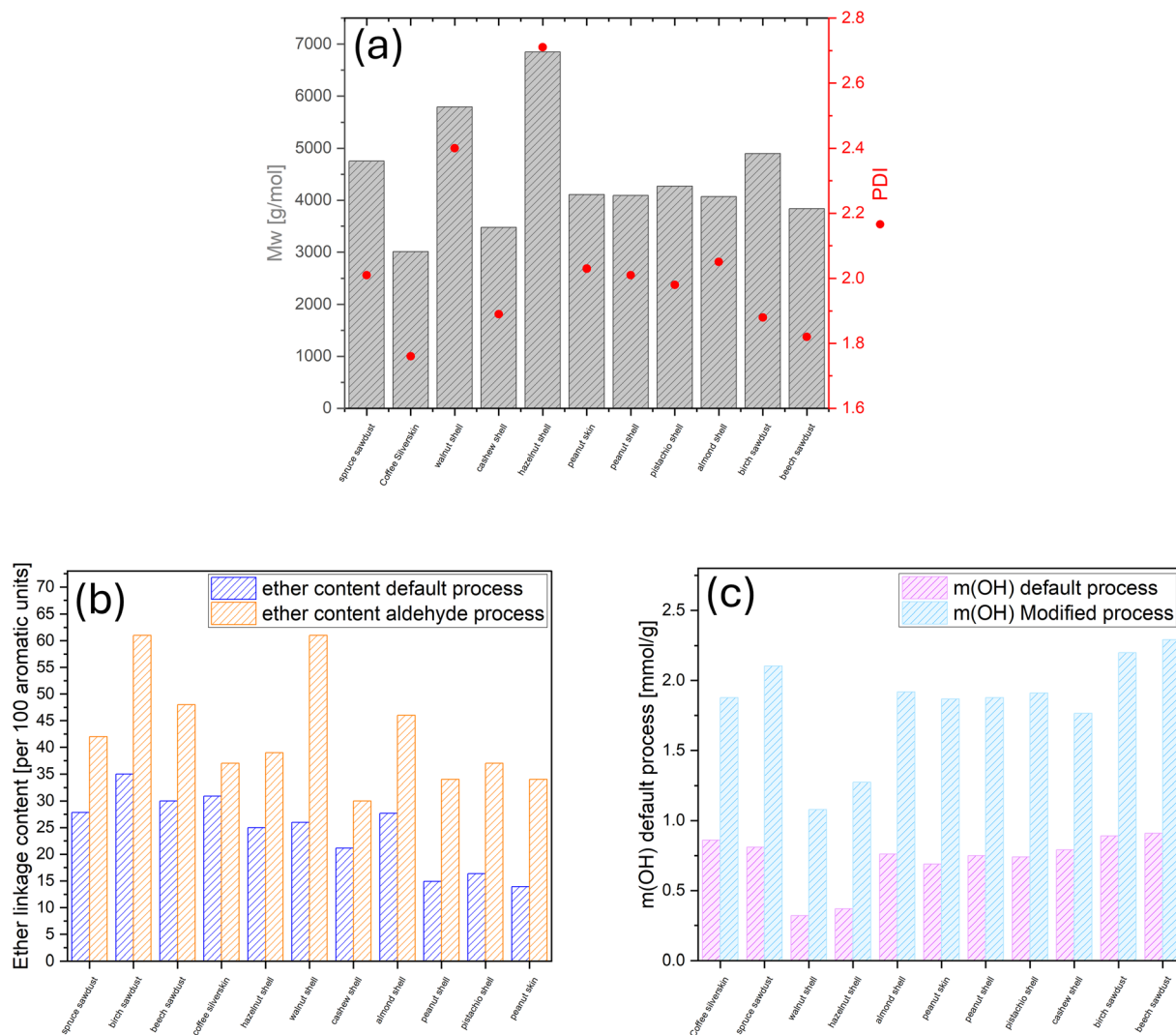


Fig. 6 Qualitative analysis of extracted lignin using the modified extraction process (acidic mixture of GVL/propionic aldehyde) compared to the default extraction process (acidic mixture of GVL/water). (a) GPC analysis of lignin extracted with the modified extraction process from all examined biomass sources. Columns show the weight average molecular mass distribution in g mol^{-1} . Points show the polydispersity index (PDI) of the molecular weight distribution. (b) Ether-content determination through 2D-HSQC-NMR spectroscopy of lignin from the modified extraction process (dark columns) compared to lignin from the default extraction process (light columns). The ether-content is depicted in ether linkages per 100 aromatic units of lignin. (c) Determination of the phenolic hydroxy group content of lignin extracted with the modified extraction process (dark columns) compared to lignin extracted with the default extraction process (light columns), through UV/Vis spectroscopy. The phenolic hydroxy group content is given in mmol of hydroxy groups per gram of lignin.

influences the solubility of the lignin in different polar solvents, and also its hydrophobicity. This can be a very interesting approach to generate even lignin with even more specific properties by simply changing the protecting agent in the fractionation process and should be studied in future research. Additionally, these protected lignin structures can be effectively converted to lignin monomers due to their high ether content, which will be addressed in the next chapter.

3.2 Lignin degradation

For subsequent hydrogenolysis experiments, instead of toxic solvents like THF or 1,4-dioxane,⁴¹ GVL or M-THF can be used, as they show great solubility of acetal-protected lignin.

However, they do not allow one to achieve the full total monomer yield like in THF. The total yield of lignin monomers is shown in Table 3 for different hydrogenolysis conditions. Three exemplary biomasses were used for lignin hydrogenolysis, namely spruce sawdust, birch sawdust, and walnut shell.

The theoretical yield is based on the squared ether content as ether units lead to monomers only if the ether unit is surrounded by two other ether units or if it is located at the chain end. This theoretical yield correlates to between 73–96% with the measured monomer yield using GC-MS measurements of decomposed lignin structures. Using the Pd/C catalyst, the conversion to monomers is lower by about 21% than using the Ru/C catalyst. Ruthenium favors the formation of propyl end groups on the monomers (72% with spruce). Palladium favors

Table 3 Theoretical and experimental monomer yields and monomer compositions for different lignins from different biomasses extracted with the modified extraction process under different hydrogenolysis conditions. 200 mg lignin, 20 mL THF, 250 °C, 15 h, Ru/C catalyst were used as default hydrogenolysis conditions. Biomass, catalyst, and reaction time were varied in small experiments. The theoretical yield is calculated through the overall ether content of the sample

| Lignin source | Cat. | Propyl guaiacol [%] | Ethyl guaiacol [%] | Guacyl propanol [%] | Propyl syringol [%] | Ethyl syringol [%] | Syringyl propanol [%] | Monomer yield [%] | Theoretical yield [%] |
|---------------|-----------|---------------------|--------------------|---------------------|---------------------|--------------------|-----------------------|-------------------|-----------------------|
| Spruce | Ru/C | 5.8 | 2.6 | 3.2 | — | — | — | 11.6 | 12 |
| Spruce | Pd/C | 1.2 | 0.4 | 7.1 | — | — | — | 8.7 | 12 |
| Birch | Ru/C | 3.2 | 1.7 | 0.5 | 8.0 | 6.5 | 1.2 | 21.1 | 27 |
| Birch | Pd/C | 0.9 | 0.3 | 2.4 | 2.0 | 1.3 | 10.8 | 17.8 | 21 |
| Walnut shell | Ru/C | 0.7 | 0.9 | 2.6 | 2.0 | 3.4 | 6.5 | 16.1 | 22 |
| Spruce | Ru/C 48 h | 0.2 | — | 0.3 | — | — | — | 0.5 | 14 |
| Spruce | Ru/C 3 h | 5.6 | 6.1 | 0.8 | 0.3 | 0.2 | — | 13.0 | 14 |

the formation of propanol end groups on the monomers (82% with spruce). Ethyl end groups on the monomers are also always present, but in lower quantities. Other monomers than shown in Table 3 were not detectable in GC-MS and GC-FID measurements of the products. Depending on the ratio of G to S for a certain biomass, certain platform chemicals can be produced from lignin using this complete process: propyl syringol/guaiacol and propanol syringol/guaiacol. The ratios of G to S for a biomass also match the ratio of those monomers from hydrogenolysis experiments. Furthermore, walnut shells show similar product yields to birch sawdust. Also, different reaction times induce different product compositions and overall yield. While longer reaction times lead to a far lower yield in monomers due to recondensation, overhydrogenation to cyclohexane compounds, or catalyst deactivation,^{42–45} the formation of propanol end groups was favored. Shorter reaction times preferred a higher ethyl/propyl end group selectivity. Detailed information on the product characterization with 2D-HSQC-NMR can be found in SI Section 2.

This clearly shows that the composition of the monomeric compounds entirely depends on the lignin subunit composition of the origin biomass source, the extraction conditions (higher ether-content leads to a larger yield of monomers and the use of different protecting agents), and the hydrogenolysis conditions (different catalysts and reaction times induce the formation of different products). This method shows a big advantage for biodiversity, as biomasses from all sources can be fractionated and their lignin selectively converted towards valuable monomers, solely depending on the G/S composition. Even a conversion to hydroxyphenyl (H) based monomers can be possible with biomasses high in H content, such as cashew shells, when methoxy groups are unfavorable for certain applications.

While the ether content for lignin extracted with the modified process is comparably high, there are still carbon–carbon linkages present in its structure, leading to a biomass-dependent amount of smaller oligomeric units. These were confirmed to be dimers, trimers and tetramers through GPC and GC-MS analysis (for detailed analysis, see SI Section 2). These residual oligomers can be separated from the monomeric products using a simple hexane extraction,^{46,47} where the

monomers dissolve in hexane while the oligomers form a precipitate. The separation efficiency of this method was confirmed through GPC analysis.

The overall process, consisting of the GVL-based lignin extraction and subsequent hydrogenolysis, was compared to a reductive catalytic fractionation (RCF) process, which is considered the most reliable method to obtain theoretical lignin monomer yields.³⁶ When using GVL as the solvent in our extraction process (GVL-AAF), the lignin monomer yield is 21.1%, which is only about 9% lower (for birch wood) than in the RCF method yielding 23.2% – meaning it achieves 91% of the theoretical monomer yield while using a non-toxic green solvent. Dioxane-AAF achieved similar values to the RCF process. Our process has clear advantages over solvents like 1,4-dioxane in terms of toxicity, while achieving similar results. In the RCF process, where biomass is directly subjected to hydrogenolysis without prior fractionation, the other biopolymer products are difficult to characterize and to recover from the other products, leading to a difficult post-hydrogenolysis fractionation of possibly degraded sugar moieties. This makes the GVL-AAF process more valuable compared to other methods, as the other biopolymers can be gained in high purities beforehand,⁵ while lignin monomer yields of similar quantities are achieved during hydrogenolysis, with the opportunity to also use the protected lignin intermediate products or the oligomer side products from hydrogenolysis as valuable chemicals in certain applications.

3.3 Summary: application-based tailoring of lignin through the extraction process

In summary, lignin could be extracted from biodiverse lignocellulosic sources with different properties. The most important for several applications, which can also be influenced by the extraction process, are molecular weight, ether content, condensation ratio, thermal stability, and free phenolic hydroxy group content. Several other properties that come from the high aromaticity of lignin can also be achieved by preserving the polyaromatic native structure of lignin. From this research, there are three different endpoints for chemical lignin treatments: (1) lignin was treated with an extraction process



involving acidic GVL/water organosolv mixtures. This led to medium molecular weight ($\sim 2500 \text{ g mol}^{-1}$) lignin oligomers with low ether content ($\sim 25\%$), low free phenolic hydroxy group content ($\sim 0.8 \text{ mmol g}^{-1}$), and a high degree of condensation, meaning a large number of C–C linkages. This is similar to the usual organosolv lignin in literature^{48,49} (2) lignin was treated with an extraction process involving acidic GVL/aldehyde organosolv mixtures, in which the aldehydes prohibit condensation by protecting the β -1,4-diol functions of lignin ether linkages through acetal formation (GVL based aldehyde-assisted fractionation – GVL-AAF). This led to high molecular weight lignin ($\sim 5000 \text{ g mol}^{-1}$) with high ether content ($\sim 50\%$), high free phenolic hydroxy group content ($\sim 2 \text{ mmol g}^{-1}$), and no condensation. Lignin is preserved in its native state by aldehyde protection. This state makes it possible to further depolymerize the lignin. (3) Lignin product (2) is subjected to hydrogenolysis with a metal catalyst (Ru/C, Pd/C) under H_2 atmosphere (40 bar) and high temperature (200–250 °C). This led to specific lignin monomers. The monomers include a monoaromatic core structure, with 0–2 phenolic methoxy groups, 1 phenolic hydroxy group, and 1 aliphatic rest (either aliphatic alcohol or alkyl group), whereas the specific structure depends on the biomass and the hydrogenolysis conditions. As a side product, oligomers composed of 2–4 lignin subunits were received, their yield depending on the carbon–carbon linkage content of the original lignin in a certain biomass. These oligomers can be separated from the monomers through a simple hexane extraction. Fig. 7 gives an overview of the named lignin products.

Overall, the process of extracting lignin with the green solvent GVL from lignocellulosic biomass and further using hydrogenolysis to receive valuable lignin monomers is of great importance for future production of bio-based materials. Creating new valuable molecules for different applications is the next step in line of complete lignin valorization. This lignocellulosic biomass fractionation and dissolution process makes it possible to separate, selectively decompose and dissolve lignin no matter the source of biomass, be it wood or different industry waste streams. It also shows the properties of lignin from different biomasses and how the main properties of lignin can be preserved during a mild green extraction process.

The different lignin products (1)–(3) can be used for different applications concerning their individual properties that stem from their extraction/degradation process and their choice of biomass origin. Key considerations for choosing a certain lignin for different applications are its reactivity towards chemical modification, thermal stability, molecular mass, and specific functionality. Lignin products can be used in adhesives and resins to replace fossil-based chemicals. Lignin can be used for partially replacing phenol in different phenolic resins due to its aromatic structure. This ability is limited by the condensation of the GVL organosolv lignin, leading to less accessibility towards the substitution in phenolic resin reactions,^{50–53} thus it is mostly used as a green filler component for composites due to its high thermal stability.⁵⁴ The protected lignin is generally more reactive due to no condensation and a higher amount of phenolic hydroxy groups, making it not only suitable for less

limited replacement of phenolic monomers, but also better for forming epoxy resins^{55,56} or polyurethane adhesives.⁵⁷ Overall, the protected lignin provides a higher reactivity and lower randomly condensed structures, thus a better performance in resin formulations. Additionally, lignin monomers could be used for synthesizing specific resins by specifically producing high purity lignin monomers with certain functional groups that induce resin formation. This would lead to tailored polymers, which in turn are less cost effective. Examples for this would include the formation of lignin monomer based curing agents or resin monomers, which will be addressed in a follow-up article. A great challenge is also the production of biodegradable polymers from lignin, which can also be possible due to the high reactivity and flexibility of protected lignin structures.

Another application for lignin is carbon-based materials such as carbon fibers, activated carbon, or carbon electrodes. For this application, high thermal stability is necessary, which coincides with the ratio of condensation in extracted lignin oligomers. For this reason, the GVL organosolv lignin provides the best starting point for producing carbon-based materials, while protected lignin and lignin monomers are either not thermally stable enough or too valuable for simply producing carbon-based materials.^{58–60}

Due to its free phenolic hydroxy group content, lignin has been commonly used as antioxidant additive in food packaging, cosmetics, and stabilizers for polymers and fuels. The ability to act as an antioxidant is solely dependent on the number of free phenolic hydroxy groups, which act as radical scavengers, inhibiting or quenching free radical reactions by forming phenoxy radicals, and thus protecting certain products from oxidative degradation.^{61,62} Another big advantage of lignin is its functionalization with methoxy groups on the aromatic ring, which enhance antioxidant activity through stabilization of the phenoxy radicals. While GVL organosolv lignin can be used for antioxidant applications only moderately due to its rather low content in free phenolic hydroxy groups, the protected lignin could be an excellent antioxidant additive due to its high free phenolic hydroxy group content. Similarly, lignin monomers can be used due to their phenolic nature but are less efficient. It was found that increased molecular weight lignin fragments exhibit better antioxidant properties compared to monomeric lignin fragments.^{63–65} Therefore, the higher molecular weight, more native structure, and higher free phenolic hydroxy group content makes protected lignin oligomers the most effective in antioxidant applications.

Additionally, lignin holds great antimicrobial properties. Lignin exhibits these properties through destroying the cell membranes of bacteria upon contact and preventing further microbial growth. The antimicrobial activity of lignin is greatly influenced by several factors: the origin biomass of the lignin is very important, as different lignins show different effects on Gram-negative and Gram-positive bacteria, probably due to its gene-based composition. The extraction process also plays a significant role, as it produces lignin with different structural properties. While organosolv lignin shows a lower antimicrobial activity than lignosulfonate, but a higher antimicrobial activity



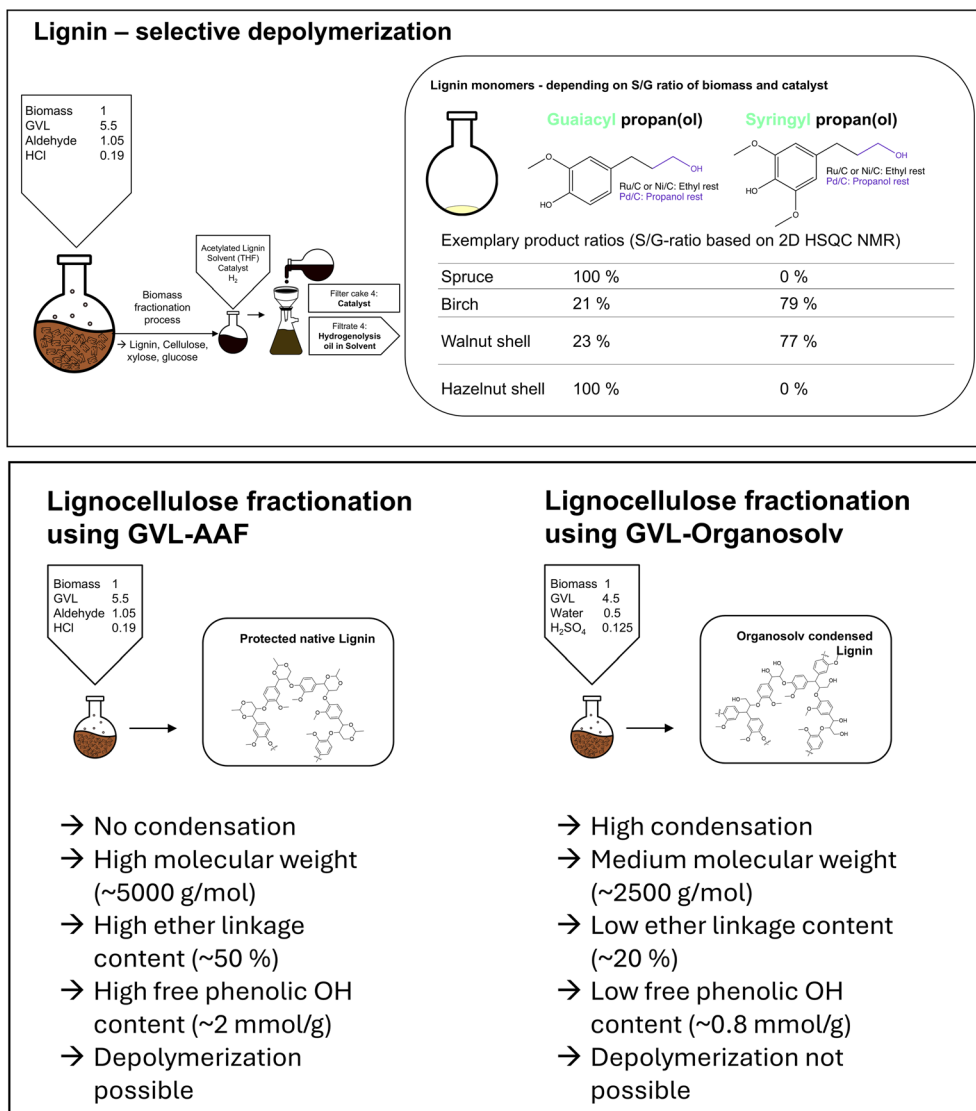


Fig. 7 Overview over the products (1)–(3) and the process of hydrogenolysis towards lignin monomers.

than Kraft lignin, enzymatically hydrolyzed (a method to mildly hydrolyze carbohydrates, leaving native high molecular weight lignin) lignin shows the overall highest antimicrobial activity.⁶⁶ This leads to the conclusion that more native structures of lignin can exhibit excellent antimicrobial properties. Additionally, phenolic hydroxy groups and methoxy groups, high surface area, high purity, low dispersion, and low molecular weight are beneficial to antimicrobial properties. Also, certain bacteria are targeted by specific lignin structures better than others.^{66–68} This makes protected lignin an excellent choice for antimicrobial use, as it has a high number of useful functional groups, a medium molecular weight compared to enzymatically hydrolyzed lignin, high purity, and an overall very native structure.

Lignin can be used as UV absorbing agent in different coatings, such as sunscreens or packaging materials. Due to its high absorptivity in the UV/Vis-range (250–400 nm), lignin can be used as a natural UV-blocker. The main chromophores in lignin include aromatic rings, conjugated double bonds,

phenolic hydroxy groups, and carbonyl groups. This makes protected native lignin without condensation a good choice for UV-blocking agents, since even more UV absorbing functional groups could be introduced through the protection agent. Organosolv GVL lignin and lignin monomers exhibit less to no UV absorbing properties due to a lack of functional groups or polymeric structure. Depending on the desired properties, GVL organosolv or protected lignin can be used,^{69,70} combined with their antimicrobial and antioxidant properties, for different coatings or films.^{71–74}

Lignin can be used as dispersants or surfactants depending on their solubility in hydrophilic and hydrophobic media. The use of lignin as a surfactant involves lignin accumulating at the interface of two phases and changing its surface tension. These can be used as wetting agents, detergents, emulsifiers, foaming agents, or dispersants. Dispersants are used to stabilize particles in colloidal suspensions, *e.g.* in cosmetics, pharmaceuticals, or cement. In the chemical industry, lignosulfonates are



commonly used as surfactants and dispersants. These come from the lignosulfonate pulping process, yielding condensed lignin with a large number of substituted sulphonate groups, increasing the lignin's dispersant ability. To achieve this, our lignin products would have to undergo similar modifications, like sulfonation, sulfomethylation, etherification, carboxymethylation or oxidation towards efficient surfactants.^{75–79} Another route for this would be to use the addition of the protection group to the lignin structure to introduce different functional groups that can improve the surfactant and dispersant ability of lignin. This would add to the more amphiphilic nature of protected lignin due to its higher ether content and free phenolic hydroxy group content, maximizing surfactant and dispersant properties. Lignin monomers would not be able to show such properties due to their lack of a polymeric structure and lower reactivity towards modification reactions.⁷⁵

Additionally, lignin can be used in agriculture for various purposes. These include pesticide and fungicide carriers, soil amendments, plant growth regulators, mulching films, and soil release fertilizers. Lignin can be used to coat fertilizers (physically impeded type fertilizers), allowing for a controlled release of nutrients into the soil while reducing the environmental impact of these fertilizers. The slow release that is achieved through the lignin is caused by strong interactions between lignin and fertilizer, slowing down their dissolution in water due to increased hydrophobicity. This makes it a strong fit for GVL organosolv lignin, which is also very stable and exhibits high hydrophobicity. Lignin can also be chemically modified to further fit the purpose of slow release fertilizers by increasing the hydrophobicity of the coating and film-forming properties. Additionally, the chemically modified type fertilizers work through a direct chemical reaction between lignin and nutrients. Both are attached to each other and can then be used for a controlled release. To achieve this, lignin has to be chemically modified *via* Mannich reaction or chelation reaction. It is necessary to use a lignin with high reactivity and purity to achieve this type of slow release fertilizer. Protected lignin can be the optimal choice due to its high reactivity and purity.^{80,81} Similarly, lignin can also protect pesticides and fungicides by encapsulation, protecting them from degradation and achieving a controlled release over time.⁸² Lignin can also be used to improve the soil structure by improving water retention and microbial activity. Lignin enhances soil aggregation and reduces erosion but also retains water due to its hydrophilic groups and serves as a carbon source for soil microbes. Organosolv lignin is typically more effective for this purpose, as it is more stable and shows slower degradation. This also makes it more effective as composting additives.⁸³ Protected lignin could increase the water retention for dry areas but also show faster degradation and thus less benefits for the soil.^{84,85} Lignin can be used as a plant growth promoter to enhance plant growth and stress resistance by improving the nutrient uptake or by coating seeds to provide protection and promote germination.^{82,86} The biostimulant effect of lignin can typically be related to reactivity of functional groups like hydroxy groups and aliphatic aromatics.⁸⁷ This makes protected lignin ideal for biostimulant applications due to its native state and high availability of

hydroxy groups, possibly also after a deprotection to achieve an even higher number of functional groups. While organosolv lignin is less effective due to its condensed structure, lignin monomers could be used as biostimulants but are less cost-efficient than lignin oligomers.

Lignin has also gained attention in biomedical applications due to its biocompatibility, antioxidant properties and reactivity towards functionalization. In drug delivery, lignin is used to form nanoparticles and hydrogels for controlled drug release.⁸⁸ Lignin can also induce tissue regeneration and provide antimicrobial properties for medical devices or wound dressings.⁸⁹ Lignin can be integrated into scaffolds to improve mechanical properties and biocompatibility.⁹⁰ For most applications, protected lignin can be ideal due to its high versatility, high reactivity, large number of free phenolic hydroxy groups for functionalization, and lack of condensation. In contrast, GVL organosolv lignin can be used for composite materials or tissue engineering due to its low reactivity and condensed structure.⁹¹ With a lack of polymeric structure, lignin monomers can still be used to synthesize bioactive compounds but are less usable for bulk applications. An example for this is syringaldehyde, which can be synthesized from lignin monomers and can be used for forming dendrimers with solid copper particles for drug delivery systems. It can also be used for reducing blood sugar and cancer treatment.⁹²

Lignin has many direct monomer applications in the flavor and fragrance industry. It is a major source of vanillin, a widely used flavoring agent and the only lignin-based product that is currently synthesized from lignin in the chemical industry. However, it only makes up around 1% of the total vanillin production. Vanillin can also be used for thermoplastic polymer synthesis.^{93,94} Additionally, there are other fragrance or flavor ingredients that are based on lignin, such as 4-propylsyringol or 4-propylguaicol, which already possess a FEMA number, which classifies them as not harmful and safe to use.⁹⁵ Lignin degradation overall leads to a great variety of different aromatic molecules, that can be used in perfumes or food flavorings.⁹⁶ The extraction of protected lignin in its native state with a high ether content also greatly improves the degradation efficiency, making the creation of lignin monomers more achievable.

Lignin is also a promising feedstock for the production of biofuels and biochemicals through various processes. Lignin can be converted into syngas, bio-oil, or lignin-based fuels through pyrolysis or gasification,⁹⁷ but also be depolymerized into aromatic chemicals or platform chemicals.^{98,99} GVL organosolv lignin is more suitable for pyrolysis or gasification due to its condensed structure. Due to its lower ether content, it yields less monomers in degradation. However, protected lignin is highly ideal for degradation towards monomers due to its high ether content and lack of condensation.

Recently, it has also been found that lignin can be degraded towards aliphatic organic molecules such as sodium levulinate or sodium acetate by using electrocatalysis in a GVL/water mixture. This also opens up a great opportunity of further using GVL-based systems to create a wide variety of target molecules for most different applications. While the GVL-based fractionation with hydrogenolysis focuses on degrading lignin



towards aromatic molecules, electrocatalysis can cover the aliphatic petroleum-based product side.¹⁰⁰ Lignin electrocatalysis typically achieve yields of around 13% for organosolv lignin, which makes it less efficient than our GVL-based process or classical RCF. However, it comes with environmental advantages such as ambient temperatures and pressures, no hydrogen gas necessity, and no chemical waste.¹⁰¹ This makes electrocatalysis viable as a possible replacement for subsequent hydrogenolysis after lignin fractionation with GVL, if the yields can be increased in the future.

Overall, lignin does have various application options, which are all dependent on specific properties of the lignin. In most cases, the protected lignin is ideal due to its native state and versatile structure, and its ability to be functionalized through different protection agents. Protected lignin is excellent for resins, antioxidants, biomedical uses and depolymerization due to its high reactivity, free phenolic hydroxy groups and lack of condensation. GVL organosolv lignin, while still usable for the other applications, is most effective in applications that require thermal, mechanical and degradation stability, like carbon materials, agricultural uses, or composting. Additionally, lignin monomers are excellent for high purity, high value applications with the need for specific monomeric structures, like flavor or fragrance production, specific resin production, or biomedical applications, but are less efficient for bulk applications.

Process parameters of the extraction processes can also be tuned to achieve certain properties, like a higher/lower molecular weight, less/more condensation, lower/higher ether content, lower/higher phenolic hydroxy group content, or a functionalization of the aromatic ring. By variation of the protection agent for the aldehyde assisted extraction process, the protection group can have different functional groups that change certain properties of the protected lignin, most likely solubility in hydrophobic and hydrophilic media, and functional group based properties like antioxidant activity.

While the current study demonstrates the effective lignin fractionation and degradation to specific monomeric or oligomeric compounds, the general operational simplicity, the use of mainly green and non-toxic solvents, essentially GVL, and the employing of mild conditions supports the scalability of our process for further optimization for industrial application. To further support this claim, the process protocol and the production of all named products were successfully adapted to scaled up reaction conditions. Further experiments with larger scale up and under continuous flow will be necessary in the next step to achieve process industrialization. Problems might be the use of aldehydes in great excess, the use of large amounts of metal catalysts during hydrogenolysis or the multistep-workup process of fractionated lignin. Addressing these problems is a good step towards industrialization. However, our process is not limited by lignin heterogeneity, being able to use the heterogeneity of biodiverse lignin to produce specific targeted product molecules. Taken together, the demonstrated efficiency, operational feasibility, and use of environmentally friendly solvents position our process as a promising candidate for future scalable lignin valorization strategies in biorefinery.

4 Conclusion and outlook

In conclusion, lignin can be isolated with different properties from lignocellulosic biomass in high yields and purities. We could show that the choice of extraction process and biomass type significantly influences the lignin structure and the ability to further depolymerize it into specific monomers, which can be valuable for various applications. We managed to modify our GVL-based biomass fractionation process, which is explained in our previous study, to yield specific lignin products through simple process modifications at mild conditions to control the application profile of the resulting lignin. Lignin oligomers with different molecular weights, phenolic hydroxy group content, and different condensation levels, structural aromatic and linkage composition, and ether content can provide the required properties for specific applications. These properties are all influenced by the choice of biomass and the choice of extraction process conditions. Therefore, lignin can be tailored *via* the chosen reagents towards specific applications. This creates a biodiverse spectrum of possible lignin valorization, as lignin from hardwood or softwood trees, different nutshells, or even waste streams like coffee silverskin can be prepared for the production of valuable starter molecules for the chemical industry. With a more profound understanding of how the extraction process can be optimized to yield specific lignin products with desired properties, future studies have to expand on specifically improving existing valorization options or create new applications that can replace petroleum-based alternatives. Additional studies could also determine the solubility of lignin with different properties for a better understanding of the behavior of lignin in mixtures of multiple components. More research could also be invested into the chemical modification of lignin during the protection/extraction process, leading to different lignin structures that can directly be implemented into different applications. Here, an interesting topic can be the influence of the protecting agent used in the fractionation process on the general properties of the resulting lignin. Overall, by increasing the knowledge of lignin tailoring, transforming the petroleum-based chemical industry into a biorefinery-based industry becomes even more of an achievable reality, using the biodiverse phenolic polymer lignin that nature provides in great abundance.

Author contributions

Moritz Schweiger: conceptualization, data curation, investigation, formal analysis, visualization, methodology, writing – original draft. Thomas Lang: investigation, formal analysis, validation, writing – SI. Eva Müller: writing – review & editing, supervision, conceptualization. Didier Touraud: conceptualization, writing – review & editing. Werner Kunz: writing – review & editing, supervision, resources, project administration, funding acquisition.

Conflicts of interest

There are no conflicts to declare.



Data availability

The data supporting this article have been included in the text and as part of the SI. Should any data files be needed in another format, they are available from the corresponding author upon reasonable request. See DOI: <https://doi.org/10.1039/d5su00324e>.

Acknowledgements

The authors acknowledge the financial support of KVT-Technology (Graz, Austria) and their cooperation with our department of physical chemistry II at the University of Regensburg. We also acknowledge the support of the project "AI-supported search for environmentally acceptable solvents for the dissolution and stabilization of biopolymers for their utilization as sustainable materials", funded by the Bayerisch-Tschechische Hochschulagentur (BTHA) as project BTHA-JC-2024-57. We also acknowledge the experimental support of the Fraunhofer Institute (Straubing, Germany) and the ability to use the high pressure reactors for hydrogenolysis at their facility.

References

- 1 Z. Usmani, M. Sharma, A. K. Awasthi, T. Lukk, M. G. Tuohy, L. Gong, *et al.*, Lignocellulosic biorefineries: the current state of challenges and strategies for efficient commercialization, *Renewable Sustainable Energy Rev.*, 2021, **148**, 111258.
- 2 C. Ververis, K. Georgiou, N. Christodoulakis, P. Santas and R. Santas, Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production, *Ind. Crops Prod.*, 2004, **19**(3), 245–254.
- 3 B. Singh, J. Korstad, A. Guldhe and R. Kothari, Editorial: Emerging feedstocks & clean technologies for lignocellulosic biofuel, *Front. Energy Res.*, 2022, **10**, 1–3.
- 4 N. Singh, R. R. Singhanian, P. S. Nigam, C. Dong, A. K. Patel and M. Puri, Global status of lignocellulosic biorefinery: challenges and perspectives, *Bioresour. Technol.*, 2022, **344**(Pt B), 126415.
- 5 M. Schweiger, T. Lang, V. Jerabek, M. Klajmon, E. Müller, J. Heyda, *et al.*, Complete biodiverse fractionation process using the green solvent γ -valerolactone, *RSC Sustainability*, 2025, Submitted.
- 6 A. Chemat, M. Schweiger, D. Touraud, R. Müller, L. Lajoie, J. B. Mazzitelli, *et al.*, Cascade extractions of coffee silverskin: towards zero solid waste valorization of a by-product, *Sustainable Chem. Pharm.*, 2024, **42**, 101779.
- 7 M. Graglia, Lignin Valorization, PhD thesis, University of Potsdam, 2017.
- 8 C. Chio, M. Sain and W. Qin, Lignin utilization: a review of lignin depolymerization from various aspects, *Renewable Sustainable Energy Rev.*, 2019, **107**, 232–249.
- 9 S. H. Ghaffar and M. Fan, Lignin in straw and its applications as an adhesive, *Int. J. Adhes. Adhes.*, 2014, **48**, 92–101.
- 10 R. M. Trevorah and M. Z. Othman, Alkali pretreatment and enzymatic hydrolysis of Australian timber mill sawdust for biofuel production, *J. Renewable Energy*, 2015, **2015**, 284250.
- 11 D. S. Bajwa, G. Pourhashem, A. H. Ullah and S. G. Bajwa, A concise review of current lignin production, applications, products and their environmental impact, *Ind. Crops Prod.*, 2019, **139**, 111526.
- 12 S. Jampa, A. Puente-Urbina, Z. Ma, S. Wongkasemjit, J. S. Luterbacher and J. A. van Bokhoven, Optimization of lignin extraction from pine wood for fast pyrolysis by using a γ -valerolactone-based binary solvent system, *ACS Sustain. Chem. Eng.*, 2019, **7**(4), 4058–4068.
- 13 D. Watkins, M. Nuruddin, M. Hosur, A. Tcherbi-Narteh and S. Jeelani, Extraction and characterization of lignin from different biomass resources, *J. Mater. Res. Technol.*, 2015, **4**(1), 26–32.
- 14 X. Lu, X. Gu and Y. Shi, A review on lignin antioxidants: their sources, isolations, antioxidant activities and various applications, *Int. J. Biol. Macromol.*, 2022, **210**, 716–741.
- 15 A. Kumar, K. J. Anushree and T. Bhaskar, Utilization of lignin: a sustainable and ecofriendly approach, *J. Energy Inst.*, 2020, **93**(1), 235–271.
- 16 L. A. Z. Torres, A. L. Woiciechowski, V. O. A. Tanobe, S. G. Karp, L. C. G. Lorenci, C. Faulds, *et al.*, Lignin as a potential source of high-added value compounds: a review, *J. Cleaner Prod.*, 2020, **263**, 121499.
- 17 L. Dessbesell, M. Paleologou, M. Leitch and R. Pulkki, Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers, *Renewable Sustainable Energy Rev.*, 2020, **123**, 109768.
- 18 D. D. S. Argyropoulos, C. Crestini, C. Dahlstrand, E. Furusjö, C. Gioia, K. Jedvert, *et al.*, Kraft lignin: a valuable, sustainable resource, opportunities and challenges, *ChemSusChem*, 2023, **16**(1), e202300492.
- 19 J. D. Gargulak, S. E. Lebo and T. J. McNally, Lignin, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2015, pp. 1–26.
- 20 T. Aro and P. Fatehi, Production and application of lignosulfonates and sulfonated lignin, *ChemSusChem*, 2017, **10**(9), 1861–1877.
- 21 S. P. S. Chundawat, V. Balan, L. Da Costa Sousa and B. E. Dale, Thermochemical pretreatment of lignocellulosic biomass, in *Bioalcohol Production*, Woodhead Publishing, 2010, pp. 24–72.
- 22 X. Li, M. Li, Y. Pu, A. J. Ragauskas, A. S. Klett, M. Thies, *et al.*, Inhibitory effects of lignin on enzymatic hydrolysis: the role of lignin chemistry and molecular weight, *Renewable Energy*, 2018, **123**, 664–674.
- 23 H.-Z. Chen and Z.-H. Liu, Enzymatic hydrolysis of lignocellulosic biomass from low to high solids loading, *Eng. Life Sci.*, 2017, **17**(5), 489–499.
- 24 X. Li, Y. Shi, W. Kong, J. Wie, W. Song and S. Wang, Improving enzymatic hydrolysis of lignocellulosic biomass by bio-coordinated physiochemical pretreatment – a review, *Energy Rep.*, 2022, **8**, 696–709.



- 25 F. Cheng, S. Liu, S. D. Karlen, H. Kim, F. Lu, J. Ralph, *et al.*, Poplar lignin structural changes during extraction in γ -valerolactone (GVL), *Green Chem.*, 2023, **25**(1), 336–347.
- 26 C. Gioia, M. Colonna, A. Tagami, L. Medina, O. Sevastyanova, L. A. Berglund, *et al.*, Lignin-based epoxy resins: unravelling the relationship between structure and material properties, *Biomacromolecules*, 2020, **21**(5), 1920–1928.
- 27 W. Lan, M. T. Amiri, C. M. Hunston and J. S. Luterbacher, Protection group effects during α,γ -diol lignin stabilization promote high-selectivity monomer production, *Angew. Chem., Int. Ed.*, 2018, **57**(5), 1356–1360.
- 28 M. A. Hossain, T. Saelee, M. S. Rahaman, T. K. Phung, T. Maihom, P. Praserttham, *et al.*, Catalytic hydrogenolysis of lignin into phenolics by internal hydrogen over Ru catalyst, *ChemCatChem*, 2022, **14**(10), e202200549.
- 29 S. Wang, X. Li, R. Ma and G. Song, Catalytic hydrogenolysis of lignin into serviceable products, *Acc. Chem. Res.*, 2025, **58**(3), 529–542.
- 30 Z. Shen, C. Shi, F. Liu, W. Wang, M. Ai, Z. Huang, *et al.*, Advances in heterogeneous catalysts for lignin hydrogenolysis, *Adv. Sci.*, 2024, **11**, 2306693.
- 31 S. Sethupathy, G. M. Morales, L. Gao, H. Wang, B. Yang, J. Jiang, *et al.*, Lignin valorization: status, challenges and opportunities, *Bioresour. Technol.*, 2022, **347**, 126696.
- 32 A. Boarino and H.-A. Klok, Opportunities and challenges for lignin valorization in food packaging, antimicrobial, and agricultural applications, *Biomacromolecules*, 2023, **24**(3), 1065–1077.
- 33 M. Ullah, P. Liu, S. Xie and S. Sun, Recent advancements and challenges in lignin valorization: green routes towards sustainable bioproducts, *Molecules*, 2022, **27**(18), 6055.
- 34 D. S. Zijlstra, A. de Santi, B. Oldenburger, J. de Vries, K. Barta and P. Deuss, Extraction of lignin with high β -O-4 content by mild ethanol extraction and its effect on depolymerization yield, *J. Visualized Exp.*, 2019, **143**, e58575.
- 35 L. Chen, X. Wei, H. Wang, H. Yao, L. Zhang, G. Gellerstedt, *et al.*, A modified ionization difference UV-vis method for fast quantification of guaiacyl-type phenolic hydroxyl groups in lignin, *Int. J. Biol. Macromol.*, 2022, **201**, 330–337.
- 36 M. T. Amiri, G. R. Dick, Y. M. Questell-Santiago and J. S. Luterbacher, Fractionation of lignocellulosic biomass to produce uncondensed aldehyde-stabilized lignin, *Nat. Protoc.*, 2019, **14**(3), 921–954.
- 37 L. D. Tolesa, B. S. Gupta and M. Lee, Treatment of coffee husk with ammonium-based ionic liquids: lignin extraction, degradation, and characterization, *ACS Omega*, 2018, **3**(9), 10866–10876.
- 38 B. Wang, S.-F. Wang, S. S. Lam, C. Sonne, T.-Q. Yuan, G.-Y. Song, *et al.*, A review on production of lignin-based flocculants: sustainable feedstock and low carbon footprint applications, *Renewable Sustainable Energy Rev.*, 2020, **134**, 110384.
- 39 L. Xiao, W. Liu, J. Huang, H. Lou and X. Qiu, Study on the antioxidant activity of lignin and its application performance in SBS elastomer, *Ind. Eng. Chem. Res.*, 2020, **60**(1), 1–12.
- 40 S. Chandna, M. C. A. Olivares, E. Baranovskii, G. Engelmann, A. Böker, C. Tzschucke, *et al.*, Lignin upconversion by functionalization and network formation, *Angew. Chem., Int. Ed.*, 2024, **63**, e202313945.
- 41 W. Lan, J. B. de Bueren and J. S. Luterbacher, Highly selective oxidation and depolymerization of α,γ -diol-protected lignin, *Angew. Chem., Int. Ed.*, 2019, **58**(9), 2649–2654.
- 42 X. Liu, F. Bouxin, J. Fan, V. Budarin, C. Hu and J. Clark, Recent advances in the catalytic depolymerization of lignin towards phenolic chemicals: a review, *ChemSusChem*, 2020, **13**(17), 4296–4317.
- 43 M. R. Chandraratne and A. Gezae Daful, Hydrothermal conversion of lignocellulosic biomass to hydrochar: production, characterization, and applications, in *From Biomass to Biobased Products*, IntechOpen, 2024.
- 44 K. Lv, Z. Chen, J. Zhang, Y. Liu and J. Long, Mechanistic insights into formation of residual solid in lignin depolymerization, *ChemSusChem*, 2023, **16**(13), e202300123.
- 45 B. Chen, Z.-Z. Cao, Z.-J. Diao, S.-J. Zhao, H. Yuan and J.-M. He, Hydrogenolysis of lignin and C-O linkages containing lignin-related compounds over a microporous silicalite-1 array-supported Ru-Ni phosphide composite, *Catalysts*, 2022, **12**(12), 1625.
- 46 E. Subbotina, L. R. Souza, J. Zimmerman and P. Anastas, Room temperature catalytic upgrading of unpurified lignin depolymerization oil into bisphenols and butene-2, *Nat. Commun.*, 2024, **15**, 5892.
- 47 Y. Liao, S.-F. Koelewijn, G. Van den Bossche, J. Van Aelst, S. Van den Bosch, T. Renders, *et al.*, A sustainable wood biorefinery for low-carbon footprint chemicals production, *Science*, 2020, **367**(6484), 1385–1390.
- 48 B. Rietzler, M. Karlsson, I. Kwan, M. Lawoko and M. Ek, Fundamental insights on the physical and chemical properties of organosolv lignin from Norway spruce bark, *Biomacromolecules*, 2022, **23**(8), 3349–3358.
- 49 J. Prajin, M. Tanase-Opedal and T. M. Storker, Polymer properties of softwood organosolv lignins produced in two different reactor systems, *Biopolymers*, 2023, **114**(3), e23566.
- 50 Z. Gao, X. Lang, S. Chen and C. Zhao, Mini-review on the synthesis of lignin-based phenolic resin, *Energy Fuels*, 2021, **35**(23), 18385–18395.
- 51 G. Foyer, B.-H. Chenfi, B. Boutevin, S. Caillol and G. David, New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors, *Eur. Polym. J.*, 2016, **74**, 296–309.
- 52 W. Su, P. Li, M. Wang, D. Yi, B. Jiang and W. Wu, Simple preparation of lignin-based phenolic resin carbon and its efficient absorption of Congo red, *Water*, 2023, **15**(15), 2777.



- 53 Y. Meng, Y. Cheng, J. Lu and H. Wang, A review on lignin-based phenolic resin adhesive, *Macromol. Chem. Phys.*, 2022, **223**(21), 2100434.
- 54 M. R. Ridho, E. A. Agustlany, M. R. Dn, E. W. Madyaratri, M. Ghozali, W. K. Restu, *et al.*, Lignin as green filler in polymer composites: developments methods, characteristics, and potential applications, *Adv. Mater. Sci. Eng.*, 2022, **2022**, 1363481.
- 55 X. Lu and X. Gu, A review on lignin-based epoxy resins: lignin effects on their synthesis and properties, *Int. J. Biol. Macromol.*, 2023, **229**, 778–790.
- 56 C. Gioia, M. Colonna, A. Tagami, L. Medina, O. Sevastyanova, L. A. Berglund, *et al.*, Lignin-based epoxy resins: unravelling the relationship between structure and material properties, *Biomacromolecules*, 2020, **21**(5), 1920–1928.
- 57 A. Shafiq, I. A. Bhatti, N. Amjed, M. Zeshan, A. Zaheer, A. Kamal, *et al.*, Lignin derived polyurethanes: current advances and future prospects in synthesis and applications, *Eur. Polym. J.*, 2024, **209**, 112899.
- 58 G. Milczarek and O. Inganas, Renewable cathode materials from biopolymer/conjugated polymer interpenetrating networks, *Science*, 2012, **335**(6075), 1468–1471.
- 59 D. A. Baker and T. G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, *J. Appl. Polym. Sci.*, 2013, **130**(2), 713–728.
- 60 J. Hayashi, A. Kazehaya, K. Muroyama and A. P. Watkinson, Preparation of activated carbon from lignin by chemical activation, *Carbon*, 2000, **38**(13), 1873–1878.
- 61 X. Lu, X. Gu and Y. Shi, A review on lignin antioxidants: their sources, isolations, antioxidant activities and various applications, *Int. J. Biol. Macromol.*, 2022, **210**, 716–741.
- 62 S. Kang, J. Chang and J. Fan, Phenolic antioxidant production by hydrothermal liquefaction of lignin, *Energy Sources, Part A*, 2015, **37**(5), 494–500.
- 63 H. Sadeghifar and A. J. Ragauskas, Lignin as a natural antioxidant: chemistry and applications, *Macromolecules*, 2025, **5**(5), 1–21.
- 64 A. Karmanov, L. Kocheva, V. Belyy, A. Kanarsky, E. Semenov, N. Bogdanovich, *et al.*, Structural features and antioxidant behavior of lignin polymers isolated from various woody plants, *Biocatal. Agric. Biotechnol.*, 2023, **54**, 102969.
- 65 G. L. Catignani and M. E. Carter, Antioxidant properties of lignin, *J. Food Sci.*, 1982, **47**(5), 1745–1748.
- 66 K. Li, W. Zhong, P. Li, J. Ren, K. Jiang and W. Wu, Antibacterial mechanism of lignin and lignin-based antimicrobial materials in different fields, *Int. J. Biol. Macromol.*, 2023, **252**, 126281.
- 67 J. Yun, L. Wie, W. Li, D. Gong, H. Qin, X. Feng, *et al.*, Isolating high antimicrobial ability lignin from bamboo kraft lignin by organosolv fractionation, *Front. Bioeng. Biotechnol.*, 2021, **9**, 1–12.
- 68 D. C. Reyes, Z. Ma and J. J. Romero, The antimicrobial properties of technical lignins and their derivatives – a review, *Polymers*, 2024, **16**(12), 2181.
- 69 H. Sadeghifar and A. Ragauskas, Lignin as a UV light blocker – a review, *Polymers*, 2020, **12**(5), 1134.
- 70 S. Lv, S. Liang, J. Zuo, S. Zhang, J. Wang and D. Wie, Lignin-based anti-UV functional materials: recent advances in preparation and applications, *Iran. Polym. J.*, 2023, **32**, 1477–1497.
- 71 Anushikha and K. K. Gaikwad, Lignin as a UV blocking, antioxidant, and antimicrobial agent for food packaging applications, *Biomass Convers. Biorefin.*, 2024, **14**, 16755–16767.
- 72 A. Halloub, M. Raji, H. Essabir, H. Chackchak, R. Boussen, M. Bensalah, *et al.*, Intelligent food packaging film containing lignin and cellulose nanocrystals for shelf life extension of food, *Carbohydr. Polym.*, 2022, **296**, 119972.
- 73 M. H. Tran, D. Phan and E. Y. Lee, Review on lignin modifications toward natural UV protection ingredient for lignin-based sunscreens, *Green Chem.*, 2021, **23**(13), 4633–4646.
- 74 K. Li, W. Zhong, P. Li, J. Ren, K. Jiang and W. Wu, Recent advances in lignin antioxidant: antioxidant mechanism, evaluation methods, influence factors and various applications, *Int. J. Biol. Macromol.*, 2023, **251**, 125992.
- 75 T. Wang, H. Li, X. Diao, X. Lu, D. Ma and N. Ji, Lignin to dispersants, adsorbents, flocculants and adhesives: a critical review on industrial applications of lignin, *Ind. Crops Prod.*, 2023, **199**, 116715.
- 76 H. A. Qulatein, W. Gao and P. Fatehi, Carboxylated lignin as a sustainable dispersant for coal water slurry, *Polymers*, 2024, **16**(12), 2586.
- 77 A. Kalliola, P. Kangas, I. Winberg, T. Vehmas, H. Kyllönen, J. Heikkinen, *et al.*, Oxidation process concept to produce lignin dispersants at a kraft pulp mill, *Nord. Pulp Pap. Res. J.*, 2022, **37**(2), 394–404.
- 78 X. Ouyang, L. Ke, X. Qiu, Y. Guo and Y. Pang, Sulfonation of alkali lignin and its potential use in dispersant for cement, *J. Dispersion Sci. Technol.*, 2009, **30**(1), 1–6.
- 79 N. Alwadani and P. Fatehi, Synthetic and lignin-based surfactants: challenges and opportunities, *Carbon Resour. Convers.*, 2018, **1**, 126–138.
- 80 J. Lu, M. Cheng, C. Zhao, B. Li, H. Peng, Y. Zhang, *et al.*, Application of lignin in preparation of slow-release fertilizer: current status and future perspectives, *Ind. Crops Prod.*, 2022, **176**, 114267.
- 81 R. Kumar, G. Naess and M. Sorensen, Slow-release fertilizers using lignin: challenges and future prospects, *Biofuels, Bioprod. Biorefin.*, 2023, **17**(6), 1368–1381.
- 82 A. Abbas, D. Y. F. Lai, P. Peng and D. She, Lignin-based functional materials in agricultural application: a review, *J. Agric. Food Chem.*, 2025, **73**(10), 5685–5710.
- 83 W. Yao, D. Cai, F. Huang, T. A. Mohamed, P. Li, X. Qiao, *et al.*, Promoting lignin exploitability in compost: a cooperative microbial depolymerization mechanism, *Process Saf. Environ. Prot.*, 2023, **174**, 856–868.
- 84 D. Savy and V. Cozzolino, Novel fertilizing products from lignin and its derivatives to enhance plant development and increase the sustainability of crop production, *J. Cleaner Prod.*, 2022, **366**, 132832.
- 85 X. Chen, Lignin-improved soil research progress, *Acad. J. Sci. Technol.*, 2024, **10**(1), 1–10.



- 86 Y. Wang, X. Yu, H. He, W. Zhu, X. Yuan and H. Wang, Engineering high-performance and multifunctional seed coating agents from lignocellulosic components, *Ind. Crops Prod.*, 2024, **222**, 119768.
- 87 J. A. Diaz-Elizondo, A. Ayala-Velazco, A. Benavides-Mendoza, F. J. Enriques-Medrano and J. Medrano-Macias, Obtaining lignin from nutshells under mild extraction conditions and its use as a biostimulant in tomato seedlings, *Horticulturae*, 2024, **10**(6), 1079.
- 88 M. Chaudhary and V. R. Sinha, Lignin-based carriers for drug delivery applications: from an industrial waste to a pharmaceutical aid, *Eur. Polym. J.*, 2023, **195**, 112306.
- 89 Z. Shan, B. Jiang, P. Wang, W. Wu and Y. Jin, Sustainable lignin-based composite hydrogels for controlled drug release and self-healing in antimicrobial wound dressing, *Int. J. Biol. Macromol.*, 2025, **285**, 138327.
- 90 R. Chavooshi, R. M. Renjkesh, B. Hashemi and L. Roshangar, Cellulose and lignin-derived scaffold and their biological application in tissue engineering, drug delivery, and wound healing: a review, *Cell J.*, 2023, **25**(3), 158–164.
- 91 J. Dominguez-Robles, A. Carcamo-Martinez, S. A. Stewart, R. F. Donnelly, E. Larraneta and M. Borrega, Lignin for pharmaceutical and biomedical applications – could this become a reality?, *Sustainable Chem. Pharm.*, 2020, **18**, 100320.
- 92 Y. Li, J. Zhu, Z. Zhang and Y. Qu, Preparation of syringaldehyde from lignin by catalytic oxidation of perovskite-type oxides, *ACS Omega*, 2020, **5**(5), 2107–2113.
- 93 M. Fache, B. Boutevin and S. Caillol, Vanillin production from lignin and its use as a renewable chemical, *ACS Sustain. Chem. Eng.*, 2016, **4**(1), 35–46.
- 94 C. Isola, H. L. Sieverding, A. M. Numan-Al-Mobin, R. Rajappagowda, E. A. Boakye, D. E. Raynie, *et al.*, Vanillin derived from lignin liquefaction: a sustainability evaluation, *Int. J. Life Cycle Assess.*, 2018, **23**, 1761–1772.
- 95 T. Ren, Z. Zhang, S. You, W. Qi, R. Su and Z. He, Isolation and purification of 4-propylguaiacol and 4-propylsyringol by extraction and crystallization from the products of reductive catalytic fractionation processes, *Green Chem.*, 2022, **24**(19), 7355–7361.
- 96 N. Zhou, W. Thilakarathna, Q. S. He and V. Rupasinghe, A review: depolymerization of lignin to generate high-value bio-products: opportunities, challenges, and prospects, *Front. Energy Res.*, 2022, **9**, 758744.
- 97 E. Kocaturk, T. Salan, O. Ozcelik, M. H. Alma and Z. Candan, Recent advances in lignin-based biofuel production, *Energies*, 2023, **16**(8), 3382.
- 98 A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, *et al.*, Lignin valorization: improving lignin processing in the biorefinery, *Science*, 2014, **344**(6185), 1246843.
- 99 W. Schutyser, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G. T. Beckham and B. F. Sels, Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerization, and upgrading, *Chem. Soc. Rev.*, 2018, **47**(3), 852–908.
- 100 L. M. Lindenbeck, S. Dahlhaus, L. M. Wende, B. B. Beele, M. Frauscher and N. H. Schebb, Breaking down lignin in gamma-valerolactone: advances into a bioelectrorefinery, *Green Chem. Lett. Rev.*, 2024, **17**(1), 2390867.
- 101 J. Xu, J. Meng, Y. Hu, Y. Liu, Y. Lou, W. Bai, *et al.*, Electrocatalytic lignin valorization into aromatic products via oxidative cleavage of C α –C β bonds, *Research*, 2023, **6**, 0288.

