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A Brief Overview of Lignin Extraction and Isolation Processes: From Lignocellulosic Biomass to Added-Value Biomaterials †

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Abstract: Lignin is one of the three major components of the cell wall of lignocellulosic biomaterials. It is the second-most abundant polymer in nature. It is a complex and heterogeneous polymer found in the cell walls of lignocellulosic biomass. Lignin's predominant composition, which is rich in carbon and aromatic structures, enhances its value by enabling the development of high-value chemicals and bio-based materials. As one of the most affluent natural renewable sources of aromatic structures and the world's second-largest renewable source of carbon, lignin possesses a thermal value comparable to that of carbon. Its aromatic constituents exhibit unique chemical properties and significant bioactive effects, making lignin a crucial material in various advanced applications. Different chemical fractionation methods have been designed to overcome the obstacles to extracting the lignin biopolymer from lignocellulosic biomass. Lignin fractionation is a process that involves separating lignin from other components of biomass feedstock, such as cellulose and hemicellulose. This process is commonly used in the paper and pulp industry to obtain valuable lignin derivatives that can be used in various applications, including, among others, biofuels, chemicals, and biomaterials. In the brief overview described in this proceedings paper, we provide a comprehensive chemical overview of the current processes for extracting technical lignin from wood and lignocellulosic biomass, critically evaluating the advantages and limitations of each method.

Keywords: wood; lignin; chemistry; fractionation; extraction; chemical pulping

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1. Introduction

Lignin is one of the three major components of the cell wall of lignocellulosic biomaterials, accounting for 10–25% of their composition as a function of their origin and environmental conditions. It is often chemically associated with cellulose and hemicellulose within the cellular structures of plants. Additionally, it is the principal recalcitrant component in these structures due to its complicated structure, which is made up of propylphenolic subunits [1,2].

Typically, lignin biopolymer consists of three repeating units: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) [3–5]. These subunits contain various chemical groups that are active sites for further chemical modifications and lignin utilization [6]. Furthermore, the ratio of these subunits can vary depending on the plant source, leading to structural diversity and tailored properties (Figure 1a). On the other hand, different types of linkages,

mainly β-O-4 ether linkages, connect the building blocks of lignin and are crucial targets for most degradation mechanisms (Figure 1b). Other bonds include β-5 phenylcoumaran, β-β resinol, α-O-4 ether, 4-O-5 diphenyl ether, 5-5 biphenyl, and β-1 diphenyl methane bonds, which make up smaller percentages [7].

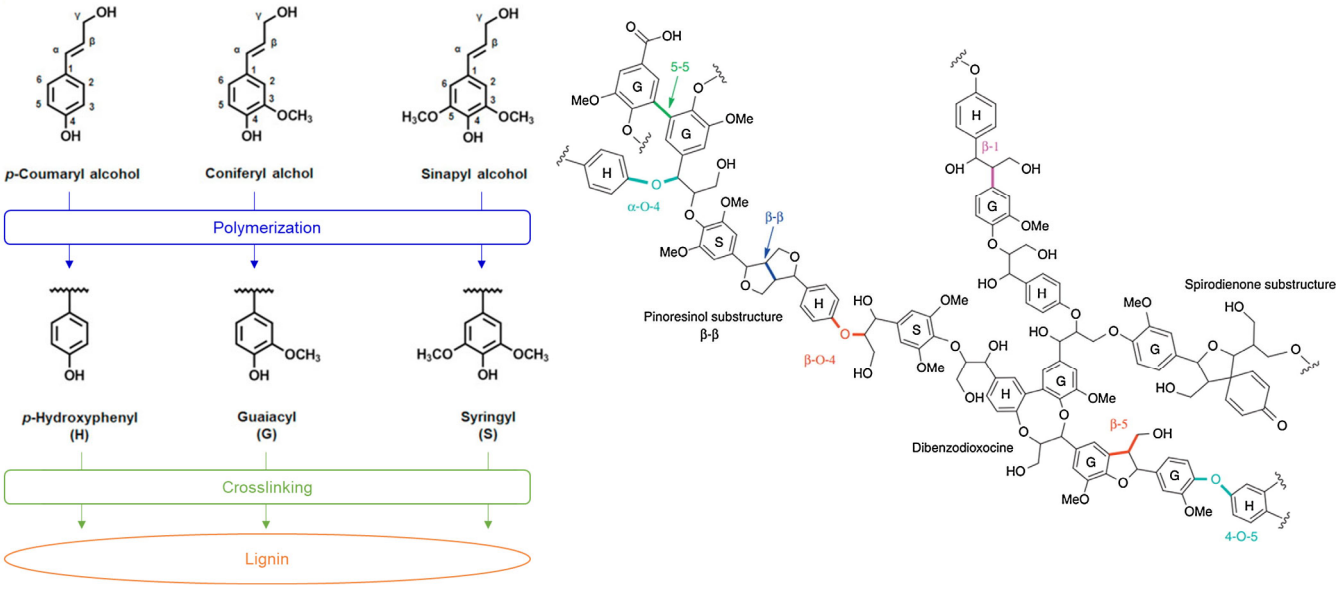

Figure 1. (**a**) Chemical structures of monolignols, which represent the precursors for the structural units in the lignin backbone. (Adapted from Hachimi Alaoui et al. (2022) [2], Copyright© 2022 MDPI under the terms of the Creative Commons Attribution 4.0 International License). (**b**) Example of lignin's structure, showing the main linkage bonds. (Reprinted from Figueiredo et al. (2018) [7], with permission from Elsevier. Published under license, Copyright© 2018 Elsevier Ltd.).

Since lignin is made up of many carbon and aromatic structures, it is more valuable because it can be used to make high-value chemicals and bio-based materials like hydrogels, films, nanofibers, and nanoparticles [8–12]. Furthermore, due to its intra- and intermolecular hydrogen bonding, lignin exhibits antioxidative and antibacterial qualities, UV-absorbing capacity, biocompatibility, and low cytotoxicity [8]. Its antioxidative activity stems from phenolic structures containing hydroxyl groups that neutralize reactive oxygen species (ROS) and free radicals [13]. The antibacterial properties arise from phenolic compounds and functional groups (hydroxyl and methoxy) that can disrupt bacterial cell membranes, making it useful in wound dressings and medical device coatings [14,15]. Finally, lignin's UV-absorbing capacity, attributed to its aromatic structure, effectively protects cells and tissues from UV-induced damage [16].

In the realm of materials science, lignin-derived carbon fibers are being utilized in lightweight, high-strength composites for the aerospace and automotive industries [12,17]. Furthermore, its inherent bioactive properties have enabled the development of lignin-based antioxidants and antimicrobial agents in food industries, biomedical fields, pharmaceuticals, and cosmetics [18–20]. In agriculture, lignin is employed in controlled-release fertilizers and as a soil conditioner due to its biodegradable nature [11,21]. These examples underscore the significance of lignin in advancing green technologies and its potential to contribute to the circular economy [9]. To fully exploit the beneficial properties of this biopolymer, several processes have been developed to optimize its isolation and recovery from lignocellulosic biomass, including Kraft, sulfite, alkaline, and steam explosion processes, among others [2,9,22].

2. Added-Value Lignin-Based Materials

Taking advantage of lignin's properties, including its antioxidative, antimicrobial, and UV-protective capabilities, may open new perspectives in the development of promising materials for various industrial applications, including those in the biomedical pharmaceutical fields and in adsorbents, supercapacitor electrodes, and adhesives. For instance, Kraft lignin was added to solid phenol and an aqueous solution of formaldehyde to prepare porous hydrogels [23]. In 2018, Sathawong et al. (2018) recovered Kraft lignin to synthesize a lignin–agarose hydrogel for cartilage neural tissue engineering and wound healing applications [24]. As well, sodium-lignosulfonate was grafted to poly(acrylic acid)co(poly(vinyl pyrrolidone) to form hydrogels for drug delivery applications [25]. Another way to use lignin biopolymer for biomedical applications is in scaffold preparation using the 3D bioprinting technique. In 2020, Jiang et al. (2020) successfully developed scaffolds using alkali lignin with Pluronic F127 [26]. In the same context, in 2022, Akhramez et al. (2022) developed and studied a novel lignin-based hydrogel for future applications in biomedical engineering using modified bagasse-sourced lignin obtained by the alkaline delignification process [9]. In the field of adsorbents, lignin-based materials have shown good promise in removing heavy metals, dyes, and other pollutants from water, highlighting their usefulness in environmental remediation. Last year, Sun et al. (2023) developed a cost-effective and environmentally friendly lignin-based network composite hydrogel adsorbent for methylene blue (MB) adsorption from wastewater by cross-linking polyacrylic acid (PAA) with sulfomethylated lignin (SML) derived from alkaline lignin [27]. In the same context, Li et al. (2016) investigated the potential of lignin in the development of high-performance of magnetic lignin hollow microspheres (MLS) with high adsorption capacity for organic dyes such as methylene blue and rhodamine B by synthesizing lignin hollow microspheres (LHM) from esterified organosolv lignin [28]. Beyond these applications, lignin has inherent adhesive properties that allow the formation of strong and durable bonds. More recently, Luo et al. (2024) developed super-tough and high-temperature-resistant hot-melt adhesives using lignin-derived elastomers [29].

3. Processing Methods for Lignin Extraction

In the literature, lignin extraction methods are broadly categorized into two main approaches: (1) methods where lignin is obtained as a residue and (2) methods where lignin is actively extracted. In the former approach, lignin is typically a byproduct of industrial processes, such as the Kraft and sulfite pulping processes, which primarily focus on cellulose and hemicellulose recovery. The resulting lignin often contains chemical impurities and modified structures due to the harsh treatment conditions. In contrast, the latter approach involves the targeted extraction of lignin using specific techniques, such as organosolv or alkaline processes, which are designed to isolate lignin with higher purity and more preserved structural properties [30]. As Holladay et al. (2007) pointed out in their comprehensive screening study, this classification highlights the variability in lignin quality and the suitability of different extraction methods for specific downstream applications [30].

Lignin can be extracted in various forms by different extraction processes [31]. Prior to extraction, lignocellulosic biomass can undergo preliminary treatments classified as chemical, physicochemical, or enzymatic pretreatments to remove the hemicellulose fraction, thereby facilitating lignin isolation [32]. It is worth noting that various physicochemical parameters and environmental conditions (i.e., temperature, solvent concentration, reaction time, and type of raw material) significantly impact the extraction yield and lignin properties [33,34]. Lignin can be obtained using Kraft, sulfite, alkaline, organosolv, steam explosion, or hydrolysis processes [35,36], as well as through "green methods" employing "eco-friendly solvents" such as ionic liquids and deep eutectic solvents [37,38]. After extraction, different techniques can be used to purify the obtained lignins, with the aim of isolating specific molecular lignin fractions with well-defined properties [39]. To enhance the comprehensibility of the differences between lignin types, Figure 2 illustrates the chem-

ical structures of lignosulfonate lignin, Kraft lignin, organosolv lignin, and soda lignin. These structures highlight the impact of different extraction and purification processes on lignin's composition and functional groups [40].

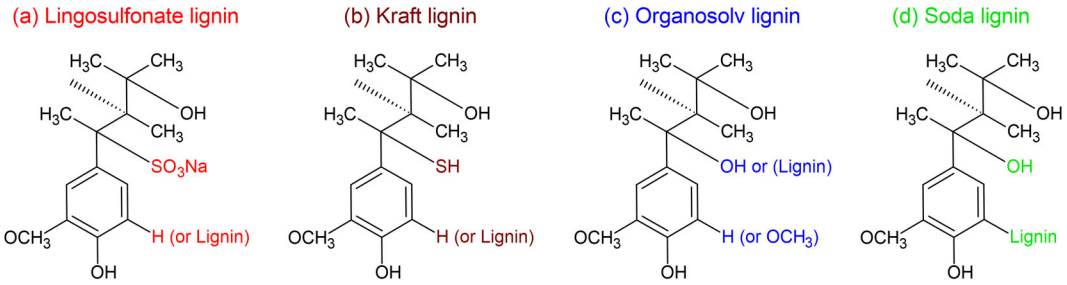

Figure 2. Chemical structures of some types of lignin obtained from various extraction and purification processes: (**a**) lignosulfonate lignin (derived from sulfite pulping processes); (**b**) Kraft lignin (produced from Kraft pulping); (**c**) organosolv lignin (isolated using organic solvent processes); (**d**) soda lignin (obtained through soda pulping). The structural differences reflect variations in extraction methods and conditions, which influence lignin's chemical properties and suitability for specific applications. (Created with ACD/ChemSketch (Freeware) 2023.1.2. Adapted from Melro et al. (2018) [40], with permission from Elsevier. Published under license, Copyright© 2018 Elsevier Ltd.).

For more details about these different methods as a function of the classifications, the following sub-sections summarize the important lignin extraction processes.

3.1. Kraft Process

The Kraft process is a widely applied method for lignin extraction that is particularly suitable for wood-based materials. This process employs a solution of sodium hydroxide and sodium sulfide, commonly known as white liquor, to dissolve lignin at an elevated temperature of approximately 170 °C and a high pH level, typically between 13 and 14. The reaction typically spans around two hours, after which lignin can be isolated from the residual pulp through precipitation, often mediated by sulfuric acid [7,41,42].

One of the main advantages of the Kraft process is its high lignin removal efficiency, which effectively liberates lignin from the wood matrix while yielding a lignin product with a relatively low ash content. Additionally, Kraft lignin is valuable due to its solubility in alkali solutions and various polar organic solvents, offering flexibility in downstream applications. However, the Kraft process has some limitations, notably its lengthy reaction time and the generation of black liquor—a byproduct rich in carbohydrates. This byproduct requires further processing, adding complexity and cost to the overall process.

To address these challenges, advanced techniques such as the LignoBoost process have been developed. The LignoBoost process builds on the traditional acidification method by introducing a two-step precipitation procedure. In the first step, carbon dioxide is used to partially precipitate the lignin, followed by sulfuric acid for further purification. This dual-step approach reduces impurities, improves the filtration performance, and lowers the resistance of the filter cake, making the process more efficient. Moreover, LignoBoost lignin exhibits higher purity and uniformity, which enhances its potential for high-value applications such as adhesives, resins, and carbon fibers [43].

3.2. Sulfite Process

The sulfite process is another key method for extracting lignin, which specifically produces lignosulfonates through a chemical reaction involving lignin, sulfur dioxide (SO_2), and a metal sulfite such as calcium sulfite ($CaSO_3$) or magnesium sulfite ($MgSO_3$). This reaction targets and cleaves α-ether and β-ether linkages in the lignin structure, facilitating lignin's release from the wood matrix. The process is typically conducted at temperatures ranging from 120 to 180 °C over a span of 1 to 5 h, and it can be adapted to operate under alkaline, neutral, or acidic conditions depending on the desired outcomes [7,41,44].

One of the primary benefits of the sulfite process is the production of lignosulfonate, a highly soluble form of lignin. This lignosulfonate demonstrates solubility in water, polar organic solvents, and amines, expanding its applicability across various industries. However, there are significant downsides to this process. It yields a lignin product with a high sulfur content, which may limit its use in some applications. Additionally, the sulfite process is less selective, often resulting in the co-extraction of both lignin and hemicellulose. This lack of selectivity, coupled with the high content of ash and carbohydrates in the end product, can complicate lignin purification. Moreover, the process alters the lignin's original structure, potentially impacting its functional properties in further applications.

3.3. Alkaline Process

The alkaline process is a commonly used approach for lignin extraction, and it is particularly effective for the delignification of non-wood lignocellulosic materials. This process employs various alkali solutions, including ammonium, sodium, and calcium hydroxide, to hydrolytically break down lignin within the biomass. Typically carried out at temperatures ranging from 140 to 170 °C, the process allows for the efficient separation of lignin, which can then be recovered through centrifugation or filtration techniques [7,41,45,46].

Among the advantages of the alkaline process is its high lignin removal efficiency, producing a product with low ash content and with minimal formation of inhibitory compounds, which can be beneficial for subsequent applications. However, some downsides are associated with this approach. The use of alkaline catalysts can incur high costs, and the process often results in significant structural alterations to the lignin, which may affect its functionality. Additionally, the lignin obtained may contain a substantial amount of residual carbohydrates, necessitating further purification steps.

3.4. Organosolv Process

The organosolv process is an advanced lignin extraction method that involves treating lignocellulosic biomass with organic solvents—such as ethanol, methanol, acetic acid, formic acid, ethylene glycol, or tetrahydrofurfuryl alcohol—that are often mixed with water. The process may also incorporate basic or acidic catalysts to enhance the extraction efficiency. Conducted at temperatures between 170 and 190 °C, this approach allows lignin to dissolve within the organic solvent medium, from which it can later be recovered by solvent evaporation or precipitation [7,41,44,45,47,48].

This method offers several advantages: it produces a lignin product with no sulfur content, making it more suitable for certain applications where sulfur-free lignin is preferred. Additionally, the organosolv process is less aggressive than other methods, resulting in lignin with low ash content and lower molecular weight, which can increase its solubility in alkali solutions and broaden its applicability. Furthermore, the relatively short reaction times make this process efficient. Despite its benefits, the organosolv process has some limitations. The primary challenge lies in the high cost of the organic solvents, which can significantly increase the overall expense. Additionally, solvent recovery is required to maintain cost-effectiveness and environmental compliance, necessitating an extra processing step. The lignin produced by this method is also notably hydrophobic, which may limit its compatibility with certain applications unless further modification is performed.

3.5. Steam Explosion Process

The steam explosion process is an innovative and cost-effective lignin extraction method that utilizes both mechanical and chemical forces to break down lignocellulosic materials. In this process, lignocellulosic biomass is subjected to high temperatures (180–250 °C) for a brief period (about 1–2 min) to reach pressures of 4–7 MPa. This rapid treatment causes the acetyl groups within hemicellulose to undergo autohydrolysis, leading to a "steam explosion" effect that aids in the disruption of the biomass structure. Following this, lignin can be separated from hemicellulose-derived products via a washing step using an alkali solution or organic solvent [41,44–46,49,50].

Steam explosion offers several advantages: it is sulfur-free, which improves the environmental profile and reduces processing costs compared with sulfur-based methods. The process is also energy efficient and produces a lignin product with low ash content while having minimal environmental impact. However, the intense conditions of steam explosion can lead to significant structural modifications to the lignin, which may impact its usability in certain applications. Additionally, the method often results in a high hemicellulose content within the extracted lignin and may generate toxic byproducts, necessitating careful handling and additional processing.

3.6. Hydrolysis Process

The hydrolysis process is a lignin extraction technique that utilizes acidic or enzymatic hydrolysis to break down lignocellulosic biomass. This approach primarily targets and dissolves the carbohydrate fraction of the biomass, after which the lignin can be isolated through precipitation. Hydrolysis can be performed using strong acids, which facilitate rapid carbohydrate dissolution, or through enzymes, which offer a more selective breakdown while being gentler on the lignin structure [6,41,46,49,51].

The hydrolysis process offers several distinct benefits. It produces sulfur-free lignin, enhancing its applicability in industries where sulfur content is undesirable. Additionally, this method yields a high glucose content from the dissolved carbohydrates, which can be valuable in biofuel and biochemical production. It is also a relatively low-energy process compared with other lignin extraction methods, making it more sustainable from an energy consumption perspective. However, the hydrolysis process is not without limitations. It requires an extended treatment duration, particularly for enzymatic hydrolysis, which may affect the process efficiency. This method can also lead to carbohydrate depletion if microbial cultures are present, complicating the product purity. Furthermore, the formation of inhibitory byproducts is a challenge, as these can affect downstream processes. Lastly, the acidic hydrolysis option necessitates the use of corrosion-resistant equipment, which can substantially increase operational costs.

3.7. Ionic-Liquid Extraction Process

The ionic-liquid extraction process represents a green and efficient method for lignin extraction that leverages ionic liquids—salts composed of inorganic anions and organic cations with unique solvent properties. These ionic liquids act as effective solvents for lignocellulosic biomass, facilitating the dissolution of both lignin and carbohydrates. This approach has the added benefit of reducing the structural rigidity of lignin, making it easier to process and utilize [41,48–50,52,53].

This method offers several advantages. Ionic liquids generally have low melting points (below 100 °C), and they exhibit high thermal stability and polarity, which enhance their effectiveness in lignin dissolution. Furthermore, ionic liquids have low toxicity and cause minimal structural alterations to lignin, preserving its native properties. They are also reusable, making them environmentally and economically favorable for sustainable biomass processing. However, the high cost of ionic liquids poses a significant barrier to the widespread application of this method. Additionally, the process requires an antisolvent to regenerate the biomass, adding complexity. An extra step for ionic-liquid recovery is also necessary, as these solvents must be recycled to offset costs. This recycling process, while feasible, is energy-intensive, which may diminish some of the environmental benefits of using ionic liquids.

3.8. Deep Eutectic Solvent Process

The deep eutectic solvent (DES) process is a novel green method for lignin extraction that employs a unique class of solvents. DESs consist of a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA), which, together, form a stable, eutectic mixture capable of efficiently dissolving lignin and other biomass components. Typically, choline chloride

is used as the HBA, while common HBDs include amines, carboxylic acids, and alcohols, resulting in a highly customizable solvent system [6,46,49,54–56].

DESs offer numerous advantages, making them well suited for sustainable lignin extraction. They are inexpensive, straightforward to prepare, and exhibit high biocompatibility and biodegradability. Additionally, DESs are non-flammable, low-volatile, and environmentally friendly, enhancing their appeal as green solvents. This method allows for the dissolution of various biomass types and produces high-purity lignin under relatively mild conditions, preserving lignin's functional integrity while reducing energy consumption. However, like other solvent-based processes, DES extraction requires solvent recovery and recycling to be cost-effective and sustainable, which adds an additional step to the process.

4. Conclusions

The various extraction techniques presented in this brief overview highlight significant progress in isolating lignin from lignocellulosic biomass. Each method, whether sulfur-based, sulfur-free, or involve novel green technologies, has distinct advantages and limitations that directly influence the structure, purity, and properties of the extracted lignin. Selecting appropriate extraction conditions and parameters is crucial for retaining the intrinsic functional properties of lignin, which is essential for its diverse applications. Green technologies, such as those employing deep eutectic solvents, ionic liquids, and organosolv processes, are particularly noteworthy for their potential to minimize environmental impacts. These methods allow for the recovery and reuse of solvents, reducing waste generation and lowering the carbon footprint of lignin extraction. Additionally, they contribute to the development of environmentally sustainable biorefinery processes by replacing conventional harsh chemical treatments with eco-friendly alternatives. The adoption of these methods not only aligns with global efforts to address environmental pressures but also enhances the feasibility of lignin-based materials as a renewable and sustainable resource. The continued advancement of lignin extraction technologies, coupled with a deeper understanding of structure–property relationships, will play a vital role in unlocking the full potential of this versatile biopolymer. This progress will facilitate the development of sustainable biomaterials, contribute to reducing environmental burdens, and support the transition toward a circular bioeconomy.

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