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Review

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A Targeted Review on Lignin and Its Depolymerization Methodologies

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Abstract: The surge in demand for renewable energy and bio-based chemicals has heightened attention on lignocellulosic biomass as an alternative to fossil-derived resources. Lignin, a major component of lignocellulosic biomass, is not used to a sufficient extent despite its potential as a renewable resource for multiple important chemicals and biofuels. This survey examines extraction, characterisation, and decomposition of lignin, highlighting recent innovations and hurdles in lignin valorisation. Various lignin isolation techniques, such as kraft lignin, soda lignin, organosolv lignin, ionic liquids, hydrolysis lignin and deep eutectic solvents, are explored, emphasizing their impact on lignin purity and structural integrity. Analytical methods including NMR, FTIR, GPC, TGA, and DSC provide critical insights into lignin's complex chemical structure and physicochemical properties. The review also investigates diverse depolymerisation strategies: acid-catalysed, base-catalysed, metal-catalysed, hydrogenolysis, electrocatalytic oxidative and reductive reaction pathways and microwave-assisted processes focusing on their efficiency, selectivity, and applicability for industrial-scale to convert lignin into value-added products. Despite technological advancements, problems such as lignin's structural heterogeneity, high energy requirements for processing, low yields, and catalyst costs impede widespread commercialisation. Future research should address cost-effective, recyclable catalysts, process integration within biorefineries, and optimisation strategies to enhance economic feasibility. Advancing lignin valorisation technologies is vital for achieving a circular bioeconomy and reducing dependence on fossil-based resources.

Keywords: lignocellulosic biomass; lignin; characterisation techniques; lignin depolymerisation; value-added products

1. Introduction

The reliance on non-renewable resources for liquid fuels and chemical production has resulted in significant greenhouse gas emissions, necessitating a shift towards sustainable practices to address environmental concerns and meet increasing energy needs [1]. The global demand for energy is growing swiftly and fossil fuels like coal and oil are becoming depleted at an accelerating rate, so the focus has definitively shifted toward cleaner, more sustainable energy sources [2]. The biorefinery industry presents a promising pathway for transitioning to a sustainable and carbon-neutral energy future by utilising inedible biomass to produce a variety of valuable products [3,4]. Lignocellulosic biomass has gained significant research attention because it is a truly important sustainable resource; it provides the possibility of acting as a renewable carbon source to address many ecological concerns, in addition to fulfilling the total demand for alternatives to fossil-based materials [5,6]. Lignocellulosic biomass is derived from diverse sources such as wood residues (forestry wastes), by-products from industrial processes (industry wastes), plant materials from coffee, rice, corn (agricultural wastes), and waste or garbage (urban areas),

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and can be used as an alternative substrate for value-added chemicals production [7]. This makes it a promising candidate for various applications, including synthesis of bio-based chemicals [8]. However, a lot of lignocellulosic waste is still not being fully utilised worldwide, with its fate being either thrown away, burnt for energy, or low value applications [9]. Therefore, recent research has shifted towards developing valuable bioproducts from lignocellulosic biomass, offering potential benefits for sustainable chemicals and material production as well as environmental protection [10].

1.1. What is Lignocellulosic Biomass

Lignocellulosic biomass presents a compelling option as a renewable resource for value-added chemicals due to its cost-effectiveness, abundant and sustainable nature, and widespread availability [8,11,12]. Lignocellulosic biomass feedstocks encompass a wide array of sources for bioenergy production, including agricultural and timber industry residues, dedicated energy crops, and both food and non-food plants [13,14]. Among these, non-food perennial lignocellulosic plants such as miscanthus, reed canary grass, short-rotation willow, and eucalyptus have gained attention as promising alternatives [15–18]. Traditional lignocellulosic feedstocks, primarily consisting of various energy crops, underscore the extensive range of biomass sources available for bioenergy production, with oil-bearing plants like jatropha and camelina also contributing to this diverse portfolio [19,20]. Byproducts of agriculture, such as corn stover and stalks, rice and wheat straw and sugarcane bagasse, are a variety of materials obtained from farming operations that have the potential to be reused and applied in a number of ways, supporting resource management and sustainable agricultural practices [10,21]. These structures display diverse relative compositions, adding to the complexity and uniqueness of each biomass type [22].

1.2. Biomass Resources and Their Proportions

Lignocellulosic biomass is composed of three main fractions: cellulose, hemicellulose, and lignin [23]. The range of these lignocellulosic biomass composition can vary drastically with the various feedstocks. The majority of lignocellulosic feedstocks, which come from grasses, agricultural waste, hardwood and softwood stems, etc., have a variety of uses [22,24]. These feedstocks do differ in terms of composition for each feedstock, such as cellulose (50%), hemicellulose (20–40%) in herbaceous biomass, in woods it is (10–30%) and lignin (in herbaceous biomass it is 10–40%, in woods it is 20–40%) [25]. These cellulose, hemicellulose and lignin ratios vary within a single plant due to age, conditions and harvesting season [9]. These components exhibit distinct chemical structures and physical properties, influencing their reactivity and suitability for various applications [26]. Economic viability of lignocellulosic biomass processing would be significantly improved by the efficient use of all three elements [24]. Table 1 depicts a summary of the compositions of a range of lignocellulosic feedstocks.

Table 1. Summary of Lignocellulosic Feedstocks and their Composition

Biomass Feedstocks	Carbohydrate Composition (% Dry Weight)			References
	Lignin	Hemicellulose	Cellulose	
Bamboo	23.0	18.0–20.0	49.0–50.0	[24]
Barley Straw	6.3–9.8	24.0–33.0	36.0–43.0	[22]
Coffee Pulp	15.6–19.1	44.2–47.5	33.7–36.9	[24]
Corn Cobs	6.1–15.9	31.9–36.0	33.7–41.2	[22]
Corn Stover	19.0	26.0	38.0	[24]
Eucalyptus	29.0	11.0–18.0	45.0–51.0	[22]
Grasses	10.0–30.0	25.0–50.0	25.0–40.0	[22]
Hardwood stems	18.0–25.0	24.0–40.0	40.0–55.0	[24]
Jute fibres	21.0–26.0	18.0–21.0	45.0–53.0	[24]
Leaves	0	80.0–85.0	15.0–20.0	[27]
Oak	24.1	35.9	40.4	[22]
Pine	23.0–29.0	13.0–25.0	42.0–49.0	[22]
Poplar wood	10.0–21.0	25.0–28.0	45.0–51.0	[24]
Softwood stem	25.0–35.0	25.0–35.0	45.0–50.0	[24]
Spruce	27.9	22.9	45.5	[22]
Sugarcane tops	14.0	32.0	35.0	[24]

1.2.1. Cellulose

Cellulose is a polysaccharide founds as a linear chain of several hundred to many thousands of D-glucose units with β (1→4) glycosidic linkages as shown in Figure 1 [27,28]. It is a crucial structural component of the primary cell wall found in green plants [29]. This linear semi-crystalline biopolymer boasts a unique composition featuring both amorphous and crystalline structures [30]. Cellulose and its derivatives find widespread use in numerous industries, including textiles, packaging, personal care, food, and engineering, owing to their abundance,

biocompatibility, biodegradability, and potential for sustainable production [31]. Cellulose, a ubiquitous natural substance primarily found in woody materials, plants, and grasses, is intimately associated with lignin and hemicellulose, forming a fundamental characteristic of numerous plant-based materials [32].

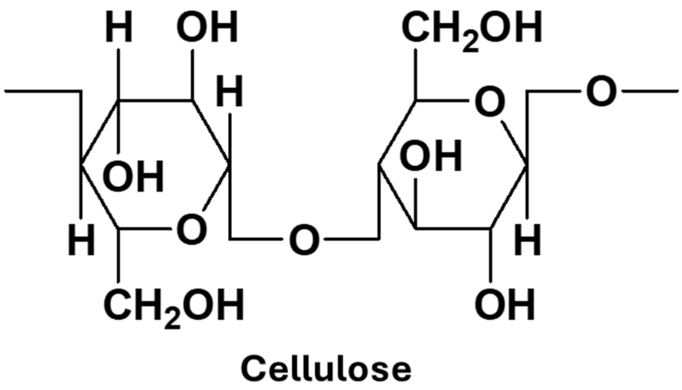


Figure 1. Structure of Cellulose

1.2.2. Hemicellulose

Hemicellulose is a complex and diverse group of polysaccharides that form the intricate structure of plant cell walls [33]. Unlike cellulose, which contains linear chains of glucose units, hemicellulose (an amorphous heterogeneous polymer) consists of branched chains made from different sugar monomers, including xylose, galactose, glucose, mannose, and arabinose [34]. These polysaccharides primarily consist of β (1 → 4) backbone linkages in their molecular structure as shown in Figure 2 [35]. Hardwoods primarily contain xylans as their main hemicellulose, whereas softwoods predominantly feature glucomannans [36]. The solubility of these polymers generally increases with temperature, but predicting this relationship for higher molecular weight polymers is challenging due to their structural properties and melting behaviour which makes it difficult to foretell how solubility will change [37]. Understanding the composition and structure of hemicellulose presents a significant intellectual challenge.

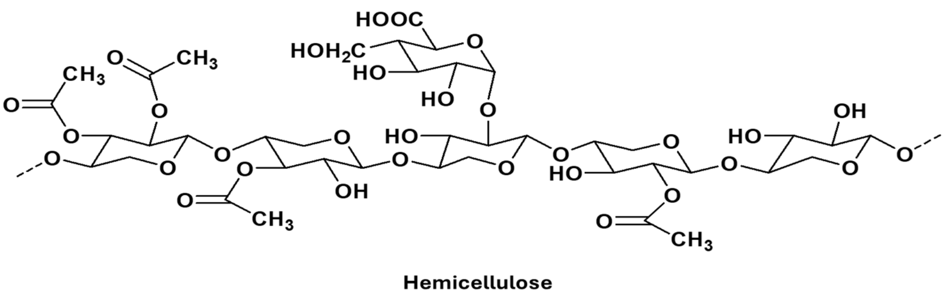


Figure 2. Structure of Hemicellulose

1.2.3. Lignin

Lignin, a highly intricate organic polymer, ranks as the second most prevalent natural polymer present in plant cells [30]. Lignin has a complex, cross-linked, highly branched, amorphous, and irregular aromatic structure (Figure 3) which distinguishes it from the other two components, cellulose and hemicellulose [30,38]. Lignin serves as a crucial structural component of the secondary cell wall of vascular plant cells, functioning in conjunction with cellulose and hemicellulose to provide essential support and rigidity [39,40]. Lignin is characterised as a complex three-dimensional amorphous polymer composed of cross-linked phenylpropane units, exhibiting intricate polyphenol structural characteristics and a high molecular weight [34,41,42]. The helical structure is a result of the polymerisation of three phenylpropanoid monomeric units: coniferyl alcohol (G), sinapyl alcohol (S), and p-coumaryl alcohol (H) shown in Figure 4 [5,40,43–46]. These phenolic monomers are interconnected by ether (-O-) and C-C linkages, forming a robust three-dimensional arrangement [40]. The individual monomeric units are distinct from each other because methoxy groups are present. The "H" moiety lacks methoxy groups, while the "G" and "S" moieties contain one and two methoxy groups, respectively [5]. The composition and properties of lignin exhibit significant variability based on factors such as plant species, age,

environment, and biomass sources [47]. In different hardwood species, lignin comprises varying quantities of lignin, G and S moieties, with S units being particularly abundant. In contrast, softwood species tend to have a higher abundance of G units, while grass lignin typically contains all three [5,48]. Furthermore, H/G/S ratios in softwoods (pinus and spruce) are 5/95/0%, in grasses are 5–35/35–80/20–55% and in hardwoods (birch, beech and aspen) are 0–8/25–50/45–75% respectively [49].

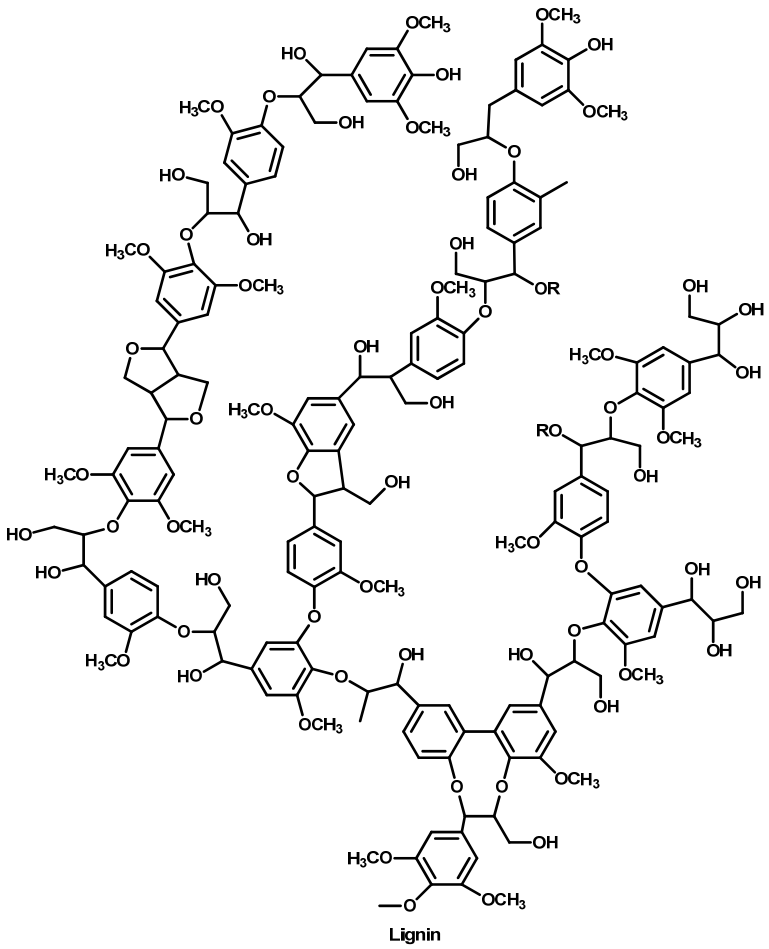


Figure 3. Structure of Lignin

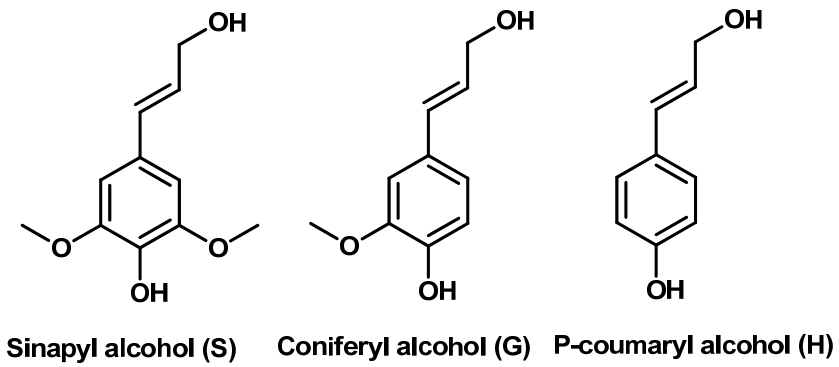


Figure 4. Common phenylpropanoid units present in lignin

The phenolic monomers, key components of lignin, include the prevalent β-O-4 (45–60%) bond, the less common 4-O-5 (2–10%) bond, the 5–5 (5–25%) bond, the β-5 (5–25%) bond, the β-1 (2–10%) bond, and the β-β (2–10%) bond [50]. The distribution of these bonds is not random but rather varies based on the botanical source [50]. Figure 5 shows the typical structure linkages present in lignin [5,40,44,46,51].

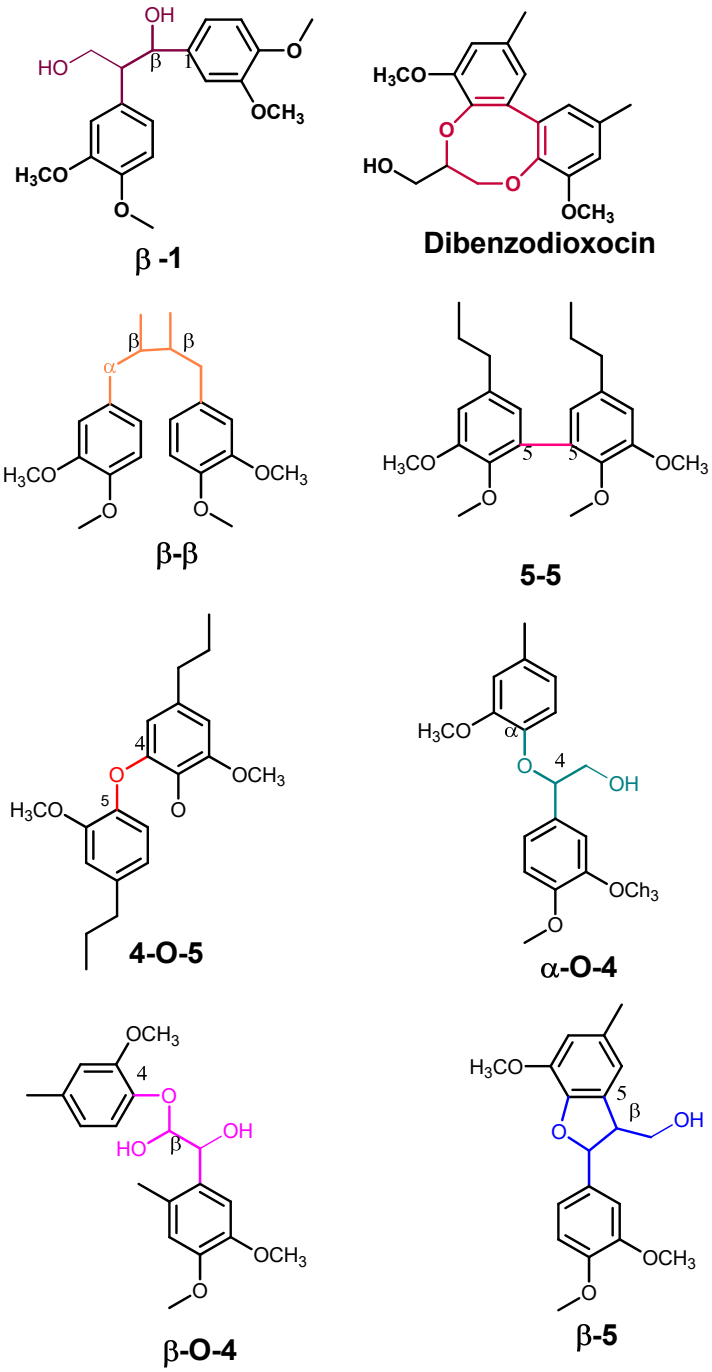


Figure 5. Typical ether and C-C linkages present in lignin

1.3. Why We Are Interested in Lignin

The proportion of lignin varies across different individual types of lignocellulosic biomass. For example, almond stem contains 20.4%, ailanthus wood includes 26.2%, spruce wood is 27.5%, barley straw is 17.13%, and stem wood is 28% [40,52–54]. There are various pretreatment methods to extract this different lignin from lignocellulosic biomass, which include physical (mechanical operations), chemical (alkali, acid), biological (microaerobic, microbiological), thermochemical and physiochemical (steam explosion, microwave irradiation) methods. Each pretreatment methods has its own advantages, limitations, and applications [55,56]. Following the deformation of the biomass structure, isolated significant components can be converted into monomeric products through acid or enzymatic processes, which can be further utilised to form desired high value-added chemicals [57]. Based on the extraction methods, isolated lignin is classified into two types: first is native lignin, and second is technical lignin. Native lignin is the unaltered, natural lignin structure within lignocellulose without any modifications [58]. It is important to emphasise that native lignin constantly forms part of lignocellulose and does not occur independently in nature [58,59]. The most researched type of lignin is modified or technical lignin,

extracted from biomass or recovered from industrial by-products. Several research studies are dedicated to transforming technical lignin into high-value chemicals and products [59]. Kraft lignin (KL) serves as the primary source of technical lignin in industries, with additional types including hydrolysis lignin (HL), soda lignin (SL), and organosolv lignin (OL) [59]. Every kind of technical lignin possesses a unique composition and molecular weight, influenced by the specific extraction methods and original sources [60]. Technical lignin extracted from industrial by-products offers a direct and efficient solution as a resource for production of various chemicals. Aliphatic and aromatic hydroxyl groups are vital components and active sites found abundantly in technical lignin [58]. This characteristic enables lignin to be utilised directly as polyols, making it possible to replace up to 30% of petroleum-based polyols in polyurethane production [60]. The quality of lignin feedstock is also crucial as it influences depolymerisation yield.

For the purpose of gaining a deeper insight into lignin in this review article, we will cover (1) numerous distinct extraction procedures that have been used to isolate various types of lignin, (2) different analytical techniques to understand the behaviour of lignin before and after depolymerisation (3) a range of catalysts employed in an attempt to break lignin it into small, valuable aromatic monomers.

The purpose of this review is to connect the upstream source of technical lignin, in particular biomass sources and isolation history and downstream depolymerisation performance. Different extraction procedures result in lignins with a wide range of molecular weights, distributions of inter-unit linkages, functional groups, and impurity levels. These properties affect catalyst compatibility, bond-cleavage mechanisms, product selectivity and ultimately the economic feasibility of lignin valorisation. Overall, this review brings together lignin isolation, structural characterisation and catalytic depolymerisation into a single feedstock-structure-conversion framework.

2. Extraction/Isolation Methods of Lignin

The extraction and isolation of lignin present significant challenges due to its complex structural diversity and robust associations with cellulose and hemicellulose. A range of extraction and isolation techniques are employed, with the method for selecting the most appropriate dependent on the intended use of lignin and the purity level. These approaches generally involve the disruption of bonds between lignin and other cell wall constituents through chemical, physical, or enzymatic processes.

2.1. Kraft Lignin

The extraction of kraft lignin occurs during the kraft pulping process, an extraction method which involves subjecting wood chips to high temperature (approximately 170 °C) and pressure in a solution known as ‘white liquor’ which primarily consists of an aqueous system of sodium sulfide and sodium hydroxide [61]. This process helps in breaking down lignin into soluble fragments and results in a liquid mixture called black liquor, which can account for up to 90% of the lignin feedstock [4]. The partial depolymerisation of lignin occurs under these conditions, leading to its substantial separation from the carbohydrate matrix through a process of solubilisation [62].

Pulp mills can either retain lignin in crude black liquor for processes like gasification or extract it through precipitation methods such as LignoBoost or Lignoforce which involves acidification and filtration to separate lignin from black liquor [63]. The LignoBoost process, a modern method for extracting kraft lignin from softwood or hardwood black liquor, offers an enhanced approach to lignin isolation from pulping waste streams that aligns more effectively with current kraft pulping technologies [64]. In kraft lignin extraction through LignoBoost process, black liquor is initially acidified with carbon dioxide to precipitate phenolic compounds, followed by filtration to obtain a high-ash lignin solid. The lignin is then re-dispersed, acidified with sulfuric acid to reduce ash content, and filtered again to produce the final product, while the liquors are recycled to regenerate process chemicals [63,65]. Another method is the LignoForce process which is a modified version of LignoBoost for extracting lignin from black liquor, featuring key differences such as a simplified process without belt filtration, reduced H_2S emissions through pre-oxidation, and altering the lignin particle formation due to initial black liquor oxidation [66]. Notably, LignoForce employs a single filter press for filtration, washing, and protonation, while still producing lignin with properties comparable to those obtained through the LignoBoost process [65,66]. Recent studies have employed a combination of solvent-mediated extractions and advanced analytical techniques (^{31}P NMR, GPC, HSQC, and ^{13}C NMR) to elucidate the molecular structure of kraft lignin, revealing two distinct fragments: first is a smaller phenol-rich fragment, as well as larger fragment of native lignin [67]. The kraft lignin isolation process yields high-purity lignin powder with minimal ash and carbohydrate content [68]. It’s heterogeneity and polydisperse nature, resulting from various process variations and feedstock variability, have been largely overlooked in structural elucidation efforts, necessitating a focus on well-defined component fractions for precise characterisation [69].

Kraft lignin has gathered significant attention for its diverse material applications, including thermoplastics, composites, and polymer blends [70–72]. Its unique polyphenolic structure imparts valuable properties such as radical scavenging, antioxidant capabilities, UV stabilization, flame retardancy, and biodegradability, making it an attractive alternative to fossil-based chemicals and polymers [73–75]. These characteristics render lignin suitable for various applications, including coatings, bioplastics, bio-composites for 3D printing, and carbon-based materials, highlighting its versatility and potential as a sustainable resource [76–79]. Various lignin types, including Kraft, Lignosulfonated, Organosolv, Pyrolytic, Steam Explosion, and Acidolysis, exhibit significant differences in properties such as inter-subunit linkages, molecular weight, and solubility, which can impact potential valorisation methods [80]. Different extraction processes, such as Sulphite, Soda, and Kraft, employ distinct chemical treatments to isolate lignin from lignocellulosic biomass, often requiring further purification steps (such as by fermentation method, chemical removal or ultrafiltration) [81]. While the Kraft process, enhanced by LignoBoost technology, is widely used, the Organosolv fractionation with ethanol-water, though not yet commercialised, produces high-purity lignin with minimal residual carbohydrate content [82]. Lignin valorisation, a key aspect of downstream processing, involves depolymerisation and chemical modification of isolated lignin streams to produce various valuable products [83]. This technology has facilitated the development of important biopolymers, including epoxies, polyesters, and polyurethanes, with conversion of lignin into biopolymers and high-value substances considered the most promising long-term sustainability approach [23]. Despite its potential for developing a sustainable, cost-effective, and green bio-based industry, commercial lignin biorefineries have not yet been established due to challenges such as lignin recovery, purification, structural complexity, and reactivity [84].

Life cycle assessment, a standardised methodology for evaluating environmental sustainability, has been increasingly applied to biorefineries, including kraft mills with lignin outtake, due to growing environmental awareness and the challenge of allocating environmental burdens in multifunctional systems. A study by Culbertson et al. revealed that recovering kraft lignin from pulp mills and using it as a phenol substitute in materials applications yielded the best environmental performance, compared to its use as fuel or in mills without lignin recovery [84,85]. While traditional sulfur cycles in lignin recovery have been identified as an environmental hotspot in unbleached pulp production, a novel sulfur recirculation cycle introduced by Manzardo et al. has shown significant potential to reduce the environmental impact of this process [86–88]. The study demonstrates that utilising kraft lignin as a substitute for chemicals like carbon black, phenol, and bisphenol A significantly enhances environmental performance compared to bitumen, while burning kraft lignin only proves beneficial when replacing highly polluting fossil fuels like coal [65,88,89].

Current lignin applications primarily focus on producing fuel, syngas, power, and macromolecules, while the valorisation of the aromatic fraction remains an active research area [90]. Therefore, the benefits for the standardisation of kraft lignin valorisation procedures and database creation aims to map feedstock variations, linking pulping conditions to raw materials and their application-specific reactivity. The pulp and paper industry is more persistent towards lignin valorisation beyond bioenergy applications, driven by the desire to improve process efficiency, advancements in kraft lignin extraction, and the potential for product diversification and revenue generation [91]. This trend is evident in manufacturers' growing practice of diverting portions of their lignin stream towards alternative uses, signalling a shift towards more sustainable and economically beneficial resource utilisation strategies in the industry [76]. There are alternative uses of lignin to extract it from black liquor, including gasification to produce syngas for derivative chemicals, and recovery of pulping chemicals, demonstrating potential applications beyond bioenergy in the pulp and paper industry [65]. This approach could enable pulp mills to produce tailored kraft lignin alongside pulp, highlighting the importance of ongoing research to fully explore kraft lignin's potential as a valuable resource.

2.2. Soda Lignin

Lignin's potential for industrial applications has driven extensive research efforts to develop sulfur-free extraction processes, despite limitations in current extraction methods. However, the absence of sulfur in lignin not only enhances its susceptibility to chemical modification but also presents opportunities to obtain economically valuable compounds suitable for diverse applications [92]. Soda lignin is lignin isolated from soda process, the oldest pulping method, and is currently employed for processing various non wood materials such as bagasse, hemp, kenaf, sisal, and wheat straw, involving a reaction between biomass and sodium hydroxide under high-pressure and high-temperature conditions [93]. The soda pulping process, which operates without sulfur-containing chemicals, produces sulfur-free alkaline lignin by reacting the biomass with 10–15% *w*/*w* alkali (typically sodium hydroxide) in a pressurised reactor at 160–170 °C [90,94]. Isolating lignin through

delignification method does affect the final structure as shown in Figure 6 [48]. While modifications like adding anthraquinone as a catalyst have improved carbohydrate stabilisation and lignin dissolution, the lignin recovery in this process remains lower compared to alternative methods [95]. Soda or soda/Anthraquinone pulping may be valuable for biorefineries due to its sulfur-free byproducts and suitability with annual plants, which are easier to delignify. This approach could overcome most challenges faced in lignin utilisation caused by sulfur content in kraft and sulfite lignins, potentially enhancing downstream catalytic processes [96]. The molecular weight of soda lignin extracted using anthraquinone as a catalyst is influenced by the choice of feedstock and organic solvent, resulting in diverse molecular weight profiles for the isolated lignin such as Bagasse (Mw = 2400), Softwood (Mw = 5500) and long fibre plants (Mw = 1300) [95,96]. Soda lignin, free from sulfur-containing compounds, presents a valuable precursor for sustainable and environment friendly raw materials [93]. Soda lignin finds diverse applications in phenolic resins, dispersants, polymer synthesis, and animal nutrition, but its usage is constrained by the scarcity of soda pulping mills and the process's low pulp yield performance [94]. The delignification method significantly influences the chemical structure of isolated lignin as shown in Figure 6; however, the final structure is also affected by its botanical origin and the native lignin composition of the feedstock. This is because of the chemical conditions used during extraction can effectively cleave/break lignin interunit linkages (such as β-O-4 and C-C bonds in kraft lignin, aryl ether bonds and loss of aliphatic phenolic OH group in soda lignin, and acidic hydrolysis in organosolv lignin), modifying hydroxyl and carbonyl functionalities, and facilitate condensation or repolymerisation reactions [48].

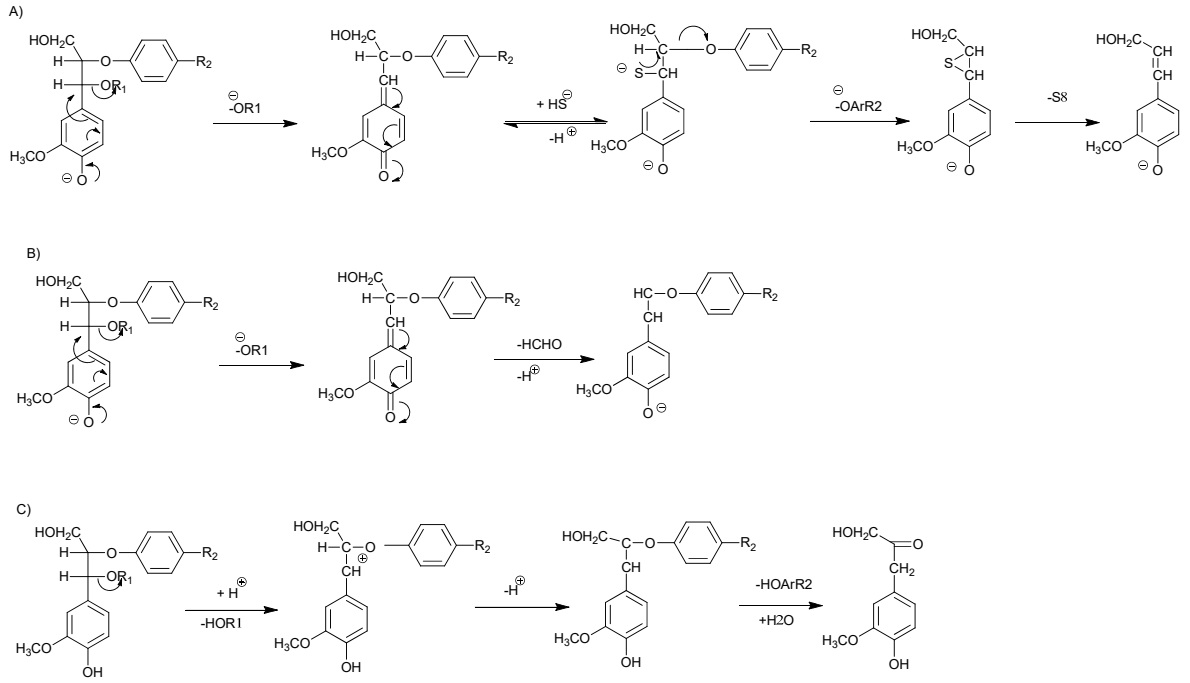


Figure 6. Schematic representation of change in lignin structure while preparing (**A**) Kraft lignin (**B**) soda lignin and (**C**) water/ethanol processes (Organosolv lignin).

2.3. Organosolv Lignin

The organosolv process encompasses a range of pulping methods which uses low-boiling organic solvents, predominantly utilising sulfur-free chemicals for delignification [91]. These processes commonly use alcohols (like ethanol or methanol, frequently blended with water), organic acids (such as formic/acetic acid), or combinations of organic solvents and inorganic alkali chemicals as the primary solvents for lignin extraction [91,97]. The organosolv process treats annual and hardwood plants using high-boiling solvents, operating at atmospheric pressure but making solvent recovery from spent liquor challenging [97]. It aims to isolate lignin from carbohydrates in lignocellulosic biomass [28]. The extracted lignin can have high purity, chemical reactivity, and be sulfur-free and non- toxic, with a homogeneous structure, low molecular weight, and low polydispersity resembling native lignin depending on the pretreatment conditions [38,97]. However, the usage of organic solvents also escalates the methodology costs as well as environmental impact [97,98]. Some research studies show that the Organosolv lignin extraction process significantly modifies lignin properties, reducing molar mass by 36% to 56% and altering the amount of syringyl phenolic units, aliphatic hydroxyl group content, and phenolic structures

compared to untreated lignin [28,99]. Some researchers have also explored the use of Lewis acid catalysts in organosolv processes, which further decreases molecular mass and amount of hydroxyl content [100]. The organic acid-based delignification process, particularly using formic acid, is highlighted as a promising organosolv technique for separating lignocelluloses, with applications in bioethanol production and cellulose-based materials using low-cost, recoverable formic acid at low temperatures [101]. The lignol process, another distinguished organosolv method, uses a 1:1 water-ethanol combination at high temperature (~200 °C) and pressure (2.76 MPa) for lignin extraction from lignocellulosic biomass [102]. These processes yield lignin that is highly soluble in organic solvents but nearly insoluble in water (due to its hydrophobic nature), necessitating specific recovery methods involving precipitation through concentration, pH, and temperature adjustments [28,103,104]. Organosolv lignin, characterised by low molecular weight and specific solubility properties, is considered a promising raw material for various applications (such as bioethanol) [89,101]. Organosolv lignin, characterised by its abundance of weaker β-O-4 aryl ether linkages, closely resembles native plant lignin and offers enhanced potential for structural modifications and decomposition [38]. Existing biomass pretreatment methods are costly and environmentally harmful, prompting the need for eco-friendly, cost-effective solvents [90]. Research should focus on integrating processes that utilise all organosolv fractionation streams for value- added products, especially valorising the hemicellulose-rich stream [90].

2.3.1. Ionic Liquids in Lignin Processing

Ionic liquids, composed of cations and anions, are low-temperature (at or below 100 °C) liquid salts with unique properties such as low volatility, high thermal stability, along with exceptional solvation capabilities for diverse compounds, making them versatile and potentially environmentally friendly alternatives to traditional/conventional solvents in various applications [105]. According to Lee and Lee (2005) ionic liquids demonstrate exceptional physical properties in chemical processes, including their capacity to dissolve various compounds such as polar and non-polar, organic and inorganic compounds, and offer nearly limitless potential for customisation through diverse anion-cation combinations [105,106]. Ionic liquids (ILs) have gained attention for treating lignocellulosic biomass, due to their excellent physical characteristics and ability to dissolve various compounds, including cellulose [107]. 1- butyl-3-methylimidazolium chloride [C4mim] [Cl] which is an Imidazolium-based ionic liquid has demonstrated remarkable efficacy in dissolving cellulose within biomass by disrupting its hydrogen bonds and coordinating chloride ions with hydroxyl groups; but this process requires extremely low moisture content to prevent water interference [108]. The dissolution of cellulose in Ionic liquids could enhance enzymatic hydrolysis, as reconstituted cellulose often exhibits lower crystallinity and improved accessibility to cellulases [109]. Originally, dissolution of cellulose with ionic liquids has been the main focus, but other components can be targeted, exemplified by the extraction of up to 40% of available lignin from olive pomace using triethylammonium hydrogen sulfate [Et_3NH] [HSO_4] [110]. This ionic liquid has also gained interest in industrial application due to its low cost and ability to solubilise 100% of hemicellulose and 85% of lignin from the energy crop miscanthus [107]. The utilisation of ionic liquids (ILs) for lignin extraction from wood faces several challenges, including the potential need for anhydrous conditions, inert atmospheres, small wood particle sizes, and extended dissolution times, with microwave heating offering a potential solution for the latter two issues [111]. Also, industrial application is further hindered by high costs, toxicity concerns, low efficiency and inefficient recovery methods, though the reuse of ionic liquids is proposed as a potential strategy to mitigate these limitations, particularly in terms of cost reduction [90]. There are multiple approaches for lignin recovery from lignin-ionic liquid solutions such as precipitation using mineral acids, extraction via a two-phase liquid system using organic solvents, and catalytic methods [112]. The precipitation of lignin from ionic liquid solutions uses various mineral acids such as HCl, H_2SO_4 and involves a complex, multi-step process that includes acidification (with 1 M HCl to pH = 2 at room temperature), heating (70 °C for 30 min) for mixing of the lignin and ionic liquid, and then washing with a large amount of water for the precipitated lignin, then neutralisation with 0.1 M NaOH under dry vacuum for 12 h, and dissolving with acetonitrile to extract the ionic liquid from salts, making it resource-intensive [112,113]. Second is the separation of lignin from water-ionic liquid mixtures using organic solvents in a two-phase system, while showing promise with tetrahydrofuran (THF) and water, is ultimately inefficient and requires additional steps for pH adjustment and recovery [113,114]. The third method is a catalyst-based method for extracting lignin from water-ionic liquid mixtures and involves converting lignin and sugar solutions into insoluble products using catalysts like $CrCl_3$ or $CrCl_3 \cdot 6H_2O$, with the latter effectively removing nearly all lignin and sugars at temperatures of 170 °C or higher [112–114]. While the ionic liquid and catalyst can be recovered through evaporation, the residual catalyst in the ionic liquid may interfere with subsequent pretreatment processes and potentially cause unwanted side reactions [112,114]. To comprehensively examine the characteristics and chemical properties of

recovered lignin and ionic liquids can be done by using various analytical procedures including Thermogravimetric analysis (TGA), NMR (^{1}H, HSQC, ^{13}C), Scanning electron microscopy (SEM), Ultraviolet-visible spectroscopy (UV-Vis) [113]. However, developing efficient separation processes to recover high-purity ionic liquids and lignin using these methods is crucial for scaling up ionic liquid-based biomass pretreatment to industrial levels, while the need to optimising purity and minimise its costs remain.

2.3.2. Deep Eutectic Solvents in Lignin Processing

Deep eutectic solvents (DESs) are the homogeneous combinations of two solid chemicals having a lower melting point compared to their independent elements, composed of a hydrogen-bond acceptor and donor, offering advantages such as low volatility, non-toxicity, and low cost [115,116]. Abbott et al. has developed one deep eutectic solvents (DESs) by combining carboxylic acids or Urea (HBD) and choline chloride (ChCl—HBA) salts together, which remain liquid at room temperature because of hydrogen bonding formed between these two compounds, as well as having advantageous properties such as ease of synthesis, biodegradability, and availability, making them potential alternatives to conventional ionic liquids [116,117]. These versatile solvents have found applications in various fields, including organic reactions, extraction processes, and azeotropic separation [117]. Deep eutectic solvents have almost identical physical properties to conventional ionic liquids (ILs) yet offer advantages such as easier preparation, cost-effectiveness, lower production costs, and well-characterised components, making them suitable for large-scale applications [118]. DES offer several advantages over ionic liquids (ILs) for biomass processing, including stability, and environmental friendliness, but require further research to address the challenges in recovery, reuse, and industrial-scale application [119]. Deep eutectic solvents have emerged as a favourable and increasingly popular method for fractionating lignocellulosic biomass in bioproduct production, attracting attention from researchers and industry professionals for their efficiency and sustainability [120]. Recent studies indicate that deep eutectic solvents (DES) can effectively extract lignin from woody plants by dissolving it and breaking β-O-4 bonds among phenylpropane units, leading to the splitting of lignocellulose components and generation of low molecular weight lignin through acid catalysis [120]. These deep eutectic solvents show a promising result as an alternative solvent for lignocellulosic separation and high-value lignin production as demonstrated by Francisco et al. (2012) who has used lactic acid-choline chloride mixtures to selectively dissolve lignin from various lignocellulosic biomass [120,121]. A study was investigated by Yiin et al. (2015) on how water influences the physiochemical properties of deep eutectic solvents (DESs), revealing that small amounts of water improve lignin solubility in DESs without having any effect on its thermal stability [121].

2.4. Hydrolysis Lignin (HL)

Hydrolysis lignin, a type of technical lignin, a by-product of sugar and bioethanol production from corn and sugarcane residues, is generated during the processing of these bio-based materials in renewable fuel and sugar manufacturing [57,122]. The HL obtained primarily consists of 56–57 wt.% lignin, along with unreacted cellulose and monosaccharides/oligosaccharides [123]. Hydrolysis lignin, despite its limited research compared to traditional industrial lignins, has undergone various chemical modifications to enhance its reactivity and properties, addressing challenges posed by high residual carbohydrate content [123,124]. Hydrolysis lignin can be classified into enzymatic and acid hydrolysis subgroups based on the hydrolysis process and further distinguished by their softwood, hardwood, or non-wood origin, can be produced using organic or inorganic acids [125]. Modern biorefinery concepts have moved away from dilute acid hydrolysis of wood for ethanol production, instead employing advanced technologies that combine pretreatments with enzymatic hydrolysis and fermentation [126]. Enzymatic hydrolysis lignin demonstrates higher activity compared to lignosulfonates and kraft lignin, making it suitable for polymeric materials and graft copolymerisation with acrylonitrile [124,127]. Hydrolysis lignin, classified into enzymatic and acid hydrolysis subgroups based on the hydrolysis process and further distinguished by their softwood, hardwood, or non-wood origin, can be produced using organic or inorganic acids [128]. These hydrolysis lignin exhibit high sorption ability and are difficult to dewater, making them useful as sorbents in various applications [126,129]. Hydrolysis lignin, despite its potential applications in various industries such as agriculture, environmental protection, and chemical recycling, remains largely underutilised due to the high costs of necessary modifications and suboptimal performance, presenting ongoing challenges for researchers seeking its valorisation [123].

Though different methods have been used to isolate lignin, Table 2 acts as a cross-comparison of isolated lignins to aid in understanding different lignin profiles. This in turn can be used to suggest which type of lignin will be better to use for various depolymerisation methods.

Table 2. Summary of relationship between lignin, its origin, structural characteristics and suitable depolymerisation strategies.

Lignin Type	Isolation Route	Key Structural Features	Characterization Method	Most Suitable Depolymerization Route	Expected Products	Major Limitations
Kraft lignin	Kraft pulping	Condensed, sulfur-containing, heterogenous	GPC, HSQC, NMR	Base catalysis, Hydrogenolysis, Selected Metal catalysis	Phenolics, aromatics	Condensation/catalyst poisoning
Soda lignin	Sulfur-free alkaline pulping	Variable Molecular weight, Sulfur-free	GPC, NMR, FTIR	Catalytic depolymerisation	Aromatic phenols	Feedstock variability
Organosolv lignin	Organic-solvent fractionation	Higher β-O-4 preservation, lower MW, sulfur-free	HSQC, GPC, FTIR	Hydrogenolysis/Solvolysis	Aromatic monomers	Solvent cost/recovery
Hydrolysis lignin	Bio-refinery residue	Residual carbohydrate, condensed structures	GPC, NMR, compositional analysis	Robust catalytic routes	Mixed phenolics	Impurities/Low recovery
DES-derived lignin	DES fractionation	Process-dependent cleavage/modification	NMR, GPC, FTIR	Route-specific	Aromatics/Phenolics	Solvent recovery/ scalability

3. Characterisation of Lignin

For a better understanding of lignin reactivity and to direct depolymerisation approach, structural characterisation is essential. This information is vital in developing effective methods for choosing multiple catalysts for depolymerisation. By studying these analytical techniques, researchers can better acknowledge the behaviour of lignin and be aware of how to manipulate its complex structure, which is crucial for enhancing its conversion into valuable products and improving depolymerisation processes.

3.1. NMR

Understanding the detailed structural analysis of isolated lignin through nuclear magnetic resonance (NMR) methodology is vital for achieving accurate qualitative and quantitative characterisation [130]. NMR assesses C-H bonds, multiple bonds, and other potential correlations in ^{1}H and ^{13}C using advanced two-dimensional heteronuclear single quantum coherence (2D HSQC) techniques. It can analyse a wide range of lignin fragments, from monomers, dimers, trimers and tetramers, providing valuable insights into lignin structure and composition. 2D HSQC reveals a clear separation of molecules by directly correlating the carbons with their attached protons [131]. This tool is incredibly effective to not only identify the structure of lignin but also estimates the relative abundance of interunit linkages and monolignol ratios within lignin composition (for example, ^{1}H NMR spectrum provides valuable information for distinguishing and characterising different hydrogen environments present in the aromatic molecule [4,132]. To identify and quantify lignin hydroxyl groups (particularly phenolics -OH groups) from aliphatic, aromatic, syringol (S), guaiacol (G), and hydroxyl (H content) unit, phosphorylation followed by ^{31}P (Phosphorus) nuclear magnetic resonance is a very useful and reliable method [133]. A good example from more recently is Zirbes et al. (2023), who looked into how peroxodicarbonate could be used to break down Kraft lignin and showed that it could selectively form vanillin. 2D-HSQC NMR spectroscopy and other diagnostic methods were used together to study how lignin breaks down and what products are made. While lignin is being converted, this study shows how useful NMR is as a non-linear analytical tool for tracking changes in structure and confirming the creation of desired low-molecular-weight aromatic products [134].

Additionally, NMR spectroscopy is very useful when lignin conversion causes major molecular changes that go beyond the formation of normal aromatic monomers. Lindenbeck et al. (2024) studied how lignin changes electrically in a system with water and γ-valerolactone and to find structurally different products made during lignin conversion, they used a method that combined ^{1}H and ^{13}C NMR spectroscopy, LC-ESI-HRMS, and infrared spectroscopy. The study shows how important it is to use both NMR and other analytical methods together when complex reaction mixes have both aromatic and aliphatic products that can't be fully described by a single analytical method alone [135].

Recent studies done by Liu et al. (2025) shows that advanced analytical methods are still needed to fully understand structures and identify compounds produced from lignin. It's clear from studies that ^{1}H NMR spectroscopy could help not only finding the specific products but also make us understand about how products are distributed and how their structures change during lignin depolymerisation [136].

A study done by Han et al. (2023) talked about how important it is to use 2D-HSQC NMR along with other methods like GPC/SEC, MALDI-TOF-MS, and FT-ICR-MS to identify oligomeric lignin-depolymerization products. They also said that structural assignments from native lignin can't always be used directly on these products because recoupling and condensation can create new C-C linkages that change the molecular structures of the oligomers that are made [137].

Moreover, recent research shows that NMR spectroscopy is a useful method for identifying both low-molecular weight and oligomeric lignin-depolymerisation products. When combined with chromatographic and mass-spectrometric methods, it gives extra information about structure, elementcomposition, quantitative product analysis, and molecular weight distributions.

3.2. FTIR

Fourier transform infrared spectroscopy (FTIR) spectroscopy, which allow determination of functional groups present in a sample. It enables determination of specific units present in lignin, such as vanillin, guaiacyl, syringyl, and p-hydroxyphenyl units. According to Wang, Pu, et al., 2018, the absorbance of lignin's distinctive aromatic skeletal occurs at 1500–1560 cm^{-1} [4,132]. According to Duan et al. (2017), when comparing the primary peaks of lignin before and after depolymerisation , the chemical functional groups that were present in lignin were found at 3423 cm^{-1} (-OH stretching absorption of the aliphatic and phenolic hydroxyl groups), 2937/2840 cm^{-1} (-CH stretching in methyl), 1720 cm^{-1} (-C=O stretching), 1654/1603 cm^{-1} (-C=C stretching), 1514 cm^{-1} (-C=C stretching in an aromatic ring), 1462/1425 cm^{-1} (-CH bending from methyl groups), 1328 cm^{-1} (-OH bending of the phenolic hydroxyl groups), 1268/1217 cm^{-1} (-CO stretching in the guaiacol and syringol rings), 1118 cm^{-1} (-CO stretching in tertiary alcohols), 1032 cm^{-1} (CO-O-CO stretching), 913/833 cm^{-1} (-C=C bending) [138]. Also, one could use Fourier transformation near-infrared spectroscopy (FT-NIR), to analyse the chemical composition of lignocellulosic biomass such as corn stover, wood and rice straw as well [139].

ATR-FTIR spectroscopy has evolved as a quick, non-destructive and green analytical approach for characterisation of lignin and lignocellulosic biomass [133]. Its low sample demand and its little or no chemical reagents and solvents make it particularly ideal for high throughput biomass screening and process monitoring [140]. Also, In-situ FTIR spectroscopy gives us more information about how the substrate's molecules change under reaction conditions in real time. It also demonstrates a sequential synthesis of phenolic, aromatic and carbonyl species which confirms a process involving initial benzylic oxidation followed by Cα-Cβ bond cleavage to provide aromatic monomers. Rather than random breaking of bonds or complete mineralisation, these potential-dependent spectral changes offer direct evidence for a selective depolymerisation mechanism [141,142].

3.3. GPC

Gel permeation chromatography (GPC) can be used to find out molecular weight distribution of isolated substances, aiding in determining average molecular weight of lignin samples before and after depolymerisation. This analysis can be done using a high-performance liquid chromatography technique, which injects a sample mixture into a column, where it filters across sorbents. This allows different components to move at varying velocities based on their size and chemical nature. When the sample emerges from the column, the measurement of retention time is crucial. Elution can be calculated using refractive index (RI), Ultraviolet absorbance (UV), or light scattering (LS) [131]. With its versatile elution calculation methods, this technique is particularly well-suited for analysing lignin dissolved in a solvent like dimethyl formamide (DMF) or tetra hydrofuran (THF) [131]. GPC provides important details like peak molecular weight (Mp), number average molecular weight (Mn), weight average molecular weight (Mw), and dispersity index (D = Mw/Mn). Whenever the values go down, it usually means that large lignin molecules have been broken apart into small oligomeric and monomeric units. According to Lindenbeck et al. (2025) study electrochemical kraft lignin depolymerisation and saw a big change in values in Mp (1931 to 154 Da), Mn (894 to 219 Da), and Mw (5689 to 572 Da), along with a drop in dispersity index from 6.37 to 2.61 which means that high molecular weight lignin could be changed into smaller, more evenly distributed products. The sudden drop in Mn, Mp and Mw values indicates that reductive electrochemical depolymerisation effectively breaks up the structure of Kraft's lignin through selective cleavage of β-O-4 bonds and other interunit linkages. Therefore, GPC is another analytical technique for checking how well depolymerisation works and how lignin molecular-weight distributions change [143].

3.4. TGA

Thermal gravimetric analysis (TGA) is a thermo-analytical method which records changes in sample mass as the temperature rises, either at a constant heating rate or as a function of time under nitrogen atmosphere [131,144].

It provides essential information about phase transition temperatures and thermal degradation. This thermo-analytical technique is beneficial for interpreting the composition of isolated lignin and thermal stability over a broad range of temperature [131,145–147].

3.5. DSC

Analysis of isolated lignin with differential scanning calorimetry (DSC) is beneficial for diagnosing glass transition temperature (Tg). DSC is a powerful thermo-analytical technique that offers valuable insights into the behaviour of materials. DSC enables accurate determination of phase transitions by precisely measuring the heat flow required to increase the temperature of a sample and a reference material at a constant rate [147]. This technique is based on the concept that when a sample goes through a phase change, the flow of heat to it differs from the reference materials, allowing for a comprehensive understanding of material characteristics and behaviour [131,145,147].

4. Depolymerisation of Lignin

Lignin depolymerisation has been widely investigated and can provide several benefits, including high selectivity and reactivity. Depending on the type of depolymerisation techniques, suitable chemical reagents can be used in different methodologies of depolymerisation, such as acid-based catalysts, base catalysts, metal catalysts, microwave-assisted, and hydrogenolysis.

4.1. Acid-Catalysed Depolymerisation

Acid-catalysed depolymerisation is an efficient method for breaking down lignin, which involves the precise cleavage of ether bonds [148]. The β-aryl ether (i.e, β-O-4) linkages, comprising over 50% of lignin's structure, are the primary targets for depolymerisation due to their predominance in the polymer [149]. Common products that originate from acid-catalysed depolymerisation are either Hibbert ketones or aldehyde-substituted phenolics as shown in Figure 7 [148]. Inorganic acids (HCl, H_2SO_4 etc.) and organic acids (HCOOH, CH_3COOH, $C_2H_2O_4$, etc.) have been extensively used to catalyse lignin depolymerisation [23]. However, using these homogenous catalysts for acid-catalysed depolymerisation can cause serious corrosion and polymerisation [150]. Compared to homogenous catalysts, solid acid catalysts are easily separable and recyclable, less corrosive and highly environmental-friendly [150]. These materials are notable for their expansive surface area, intricate pore structure, and abundance of acid sites, all of which contribute to accelerating the rate of C-O bond cleavage and effectively preventing coke formation during lignin conversion [151]. Common solid acid catalysts are zeolites (such as H-ZSM-5, H-MOR, etc.), Lewis acids ($NiCl_2$, $AlCl_3$, Cu $(OAc)_2$, etc.), and amorphous silica-alumina (SiO_2-Al_2O_3) [151,152]. The efficiency of solid acid catalysis and product composition is influenced by factors such as acidic strength, specific surface area, and pore size, with diffusion limitation potentially decreasing catalytic efficiency if pores become clogged [151]. The extensive surface area and distinctive pore structure of zeolites make them an appropriate support for lignin depolymerisation [153,154]. A study on kraft lignin depolymerisation using various zeolites found that catalysts with large pore sizes and high acidity yielded more cycloalkanes, while those with small pore sizes and low acidity produced more cyclic ketones/alcohols and alkanes [150]. Lewis acids work as solid acid catalysts to depolymerise the lignin function through two mechanisms, with the first involving the valence state of metal ions, where higher valence states enhance the bond formation that react with ether bonds, while the other involves an oxidation mechanism, where the Cα-OH in the β-O-4 aryl ether bond is activated and selectively oxidised to Cα=O [155].

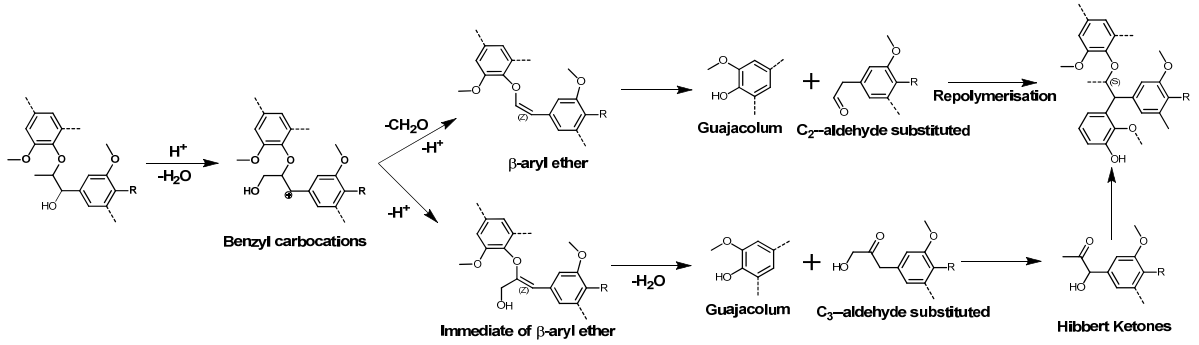


Figure 7. Schematic representation of Acid-catalysed depolymerisation.

This method effectively limits the formation of β-O-4 carbocations, thus reducing the energy of C-O bond in β-O-4 linkages [156]. Acid-catalysed depolymerisation, despite its widespread industrial adoption, presents critical challenges, including high energy consumption, repolymerisation issues, environmental concerns, and inefficiency, rendering it increasingly unsustainable and incompatible [40]. This method's unavoidable aspects are extreme reaction conditions, repolymerisation, toxic chemicals, and extended processing times which not only compromise product quality but also significantly increase operational costs and environmental impact [40,147]. These limitations underscore the need for developing alternative, more efficient, and environmentally friendly approaches to lignin depolymerisation [157]. The examples outlined in Table 3 have been carefully chosen to exemplify the key acid-catalysed depolymerisation strategies, as well as to demonstrate the influence of catalyst type and reaction conditions on the conversion of lignin. The studies chosen for this review encompass a range of representative acidic systems that illustrate variations in C-O bond cleavage, product selectivity, and competing risks associated with condensation and repolymerisation.

Table 3. Summary of various acid catalysts to depolymerise the lignin.

Type of Lignin	Reaction Conditions	Major Products	Results	References
Lignin	$ZnCl_2$ (260 °C)/5 h	Phenolic monomers	11.0%	[158]
Lignin	$CrCl_3$ (260 °C)/5 h	Phenolic monomers	24.0%	[158]
Alkali lignin	Pd/C + $CrCl_3$ (260 °C)/5 h	Phenolic monomers	28.5%	[159]
Kraft lignin	Ni-Cu/H-Beta (330 °C)/3 h	Cycloalkanes, Aromatics, Cyclic alcohols, Alkanes	50.8 wt.%	[154]
Birch lignin	Ru/Nb_2O_5 (250 °C)/20 h	Hydrocarbons	35.5 wt.%	[160]
Bagasse lignin	H-USY in MIBK (350 °C)/1 h	Phenol, 4-ethyl phenol, Guaiacol	Guaiacol (7.9 wt.%), 4-ethylphenol (6.0 wt.%), and phenol (3.4 wt.%)	[161]
Soda lignin	Aluminum/copper/nickel triflates in ethanol/water (400 °C)/4 h	Aliphatic and aromatic products	Aliphatic products (~67 wt.%) and aromatic products (~18 wt.%) in $Al(OTf)_3$, ~75 wt.% aliphatic product and ~13 wt.% aromatic products in $Cu(OTf)_2$, and in $Ni(OTf)_2$, ~73 wt.% aliphatic product and ~14 wt.% of aromatic product	[162]

4.2. Base-Catalysed Depolymerisation

Base-catalysed depolymerisation is a traditional method for breaking down lignin, utilising inorganic or organic bases, by cleaving its weakest ether bonds, especially α-aryl and β-aryl ether linkages [148,163]. The process primarily breaks the weakest β-O-4 linkages/bonds in the structure of lignin through two mechanisms involving phenolic and non-phenolic units, specifically targeting α-O-4 and β-O-4 bonds, respectively [164]. Most of the research studies have focused on the following catalyst types: solid catalysts (MgO, Na_2CO_3), organic bases (ethylenediamine), homogeneous catalysts (NaOH, KOH) in addition to other base catalysts such as CsOH and Ca $(OH)_2$ as well [4,58,148,165]. These base catalysts have been widely used for their high catalytic activity, efficacy and cost-effectiveness but often necessitate harsh reaction conditions, resulting in side reactions and reduced selectivity [166]. Strong bases outperform weak bases in depolymerisation due to their higher polarity, which accelerates degradation, minimises carbon formation, and enhances reaction kinetics and efficiency in polymer breakdown [148,167]. To enhance base-catalysed depolymerisation and phenolic product yield, it is crucial to minimise the condensation and repolymerisation of intermediate products, as these processes contribute significantly to solid residue formation and hinder overall depolymerisation efficiency [168]. This depolymerisation of lignin has faced many challenges, such as poor product specificity and extreme reaction conditions (such as high temperature and high pressure), which increases its cost and operational complexity [168]. As a result, researchers are actively exploring alternative approaches, including the use of metal catalysts, to achieve selective lignin depolymerisation under milder conditions [169]. Combining base- catalysed depolymerisation with other lignin valorisation techniques (such as oxidative depolymerisation, hydrogenolysis and pyrolysis) can help in improving product yield, specificity, and overall selectivity and efficiency [157,165]. The industrial-scale implementation of lignin depolymerisation processes encounters substantial hurdles in product selectivity, process efficiency, and economic viability, despite encouraging laboratory outcomes, thereby requiring innovative approaches for successful commercialisation [166,170]. The examples in Table 4 were chosen to show how the alkaline reaction environment changes the breaking of lignin bonds and the distribution of products. The chosen studies use a range of lignin feedstocks and reaction conditions to show the importance of base-assisted cleavage, solvent effects, and the intensity of the reaction.

Table 4. Summary of the details of various base catalysts used for lignin depolymerisation.

Type of Lignin	Reaction Conditions	Major Products	Results	References
Walnut-shell EtOH lignin	$Bi(OTf)_3$, 1,4-dioxane + ethylene glycol, (150 °C)/15 min	Aromatic phenols	18 wt.%	[171]
Pine lignin	NaOH, Ru/C, (260 °C)/4 h	Syringol and Guaiacol	N/A	[172]
Alkaline lignin	NaX (sodium zeolite X), (250 °C)/1 h	Guaiacol, 4-hydroxy benzyl alcohol, and 2-methoxy-4-methyl phenol, vanillin	1.0 wt.%, 1.4 wt.%, 3.7 wt.% and 3.6 wt.%	[173]
Organosolv oak lignin	Cs_2CO_3, 10 wt.% DMC, (180 °C)/1 h	1,2-dimethoxybenzene, 3,4-dimethoxybenzoate	Within 52–67 wt.%	[174]
Organosolv lignin	NaOH, (230 °C)/20 h	Guaiacol, Vanillin, Dihydroconiferyl alcohol and Coniferyl aldehyde	N/A	[172]
Kraft lignin	NaOH, (250 °C)/120 min.	Aliphatic and Phenolic OH	92 wt.% of depolymerised lignin	[175]
Organosolv lignin	NaOH, (300 °C)/80 min/9 MPa	Phenolic monomers	28.2 wt.%	[176]

4.3. Metal-Catalysed Depolymerisation

Recent lignin depolymerisation research has shifted focus from conventional acid/base catalysis to metallic catalysts, aiming for improved reaction conditions and selectivity in lignin breakdown, potentially enhancing efficiency and sustainability in lignin valorisation strategies [165]. Metal catalysts, including transition metals, noble metals, and bimetallic combinations, are widely employed in lignin depolymerisation, often supported on carriers to enhance their catalytic potential [4]. Transition metals like Fe, Ni, Cu, Co, and Mo are favoured for their economic viability and efficiency, while Platinum group metals such as Ru, Rh, Pd, or Pt has also been broadly studied for their catalytic properties in lignin depolymerisation [177]. The selection of appropriate support materials for catalysts plays a crucial role in enhancing lignin depolymerisation by improving catalyst performance, stability, and selectivity, ultimately influencing overall efficiency and product distribution [178]. Nickel has emerged as a promising metallic catalyst for lignin depolymerisation, demonstrating high efficiency and selectivity in breaking down lignin structures [165]. Research has shown that nickel effectively cleaves ether linkages and carbon-hydroxyl bonds in lignin [179]. A notable study by Song et al. reported that nickel could convert more than half of birch wood lignin into valuable monomers, specifically propyl guaiacol and propyl syringol, under relatively mild conditions [180]. These findings highlight nickel's potential as an effective catalyst for lignin valorisation, offering a sustainable approach to biomass utilisation.

Bimetallic catalysts (such as Ni-M, where M can be Ru, Rh, Pd, Pt, Au, Fe, and Mo) have attracted considerable interest in catalysis research due to their ability to enhance reactivity and selectivity through synergistic effects between two metal species, resulting in superior performance compared to monometallic catalysts [165,179–183]. These bimetallic catalysts, exhibit electronic modifications, geometric alterations, bifunctionality, and improved stability, resulting in superior activity, selectivity, and resistance to deactivation compared to monometallic catalysts [184]. But the use of nickel- bimetallic catalysts for depolymerisation faces challenges due to the rising cost of Platinum group metals (PGM) and risk of over- hydrogenation of aromatic compounds under various reaction conditions, which can reduce phenolic product yields [4,165]. Despite the high selectivity of metallic catalysts in lignin depolymerisation, their widespread application is hindered by multiple factors, such as the use of expensive noble metals, catalyst deactivation, and relatively low conversion rates compared to more cost-effective alternatives like acids and bases [165]. To address these issues, researchers are exploring cost-effective alternatives, such as replacing noble metals with cheaper options and enhancing catalyst reusability, to improve affordability and process efficiency [180,183]. Table 5 compares sample metal-catalysed systems with varied catalytic functionalities. We focused on several catalyst classes and compositions to show how the active metal affects C-O bond cleavage, hydrogenation, hydrodeoxygenation, and product selectivity.

Table 5. Summarises the various metal-based catalysts for lignin depolymerisation.

Type of Lignin	Reaction Condition	Major Products	Results	References
Birch sawdust	Ni/C, (200 °C)/6 h	Propenylguaiacol, Propenylsyringol, Ethyl guaiacol	54 wt.%	[179]
Corn stalk lignin	Ru/C, Methanol (250 °C)/3 h	4-ethylphenol, 4-ethylguaiacol	51 wt.%	[185]
Organosolv lignin (switchgrass)	Pt/C, (230 °C)/3 h/30 bar N_2	Monophenols	45 wt.%	[186]
Organosolv poplar lignin	NiCu/C, Ethanol/Isopropanol (270 °C)/ 4 h/1 MPa N_2	Monomeric phenols	63.4 wt.%	[187]
Organosolv lignin	Cu-PMO, Methanol (300 °C)/24 h	Monomeric cyclohexyl derivatives	N/A	[188]

4.4. Hydrogenolysis

Hydrogenolysis is a chemical process that uses hydrogen to break specific chemical bonds, particularly carbon-carbon single bonds or bonds between carbon and heteroatoms (C-O bonds), results in the formation of small molecular components [189]. Therefore, hydrogenolysis of lignin's C-O bonds using hydrogen gas and metal catalysts is considered an efficient method for breaking down lignin into simpler aromatic compounds [190]. This depolymerisation method, employing molecular hydrogen or a hydrogen-donor solvent, stands out as a promising approach for lignin depolymerisation, potentially yielding higher quantities of aromatic monomers than other depolymerisation methods [191]. Alcohols, formic acid, and formates act as hydrogen donors, offering a sustainable approach to lignin valorisation under mild conditions [192]. The proposed mechanism of lignin hydrogenolysis involves direct cleavage of C-O bonds, particularly β-O-4 ether linkages, and results in phenolic monomers while retaining aromatic structures [193]. Alternatively, some catalysts employ sequential hydrogenation and cleavage or utilise bifunctional catalysis with acid-base synergy to enhance selectivity and promote both hydrogenation and hydrolysis reactions [193]. The complex and varied lignin structures derived from different biomass sources (softwoods, herbaceous, hardwoods) require customised reaction conditions and carefully chosen catalysts to enhance the hydrogenolysis process and maximise production of valuable monomeric compounds [177]. Nickel-based, PGM-based or molybdenum-based catalysts are the most preferred metal centres for lignin hydrogenolysis [194]. Nickel catalysts are commonly chosen because they offer a good balance of affordability and effectiveness [194]. Bimetallic NiM catalysts and modified nickel catalysts, such as graphene-protected Ni-Co nanoparticles and Nb_2O_5-modified Ni, have appeared as positive research directions because of their enhanced ability to cleave C-O bonds and depolymerise lignin [195]. Platinum group metal (PGM) catalysts, often supported on materials like carbon or silica, are widely used for lignin hydrogenolysis owing to their high activity, mild reaction conditions and high selectivity, ensuring retention of aromaticity within the product stream [196]. Recent studies have investigated various PGM catalysts on different supports for lignin depolymerisation, with Ru/SiC demonstrating improved performance compared to Ru/C in lignin-first biorefinery applications [197]. SiC-supported catalysts exhibit high thermal and/or oxidative stability but also possess low surface area [197]. Mo-based catalysts offer cost-effective and efficient hydrodeoxygenation (HDO) bio-based oxygenates, operating at moderate temperatures as well as low H_2 pressure [198]. Various forms of Mo catalysts, including oxides, carbides, nitrides, and sulfides, have been studied with MoO_3 catalysts showing high activity for cleaving phenolic bonds [194]. The performance and stability of Mo- based catalysts is influenced by different factors like support material, dispersion, as well as the presence of other elements like Co, with some catalysts demonstrating excellent recyclability and high bio-oil yields without char or tar residues [194,199]. The addition of a base (for example, NaO^tBu) has been shown to potentially improve selectivity for monomeric aromatic compounds in various studies, indicating that basic conditions may influence product distribution in certain chemical processes involving aromatic structures [181]. In terms of efficiency, selectivity and cost-effectiveness of using these various catalysts, Nickel-based catalysts offer a cost-effective solution with moderate performance, PGM-based catalysts provide superior efficiency and selectivity at a premium cost, while molybdenum- based catalysts strike a balance between performance and affordability [178,194–196,198,200–202].

The hydrogenolysis of lignin is significantly influenced by reaction conditions, including temperature, pressure, and solvent choice, with each parameter affecting conversion rates, product distribution, and overall efficiency [203]. Temperature typically ranges from 200–350 °C, while pressure (1–10 MPa) and solvent selection impact lignin solubility and product yield, with polar and hydrogen- donor solvents offering specific advantages [204]. The unintended hydrogenation of benzene rings during lignin hydrogenolysis poses significant challenges, including increased hydrogen consumption, reduced efficiency, and formation of stable, fully saturated products resistant to further hydrogenolysis [205–207]. Optimising these conditions requires balancing efficiency, selectivity, and economic factors to achieve desired outcomes in lignin conversion processes [208]. Table 6 compares the main lignin hydrogenolysis catalyst classes and feedstocks. The selected research uses genuine and model lignins from Ni, Pd, Pt, and Ru-based systems. This selection compares hydrogenolytic C-O bond cleavage and product selectivity effects of catalyst identity, lignin complexity, solvent, and reaction conditions.

Table 6. Summarises the details of the type of lignin, catalyst, solvent and major products for the hydrogenolysis of lignin.

Type of Lignin	Reaction Conditions	Major Products	Results	References
Organosolv lignin	Pd/C, (195 °C)/2–24 h	4-propyl guaiacol, Dihydroconiferyl alcohol	2%, 19–21%	[209]
Ammonia lignin	Pt/Al_2O_3, $MeOH/H_2O$ (300 °C)/2 h/30 bar H_2	Syringol, 4- propyl syringol, 4-n-propanol syringol	18.9 wt.%	[210]

Table 6. *Cont*.

Type of Lignin	Reaction Conditions	Major Products	Results	References
Lignin rich residue	Ru/C, Isopropanol (300 °C)/3 h/2 MPa N_2	Monophenols	27 wt.%	[211]
Glycerol	Pd/Fe_2O_3, Isopropanol (180 °C)/24 h/5 bar inert gas	1,2-propanediol	94% selectivity	[212]
Organosolv Lignin	Ni-SBA-15, (150 °C)/0.5 h	Monomers (phenols, guaiacol derivatives), oligomers	35–45 wt.%	[213]
Lignin	Ni/C, (190 °C)/3 h	4-propanol guaiacol and 4-propanol syringol	17.2 wt.%	[214]
Pine wood lignin	Pd/C, 1:1 ethanol/water mixture/(195 °C)/1 h	2-methoxy-4-(prop-1-enyl)-phenol	23%	[159]
Lignin	NiCo/C, Ethanol, (260 °C)/4 h	Hydrocarbon monomers	20.8 wt.%	[215]

4.5. Microwave-Assisted Depolymerisation

Microwave-assisted depolymerisation utilises microwave heating to break down large molecules, such as lignin, into smaller, more useful chemical compounds or monomers [40]. The process of microwave-assisted depolymerisation of lignin has been capturing growing interest compared to traditional heating methods [216]. This is primarily due to its ability to achieve a fast-heating rate and high heating efficiency, making it a promising alternative in lignin depolymerisation processes [217]. In contrast traditional heating method highlights slower external heat transfer, longer reaction, high energy use, moderate yield with more by-products and reduced catalyst interaction [40]. Under microwave irradiation, microwave heating occurs when polar solvents, which possess high microwave absorption abilities, undergo dipole rotation and ionic conduction [218]. However, introducing molecular hydrogen by using solvents could significantly elevate costs and risks associated with the process [219]. As a result, using polar hydrogen donor solvents like methanol, ethanol, formic acid, etc. in the presence of various catalysts presents a compelling opportunity for cost-effectiveness and safety with the help of microwave heating [220]. Pd, Pt, and Ru (noble metal-based catalysts) have highly influenced depolymerising lignin [184]. Pd-based catalysts demonstrate high selectivity for phenolic monomers at moderate temperatures, while Pt catalysts offer a balanced approach, producing a mix of monomers and deoxygenated products, and Ru catalysts excel at hydrodeoxygenation, yielding highly deoxygenated hydrocarbons for bio-oil applications [221,222]. A study done by Liu et al., (2021) for Microwave-assisted catalytic depolymerisation of lignin from birch sawdust was investigated using water-alcohol co-solvents and commercial catalysts (such as Pt/C, Pd/C, Ru/C) at 190 °C for 3 h, resulting in a 65 wt% yield of phenolic monomers without using external hydrogen [223]. This single-step process not only demonstrated potential for integrated biorefinery applications (such as pulp industry) by retaining significant portions of cellulose and hemicellulose in solid residues but also introducing new perspectives for efficient and cost-effective production of value- added phenolic compounds from lignin in agro-industrial wastes [223]. Microwave-assisted depolymerisation of lignin exhibits temperature-dependent selectivity, with lower temperatures favouring ether linkage cleavage and higher temperatures promoting more extensive bond breaking and hydrodeoxygenation, while microwave radiation enhances overall efficiency by selectively heating reactive groups and reducing side reactions [217]. Microwave- assisted depolymerisation is grouped into two types based on temperature variation: solvolysis at low temperatures (<200 °C) or pyrolysis at high temperatures (>400 °C) [224]. Solvolysis of lignin is an innovative approach to converting lignin into a diverse array of valuable chemicals using specific solvents [225]. Solvolysis at lower temperatures (150–250 °C) selectively cleaves C-O bonds, preserving aromaticity and yielding specific aromatic monomers with minimal char formation [225]. In contrast, high-temperature pyrolysis (350–500 °C) cleaves either C-O bond or C-C bonds, resulting in diverse products including gases, bio-oils, and char, but with reduced aromaticity and higher energy input [226]. Therefore, both solvolysis and pyrolysis show promising results, but challenges remain in controlling product selectivity and minimising char formation, necessitating further research into optimised microwave systems and hybrid approaches to enhance efficiency and yield of valuable monomers [226,227]. The optimisation of lignin depolymerisation processes and maximization of valuable aromatic compound production rely heavily on understanding the complex relationships between reaction conditions, catalyst selection, and product distribution [227]. The cases chosen in Table 7 shows how different feedstocks, reaction media, catalysts, microwave settings, and product distributions can affect microwave-assisted lignin depolymerisation. From liquefaction of lignin and generation of polyols to production of aromatic monomers and bio-oil, the chosen research shows the divergent results of low-temperature solvolytic and catalytic processes.

Table 7. A summary of lignin source, reaction conditions, and major products for microwave-assisted depolymerisation.

Type of Lignin	Reaction Conditions	Major Products	Results	References
Lignin	Glycerol and 1,4-butanediol (130–170 °C)/5 min.	Polyols	93 wt.%	[228]
Alkali lignin	Methanol/formic acid (160 °C)/30 min.	Vanillin, Syringaldehyde, Methyl syringate, Methyl vanillate	6.7 wt.%	[229]
Pine sawdust lignin	H_2SO_4, (185–190 °C)/5–20 min./700 W	2-methoxy-4-propyl phenol	N/A	[172]
Organosolv lignin	Hydrochloric acid (160 °C)/30 min./80 W	Mono- aromatics and C5-C12 aliphatics	96 wt.%	[229]
Alkali lignin	CuNiAl, Methanol (100–120 °C)/60 min.	Bio-oil, Phenolic monomers	N/A	[219]

4.6. Electrochemical Lignin Depolymerisation (Oxidative and Reductive)

In recent years, electrochemical conversion has gained prominence as a viable alternative to thermochemical and traditional catalytic methods for the depolymerisation and valorisation of lignin. When it comes to converting lignin, electrochemical methods are seen as being cost-effective, reagent-free, and environmentally benign. What's more, these procedures can be carried out at moderate reaction conditions [230]. Effective electrochemical conversion of lignin is strongly dependent on understanding its unique structural properties rather than its generic macromolecular structure. Targeted depolymerisation relies heavily on the presence of β-O-4 linkages [231]. Product selectivity is frequently hindered by lignin's numerous reactive functional groups and inherent structural heterogeneity, which cause it to have varying redox potentials and electron-transfer processes. Mass transfer at the electrode surface is also limited due to substantial solubility problems created by the recalcitrant nature of lignin [232]. There are two types of electrochemical reaction i.e., electrochemical oxidation and reduction. Electrochemical oxidation and reduction are phenomena in which chemical entities experience oxidation (electron loss) at anode and reduction (electron gain) at the cathode [233].

4.6.1. Electrochemical Oxidation

Comprehensive research has established that electrochemical oxidation or electrooxidation at the anode is one of the predominant methods for lignin transformation. The procedure uses anodic potentials to break down lignin, primarily focusing on α-carbonylation and C-O and C-C linkages to provide low molecular weight aromatic compounds [234,235].

Two primary pathways are involved in electrooxidation: one is the direct reaction between the electrode and lignin (Figure 8a), and the other is the indirect reaction between the electrode and a redox mediator (Figure 8b) [236]. The electrode usually uses heterogeneous catalyst for direct electrooxidation, like Ni, PbO_2, or RuO_2 [237,238]. These catalysts may also be fixed directly onto the electrode surface thus allowing depolymerisation to occur at the electrode. However, electrochemical stability of the electrolyte, the solubility of lignin, and the conduction of electrons or protons provide significant challenges in this procedure [239]. For indirect electrooxidation, homogeneous catalysts like ferric chloride, N-hydroxyphthalimide, or polyoxometalates are usually used [232,240,241]. In addition to being an oxidant, these catalysts can also serve as proton and/or electron donors. The catalyst undergoes reduction under an applied voltage when it oxidises lignin to produce or convert it to another chemical product which regenerates it at the anode which allows better control over selectivity (233,240). However, direct electrolytic oxidation of lignin can either make it more useful or break it down into smaller units. During functionalisation, the α-hydroxyl group in β-O-4 links is often oxidised to an α-carbonyl group [235]. This can make it easier for the next C-O bond to break. Depolymerisation breaks down C-O and sometimes Cα-Cβ bonds to make aromatic compounds with lower molecular weight [233,242]. More oxidation and radical-mediated binding of phenolic products, on the other hand, can lead to repolymerization and electrode fouling [242,243].

In terms of lignin conversion and product selectivity, anode materials play a significant role. Metal oxides and mixed-metal oxides, carbon-based electrodes, and transition metals like Ni and Co have all been studied extensively [244–252]. Ni-based electrodes are appealing because they are cheap but effective in catalysis, with the shape of the electrode also having a big effect on how well it works [253]. Impressive selectivity for aromatic aldehydes, such as vanillin, has been demonstrated by Co-based electrodes [252,254]. The interaction between metal mixed oxides electrodes and reactive oxygen species determines whether they induce selective oxidation or widespread mineralisation [255–258]. Electrodes made of carbon, such as graphite, glassy carbon, or diamond doped with boron, have large potential windows and are resistant to deactivation rather well [259].

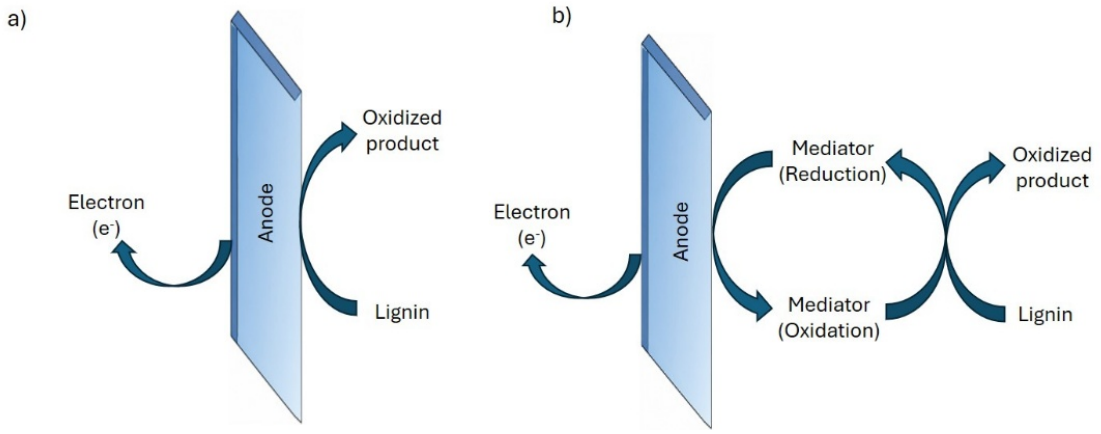


Figure 8. (**a**) conversion of lignin via oxidative direct electrochemical reaction and (**b**) and via indirect electrochemical reactions.

To summarise, the selection of an anode should be determined by the intended oxidation pathway and target product distribution. Direct electrochemical oxidation of lignin is very promising but is hampered by anode deactivation, poor lignin solubility and product overoxidation. Alkaline electrolytes have restricted operating windows, ionic solutions are expensive and phenolic polymerisation can clog the anode [260–264]. Moreover, important monomers can be excessively oxidised, leading to lower product yields. Product-removal techniques such as membrane separation, extraction and adsorption have been investigated, but these are still mostly at laboratory scale [232,265–267].

Indirect electrooxidation, which uses a redox mediator or electron shuttle, is an alternative to direct lignin oxidation. The mediator is electrochemically activated at the anode and then oxidises lignin in the bulk solution before being regenerated at the electrode, which completes the catalytic cycle [268,269]. By physically separating lignin from the electrode, electrode deactivation/poisoning can be decreased, and reaction selectivity can be better controlled by using well-designed mediators [270,271]. The valorisation of lignin has been investigated using other several mediator systems such as nitroxyl mediators, like TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and NHPI, (N-hydroxyphthalimide), can aid in depolymerisation by oxidising benzylic α-hydroxyl groups in β-O-4 links to carbonyl groups [268,272–274]. Lignin model compounds and native lignin can now be sequentially oxidised and fragmented using integrated systems that combine NHPI-mediated electrocatalytic oxidation with photocatalytic C-O bond cleavage [275,276]. Polyoxometalates, Fe^{3+}/Fe^{2+} redox couples, and halides are some of the other mediators that offer different methods for lignin to be oxidised and selective bonds to be broken [259,268,277,278]. When it comes to enhancing selectivity and minimising electrode deactivation, indirect electrooxidation offers a flexible technique. However, the choice of mediator and reaction conditions greatly impact its effectiveness.

4.6.2. Electrochemical Reduction

Unlike electrooxidation, cathodic electroreduction is less commonly studied yet continues to be a potential approach for lignin valorisation as shown in Figure 9a and oxidative-reductive electrochemical reaction in 9b [268]. Reductive processes often diminish oxygen levels while enhancing hydrogen content in lignin-derived products, rendering them appealing for generation of energy-rich fuels and chemicals [279–281]. Electrocatalytic hydrogenolysis (ECH) represents a significant reductive method that offers a gentler substitute for traditional hydrotreating techniques characterised by elevated temperatures and pressures [282,283].

In ECH, reactive adsorption hydrogen is produced in situ at the cathode via electrochemical reduction of protons or water, which then interacts with lignin-derived substrates, facilitating reductive bond cleavage and hydrogenation [280,284,285]. Hydrogenolysis cleaves lignin ether linkages to form phenolic monomers, but excessive hydrogenation can convert aromatics into saturated cycloalkyl compounds in ECH. Thus, cathode material and reaction conditions must be optimised for selective hydrogenolysis and aromatic product yields [202,286–288].

The selectivity of electrocatalytic hydrogenolysis (ECH) is significantly influenced by the cathode materials, which regulate the equilibrium between aromatic-ring hydrogenation and cleavage of C-O bond. Noble-metal catalysts may facilitate extensive hydrogenation of aromatic compounds, while non-noble metals, such as Ni and Cu, generally favour selective hydrogenolysis due to their moderate hydrogen-binding properties. Raney Ni has demonstrated exceptional activity in cleavage of β-O-4 ethers, whereas Cu-based cathodes are particularly advantageous in paired electrolysis systems due to their ability to prevent excessive reduction [277,287,289–294].

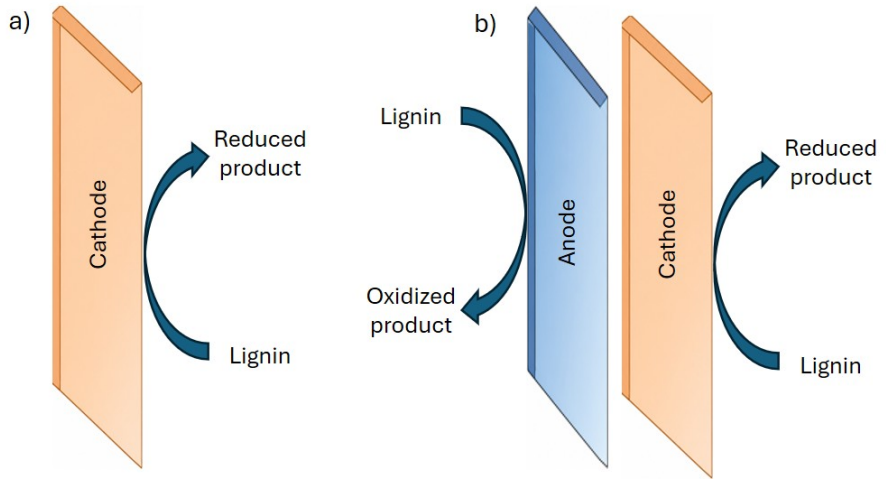


Figure 9. (**a**) Conversion of lignin via reductive electrochemical reaction and (**b**) via oxidative-reductive electrochemical reaction.

In paired electrolysis, lignin undergoes oxidative depolymerisation at the anode, yielding aromatic chemicals such vanillin and syringaldehyde, while the cathode facilitates hydrogen evolution or produces reactive species that enhance the overall reaction [268,295–298]. By combining oxidative and reductive reactions that work well together in one electrochemical process, these integrated systems can save energy and produce higher value products. Still, more work needs to be done on the catalyst to get precise control over selective ether-bond cleavage while reducing unwanted aromatic-ring hydrogenation [239].

Simultaneously, the cathode facilitates a reductive process, typically characterised by the hydrogen evolution reaction (HER), which serves either for the production of green fuels or for the generation of reactive species such as H_2O_2, which further contribute to the oxidation process [268,298]. This cohesive strategy guarantees that each electron passed through the external circuit plays a crucial role in generating a value-added product, thus enhancing both the atom economy and the economic feasibility of the biorefinery process. The examples in Table 8 were chosen to show how different cathode materials work when lignin-derived compounds are reduced and hydrogenated using electricity. Noble-metal and non-noble-metal catalysts were used to show how hydrogen adsorption works differently and how this affects the balance between selectively breaking C-O bonds and hydrogenating aromatic rings. So, the chosen substrates and reaction conditions let us compare and learn how the makeup of the cathode affects conversion and product selectivity.

Table 8. Represents the details of electrocatalytic hydrogenation of lignin derivatives.

Type of Substrate	Reaction Conditions	Major Products	Results	References
Phenol (50 mM)	Pt (2% loading) on Vulcan XC-27R, 0.05 M H_2SO_4/H-cell/60 °C	Cyclohexanol	N/A	[299]
Phenol (20 mM)	Ru/ACC, 0.2 M HCl/H-cell/80 °C/2.3 h	99% Cyclohexanol, 1%Cyclohexane	89% conversion	[300]
Guaiacol (10–20 mM)	Raney nickel/Potassium borate buffer (pH = 8)/60 °C/1 h	Cyclohexanol	<100% conversion	[288]
Phenol (20 mM)	Ni_{10}/MoO_2−@C/0.1 M H_2SO_4/H-cell/60 °C/2 h	99% Cyclohexanol, 1%Cyclohexane	N/A	[301]
Phenol (100 mM)	Pt/C-Pt/0.2 M H_2SO_4 (catholyte)/0.2 M NaCl/50 °C/2 h	74.33% Cyclohexanol, 25.67%Cyclohexane	38.95% conversion	[302]

5. Conclusions

Lignin depolymerisation continues to represent a significant challenge in the advancement of sustainable and economically feasible biorefineries. Nevertheless, the evidence presented in this review indicates that a universally optimal depolymerisation technology or catalyst for lignin valorisation does not exist. The efficacy of any conversion strategy is inherently dictated by the properties of the lignin feedstock, which are significantly shaped by its botanical origin and, importantly, its history of extraction and processing. These factors play a crucial role in determining molecular weight, distribution of functional groups, abundance and accessibility of cleavable interunit linkages, compatibility with catalysts, and ultimately the distribution of products that can be achieved.

The primary takeaway from this research is that lignin depolymerisation should not be viewed merely as an issue of catalyst selection, but rather as a challenge of aligning feedstock, structure, and method. Traditional extraction

methods, such as Kraft and soda pulping, produce lignins that are markedly different in structure and reactivity compared to organosolv or newly developed solvent-derived lignins. Thus, the appropriateness of acid-, base-, metal-catalyzed, hydrogenolytic, microwave-assisted, or electrochemical depolymerisation cannot be assessed in isolation from lignin from which the resultant compounds are derived. Characterisation is thus not solely an analytical phase but an essential condition for logical process selection.

As a result, the various depolymerisation techniques covered in this paper are best understood as supplementary tools, not alternatives. Although acid-and base-catalyzed pathways can efficiently cleave bonds, they also carry the risk of promoting condensation and non-selective reactions. Selective cleavage and stabilisation of reactive intermediates can be achieved using hydrogenolytic and metal-catalyzed methods; nevertheless, deactivation, catalyst cost, and hydrogen needs are still significant factors to be taken into account. It is important to consider scalability and energy usage when evaluating the benefits of microwave-assisted procedures, which can enhance heating efficiency and decrease reaction times. Electrochemical methods allow for a higher level of control by utilising factors like as electrolyte composition, paired electrolysis, electrode potential, catalyst and electrode design. Specifically, oxygenated aromatic compounds are best produced by oxidative electrochemistry, while ether-bond breakage and hydrogenative upgrading can be enhanced under very mild conditions by reductive electrochemical methods.

A thorough comparison between these methods necessitates a level of caution that is frequently overlooked in existing literature. Direct comparisons of reported yields are not feasible when various lignin sources, isolation methods, molecular-weight distributions, reaction scales, and product definitions are employed. High yields derived from lignin model compounds offer valuable mechanistic insights; however, these results should not be interpreted as direct indicators of performance when applied to heterogeneous technical lignins. Future research endeavours should prioritise standardised reporting of various factors, including lignin source and composition, structural characterisation, catalyst loading, reaction severity, carbon balance, product selectivity, energy consumption, and catalyst recyclability.

As a result, making progress in the future will depend on combining lignin extraction, structural characterisation, reaction engineering, catalysis, and product separation into a single biorefinery strategy. It is important to focus on making low-cost catalysts that can be recycled, better ways to separate lignin, continuous-flow and scalable reactor systems, integrated strategies for removing waste, and doing techno-economic and life-cycle studies under real-life process conditions. The change from studying model compounds to using well-known technical lignins for systematic review is also very important.

Therefore, the primary inference drawn from this review is that the problem of lignin depolymerisation should no longer be viewed solely as a catalyst-selection issue. It is a problem of harmonising the feedstock, conversion pathway, structure, catalyst and product. Structural descriptors of technical lignin are determined by the extraction history, which in turn determines the accessibility of cleavable bonds, catalyst compatibility, and achievable product selectivity.

Author Contributions

A.K.: Writing—original draft, Writing—review & editing, Data curation, Formal analysis, Methodology, Visualization. C.R.M.: Concept, Methodology, Supervision, Writing—review & editing. G.P.: Concept, Methodology, Supervision, Writing—review & editing. J.Z.: Concept, Supervision, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the author used Quillbot to improve the clarity and grammar of the manuscript. After using this tool, the author reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

Abbreviations

NMR, Nuclear magnetic resonance; FTIR, Fourier transformation infrared spectroscopy; TGA, Thermogravimetric analysis; DSC, Differential Scanning colorimetry; ILs, Ionic liquids; DES, Deep eutectic solvents; SEM, Scanning electron microscope; GPC, Gel-permeation chromatography; HL, Hydrolysis lignin; HSQC, heteroatom single quantum coherence; Tg, Glass transition; KL, Kraft lignin; SL, Soda lignin; OL, Organosolv lignin; ECH, Electrocatalytic hydrogenolysis.

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