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Conventional and Advanced Lignin Extraction Technologies from Lignocellulosic Biomass: A Review

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ABSTRACT: The chemical engineering field has shown growing interest in the valorization of lignocellulosic biomass, driven by its abundance, renewability, and potential as an alternative to petroleum-based feedstocks. Despite this, the selective and efficient extraction of structurally intact, high-purity lignin continues to pose significant technical challenges. This review synthesized secondary data from peer-reviewed journal articles, conference papers, and authoritative texts to examine conventional, environmentally benign, and emerging lignin extraction techniques. Emphasis was placed on subcritical and supercritical fluid technologies, with detailed analysis of how operational parameters—such as temperature, pressure, residence time, and solvent selection—influence lignin yield and structural integrity. Findings suggested that sub- and supercritical fluid extraction methods present a promising alternative to traditional approaches, offering tunable solvent properties that enable selective lignin isolation and the potential for enhanced purity. These advancements could play a pivotal role in enabling the commercial-scale production of lignin-derived biomaterials and accelerating the transition toward a more sustainable, bio-economy and bio-based chemical industry.

KEYWORDS: Lignin isolation, lignocellulosic biomass, valorization, sub- and supercritical fluids, bio-materials, bio-economy, bio-based chemicals.

1. INTRODUCTION

Lignocellulosic biomass constitutes the Earth's most plentiful renewable organic material, with global annual production estimates surpassing 170 billion metric tons [1]. This biomass consists of three primary components: cellulose, hemicellulose, and lignin [2]. The strategic utilization of these lignocellulosic constituents provides promising avenues for establishing environmentally sustainable substitutes for petroleum-derived materials [3]. It represents approximately 15-30% of lignocellulosic biomass by mass and exhibits a complex three-dimensional amorphous polymeric structure. This biopolymer is constructed from phenylpropane monomeric units, specifically p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which are interconnected through diverse chemical linkages including β-O-4, β-β, β-5, and 5-5 bonds, as illustrated in Figure 1. Given its status as the second most prevalent biopolymer following cellulose, lignin demonstrates significant promise as an environmentally responsible raw material for diverse industrial applications [1], [4].

Current industrial processing yields an estimated 70-80 million tons of lignin annually, with approximately 70 million tons originating from pulp and paper manufacturing operations [5]. Despite this substantial production volume, only 2% of the total lignin output is recovered and utilized for commercial applications, while the remaining 98% is combusted for energy generation [1], [6], [7]. This represents a significant underutilization of a valuable biopolymer resource. Beyond industrial sources, agricultural residues present considerable additional potential for lignin recovery. Preliminary assessments indicate that agricultural waste streams, particularly crop stalks and straw materials, could potentially yield an additional 730 million tons of lignin per year (Table 1) [8], [9], [10]. This agricultural lignin resource remains largely untapped, representing a substantial opportunity for expanding the availability of sustainable biomass-derived materials for industrial applications.

Lignin recovery from lignocellulosic biomass can be accomplished through diverse extraction methodologies. Initial biomass processing typically involves pretreatment strategies categorized as chemical, physicochemical, or enzymatic approaches, which selectively remove hemicellulose components to enhance subsequent lignin isolation efficiency [11], [12]. Conventional extraction techniques encompass Kraft pulping, sulfite processing, alkaline treatment, steam explosion, and hydrolysis methods. In parallel, environmentally conscious extraction approaches have gained prominence, utilizing sustainable solvents including organosolv systems, ionic liquids, and deep eutectic solvents [13].

Contemporary research has increasingly focused on advanced extraction technologies such as subcritical and supercritical fluid processing, as well as non-thermal plasma treatment, which offer both environmental compatibility and the ability to produce lignin with tailored physicochemical characteristics [12], [13]. Following extraction, various purification protocols may be implemented to refine the recovered lignin, with the objective of isolating distinct molecular lignin fractions

possessing well-characterized and reproducible properties [11]. This multi-step approach enables researchers to obtain lignin materials suitable for specific downstream applications while maintaining structural integrity and desired functional attributes.

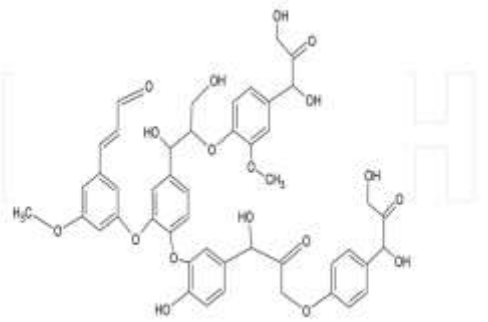

Figure 1: structure of lignin showing the three monolignol units [14]

Table 1 presents the composition of major biomass components in different lignocellulosic sources [9], [10], [15], [16]

Lignocellulosic biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	41-55	24-40	19-25
Softwood stems	41-50	26-35	24-35
Nut shells	25-30	25-30	30-40
Corn cobs	44	36	15
Grasses	25-40	35-50	10-30
Wheat Straw	30	50	15
Sorted refuse	61	20	20
Newspaper	40-55	25-40	18-30
Waste papers from chemical pulp	60-70	10-20	5-10
Primary waste-water solid	8-15	0	20-29
Switchgrass	45	31.4	12

Lignin demonstrates considerable potential across diverse industrial sectors, presenting researchers and engineers with exciting opportunities to develop sustainable material solutions. The textile, food packaging, and biomedical industries have emerged as particularly promising domains where lignin-derived materials could replace conventional petroleum-based compounds. For chemical engineers working in sustainable materials development, lignin's ability to serve as a precursor for bio-based polymers, phenolic resins, polyurethane foams, and carbon fibers represents a significant advancement toward circular economy principles [9],[17],[18],[19]. Nevertheless, the industrial utilization of lignin faces substantial technical hurdles that continue to challenge researchers in the field. The extraction of structurally intact, high-quality lignin from lignocellulosic biomass remains problematic due to lignin's intricate three-dimensional network and its extensive covalent bonding with cellulose and hemicellulose components.

Traditional extraction methodologies, while commercially established, frequently induce deleterious structural alterations to the lignin macromolecule, thereby compromising its suitability for high-value applications such as carbon fiber manufacturing [20]. Recent advances in extraction technology have directed attention toward sub- and supercritical fluid systems, which offer chemical engineers enhanced process control through adjustable solvent properties. These innovative approaches provide the dual benefits of potentially preserving lignin's native structure while simultaneously reducing the environmental footprint of the extraction process, addressing both technical and sustainability concerns that drive modern chemical engineering practice [21], [22].

This review presents both traditional and emerging technologies for lignin extraction, with particular emphasis on recent advances involving subcritical and supercritical fluid methods. The discussion explores a range of extraction techniques, highlighting their respective advantages and challenges. Furthermore, it examines how key process variables—such as temperature, pressure, residence time, and solvent selection—influence the efficiency of lignin recovery and the quality of the extracted lignin for potential industrial use employing the sub and supercritical technologies.

2. MATERIALS AND METHODS

This review was carried out using secondary sources of data from journal articles, conference proceedings, textbooks, unpublished materials and recognized websites. The method adopted included reviewing the conventional and advanced technologies for lignin isolation with emphasis on sub and super-critical fluid technologies.

3. RESULTS AND DISCUSSION

3.1. Conventional Lignin Extraction Technologies

A variety of established techniques are available for lignin extraction, each offering distinct advantages and inherent limitations. Gaining insight into these conventional and environmentally sustainable approaches is essential for contextualizing the potential benefits of more advanced methods, such as subcritical and supercritical fluid extraction technologies.

3.1.1 Kraft Pulping

The Kraft pulping process is the most widely adopted industrial technique for lignin extraction, accounting for approximately 70 million tons of lignin produced annually worldwide [23], [24]. It involves the treatment of wood chips with white liquor—an aqueous solution of sodium hydroxide and sodium sulfide—at elevated temperatures (150–170 °C) for 1–2 hours, leading to the cleavage of α-O-4 and β-O-4 ether bonds in lignin and its subsequent dissolution [25], [26]. This method is employed in over 80% of global cellulosic pulp production due to its high delignification efficiency (>90%) and suitability for producing bleachable-grade cellulose [2], [26].

During pulping, the molecular weight of lignin is significantly reduced, and the final composition may vary depending on wood type. The resulting brown-colored solution, known as black liquor, contains dissolved lignin, which can be recovered through acid or CO_2 precipitation at controlled pH levels [27]. Although Kraft lignin typically contains residual impurities, including 1–2% sulfur and traces of carbohydrates [25], [28], it remains a valuable feedstock for further refinement and utilization in industrial products such as adhesives, biofuels, and polymeric binders [29].

3.1.2 Lignosulfonate/Sulphite process

The sulfite pulping process represents a well-established industrial pathway for lignin recovery, operating across a broad pH spectrum (2-12) depending on the cationic composition of the processing medium [30], [31], [32]. This aqueous-based delignification technique employs sulfurous acid salts at elevated temperatures (130-180°C) to systematically deconstruct lignocellulosic matrices through targeted cleavage of α-ether and β-ether bonds within the lignin macromolecule. The process utilizes metal sulfites, predominantly calcium or magnesium variants, in conjunction with sulfur dioxide to facilitate lignin solubilization over residence times of 1-5 hours under controlled thermal conditions (120-180°C) [11], [12].

The sulfite method yields lignosulfonates, which exhibit exceptional solubility characteristics in aqueous and polar organic media, making them attractive for diverse industrial applications. However, chemical engineers must consider several process limitations that impact product quality and downstream processing requirements. The resulting lignin fraction contains elevated sulfur concentrations that may restrict its utility in certain high-value applications [33]. Furthermore, the process demonstrates limited selectivity, frequently co-extracting hemicellulose components alongside lignin, while introducing substantial ash and carbohydrate contamination that complicates subsequent purification steps. These structural modifications fundamentally alter lignin's native properties, potentially constraining its performance in advanced material applications [13].

3.1.3 Soda pulping process

The soda pulping methodology constitutes a foundational chemical delignification approach primarily employed for processing non-wood biomass feedstocks, including agricultural residues such as bagasse, wheat straw, hemp, kenaf, and sisal [10], [16], [33]. This alkaline extraction process utilizes concentrated sodium hydroxide solutions (13-16 wt%) as the active delignifying agent, operating under pressurized conditions at temperatures of 140-170°C to facilitate lignin removal from the lignocellulosic matrix [34]. A distinguishing characteristic of soda pulping lies in its exclusion of sodium sulfide, differentiating it from the more aggressive Kraft process. While this absence of nucleophilic sulfur species results in reduced delignification efficiency compared to Kraft technology, it simultaneously produces lignin with minimal structural perturbation [35].

The resulting soda lignin exhibits several advantageous properties for chemical engineers developing sustainable materials: it remains sulfur-free, requires minimal purification, and can be readily recovered through simple precipitation techniques. These characteristics render soda lignin particularly attractive as a feedstock for high-value applications compared to sulfur-containing alternatives such as Kraft lignin or lignosulfonates. However, process engineers must address the inherent limitation of extensive lignin condensation reactions that occur during soda pulping, which can compromise the reactivity and processability of the recovered lignin for certain downstream applications [36].

3.1.4 Alkaline Process

Alkaline delignification represents a widely adopted industrial approach for lignin recovery, demonstrating particular efficacy in processing non-wood lignocellulosic feedstocks. Chemical engineers employ various hydroxide-based systems, including ammonium, sodium, and calcium variants, to achieve hydrolytic cleavage of lignin-carbohydrate complexes within the biomass matrix. Operating at moderate temperatures (140-170°C), this methodology enables efficient lignin-cellulose separation, with subsequent lignin recovery accomplished through conventional solid-liquid separation techniques such as centrifugation or filtration [12], [13].

The alkaline extraction process offers several operational advantages that make it attractive for industrial implementation, including high delignification yields, minimal ash contamination, and reduced formation of process inhibitors that could complicate downstream biorefinery operations. However, process engineers must consider significant economic and technical challenges inherent to this approach. The alkaline catalysts impose substantial operating costs, while the harsh chemical environment induces considerable structural modifications to the native lignin architecture, potentially compromising its utility in high-performance applications. Furthermore, the recovered lignin fraction typically contains appreciable carbohydrate residues, necessitating additional purification protocols that increase process complexity and operational expenses [1], [7], [13]. These trade-offs require careful evaluation when selecting alkaline extraction for specific lignin valorization strategies.

3.1.5 Hydrolysis (acid treatment) Process

Hydrolysis-based lignin extraction employs either acidic or enzymatic pathways to selectively depolymerize carbohydrate components within lignocellulosic matrices, enabling subsequent lignin recovery through precipitation mechanisms. This approach offers chemical engineers flexibility in process design, with strong acid systems providing rapid carbohydrate solubilization or enzymatic alternatives delivering enhanced selectivity while preserving lignin structural integrity [13], [37].

The hydrolysis methodology presents several compelling advantages for sustainable biorefinery operations. The process generates sulfur-free lignin products suitable for applications requiring high purity standards, while simultaneously producing glucose-rich streams valuable for biofuel synthesis

and biochemical manufacturing. Additionally, the relatively modest energy requirements compared to thermochemical alternatives enhance the overall process sustainability profile [2], [38].

However, process engineers must address significant operational challenges inherent to hydrolysis systems. Extended residence times, particularly in enzymatic configurations, can compromise throughput efficiency and economic viability. The presence of microbial contaminants poses risks of carbohydrate consumption, potentially reducing product yields and complicating purification protocols. Furthermore, the formation of inhibitory compounds during hydrolysis can negatively impact downstream processing operations. For acidic hydrolysis variants, the corrosive operating environment necessitates specialized materials of construction, substantially increasing capital expenditure requirements and operational complexity [11], [12], [29], [39]. These factors require careful economic evaluation when implementing hydrolysis-based lignin recovery strategies.

3.2 Eco-Friendly technologies

3.2.1 Organosolv Process

In recent years, organosolv fractionation has emerged as a promising biorefinery strategy for the selective separation of cellulose, hemicelluloses, and lignin from lignocellulosic biomass [40]. This pretreatment technique employs aqueous-organic solvent mixtures—such as methanol, ethanol, acetone, ethylene glycol, and triethylene glycol—with or without acid catalysts to facilitate the fractionation process [41], [42]. Operating typically within the temperature range of 140–200 °C, the method effectively disrupts lignin–carbohydrate complexes, enabling hemicellulose removal and reducing the formation of degradation products from sugars and lignin. Compared to lignin obtained from kraft pulping, organosolv-derived lignin is generally less condensed, sulfur-free, and of higher purity, making it more suitable for downstream catalytic applications [43].

The absence of sulfur-containing compounds also circumvents catalyst deactivation associated with traditional pulping methods, although large-scale deployment remains constrained by the lack of commercially viable pathways for converting high-quality sulfur-free lignin into value-added products [41], [44]. One of the notable advantages of organosolv processing is its ability to separate hemicellulose directly, without requiring prior lignin removal. Furthermore, this approach enables mild processing conditions, efficient solvent recovery, and the isolation of structurally preserved lignin. Nevertheless, its industrial applicability is limited by high operational costs, solvent safety concerns, and the technical demands of solvent recycling infrastructure [7].

3.2.2 Ionic-Liquids (ILs)

Ionic liquid (IL) extraction has emerged as a sustainable and effective approach for lignin recovery, capitalizing on the unique physicochemical properties of ionic liquids—salts formed from organic cations and either inorganic or organic anions [45], [46]. These solvents, typically characterized by melting points below 100 °C, are composed of cationic species such as imidazolium, pyridinium, aliphatic ammonium, alkyl phosphonium, or sulfonium ions, paired with suitable anions [7], [47]. Due to their dual role as solvents and reagents, ILs have gained considerable attention as environmentally benign agents for lignocellulosic biomass pretreatment [7], [48], [49]. Their high polarity, thermal stability, and low volatility contribute to their efficacy in dissolving both lignin and carbohydrates, often with minimal structural disruption to the lignin matrix [45], [50].

Additionally, ionic liquids are generally non-volatile and exhibit low toxicity, making them attractive for green processing routes. The ability to preserve lignin's native structural features enhances their suitability for applications that require high-purity lignin. Furthermore, their reusability supports the economic and environmental feasibility of the process. Nonetheless, the high cost of most ILs remains a critical limitation for large-scale deployment. The process also necessitates the use of an antisolvent for biomass regeneration, along with a recovery system for recycling the ionic liquid, which introduces additional operational complexity and energy demands [7], [51]. Although technically feasible, the energy-intensive nature of IL recovery could potentially offset some of the environmental advantages of this otherwise promising method.

3.2.3 Deep Eutectic Solvents

The deep eutectic solvent (DES) method represents an emerging green technology for lignin extraction, utilizing a novel class of designer solvents formed through the combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). These components interact to form a thermodynamically stable eutectic mixture capable of selectively dissolving lignin and other structural components of lignocellulosic biomass [7], [52], [53]. Commonly, choline chloride serves as the HBA, while a variety of HBDs—such as carboxylic acids, alcohols, and amines—can be employed, allowing for the development of highly tunable solvent systems tailored to specific biomass types [54], [55].

DESs offer several key advantages that make them suitable for sustainable lignin valorization, including low cost, ease of synthesis, and favorable environmental properties such as biodegradability, non-flammability, and low vapor pressure [13], [56], [57], [58], [59], [60]. These solvents enable the processing of diverse biomass feedstocks under relatively mild operating conditions, which contributes to energy efficiency and helps preserve the native structure and functionality of the extracted lignin [61], [62], [63], [64]. Despite their promising potential, DES-based extraction processes still face practical challenges, particularly regarding solvent recovery and recycling. To ensure economic viability and environmental sustainability, effective regeneration strategies are necessary, introducing an additional layer of process complexity [13], [65], [66], [67], [68].

3.2.4 Microwave-Assisted Extraction (MAEx)

Microwave-Assisted Extraction (MAEx) has emerged over the past decade and a half as a sustainable and efficient technique for the extraction of lignocellulosic components, particularly lignin and hemicelluloses, due to its reduced environmental impact and operational effectiveness [7], [13]. Unlike traditional methods, MAEx utilizes microwave (MW) radiation to accelerate the dehydration of biomass and disrupt plant cell wall structures, thereby enhancing the diffusion and release of target compounds [2], [69], [70]. This approach facilitates rapid heating, which contributes to the effective degradation of lignocellulosic matrices and improves mass transfer processes.

The efficiency of MAEx is governed by a combination of physical and chemical phenomena, including solvent penetration into plant tissues, microwave reflection and refraction behavior, and the solubility and diffusion characteristics of cellulose within the solvent medium [71], [72]. During MW pretreatment, electromagnetic radiation interacts with polar molecules in the biomass, causing localized heating and structural disruption of the cellulosic and lignin components [73]. This effect can partially degrade lignin and increase cellulose accessibility to enzymatic or chemical hydrolysis during subsequent processing steps [74].

Several parameters influence the success of microwave-assisted treatments, such as biomass type, inherent moisture content, particle size, solvent choice, and the intensity and duration of microwave exposure [2]. Due to the targeted nature of microwave heating, energy losses to the environment are minimized, contributing to overall process efficiency and sustainability [73]. The enhanced internal heating provided by microwave energy outperforms conventional thermal systems, which typically rely on slower and less efficient conductive heat transfer [76]. As a result, MAEx not only improves extraction yield and reduces solvent usage but also significantly shortens processing time, reinforcing its potential as a green and scalable technology for biomass valorization [75].

3.2.5 Steam Explosion

Steam explosion is a widely recognized hydrothermal pretreatment technique that involves subjecting lignocellulosic biomass to high-pressure saturated steam—typically within the range of 0.7 to 4.8 MPa—at elevated temperatures between 160 °C and 260 °C for short residence times, followed by sudden depressurization [7], [13]. This rapid decompression causes structural disruption of the biomass, facilitating hemicellulose hydrolysis and partial modification of lignin through autohydrolysis reactions. As a result, steam explosion offers a combined mechanical and chemical mechanism for effective lignocellulosic fractionation, presenting itself as a promising and cost-efficient method for lignin recovery [77].

During treatment, the biomass is exposed to temperatures around 180–250 °C for approximately 1–2 minutes, reaching pressures of up to 4–7 MPa. The release of acetyl groups from hemicellulose triggers autohydrolysis, creating internal pressure that aids in the disintegration of the lignocellulosic matrix. Subsequent separation of lignin from hemicellulose-derived compounds can be achieved through washing with alkaline or organic solvents [78]. Notably, this method avoids the use of sulfur-based chemicals, which enhances its environmental performance and lowers processing costs.

Steam explosion also provides additional benefits, including relatively low energy consumption and the production of lignin with reduced ash content. However, the high-temperature, high-pressure environment can cause substantial structural alterations in the lignin, potentially limiting its suitability for certain downstream applications [2], [13]. Moreover, the extracted lignin often contains significant hemicellulosic residues and may be accompanied by inhibitory byproducts, necessitating further purification and handling measures to ensure its compatibility with targeted value-added uses.

For comparative analysis of these technologies, the benefits and limitations of each technology are summarized in Table 2.

Table 2: Summary of the comparative analysis of the different technologies

S/No	Technologies	Mechanism	Benefits	Limitations	Applications/References
1	Kraft pulping	Nucleophilic attack on lignin linkages by NaOH and Hydrosulfide ions	High delignification efficiency (85-95%) Produces high quality cellulose pulp Economically viable for large scale operations.	Severe lignin degradation and condensation reactions. Low lignin yield in pure form. Environmental concerns due to sulphur compounds.	Pulp and paper industry Biochemicals Carbon fibre production. Adhesives, binders [13], [24], [27]
2	Sulphite pulping	Sulphonation of Lignin sidechains particularly at benzylic positions.	Produces Lignosulphonates. Lower cooking temperature	Lower delignification efficiency than kraft	Production of Lignosulphonates for concrete admixture Animal feed binder

			Better preservation of carbohydrate function	Environmental issues with SO_2 emissions Lignin structure heavily modified by sulfonation.	Oil drilling muds, dispersants, binder [13], [30],[31]
3	Soda pulping	Alkaline hydrolysis of lignin ether linkages Similar to kraft but without sulfur chemistry enhancement	Sulfur-free process eliminates odor issues Simpler chemical system Produces relatively unmodified lignin Lower capital investment for chemical recovery	Lower delignification rate compared to kraft Requires higher alkali charge and longer cooking times Higher energy consumption per unit of delignification	Primarily used for non-wood fibers and in regions where sulfur availability is limited. Silica Recovery Operations Biorefinery Applications for Agricultural Residues Anthraquinone-Modified Soda (AMS) Process [13], [33], [34]
4	Alkaline treatment	Hydroxyl and perhydroxyl radicals attack lignin aromatics Oxidative cleavage of lignin bonds Formation of carboxylic acids and aldehydes	Selective lignin removal Mild reaction conditions (room temperature to 80°C) No sulfur compounds involved Preserves cellulose quality	Low lignin recovery due to extensive degradation Requires pH control and stabilizers Limited commercial viability for lignin isolation Safety concerns with concentrated peroxide	Research applications and specialty pulping; Oxygen bleaching in pulp industry. Carbon Materials Manufacturing Phenolic Resin Substitution [12], [13], [37].
5	Hydrolysis (Acid) process	Acid-catalyzed hydrolysis of glycosidic bonds Protonation of lignin ether linkages promotes cleavage Partial lignin solubilization and structural modification Hemicellulose hydrolysis to simple sugars	Cost-effective and simple process Effective hemicellulose removal Relatively mild conditions (120-160°C)	Low lignin yield and purity Formation of fermentation inhibitors Corrosive conditions require specialized equipment Environmental concerns with acid waste	Pretreatment step in bioethanol production; Produces low-grade lignin as byproduct. Membrane Separation Integration [13], [39]

6	Organosolv	Organic solvents swell lignin structure Acid catalysis (when used) promotes lignin fragmentation Lignin dissolves preferentially in the organic phase	Produces high-purity, sulfur-free lignin Excellent lignin recovery (60-85%) Minimal lignin structural modification Environmentally friendly with proper solvent recovery Lower processing temperatures (150-200°C)	High capital costs for solvent recovery systems Requires specialized equipment for solvent handling Energy-intensive distillation for solvent recovery	Research and pilot-scale biorefineries; promising for integrated lignocellulosic processing. Electrochemical Applications Antimicrobial and Antioxidant Products Polyurethane Foam Production [41], [42], [44].
7	Ionic Liquids	Inorganic anions and organic cations facilitate dissolution of lignin	High quality lignin recovery Low melting points High thermal stability and polarity Low toxicity	High cost of ionic liquids Requires antisolvent to regenerate the biomass	Pharmaceutical and Biomedical Applications 3D Printing and Additive Manufacturing Nanocomposite Reinforcement [13], [46], [48]
8	Deep Eutectic Solvent	Hydrogen-bond donor (HBD) and a Hydrogen-bond acceptor (HBA) form a stable eutectic mixture dissolving lignin	Biocompatible and biodegradable liquids Non flammable High purity lignin	Require solvent recovery	Food processing, Textile Bio-based Antioxidant Production Thermoplastic Polymer Applications [13], [61], [62], [68],
9	Microwave-assisted Extraction	Interaction between the microwave electromagnetic field and the polar molecules in the biomass	Less energy is wasted Solvent consumption is reduced	Non uniform penetration of biomass Depends on dielectric properties of the solvent	Polyurethane foams Textile Food processing Carbon Fiber Precursor Manufacturing [13], [70], [71]
10	Steam explosion	High-temperature steam penetrates biomass structure Partial hydrolysis of hemicellulose and lignin-carbohydrate bonds	No chemical additives required Increases accessibility for subsequent processing Relatively simple process	Limited lignin isolation (more of a pretreatment) Incomplete lignin removal Formation of inhibitory compounds	Pulp and Paper Industry Applications Bio-Oil Production Enhancement. Biorefinery Feedstock Preparation Composite Materials Manufacturing

		Rapid pressure release causes physical disruption	Short residence times (seconds to minutes)	Requires high-pressure equipment Energy-intensive process	Enzymatic Treatment Enhancement [77], [78]

3.3 Advanced Lignin Extraction Technologies

3.3.1 Non - Thermal plasma treatment

Plasma technology has recently gained attention as an innovative and environmentally friendly approach for the pretreatment of lignocellulosic biomass within biorefinery frameworks [79]. Based on fundamental physical principles, plasma represents the fourth state of matter, achieved when a gas is energized beyond its typical state, following the transitions from solid to liquid, and liquid to gas. Plasma systems are generally categorized into thermal (hot) and non-thermal (cold) plasmas, distinguished by the thermodynamic equilibrium among constituent particles. In thermal plasma, all species exist at similar temperatures, whereas non-thermal plasma (NTP) features a significant thermal disparity between electrons and heavier particles, with electrons attaining much higher energies [13], [80]. Owing to its relatively low gas temperature, NTP is often referred to as cold plasma, making it suitable for treating heat-sensitive materials under ambient conditions.

The unique physicochemical characteristics of plasma—particularly its high-energy electrons—enable the effective cleavage of carbon–carbon (C–C) and carbon–hydrogen (C–H) bonds in organic substrates, which can enhance the depolymerization of lignocellulosic structures and alter pyrolysis product composition, including compounds such as guaiacol [13]. Application of NTP in biomass pretreatment facilitates the selective removal of lignin, leading to the production of holocellulose, a component rich in cellulose and hemicellulose that can be further converted into value-added products. From a sustainability perspective, NTP offers multiple advantages, including operation under mild temperatures and atmospheric pressure, absence of harsh chemical reagents, and minimal formation of fermentation inhibitors or chemical waste [81], [82]. These attributes contribute to shorter processing times and align well with the principles of green chemistry and environmentally responsible manufacturing [83].

3.3.2 Subcritical and Supercritical Fluids

Subcritical and supercritical fluids exhibit tunable physicochemical properties—such as low viscosity, high diffusivity, and variable solvating power—that make them highly effective for processing lignocellulosic biomass, particularly in lignin extraction and depolymerization [13], [84]. A supercritical state is achieved when both temperature and pressure exceed a fluid's critical point, combining liquid-like solvency with gas-like mass transfer properties (Table 3). In contrast, subcritical conditions involve only one of these parameters [21], [22]. Water and CO_2 are the most commonly used solvents due to their low toxicity, availability, and favorable critical properties.

Supercritical CO_2 (SC-CO_2), in particular, has gained prominence due to its mild critical conditions (31.1°C, 73.8 bar), non-flammability, low polarity, and ease of recovery via depressurization—making it environmentally and operationally advantageous [2], [21], [22], [91], [92]. The integration of co-solvents further enhances lignin solubility during SC-CO_2 extraction, improving process efficiency and selectivity [89], [90]. Since the 1990s, supercritical fluid technologies have been employed for lignin valorization using various solvents like methanol, ethanol, water, and CO_2, with growing success in minimizing polymer condensation and reducing processing time [85], [88]. Despite the energy demands of high-pressure systems, their ability to yield cleaner and more tailored lignin fractions support their potential for sustainable biorefinery applications [84], [85], [86], [87].

Table 3: Critical properties of common fluids used in biomass processing [13], [21], [22]

Fluid	Critical Temperature (°C)	Critical Pressure (MPa)	Critical Density (g/cm³)
Water	374.0	22.1	0.322
Carbon dioxide	31.1	7.38	0.468
Methanol	240.0	8.09	0.272
Ethanol	241.0	6.14	0.276
Acetone	235.0	4.70	0.278
Phenol	421.0	6.13	0.346

The tunable nature of subcritical and supercritical fluids—achieved by varying temperature and pressure—enables selective control over extraction and reaction processes. In particular, water demonstrates significant changes in its physicochemical properties under these conditions. As it approaches the supercritical state, its dielectric constant drops from around 80 to below 10, shifting its behavior toward that of a non-polar solvent capable of dissolving hydrophobic compounds such as lignin [87]. Moreover, within the subcritical region, the ionic product of water increases substantially—up to approximately 10 at 250 °C and 25 MPa—enhancing its ability to promote acid- and base-catalyzed reactions without the need for added catalysts [22], [91]. These characteristics underscore the versatility of water as a reaction medium in biomass conversion and lignin valorization.

1. **Sub and Supercritical Water Process**

Subcritical and supercritical water (as outlined in Table 4) have gained recognition as effective solvents for lignin extraction,

primarily due to their capacity to cleave ether linkages within lignin and the broader lignocellulosic network—without the need for added catalysts [93]. In the subcritical range (100–374 °C, <22.1 MPa), water demonstrates an elevated ionic product, reduced dielectric constant, and improved mass transfer properties compared to its ambient state, thereby enhancing both hydrolysis efficiency and lignin solubility. When water reaches supercritical conditions (>374 °C, 22.1 MPa), these solvent properties become even more pronounced, although the risk of excessive lignin degradation increases under such extreme conditions [21], [91]. These features position water as a versatile and sustainable medium for catalytic-free biomass processing.

Table 4: properties of water under different thermodynamic conditions [7], [13], [88]. [97]

Water properties/ Units	Ambient water	Subcritical water	Supercritical water
Dielectric constant - $\mathscr{E}$	~ 80	~ 20 – 30	~ 2 – 5
Ionic product (Kw)	10^{-14}	10^{-11}	10^{-23}
Density (Kg/m^3)	1000	600 - 800	200 - 500
Viscosity (mPa.s)	0.89	0.1 – 0.2	0.03 – 0.05
Behaviour	Polar solvent	Moderate Polar solvent	Non-Polar solvent

Lignin depolymerization in supercritical water has been shown to occur remarkably quickly, with complete conversion achieved in as little as 5 seconds of residence time, primarily due to the rapid cleavage of ether linkages—particularly the prevalent β-O-4 bonds [94]. In subcritical water conditions, the impact of temperature on lignin extraction has also been investigated. For instance, [92] reported that lignin recovery from Japanese rice straw increased between 170 °C and 200 °C, attributed to enhanced hydrolysis of lignin–carbohydrate complexes. However, a decline in recovery was observed at 230 °C, likely due to excessive breakdown of lignin into low molecular weight phenolics [22].

Flow rate plays a critical role as well. Higher flow rates, such as 4.67 mL/min, resulted in greater lignin yields compared to lower rates (1.42 mL/min), suggesting that rapid removal of solubilized lignin minimizes secondary reactions and prevents undesired repolymerization [21], [91]. These findings underscore the significance of fine-tuning operating parameters—such as temperature and flow rate—for maximizing efficiency and selectivity in lignin extraction using sub- and supercritical water systems.

2. Supercritical CO_2, Process

In its supercritical state, CO_2 exhibits both liquid-like solvent capacity and gas-like diffusivity, enabling effective extraction of non-polar compounds. Its non-toxicity, non-flammability, and ease of removal via depressurization make it attractive for industrial applications, including food, pharmaceutical, and bioresource processing [7], [93], [94], [96]. Although SC-CO_2 alone is limited in lignin solubility due to lignin's polar and heterogeneous nature, co-solvents such as ethanol can improve extraction efficiency by enhancing hydrogen bonding and solvent polarity [96], [97].

For instance, [90] reported up to 85% lignin removal using SC-CO_2, with improved mass transfer and simplified solvent recovery compared to traditional methods. In the SC-CO_2 ethanol solution (SCES) approach, [98] achieved 75.41% lignin extraction at 206.63 °C, 10.29 MPa, and 58% ethanol, with the extracted lignin exhibiting strong antioxidant activity. Further studies demonstrated the effectiveness of CO_2-expanded liquids and supercritical water oxidation for lignin depolymerization and fractionation, yielding structurally diverse lignin monomers and oligomers [88], [97]. These insights reinforce SC-CO_2's potential as a green extraction platform for generating high-value lignin-based bio-products in biorefinery applications.

3. Other Sub- and Supercritical Fluids

A variety of alternative solvents have been explored for lignin extraction under subcritical and supercritical conditions, offering promising routes for efficient biomass valorization. Alcohols such as methanol and ethanol, when employed at elevated temperatures and pressures, demonstrate strong solvating power for lignin. In addition to dissolving lignin, these alcohols act as hydrogen donors, stabilizing reactive intermediates and reducing the likelihood of repolymerization during extraction. Furthermore, subcritical mixtures of organic acids—particularly acetic and formic acids—with water have exhibited selectivity in lignin solubilization. Notably, formic acid serves a dual function: it acts as both a solvent and a hydrogen donor, undergoing thermal decomposition to yield hydrogen and carbon dioxide, which promotes ether bond cleavage and suppresses condensation reactions [99].

Economic and environmental considerations have also been addressed in recent studies. For instance, [100] reported that solvent recovery—particularly for carbon dioxide and ethanol–water mixtures—can be achieved with relative ease in supercritical pretreatment systems. However, the energy-intensive nature of supercritical processes, primarily due to the high-pressure requirements and CO_2 liquefaction demands, contributes to elevated utility costs. Despite these challenges, supercritical pretreatment has been recognized for its favorable environmental performance and process efficiency. Ongoing research is needed to reduce residual energy consumption and enhance cost-effectiveness in order to facilitate broader industrial adoption.

3.4 Factors Affecting Lignin Extraction Efficiency and Quality

Several process parameters significantly influence both the efficiency of lignin extraction and the quality of the extracted lignin using the sub and supercritical fluids.

3.4.1 Temperature and Pressure

Temperature plays a pivotal role in lignin extraction using sub- and supercritical fluids, primarily by enhancing bond cleavage, which facilitates lignin dissolution and depolymerization. Moderate increases in temperature typically improve extraction yields, as demonstrated in microwave-assisted acetosolv extraction where yields rose from 43.07% to 76.98% between 90–110 °C. Similar trends have been observed in organosolv processes operating between 80–180 °C. Optimal operating ranges vary by solvent system: 180–260 °C for subcritical water, 374–400 °C for supercritical water (under short residence times), and 100–200 °C for subcritical CO_2 with co-solvents [93], [94], [95]. However, elevated temperatures may also lead to lignin degradation or unwanted condensation, affecting purity. In fact, there is often a trade-off between yield and purity, as higher temperatures can increase the co-extraction of other biomass components.

Pressure, on the other hand, influences the solvent density and thereby its solvating power. While higher pressures can enhance extraction efficiency, they may also promote side reactions. For instance, [101] observed reduced residual lignin in yellow poplar when extracted with supercritical ammonia-water mixtures at elevated temperatures. Kinetic studies further illustrate temperature-dependent behavior. In subcritical phenol, [102] identified two distinct liquefaction regimes: moderate temperatures (160–290 °C) favored ether bond cleavage but did not achieve full liquefaction, whereas nearly complete depolymerization occurred at 350 °C after 30 minutes. This reflects the higher thermal stability of C–C linkages compared to ether bonds [102], [103].

Nonetheless, findings on temperature effects remain inconsistent. For example, [104] reported improved liquefaction with increasing temperature, while [92] found reduced lignin recovery at 230 °C compared to 200 °C—attributed to excessive depolymerization. These variations underscore the critical role of solvent choice and process conditions in optimizing lignin extraction outcomes [13], [93].

3.4.2 Reaction Time

Reaction time is a critical factor influencing both the yield and structural integrity of lignin during biomass processing with sub- and supercritical fluids. While short durations may enhance product quality, excessively prolonged reaction times can promote lignin degradation. For example, [94] reported complete depolymerization of lignin within just 5 seconds under supercritical water conditions, emphasizing the rapid kinetics possible at such elevated states. Similarly, [92] examined lignin recovery from Japanese rice straw in a subcritical water system and observed maximum removal (85%) at a flow rate of 4.67 mL/min at 170–200 °C. This highlights the importance of efficient flow conditions in continuous systems, where rapid removal of solubilized lignin minimizes secondary reactions such as repolymerization or precipitation. Overall, optimizing reaction time and flow rate is essential to maximizing lignin yield while preserving quality.

3.4.3 Solvent Systems and Co-solvents

The selection of solvent plays a pivotal role in determining both the efficiency and selectivity of lignin extraction from biomass under subcritical and supercritical conditions [101]. Solvent type influences lignin solubility and reactivity, ultimately affecting yield and structural characteristics of the recovered product. Common solvents include water, alcohols (e.g., methanol, ethanol), acetone, and their combinations—chosen based on the feedstock and desired lignin properties. In a comparative study, [105] observed that supercritical ammonia alone resulted in poor lignin extraction. However, the introduction of water as a co-solvent (20% water in ammonia) significantly enhanced extraction efficiency, reducing lignin content from 20.6% to 14.6%. This improvement was attributed to water's ability to enhance solubilization and modify biomass porosity, facilitating more effective lignin release.

3.4.4 pH and Catalyst Effects

Although sub- and supercritical water can facilitate lignin extraction without the need for added catalysts, the solvent's pH plays a crucial role in dictating reaction pathways and extraction efficiency [13]. Alkaline conditions generally promote lignin solubilization and depolymerization, resulting in higher yields of soluble fragments, whereas acidic environments tend to favor lignin condensation and char formation. The optimal pH for extraction varies depending on the biomass type, extraction system, and desired lignin characteristics [102], [103]. Additionally, the use of catalysts—such as alkali or metal-supported variants—can further enhance lignin depolymerization, increase bio-oil yield, and tailor the product profile, thereby improving the efficiency and selectivity of sub- and supercritical fluid processes [101].

3.4.5 Biomass Type and Particle Size

The nature of lignocellulosic biomass plays a crucial role in determining lignin structure, which directly influences its extractability during sub- and supercritical fluid processing. Biomass type and process conditions markedly affect both lignin yield and quality [18], [91]. For instance, hardwoods—characterized by higher syringyl content—tend to yield lignin more readily than softwoods, which are richer in guaiacyl units and more prone to condensation due to greater steric hindrance. Solvent systems such as sub- or supercritical water and organic solvents exhibit varying efficiencies depending on the biomass composition and operational parameters. Particle size also significantly impacts extraction; smaller particles enhance mass transfer due to increased surface area, thus improving lignin recovery [89], [90]. However, overly fine particles may lead to channeling effects and undesired changes in lignin structure, including reduced molecular weight and modified chemical properties [104], [105], [106].

Table 5: Lignin yield and purity for different technologies [7], [13], [105]

Technology	Lignin Yield	Purity	Structure Preservation	Industrial application maturity	Environmental concerns
Kraft	Low	Low	Poor	High	Moderate
Sulfite	Moderate	Low	Poor	High	Moderate
Soda	Low	Moderate	Fair	Moderate	Low
Organosolv	High	High	Excellent	Low	Low
Steam Explosion	Very Low	Low	Poor	Moderate	Low
Dilute Acid	Low	Low	Poor	High	Moderate
Alkaline	Very Low	Low	Very Poor	Low	Very Low
Ionic liquids	High	High	Fair	Moderate	Low
Dilute eutectic solvents	High	High	Fair	Moderate	Low
Microwave-assisted extraction	Good	High	Excellent	Low	Low
Non-Thermal Plasma Treatment	Good	High	Moderate to High	Low to moderate	Low
SC-CO_2	Moderate to high	High	Excellent	Low to moderate	Low

Table 6: Properties of lignin extracted using various methods [13], [105], [106].

Extraction Technology	Mw (g/mol)	Polydispersity Index (PDI)	T (°C)	Impurities	Structural preservation
Kraft	2,000-5,000	25-35	140-150	Sulfur, ash	Low
Organosolv	1,000-3.000	1.5-2.5	90-110	Residual solvents	Medium
Steam explosion	2500–5000	2.0-3.0	120-140	Carbohydrates	Medium-low
Subcritical water	1000 - 2500	1.8-2.5	100-130	Minimal	Medium high
Supercritical water	800 - 1500	1.5-2.0	90-110	Minimal	Medium
Subcritical CO_2 + co-solvent	1200 - 2800	1.7-2.3	100-120	Co-solvent residues	High

6. CONCLUSIONS AND FUTURE RESEARCH

This review highlights the comparative advantages of conventional and emerging technologies for lignin extraction, with particular focus on sub- and supercritical fluid systems. Eco-friendly techniques such as Deep Eutectic Solvents, Microwave-Assisted Extraction, and Ionic Liquids have demonstrated enhanced extraction rates and superior preservation of lignin's native structure compared to traditional methods. Likewise, Non-Thermal Plasma and sub-/supercritical fluid technologies have shown potential for producing high-purity, minimally degraded lignin, offering opportunities to tailor lignin characteristics—such as molecular weight and functional groups—for specific industrial applications.

Sub- and supercritical fluid extraction presents a compelling alternative, overcoming key limitations of conventional processes through (1) adjustable solvent properties enabling selective solubilization, (2) minimal reliance on hazardous chemicals or catalysts, (3) improved structural integrity of recovered lignin, and (4) the ability to yield high-purity products. The performance of these processes is highly sensitive to operating conditions—namely, temperature, pressure, residence time, and solvent type—which must be optimized based on biomass composition and desired product specifications. Future research should aim to:

- Uncover the fundamental reaction mechanisms under sub- and supercritical conditions
- Develop preventive measures against lignin repolymerization
- Integrate these technologies within holistic biorefinery frameworks
- Evaluate scale-up potential and conduct comprehensive techno-economic assessments

Successfully advancing these technologies could accelerate the commercialization of lignin-derived biomaterials, contributing to a sustainable and circular bioeconomy.

REFERENCES

1. Hassan, N.S.; Badri, K.H. 2014. Lignin recovery from alkaline hydrolysis and glycerolysis of oil palm fiber. AIP Conf. Proc., 1614, 433–438.
2. Abolore, R.S., Jaiswal, S., Jaiswal, A.K. 2024. Green and sustainable pretreatment methods for cellulose

extraction from lignocellulosic biomass and its applications: A review. Carbohydr. Polym. Technol. Appl. 7, 100396 https://doi.org/10.1016/j.carpta.2023.100396.

3. Wertz J. L. and Bedue, O. 2013. Lignocellulosic Biorefineries EPFL Press
4. Li O., Serem W. K., Dai W., Yue Y., Naik M. T., Xie S., Karki P., Liu L., Sue H. J., Liang H. & Sun F. 2018. Molecular weight and uniformity define the mechanical performance of Lignin-based Carbon Fibre. Journal of materials chemistry A. 6(42), 19954-19960.
5. Lignin Market Size, Share And Growth Analysis Report, 2030 [WWW Document], n.d.URL https://www.grandviewresearch.com/industry-analysis/lignin-market (accessed 5.20.24).
6. Covinich, L. G., and Area, M. C. 2024. Trends and limitations of lignin as a starting material. BioResources 19(1), 6-9.
7. Mohammad M. A, Carola E. C, Antonio G. Zahra R. 2024. Efficient and environmentally friendly techniques for extracting lignin from lignocellulose biomass and subsequent uses: A review. Cleaner Materials 13, 100253
8. Tardy, B.L., Lizundia, E., Guizani, C., Hakkarainen, M., Sipponen, M.H., 2023. Prospects for the integration of lignin materials into the circular economy. Mater. Today 65, 122–132. https://doi.org/10.1016/j.mattod.2023.04.001.
9. Ahmad, U.M., Ji, N., Li, H., Wu, Q., Song, C., Liu, Q., Ma, D., Lu, X., 2021. Can lignin be transformed into agrochemicals? Recent advances in the agricultural applications of lignin. Ind. Crop. Prod. 170, 113646 https://doi.org/10.1016/j.indcrop.2021.113646.
10. Balk, M., Sofia, P., Neffe, A.T., Tirelli, N., 2023. Lignin, the lignification process, and advanced, lignin-based materials. Int. J. Mol. Sci. 24, 11668. https://doi.org/ 10.3390/ijms241411668.
11. Baruah, J.; Nath, B.K.; Sharma, R.; Kumar, S.; Deka, R.C.; Baruah, D.C.; Kalita, E. 2018. Recent Trends in the Pretreatment of Lignocellulosic Biomass for Value-Added Products. Front. Energy Res. 2018, 6, 141.
12. Lobato-Peralta, D.R.; Duque-Brito, E.; Villafán-Vidales, H.I.; Longoria, A.; Sebastian, P.J.; Cuentas-Gallegos, A.K.; Arancibia-Bulnes, C.A.; Okoye, P.U. 2021. A review on trends in lignin extraction and valorization of lignocellulosic biomass for energy applications. J. Clean. Prod. 2021, 293, 126123.
13. Saadan, R.; Hachimi Alaoui, C.; Ihammi, A.; Chigr, M.; Fatimi, A. 2024. A Brief Overview of Lignin Extraction and Isolation Processes: From Lignocellulosic Biomass to Added-Value Biomaterials. Environ. Earth Sci. Proc. 2024, 31, 3.https://doi.org/10.3390/eesp2024031003.
14. Zadeh, E.M., O'Keefe, S.F., Kim, Y.-T., 2018. Utilization of lignin in biopolymeric packaging films. ACS Omega 3, 7388–7398. https://doi.org/10.1021/acsomega.7b01341.
15. Díez, D., Uruena, A., Pinero, R., Barrio, A., Tamminen, T., 2020. Determination of hemicellulose, cellulose, and lignin content in different types of biomasses by thermogravimetric analysis and pseudocomponent kinetic model (TGA-PKMMethod). Processes 8, 1048. https://doi.org/10.3390/pr8091048.
16. Blasi, A., Verardi, A., Lopresto, C.G., Siciliano, S., Sangiorgio, P., 2023. Lignocellulosic agricultural waste valorization to obtain valuable products: An overview. Recycling 8, 61. https://doi.org/10.3390/recycling8040061.
17. Gan, M.J., Niu, Y.Q., Qu, X.J., Zhou, C.H., 2022. Lignin to value-added chemicals and advanced materials: extraction, degradation, and functionalization. Green Chem. 24, 7705–7750. https://doi.org/10.1039/D2GC00092J.
18. Abdullah, T. Ilyasoglu, G. Memic, A. Designing Lignin-Based Biomaterials as Carriers of Bioactive Molecules. Pharmaceutics 2023, 15, 1114.
19. Sun, B.; Liu, Y.; Li, J.; Liu, C.; Liu, Z.; Zhao, X.; Liu, B.; Hu, W.; Liu, X. Lignin-Based Carbon Fiber/Epoxy Resin Biocomposites with Excellent Fire Resistance and Mechanical Properties. Macromol. Rapid Commun. 2024, 45, 2400414.
20. Ranaldi R., Jashebski R., Clough M. T. Ralph J. Kemena M. Bruima P.C., Weckhuysen B. 2016. Paving the way for lignin valorisation: Recent advances in Bioengineering, biorefining and catalysis. Angewandte Chem Int. Edition 55(29)8164-8215.
21. Khalid, K.A., Ahmad, A.A., Yong, T.-L.-K., 2017. Lignin Extraction from Lignocellulosic Biomass Using Sub- and Supercritical Fluid Technology as Precursor for Carbon Fiber Production. 日本 エネルギー学会誌 96, 255–260. https://doi.org/10.3775/jie.96.255.
22. Jiang, Y., Feng, Y., Lei, B., Zhong, H., 2020. Impact mechanisms of supercritical CO2–ethanol–water on extraction behavior and chemical structure of eucalyptus lignin. Int. J. Biol. Macromol. 161, 1506–1515. https://doi.org/10.1016/j.ijbiomac.2020.07.318.
23. Chen, Y., Yan, Z., Liang, L., Ran, M., Wu, T., Wang, B., Zou, X., Zhao, M., Fang, G., Shen, K., 2020b. Comparative evaluation of organic acid pretreatment of eucalyptus for kraft dissolving pulp production. Materials 13,361. https://doi.org/10.3390/
24. Jardim, J.M., Hart, P.W., Lucia, L., Jameel, H., 2020. Insights into the potential of hardwood kraft lignin to

be a green platform material for emergence of the biorefinery. Polymers 12, 1795. https://doi.org/10.3390/polym12081795.

25. Jardim, J.M., Hart, P.W., Lucia, L.A., Jameel, H., Chang, H., 2022. The effect of the kraft pulping process, wood species, and pH on lignin recovery from black liquor. Fibers 10, 16. https://doi.org/10.3390/fib10020016.
26. Lahtinen, M.H., Mikkila, J., Mikkonen, K.S., Kilpelainen, I., 2021. Kraft process—formation of secoisolariciresinol structures and incorporation of fatty acids in Kraft lignin. J. Agric. Food Chem. 69, 5955–5965. https://doi.org/10.1021/acs.jafc.1c00705
27. Chen, H., 2015. 3 - Lignocellulose biorefinery feedstock engineering. In: Chen, H. (Ed.), Lignocellulose Biorefinery Engineering. Woodhead Publishing, pp. 37–86. https://doi.org/10.1016/B978-0-08-100135-6.00003-X.
28. Yiamsawas, D., Watcharin, K., Pongprayoon, T., 2023. Enhanced performance of lignin recovery with a carbon dioxide acidification method. ACS Omega 8, 7438–7447. https://doi.org/10.1021/acsomega.2c06153.
29. Vasile, C., Baican, M., 2023. Lignins as promising renewable biopolymers and bioactive compounds for high-performance materials. Polymers 15, 3177.
30. Sutradhar, S., Fatehi, P., 2023. Latest development in the fabrication and use of lignin-derived humic acid. Biotechnol. Biofuels Bioprod. 16, 38. https://doi.org/10.1186/s13068-023-02278-3.
31. Vinod, A., Pulikkalparambil, H., Jagadeesh, P., Rangappa, S.M., Siengchin, S., 2023. Recent advancements in lignocellulose biomass-based carbon fiber: Synthesis, properties, and applications. Heliyon 9, e13614.
32. Ajala, E.O., Ighalo, J.O., Ajala, M.A., Adeniyi, A.G., Ayanshola, A.M., 2021. Sugarcane bagasse: a biomass sufficiently applied for improving global energy, environment and economic sustainability. Bioresources and Bioprocessing 8, 87. https://doi.org/10.1186/s40643-021-00440-z
33. Wang, S., Innocent, M.T., Wang, Q., Xiang, H., Tang, J., Zhu, M., 2020b. Kraft lignin-based piezoresistive sensors: Effect of chemical structure on the microstructure of ultrathin carbon fibers. Int. J. Biol. Macromol. 151, 730–739. https://doi.org/10.1016/j.ijbiomac.2020.02.225.
34. Shah, T.A., Khalid, S., Nafidi, H.-A., Salamatullah, A.M., Bourhia, M., 2023. Sodium hydroxide hydrothermal extraction of lignin from rice straw residue and fermentation to biomethane. Sustainability 15, 8755. https://doi.org/10.3390/su15118755.
35. Fernandez-Rodríguez, J., Erdocia, X., Ramos, F., Alriols, M., Labidi, J., 2019. Lignin Separation and Fractionation by Ultrafiltration. pp. 229–265. https://doi.org/10.1016/B978-0-12 81505/6.00007-3.
36. Brienza, F., Cannella, D., Montesdeoca, D., Cybulska, I., Debecker, P., D. 2024. A guide to lignin valorization in biorefineries: traditional, recent, and forthcoming approaches to convert raw lignocellulose into valuable materials and chemicals. RSC Sustainability. https://doi.org/10.1039/D3SU00140G.
37. John M. J., Lefatle M.C., Sithole B. 2022. Lignin fractionation and conversion to biobased functional products. Sustain. Chem. Pharm, 2022, 25, 100594.
38. Liao J. J. Lahtif N. H. A. Trache D., Brosse N., Hassein M. H. Current advancement on the isolation, characterization and application of lignin. Int. j. Biol. Macromol.2020. 162, 985-1024.
39. Ovejero-Perez, A., Rigual, V., Domínguez, J.C., Alonso, M.V., Oliet, M., Rodriguez, F., 2020. Acidic depolymerization vs ionic liquid solubilization in lignin extraction from eucalyptus wood using the protic ionic liquid 1-methylimidazolium chloride. Int. J.Biol. Macromol. 157, 461–469. https://doi.org/10.1016/j.ijbiomac.2020.04.194
40. Zhang, Y., Ni, S., Wu, R., Fu, Y., Qin, M., Willfor, S., Xu, C., 2022. Green fractionation approaches for isolation of biopolymers and the critical technical challenges. Ind. Crop. Prod. 177, 114451 https://doi.org/10.1016/j.indcrop.2021.114451.
41. Bhattacharyya, S., Matsakas, L., Rova, U., Christakopoulos, P., 2020. Melt Stable functionalized organosolv and kraft lignin thermoplastic. Processes 8, 1108. https:// doi.org/10.3390/pr8091108.
42. Beluhan, S., Mihajlovski, K., Santek, B., Ivancic Santek, M., 2023. The production of bioethanol from lignocellulosic biomass: pretreatment methods, fermentation, and downstream processing. Energies 16, 7003. https://doi.org/10.3390/en16197003.
43. Vaidya, A.A., Murton, K.D., Smith, D.A., Dedual, G., 2022. A review on organosolv pretreatment of softwood with a focus on enzymatic hydrolysis of cellulose. Biomass Conv. Bioref. 12, 5427–5442. https://doi.org/10.1007/s13399-022-02373-9.
44. Linan, L.Z.; Gonçalves, M.P.X.; Cidreira, A.C.M.; Hatami, T.; Junior, A.A.C.; Mei, L.H.I. Acid-based organosolv lignin extraction from acai berry bagasse. Bioresour. Technol. Rep. 2023, 22, 101493.
45. Bo, L., Zhang, X., Luo, Z., Saboori, T., Dehghan, M., Ghasemizadeh, M., Karimi- Maleh, H., Alagumalai, A., Mahian, O., 2022. An overview of the applications of ionic fluids and deep eutectic solvents enhanced by nanoparticles. J. Therm. Anal. Calorim. 147, 7589–7601. https://doi.org/10.1007/s10973-021-11097-3
46. Hasanov, I., Raud, M., Kikas, T., 2020. The role of ionic liquids in the lignin separation from lignocellulosic biomass. Energies 13, 4864. https://doi.org/10.3390/en13184864.

47. Hasanov, I., Shanmugam, S., Kikas, T., 2022. Extraction and isolation of lignin from ash tree (Fraxinus exselsior) with protic ionic liquids (PILs). Chemosphere 290, 133297. https://doi.org/10.1016/j.chemosphere.2021.133297.
48. Haykir, N.I., Nizan Shikh Zahari, S.M.S., Harirchi, S., Sar, T., Awasthi, M.K., Taherzadeh, M.J., 2023. Applications of ionic liquids for the biochemical transformation of lignocellulosic biomass into biofuels and biochemicals: A critical review. Biochem. Eng. J. 193, 108850 https://doi.org/10.1016/j.bej.2023.108850
49. Margarida Martins, M., Carvalheiro, F., Gírio, F., 2022. An overview of lignin pathways of valorization: from isolation to refining and conversion into value-added products. Bioref. Biomass Conv. https://doi.org/10.1007/s13399-022-02701-z.
50. Abranches, D.O., Martins, M.A.R., Silva, L.P., Schaeffer, N., Pinho, S.P., Coutinho, J.A.P., 2019. Phenolic hydrogen bond donors in the formation of non-ionic deep eutectic solvents: the quest for type V DES. Chem. Commun. 55, 10253–10256. https://doi. org/10.1039/C9CC04846D.
51. Acosta, J., Torres-Chavez, P.I., Carvajal-Millan, E., Ramirez-Wong, B., Bello-Perez, L., Montano Leyva, B., 2014. Ionic liquids and organic solvents for recovering lignin from lignocellulosic biomass. BioResources 9, 3660–3687. https://doi.org/10. 15376/biores.9.2.3660-3687.
52. Bai, Y., Zhang, X.-F., Wang, Z., Zheng, T., Yao, J., 2022. Deep eutectic solvent with bifunctional Brønsted-Lewis acids for highly efficient lignocellulose fractionation. Bioresour. Technol. 347, 126723 https://doi.org/10.1016/j.biortech.2022.126723.
53. Chen, Z., Jacoby, W.A., Wan, C., 2019b. Ternary deep eutectic solvents for effective biomass deconstruction at high solids and low enzyme loadings. Bioresour. Technol. 279, 281–286. https://doi.org/10.1016/j.biortech.2019.01.126.
54. Chen, Y., Zhang, L., Yu, J., Lu, Y., Jiang, B., Fan, Y., Wang, Z., 2019a. High-purity lignin isolated from poplar wood meal through dissolving treatment with deep eutectic solvents. R. Soc. Open Sci. 6, 181757 https://doi.org/10.1098/rsos.181757.
55. Cronin, D.J., Chen, X., Moghaddam, L., Zhang, X., 2020. Deep eutectic solvent extraction of high-purity lignin from a corn stover hydrolysate. ChemSusChem 13, 4678–4690. https://doi.org/10.1002/cssc.202001243
56. Fernandes, C., Melro, E., Magalhaes, S., Alves, L., Craveiro, R., Filipe, A., Valente, A.J.M., Martins, G., Antunes, F.E., Romano, A., Medronho, B., 2021. New deep eutectic solvent assisted extraction of highly pure lignin from maritime pine sawdust (Pinus pinaster Ait.). Int. J. Biol. Macromol. 177, 294–305. https://doi.org/10.1016/j.ijbiomac.2021.02.088.
57. Cui, P., Ye, Z., Chai, M., Yuan, J., Xiong, Y., Yang, H., Yao, L., 2023. Effective fractionation of lignocellulose components and lignin valorization by combination of deep eutectic solvent with ethanol. Front. Bioeng. Biotechnol. 10.
58. Abranches, D.O., Coutinho, J.A.P., 2022. Type V deep eutectic solvents: Design and applications. Curr. Opin. Green Sustainable Chem. 35, 100612 https://doi.org/ 10.1016/j.cogsc.2022.100612.
59. Hu, M., Yu, Y., Li, X., Wang, X., Liu, Y., 2023a. The dawn of aqueous deep eutectic solvents for lignin extraction. Green Chem. 25, 10235–10262. https://doi.org/ 10.1039/D3GC03563H.
60. Jagirani, M., Soylak, M., 2022. Deep eutectic solvents-based adsorbents in environmental analysis. TrAC Trends Anal. Chem. 157, 116762 https://doi.org/10.1016/j.trac.2022.116762.
61. Kumar, S., Sharma, S., Arumugam, S.M., Miglani, C., Elumalai, S., 2020. Biphasic separation approach in the DES biomass fractionation facilitates lignin recovery for subsequent valorization to phenolics. ACS Sustain. Chem. Eng. 8, 19140–19154. https://doi.org/10.1021/acssuschemeng.0c07747
62. Lim, W.-L., Gunny, A.A.N., Kasim, F.H., AlNashef, I.M., Arbain, D., 2019. Alkaline deep eutectic solvent: a novel green solvent for lignocellulose pulping. Cellul. 26, 4085–4098. https://doi.org/10.1007/s10570-019-02346-8.
63. Owhe, E.O., Kumar, N., Lynam, J.G., 2021. Lignin extraction from waste biomass with deep eutectic solvents: Molecular weight and heating value. Biocatal. Agric. Biotechnol. 32, 101949 https://doi.org/10.1016/j.bcab.2021.101949.
64. Park, C.-W., Han, S.-Y., Park, J.-S., Lee, E.-A., Bandi, R., Dadigala, R., Kim, J.K., Kwon, G., Kim, N., Lee, S.-H., 2022. Deep eutectic-like solvent-assisted isolation of lignin from pinus densiflora and its characteristics. BioResources 17, 5600–5611. https://doi.org/10.15376/biores.17.4.5600-5611
65. Scelsi, E., Angelini, A., Pastore, C., 2021. Deep eutectic solvents for the valorisation of lignocellulosic biomasses towards fine chemicals. Biomass 1, 29–59. https://doi.org/10.3390/biomass1010003
66. Suthar, P., Kaushal, M., Vaidya, D., Thakur, M., Chauhan, P., Angmo, D., Kashyap, S., Negi, N., 2023. Deep eutectic solvents (DES): An update on the applications in food sectors. J. Agric. Food Res. 14, 100678 https://doi.org/10.1016/j.jafr.2023.100678.
67. Ma, H., Fu, P., Zhao, J., Lin, X., Wu, W., Yu, Z., Xia, C., Wang, Q., Gao, M., Zhou, J., 2022. Pretreatment of wheat straw lignocelluloses by deep eutectic solvent for lignin extraction. Molecules 27, 7955. https://doi.org/10.3390/molecules27227955.

68. Kwon, G.-J., Bandi, R., Yang, B.-S., Park, C.-W., Han, S.-Y., Park, J.-S., Lee, E.-A., Kim, N.- H., Lee, S.-H., 2021. Choline chloride based deep eutectic solvents for the lignocellulose nanofibril production from Mongolian oak (Quercus mongolica). Cellul.28, 9169–9185. https://doi.org/10.1007/s10570-021-04102-3.
69. Kwon, G.-J., Cho, S.-W., Bandi, R., Yang, B.-S., Dadigala, R., Han, S.-Y., Ma, S.-Y., Kim, J.-K., Kim, N.-H., Lee, S.-H., 2023. Production of lignocellulose nanofibrils by conventional and microwave-assisted deep-eutectic-solvent pretreatments: mechanical, antioxidant, and UV-blocking properties. Cellul. 30, 4277–4292. https://doi.org/10.1007/s10570-023-05164-1.
70. Grillo, G., Calcio Gaudino, E., Rosa, R., Leonelli, C., Timonina, A., Grygiskis, S., Tabasso, S., Cravotto, G., 2021. Green deep eutectic solvents for microwave-assisted biomass delignification and valorisation. Molecules 26, 798. https://doi.org/10.3390/molecules26040798.
71. Mankar, A.R., Pandey, A., Pant, K.K., 2022b. Microwave-assisted extraction of lignin from coconut coir using deep eutectic solvents and its valorization to aromatics. Bioresour. Technol. 345, 126528 https://doi.org/10.1016/j.biortech.2021.126528.
72. Mao, Y., Gerrow, A., Ray, E., Perez, N.D., Edler, K., Wolf, B., Binner, E., 2023a. Lignin recovery from cocoa bean shell using microwave-assisted extraction and deep eutectic solvents. Bioresour. Technol. 372, 128680 https://doi.org/10.1016/j. biortech.2023.128680.
73. Reddy, A.V.B., Moniruzzaman, M., Madhavi, V., Jaafar, J., 2020. Chapter 8 – Recent improvements in the extraction, cleanup and quantification of bioactive flavonoids, in: Atta-ur-Rahman (Ed.), Studies in Natural Products Chemistry, Bioactive Natural Products. Elsevier, pp. 197–223. https://doi.org/10.1016/B978-0-12-817907-9.00008-8.
74. L´opez-Salazar, H., Camacho-Díaz, B., Ocampo, M., Jimenez-Aparicio, A., 2023. Microwave-assisted extraction of functional compounds from plants: A review. BioResources 18. https://doi.org/10.15376/biores.18.3.Lopez-Salazar.
75. Isci, A., Erdem, G.M., Bagder Elmaci, S., Sakiyan, O., Lamp, A., Kaltschmitt, M., 2020. Effect of microwave-assisted deep eutectic solvent pretreatment on lignocellulosic structure and bioconversion of wheat straw. Cellul. 27, 8949–8962. https://doi.org/10.1007/s10570-020-03371-8.
76. Kohli, K., Katuwal, S., Biswas, A., Sharma, B.K., 2020. Effective delignification of lignocellulosic biomass by microwave assisted deep eutectic solvents. Bioresour. Technol. 303, 122897 https://doi.org/10.1016/j.biortech.2020.122897.
77. Brodens G. Yau E. Badal K. Collier J. Ramachandran K. B., Ramakrishnan S. Chemical & Physiochemical Pretreatment of Lignocellulosic Biomass. A review. Enzym. Res. 2011, 787532.
78. Rajesh Bam J., Karitha S. Yukesh Kamah R, Poornma Devi T., Gunesekaron M., Kim S. H. Kumar G. A review on biopolymer production via lignin valorization. Bioresourc. Techno. 290-121790
79. Meoli, C.M., Iervolino, G., Procentese, A., 2023. Non-thermal plasma as a biomass pretreatment in biorefining processes. Processes 11, 536. https://doi.org/10.3390/pr11020536.
80. Merche, D., Vandencasteele, N., Reniers, F., 2012. Atmospheric plasmas for thin film deposition: A critical review. Thin Solid Films 520, 4219–4236. https://doi.org/10.1016/j.tsf.2012.01.026.
81. Pereira, G.N., Cesca, K., Cubas, A.L.V., Bianchet, R.T., Junior, S.E.B., Zanella, E., Stambuk, B.U., Poletto, P., de Oliveira, D., 2021. Non-thermal plasma as an innovative pretreatment technology in delignification of brewery by-product. Innov. Food Sci. Emerg. Technol. 74, 102827 https://doi.org/10.1016/j.ifset.2021.102827.
82. Pereira, G.N., Cesca, K., Pereira, M.A.F., Monteiro Rudke, C.R., Borges, O.M.A., Cubas, A. L.V., Zanella, E., Stambuk, B.U., Poletto, P., de Oliveira, D., 2023. Non-thermal plasma as an efficient pretreatment to lignocellulosic raw materials. J. Food Process Eng 46, e14233. https://doi.org/10.1111/jfpe.14233
83. Shao, S., Ye, Z., Sun, J., Liu, C., Yan, J., Liu, T., Li, X., Zhang, H., Xiao, R., 2022. A review on the application of non-thermal plasma (NTP) in the conversion of biomass: Catalyst preparation, thermal utilization and catalyst regeneration. Fuel 330, 125420. https://doi.org/10.1016/j.fuel.2022.125420.
84. Gosselink, R., Teunissen, W., Dam, J., de Jong, E., Gellerstedt, G., Scott, E., Sanders, J., 2011. Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals. Bioresour. Technol. 106, 173–177. https://doi.org/10.1016/j.biortech.2011.11.121.
85. Roy, R., Rahman, M.S., Amit, T.A., Jadhav, B., 2022. Recent advances in lignin depolymerization techniques: A comparative overview of traditional and greener approaches. Biomass 2, 130–154. https://doi.org/10.3390/biomass2030009.
86. da Silva, R.P.F.F., Rocha-Santos, T.A.P., Duarte, A.C., 2016. Supercritical fluid extraction of bioactive compounds. TrAC Trends Anal. Chem. 76, 40–51. https://doi.org/ 10.1016/j.trac.2015.11.013.
87. Escobar, E.L.N., da Silva, T.A., Pirich, C.L., Corazza, M.L., Pereira Ramos, L., 2020. Supercritical fluids: A promising technique for biomass pretreatment and fractionation. Front. Bioeng. Biotechnol. 8.

88. Nardella, F., Prothmann, J., Sandahl, M., Spegel, P., Ribechini, E., Turner, C., 2023. Native lignin extraction from soft- and hardwood by green and benign sub/supercritical fluid extraction methodologies. RSC Adv. 13, 21945–21953. https://doi.org/10.1039/D3RA01873C.
89. Abbas, K. A., Mohamed, A., Abdulamir, A. S., & Abas, H. A. (2008). A review on supercritical fluid extraction as new analytical method. American Journal of Biochemistry and Biotechnology, 4(4), 345-353. https://doi.org/10.3844/ajbbsp.2008.345.353
90. Neata, G., Campeanu, G., Popescu, M.I., Popa, O., Babeanu, N., Basaraba, A., Popescu, D. 2015. Lignin extraction from corn biomass using supercritical extraction. Romanian Biotechnol. Lett. 20, 10406–10412.
91. Wahyudiono, Sasaki, M., & Goto, M. (2013). Decomposition of lignin alkaline and chemicals recovery in sub- and supercritical water. Procedia Earth and Planetary Science, 2(1), 1-6.
92. Machmudah, S., Diono, W., Kanda, H., Sasaki, M., Goto, M., 2015. Hot compressed water extraction of lignin by using a flow-through reactor. Eng. J. 19, 25–44. https://doi.org/10.4186/ej.2015.19.4.25
93. Toor, S. S., Rosendahl, L., & Rudolf, A. (2011). Hydrothermal liquefaction of biomass: A review of subcritical water technologies. Energy, 36(5), 2328-2342. https://doi.org/10.1016/j.energy.2011.03.013
94. Yong, T.-L.-K., Matsumura, Y., 2012. Reaction kinetics of the lignin conversion in supercritical water. Ind. Eng. Chem. Res. 51, 11975–11988.
95. Yang, S.M., Shaffer, M.S.P., Brandt-Talbot, A., 2023. High lignin content carbon fiber precursors wet-spun from low-cost ionic liquid water mixtures. ACS Sustain. Chem. Eng. 11, 8800–8811. https://doi.org/10.1021/acssuschemeng.3c00234.
96. Badgujar, K.C., Dange, R., Bhanage, B.M., 2021. Recent advances of use of the supercritical carbon dioxide for the biomass pre-treatment and extraction: A mini- review. J. Indian Chem. Soc. 98, 100018 https://doi.org/10.1016/j.jics.2021.100018.
97. Ho Seo, J., Jeong, H., Lee, H.W., Choi, C.S., Bae, J.H., Lee, S.M., Kim, Y.S., 2019. Characterization of solvent-fractionated lignins from woody biomass treated via supercritical water oxidation. Bioresour. Technol. 275, 368–374. https://doi.org/ 10.1016/j.biortech.2018.12.076.
98. Yang, T., Li, Z., Wei, W., Wang, X., Liu, F., Xu, X., Liu, Z., 2022. Antioxidant properties of lignin extracted from cotton stalks by ethanol solution-assisted liquid hot water before and after adding supercritical CO2. J. CO2 Util. 58, 101892 https://doi.org/ 10.1016/j.jcou.2022.101892.
99. Grbic, J., Đukic-Vukovic, A., Mladenovic, D., Lazovic, S., Mojovic, L., 2022. Effect of non-thermal plasma on cellulose crystallinity and lignin content in corn stalks. 1 26. https://doi.org/10.5937/jpea26-36871.
100. Daza Serna, L.V., Orrego Alzate, C.E., Cardona Alzate, C.A., 2016. Supercritical fluids as a green technology for the pretreatment of lignocellulosic biomass. Bioresource Technology, Pretreatment of Biomass 199, 113–120. https://doi.org/10.1016/j.biortech.2015.09.078.
101. Mishra, G., & Saka, S. (2011). Kinetic behavior of liquefaction of Japanese beech in subcritical phenol. Bioresource Technology, 102(23), 10946-10950. https://doi.org/10.1016/j.biortech.2011.09.008
102. Bludworth, J., & Knopf, F. C. (1993). Reactive extraction of lignin from wood using supercritical ammonia-water mixtures. The Journal of Supercritical Fluids, 6(4), 249-254. https://doi.org/10.1016/0896-8446(93)90033-5
103. Wan, Z., Zhang, H., Niu, M., Guo, Y., Li, H., 2023. Recent advances in lignin-based 3D printing materials: A mini-review. Int. J. Biol. Macromol. 253, 126660 https://doi.org/10.1016/j.ijbiomac.2023.126660.
104. Sathawong S. Sridach W. Techato K. 2018. Lignin: Isolation and preparing the lignin based hydrogel. J. environ. Chem. Eng 6, 5819 – 5888.
105. Jiang B., Yao Y., Liang Z, Gao J., Chen G. Xia Q., Mi R., Jiao M., Wang X., Hu L. Lignin based direct link printed structural scaffold. Small 2020, 16, 1909212.
106. Akhramez S., Fatimi A., Okoro O., V. Hajiabbas M., Brusiatta A., Moubank A. Hafid A., Khoisili M., Simifiska-Stanny J., Brigade C. 2022. The circular economy paradigm. Modification of bagasse-derived lignin as a precursor to sustainable hydrogel production. Sustainability,14, 8791.