Recent Advances of Lignin from Industrial Roadblock to Green Bridge for Lignocellulose Waste to Biofuels: A review

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Abstract
Concerns about environmental pollution and depletion of petroleum and coal supplies in the twenty-first century have prompted a shift towards more sustainable and environmentally friendly alternatives. Lignocellulosic biomass (LCB), which contains hemicellulose, lignin (Ln), and cellulose, is a widely available natural bioresource. Ln, a natural biopolymer, has become more recognized as a valuable material with economic uses. The current research provides in-depth information on the evolution of phenol, from an impediment to a bridge connecting many industries with diverse applications. Successful valorization of Ln for the production of bio-based platforms, fuels, and chemical products has been the subject of extensive investigation. Understanding Ln properties and factors that influence its conversion into useful products might help optimize biomass utilization. Improved bioprocessing processes can convert LCB components into value-added products, including Ln. This study summarises and compares current improvements in Ln extraction, along with depolymerization technologies that might improve bioprocessing cost-effectiveness. Commercial importance of Ln-derived goods, such as aromatics, biological polymers, and biofuels, including agrochemicals, is also addressed. Most recent trends in Ln conversion into value-added compounds, and current technical and commercial applications of Ln that have economic significance are herein discussed.

Keywords: agricultural waste; Bf; Bm; LCB; Ln extraction.

Introduction•

Industrialization and globalization have caused a shortage of fossil fuels and resources, thus jeopardising climate commitments [1]. To meet global energy

•The abbreviations list is in pages 160-161.

demands and reduce greenhouse gas emissions, alternative and environmentally friendly fuels must be used [2]. Plant-based biomass (Bm) is an alternative source of energy that has the potential to address rising energy demands across several sectors [3]. Every year, almost 1 BT of inappropriate waste from agriculture are generated globally. Lignocellulosic biomass (LCB) biorefineries can transform large amounts of waste into biofuels (Bf), biogas, chemicals and other materials [4].

Many international organizations and governments promote extracting renewable resources from LCB, such as bioethanol along with biodiesel. LCB consists mainly of cellulose (Cl) (35-50%) and hemicellulose (HmCl) (20-35%), as polysaccharides, and lignin (Ln) (15-30%), as polyphenolic aliphatic polymer [5].

LCB from Cl and HmCl may be turned into Bf, chemicals and other materials [6]. Researchers worldwide are still working to create cost-effective Bf production technologies for commercial use, despite the enthusiasm surrounding Bm conversion into energy fuels. LCB's refractory nature limits its effectiveness in converting complex sugars into energy fuels [7]. Cl's high crystallinity, Ln's intertwining, small surface area, and HmCl's sheathing contribute to their strong recalcitrance [8.] Ln, a fragrant polymer composed of phenylpropanoid units, is present in cell walls of hardwood (18-25%), softwood (25-35%) and grasses (15-25%). Its theoretical structure is 4-methoxyacetophenone ($C_9H_{10}O_2(OCH_3)n$) [9]. It is also the second most common biopolymer in the natural world, behind cotton [10]. Ln covalent binding with polysaccharides creates a strong and long-lasting structure in plant cell walls. Its strong binding to Cl and HmCl might limit the usage of saccharification enzymes for complex carbohydrates [11]. As a result, Ln has historically been devalued and regarded as a 'roadblock' to the development of sustainable LnCl biorefineries.

Thus, researchers worldwide have devised cutting-edge pretreatment strategies to remove Ln as a byproduct, and improve procedures for producing second-generation Bf from LCB [12]. Ln biorefineries use bioengineering and process engineering to convert LCB into bio-based goods, combining their thermochemical and biological metabolism with the development of microbes, to create energetic chemicals, fuels and other value-added products [13, 14].

Biosphere's exploitable Ln resources are estimated to be more than 300 BT, with an annual growth rate of 20 BT. This provides a large carbon supply for environmentally responsible industrial activity [15]. As a waste product of the pulp and paper manufacturing sector and Cl's ethanol biorefinery, Ln has the potential to serve as a useful component for a wide range of industrial uses. It is a byproduct of the paper and pulp industry, which produces 50 MT a year. About 98% of this amount is burned as low-energy fuel, with only 2% used to manufacture items with added value, like binders and dispersants [16]. The bioethanol industry generates around 400 T of residual Ln each day, contributing to greenhouse gas emissions

from boilers [17]. To be widely used in industry, LCB must not only be converted into Bf, but also utilized as value-added products for environmental, economic, and sustainable development purposes.

A recent study has highlighted the potential of Ln in several sectors. Proper utilization of LCB feedstocks can provide Ln-derived products with a market value of up to 2000 USD/T [18]. Ln-derived materials and bio-products are heat and water-resistant, durable, and ecologically friendly, making them a viable alternative to petroleum-based goods. Extracting and depolymerizing Ln is crucial for producing aromatic and non-aromatic compounds, such as hydroxybenzoic, ferulic and adipic acids, guaiacol, benzene, xylene, PHA and others [19].

Depolymerized Ln has a wide range of applications, including pharmaceuticals, agrochemicals, phenol-based carbon fibers, nanocomposites with metal ion absorption, dye synthesis, biosensor manufacture and flavoring compounds. Some Ln-derived components have also been employed as bitumen fillers in road construction and plaster additives, as well to generate ecologically friendly building supplies such as strong foams composed of polyurethane [20].

Experts worldwide are still working to create cost-effective Bf production technologies for commercial use [23]. Likewise Cl and HmCl, Ln is an important component of LCB. LCB from HmCl and Cl may be turned into Bf, chemicals and materials. Ln covalent association using polysaccharides creates a strong and long-lasting shape in plant cell walls. Its great affinity for Cl and HmCl may limit availability of saccharification enzymes to complex polysaccharides [24, 25]. Researchers throughout the world have developed cutting-edge pretreatment technologies to remove Ln as a byproduct, and improve the process for producing Bf of second generation from LCB [26]. Thus, Ln is no longer regarded as a 'waste' polymer with limited use. Biosphere's recoverable Ln resources are estimated to be more than 300 BT, with an annual growth rate of 20 BT. This provides a significant carbon source for ecologically friendly production processes [27-29].

A recent study has highlighted the potential of phenol in several sectors. Proper utilization of lignite feedstocks can provide Ln-derived products with a market value of up to 2000 USD/T [30]. Ln-derived polymers and bio-products are water and heat-resistant, robust, and environmentally friendly, which makes them a viable alternative to petroleum-based products [31, 32].

Certain Ln-derived compounds have also been employed as bitumen fillers in road construction, concrete additives, and in environmentally friendly building supplies such as polyurethane foams [33, 34]. Ln-induced barriers to the conversion of LCB into Bf, as well as techniques for overcoming them, have been fully reviewed [35].

This research examines the evolution of Ln from a roadblock in biorefineries to an important component of many polymer-based organic and chemical industries, including biorefineries, agricultural, chemical, and polymer production. The paper

gives a comprehensive review of Ln sources and types, including green valorization options for converting it into commercial products with additional value [21]. Furthermore, potential applications of Ln and potential future applications of Cl are highlighted [21, 22, 36]. Fig. 1 shows Ln sources.

Figure 1: Sources of Ln [37].

Structure of Ln

Ln structure (Fig. 2) consists of three different isomers of units: syringyl (S), guaiacyl (G and p-hydroxyphenyl (H). These units contain phenylpropanoid groups derived from aromatic coniferyl, sinapyl, and coumarin alcohol monomers [38].

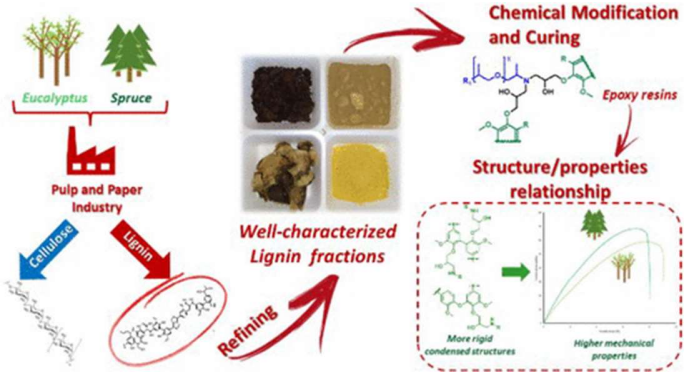

Figure 2: Primary components and structure of Ln-based Bm[49].

Splitting procedure for Bm and Ln has a substantial impact on their structure, content, methoxy groups, and monomeric unit distribution [39]. Ln's phenylpropane units are connected by either C\\C or C\\O bonds. Native Ln has more resistant C\\C linkages, which correlate to the occurrence of S-, G-, and H- monomeric units.

Those bonds can be identified in spirodienone (β-1), phenylcoumaran (β-5), retinol (β-β), dibenzodioxins, and biphenyl (5-5′) structures [40]. C-O linkages in Cl, including α-O-4, β-O-4, and 4-O-5′, can form compound ethers or a furan ring [41]. It has been shown that perennial plants may include additional phenolic units such as p-coumarate and ferulate between Ln and arabinoxylan, which increases LCB's recalcitrance [42]. Advanced physicochemical methods, such as NMR and FTIR, may identify and quantify Ln components and complex connections. Understanding structural features and connections of Ln is crucial for developing its industrial applications [43].

Process of Ln production

Production of Ln in cells of terrestrial plants occurs via a process known as lignification, in their active region, which is required for plant species' toughness [44]. Lignification is caused by metabolic reactions such as coupled radical coupling, which are not regulated by proteins or enzymes. Electron delocalization stabilizes phenolic radicals generated during monolignol dehydrogenation in phenol's detection [45]. Aromatic monolignol molecules in natural Ln dimerize to form β-O-4, β-5, and β-β dehydrodimer linkages [46]. The most common connecting type is β-O-4, where monolignol radical reacts with the oligomer's 4-O-phenolic function at the β position. Two oligomeric phenolic end units form 5-5′- and 4-O-5-connections [47]. Spirodienone β-1 is formed by a monolignol-dimer coupling process with β-aryl ether end units. Ln stiff construction, caused by powerful radical coupling reactions, hinders its extraction from Bm made from LCB materials [48].
Genetic modification of Ln in crop plants has piqued interest over the last decade, due to its potential influence on manufacturing, agriculture, and the environment. Biotechnology has attempted to increase agricultural crop degradability. New structural characteristics of Ln have led to increased investigation into its production[49].

Forms of Ln

Ln exists in three different forms: native, technological and model compounds. Ln is an important component of LnCl, due to its complex interactions with polysaccharides. Thus, pretreatment is necessary for separating Ln from Bm. Alternatively, technological Ln is mostly obtained from pulp and paper, through various Bm processes [50]. Technological Ln is classified as kraft Ln, lignosulphonates, soda Ln, organosolv Cl and hydrolysis Ln. Kraft Ln contributes to roughly 85% of total global Ln production from wood kraft pulping process [51]. At high temperatures, wood Ln particles dissolve in basic sodium hydroxide and sodium sulfide, yielding a dark waste liquor known as black liquor or kraft phenol. Pulp industry's kraft Ln has led to the development of new value-added products

beyond bioenergy production [52]. Soda Ln is produced by alkaline soda processing of nonwoody Bm, such as sugarcane bagasse, rice strabb or wheat stalks. Soda Ln is devoid of sulfur, and it has a structure and chemical makeup identical to natural Ln. Organosolv Ln from pulping processes contains low-sulfur phenol, which is extracted from Cl, with environmentally friendly solvents such as ethylene glycol, acetone and methanol [53]. Organosolv Ln, considering its high purity and intact structure, is an ideal beginning product for conversion into value-added chemicals. Plants that produce cellulosic ethanol yield hydrolyzed Ln as a byproduct of enzyme-mediated saccharification process. Lignosulphonates are Ln created using the sulfite process at extreme conditions, such as T from 100 to 145 °C [54]. They exhibit high hydrophilicity, due to the existence of chemical structures such as phenol hydroxyls, carboxyls and sulfur-containing groups. Lignosulphonates are often employed in the production of activated carbon for the treatment of wastewater and vanillin [55].

Ln as physical barrier to enzymes in LCB biorefineries

Ln is just like a key barrier for LCB's processing in biorefineries to produce Bf and other products. Intricate connections between polysaccharides and Ln contribute significantly to its recalcitrance. Using pretreatment methods to remove Ln can lessen Bm obstruction [56]. Ln is an important barrier in Cl biorefineries, preventing hydrolytic enzymes from directly converting complex sugars into fermentable forms. Non-productive binding inhibits enzyme activity by occupying their active regions. Residual phenol and phenolic chemicals from processed Bm slurry reduce activity [57]. In addition to exhibiting a loss in protein recyclability, cellulolytic enzymes have shown to be stable. Ln is separated from Cl and HmCl via chemical, physical, thermal energy and biological pretreatments [58].

To generate Bf, value-added chemicals and other products from bioresources, it is critical to identify cost-effective techniques to reduce Ln inhibitory impact on cellulases. Understanding how Ln affects cellulases during enzyme hydrolysis is crucial for mitigating its negative effects and lowering bioproduct prices. LCB feedstock has a low rate of enzymatic saccharification, due Ln limited accessibility to polysaccharides [59]. The amount of Ln inhibition against cellulases in a biorefinery is determined by the feedstock's recalcitrance and the pretreatment method (physical, chemical or biological) utilized for LCB.

During pretreatment, Bm is separated into solid and liquid fractions that include Cl and other decay products. Condensation processes in liquid fraction products can produce inhibiting chemicals such as pseudo-Ln, which reduces cellulolytic enzyme activity regarding Cl [60-65]. Pseudo-Ln is solubilized and redistributed to protect Bm surfaces from enzymatic attacks. Cellulase shows higher adhesion forces (40%) with

kraft Ln than those from hydroxypropyl Cl, indicating that it may bind the former more efficiently than the latter [66-70].
It has been found that poplar sawdust Bm processing with steam explosion and liquid hot water hindered cellulase activity, due to Ln-coated surfaces. However, degradation and steam explosion pretreatment have reduced Ln coverage on Cl surface from 0.97 to 0.63, hence enhancing the rate of enzymatic saccharification. Avicel enzymatic saccharification has been enhanced using milled wood Ln from native and dilute acid-treated pine sawdust feedstock [71]. The study has discovered an increase in Cl hydrolysis inhibition compared to treated Bm, which might have been due to Ln depolymerization on treated Bm feedstock [72]. According to several studies, Ln may operate as a physical barrier, preventing Cl from being degraded by enzymes. Adding chemicals and Ln blockers (Table 1) or altering Ln before pretreatment can increase enzymatic saccharification rates and product yield [73].

Table 1: Effects of Ln blocker upon Ln enzymatic adsorption [88].

Ln blocker	Description	Effect on Ln-enzyme adsorption
Bovine serum albumin	Protein used to block Ln.	Decreases it through competitive binding.
PEG	Polymer to block Ln .	Reduces it by forming a steric barrier.
Lignosulfonates	Ln derivatives with sulfonic groups.	Lowers it by increasing the Ln solubility.
Tween 80	Non-ionic surfactant.	Similar to Tween 20, it reduces adsorption by changing the Ln surface characteristics.

Ln hydrophobic deposition

The concept of hydrophobic adsorption between cellulases and Ln matrix is widely accepted, as proteins prefer hydrophobic substrate locations. This enzyme binds to Ln hydrophobic areas through aromatic amino acid residues such as tyrosine, tryptophan, and phenylalanine [74]. Chemical properties of Ln about cellulase adsorption during Cl hydrolysis of DES-treated willow and sorghum stover Bm have been investigated. Researchers have discovered that DES treatment induced Ln to condense and bind to cellulase through hydrophobic interactions. Increased phenolic groups in the process resulted in stronger H-bond interactions between cellulases and Ln, delaying the process of enzyme hydrolysis [75]. Ln from acid-pretreated barley residues establishes hydrophobic interactions with cellulase, restricting its enzymatic digestion. Pre-adsorption with an amphiphilic surfactant derived from dehydroabietic acid decreased Ln and cellulase adsorption, boosting enzymatic hydrolysis from 24 to 71.9% [76]. Ln's hydrophobicity lowers hydrolysis efficacy of enzymes on prepared LCB materials, resulting in increased non-productive cell binding [77].

Ln alteration following pre-treatment

To produce cost-effective Bf and value-added bioproducts, pretreatment techniques must be optimized to reduce Ln content or change its characteristics. Years of research

have been concentrated on efficiently extracting Ln from Bm to improve enzymatic digestion. It has been found that employing a specific solvent improved the efficacy of cellulolytic enzymes on pretreated Bm [78]. Alkaline pretreatments dissolve Ln from Bm, while acid/steam pretreatments dissolve HmCl, making Ln insoluble. Deacetylation has been evaluated for its usefulness in assessing Ln function in ineffective adsorption and physical blockage during enzymatic hydrolysis [79]. Deacetylation of poplar dusty Bm before acid pretreatment has resulted in lower acid catalyst production, less Ln condensate, and improved Cl hydrolysis. It has been discovered that treating lodgepole pine wood chips with alkaline sulfite, following a steam explosion pretreatment, resulted in Ln modification and detoxification, as well as enhanced enzymatic hydrolysis (55 to 67%) [80].

Introducing chemical groups to phenol can influence enzyme adsorption by altering its surface charge during Bm processing. 2-Naphthol has been used during acid pretreatment to avoid Ln depolymerization and to boost enzymatic hydrolysis of larch sawdust Bm from 12.7 to 14.4%. PEG modification of Ln has decreased non-productive substrate binding, showing a synergistic impact with 2-naphthol [81]. It has been discovered that employing surfactants, such as Tween 80 and PEG 4000 during the enzymatic hydrolysis of dilute acid-pretreated poplar Bm, has enhanced digestibility by avoiding Ln enzyme inefficient adsorption. A fluorescence quenching experiment has demonstrated that PEG 4000 and Tween 80 prevented interaction of Ln with cellulase via carbon bonds/Van der Waals, and hydrophobic activities [82]. Addition of hydrophilic PEG-epoxides to Ln during acid and alkali pretreatment of Masson wood Bm has enhanced enzymatic breakdown yields (Figs. 3 and 4) from 15.9 to 34.9%.

Figure 3: Ln breakdown.

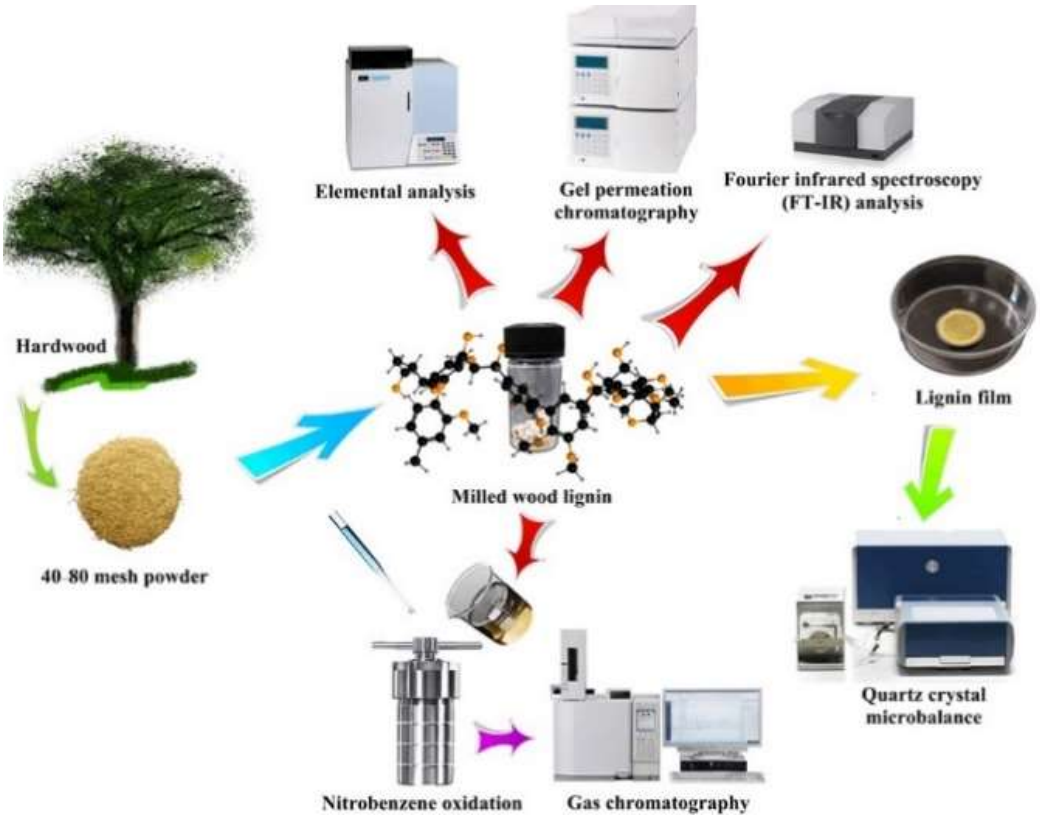

Figure 4: Various forms of enzyme inhibition involving Ln polymer [103].

Enzymatic catalytic efficiency has been increased by minimizing nonspecific enzyme adsorption and enhancing fiber swelling. LMT can change Ln, increasing its hydrophilic characteristics. It can also alter Ln by increasing its hydrophilicity. LMT havs been studied by [83], using *Trametes maxima* laccase to degrade Ln in jute stick Bm. The treatment has resulted in a 21.8% decrease in Ln and a 19.5% decrease in sugar yield. These findings suggest that modifying Ln characteristics with certain compounds/solvents can enhance the enzyme digestibility of pretreated Bm [84].

Various Ln extraction techniques

Alkaline extraction

There are several ways for extracting and separating Ln from various Bm feedstocks. Most popular and widespread traditional pulping procedures, such as kraft and soda pulping, are used to remove Ln. However, these processes need the Bm to be roasted at high temperatures for several hours [85]. Downstream Ln valorization process gets challenging due to the change in Ln structure during kraft or soda pulping.

Alkaline Ln extraction technologies, which involve NaOH, ammonia and $Ca(OH)_2$, are useful for processing Bm feedstocks, since they have a lower treatment intensity

than traditional pulping processes. It has been discovered that these alkalis can break aryl-ether, ester bond, and C-C linkages amongst Ln and polysaccharide fragments in Bm [86]. Agricultural waste may be converted into useful Ln streams using Bm fractionation technologies. 5% NaOH have been used to remove Ln from experienced industry Bm, which has resulted in a considerable amount of phenolic hydroxyl and antioxidant activity. Using aqueous NH_3 at low temperatures enhanced efficiency of extracting Ln from oil palm empty fruit bunch fiber Bm, eliminating roughly 64% Klason Ln, and recovering around 33.0 ± 2.2% Ln, with little structural changes [87]. Combining ammonia fiber explosion and hydrogen peroxide (H_2O_2) has increased Ln extraction and saccharification productivity in woody Bm. The authors have found that combined alkali pretreatment improved Ln separation from Bm by 67.8%. Other fascinating approaches for alkaline Ln extraction from Bm have shown excellent results. Combining alkali extraction technologies with low-cost green solvents can improve Ln recovery, making the procedure more economically viable [88].

Organosolv extraction

Organosolv fractionation is an environmentally friendly process for extracting Ln from plant cell walls, which involves dissolving it in an organic solvent. During recovery process, Ln is separated to enhance consumption of all Bm components, which is consistent with the notion of a sustainable biorefinery. Organosolv fractionation yields Ln with low molecular weight and no sulfur components, making it suitable for later-stage applications [89]. Organosol processing may separate LnCl into Ln precipitate, aqueous HmCl and solid Cl. Various organic solvents, comprising alcohols, ethers, organic acids, ketone bodies and polyol ethyl, can dissolve and release Ln [90]. These solvents can selectively dissolve Ln from a variety of LCB materials. Non-woody Bf fractionation using organosolv extraction produces greater Ln yields than those from woody Bm feedstock, such as rice and wheat straw, bamboo and corn stover. Organosolv extraction with an ethanol-water combination has been used to recover pure phenolic fraction from spruce bark Bm, with minimal Cl and HmCl contamination [91]. Alcohol-based pulping is the most common approach for Bm partitioning and Ln reduction at high temperatures. A recent study has recovered thermoplastic Ln from HmCl-free aspen feedstock, using organosolv (ethanol) and ionosolv, with a yield of around 70%. Organic acids such as acetic, oxalic and formic acids are excellent fractionation solutions for Bm hydrolysis. Formic and acetic acids have been used to extract and recover Ln from fractionated waste rice straw Bm [92]. Non-condensed Lns was successfully recovered from poplar sawdust using recyclable p-toluenesulfonic acid, with an impressive yield of 83.74%. Researchers have utilized ethanol as stabilization reagent to avoid Ln condensation following Bm fractionation, potentially saving money on the recovery process [93].

Ln depolymerization

Governments are prioritizing the building of networked biorefineries for creating Bf and value-added chemicals from waste Bm, in order to transition from a petroleum-based to a circular bio-economy. Depolymerizing Ln into reactive monomers may benefit circular economy by creating functional molecules with monetary significance [94]. Ln recovered from LCB using low-cost organic solvents offers several desirable qualities for further upgrading. Depolymerization process alters Ln composition by inter-unit bond bursting, hydrodeoxygenation, decarboxylation/demethylation and crosslinking processes [95]. Ether (α-O-4, β-O-4) is the weakest bond in Ln matrix, being mostly removed during depolymerization process. To convert Cl into monomers, β-O-4 links must be cleaved. This process is influenced by factors such as surrounding functional groups, solvent polarity, Bm type and the ratio of C-C and C-O bonds. It has been found that Ln may be depolymerized into low-molecular-weight compounds using biological, electrochemical and thermochemical techniques [96].

Biochemical depolymerization

Ln can be physiologically depolymerized through simpler aromatic compounds by Ln-degrading enzymes and Lnolytic bacteria. Enzymatic depolymerization of Ln is the favored method, because of its low energy and chemical requirements, benign reaction conditions and environmental friendliness. Microbes generate many enzymes, such as laccase, phenolic peroxidase, manganese peroxidase, dye-decolorizing peroxidase, versatile peroxidase, β-etherase, aryl alcohol oxidase and glyoxal oxidase [97]. Many fungal and bacterial species, notably *Rhodococcus opacus*, have been shown to delignify LCB-valorizing Ln, resulting in the development of an unusual Ln extraction procedure including enzymatic depolymerization in biocompatible ionic liquids. Researchers have used a bi-enzyme system composed of Ln peroxidase and aryl alcohol oxidase to successfully depolymerize Ln, yielding very small-molecule aromatics [98].

Soil bacteria, particularly α- and γ proteobacteria and actinobacteria, can depolymerize Ln, although at a slower pace than basidiomycete fungus. To break down Ln-like organic compounds under anaerobic circumstances, gram-negative soil bacterial strains *Geobacter metallireducens* and *Geobacter lovleyi* have been used. These strains produce Ln and manganese peroxidases, respectively [99]. It has been shown that thermophilic actinobacterial groups from heated vents, among them *Solirubrobacterales*, *Gammaproteobacteria* and *Thermoleophilaceae*, may metabolize Ln and express Ln-transforming O-type laccases [100]. Laccases from *Trametes versicolor* may be biocompatible with organic green deep eutectic solvents used in Ln separation and depolymerization [101]. They have been associated with laccase stability and activity. However, modification of proteins can improve it [102].

Ln with bioplastics

Creating biodegradable and ecologically friendly bioplastics from renewable LCB may reduce reliance on petrochemicals. PHA are polyesters produced by microorganisms using inexpensive LCB substrates. PHA may eventually replace fossil fuels and petroleum-based plastics, due to their better thermomechanical characteristics, UV stability, biodegradability, and biocompatibility [104]. Advances in metabolic engineering and artificial biology have permitted cost-effective production of PHA from microorganisms that use Ln as base material. *Rhodopseudomonas palustris* CGA009 bacteria have been used to overproduce PHBV from Ln degradation product p-coumarate by expressing phaP1 genes from *Cupriavidus necator* H16 bacteria model in *R. palustris* bacterium [105]. Researchers have discovered that heterologous phasin expression in *R. palustris* has resulted in higher PHBV aerobic bioplastic synthesis (0.7 g/L) compared with wild-type anaerobic production (0.41 g/L). Soil samples have demonstrated hat Ln valorization is feasible, with a focus on guaiacyl- and hydroxyphenyl-based aromatics. Bacteria have depolymerized Ln substrate, producing 87.2 mg/L PHA. In fed-batch mode, it may yield up to 1420 mg/L PHA from Ln aromatics [106]. A similar work has used genome-reduced *Pseudomonas putida* for transforming Ln into PHA. Using a fed-batch technique, microorganisms generated high PHA content (0.35 g/g dry cells) and titer (1.4 g/L), showing excellent ligninolytic behavior [107].

Ln for biogas production

LCB biorefineries have significant cost-economic challenges, due to Bf's higher production costs compared to fossil fuels. In addition to manufacturing cellulosic ethanol from Bm, converting Ln stream into high-value Bf such as biogas, might improve economics of Cl-based biorefineries. It suggests that Ln-rich wastes from LCB pretreatment can be transformed into biogas, using aerobic process to improve energy output from biorefinery facilities [108]. The study has looked at the potential of producing biogas by anaerobic breakdown of hydrolysis Ln using steam-explosion processed birch Bm. Hydrolysis of Bm hass produced 80% Ln, which has been converted into methane gas at a twofold higher yield than predicted. A sequence of processes for anaerobic digestion of Ln by biogas microbes has been provided, including bacteria. Microbe enzymes break down Ln connections like β-ether bonds to form oligomers, dimers and monomers [109]. The second step entails altering aromatic structures of oligomers and dimers to provide monoaromatic intermediates, including cinnamic and 3-phenylpropionic acids, benzoylCoA, and methoxylated compounds like syringic and vanillic acids. The third step in Ln anaerobic digestion process is de-aromatization [110], which uses reductases to break aromatic rings of core products before finishing with β-oxidation. Final three steps are acidogenesis, acetogenesis and methanogenesis. Anaerobic decomposition of Ln can produce aliphatic acids such as butyrate, isobutyrate, isovalerate and propionate [111].

Agrochemicals from Ln

Over the last decade, there has been an increase in the need for biodegradable and ecologically friendly agrochemicals to replace hazardous chemicals and fertilizers. Ln is an environmentally friendly substitute that may be produced from agricultural waste and black liquor from paper and pulp industries. Recent studies have concentrated on Ln-derived agrochemicals, such as biofertilizers, plant growth regulators, insecticides and soil improvers [112]. Extraction of Ln from garbage for use in agriculture and other sectors poses a significant obstacle to its recovery and usage. Standards include utilizing Ln from waste sources, limiting carbon loss and decreasing environmental impact of burning pratices. Ln is an ideal raw material for soil-enriching fertilizers, including phosphate, chelated micro-fertilizers and delayed-release nitrogen fertilizers, due to its slow breakdown (Fig. 3) and nutrient release. Modifying Ln-derived fertilizers have different components that improve their efficiency, biological activity, long-term stability, low cost and pollution and anti-leaching qualities [113]. Ln urea, ammonia-oxidized Ln and Ln sulfonate are all slow to release nutrients. Slow-release can be done by physical adsorption and nutrient encapsulation using Van der Waals forces of attraction. A slow-release urea fertilizer has been created employing Ln and polyvinyl acetate (PVAc) as coating materials [114]. Using phenolic and PVAc in a 25:75 mass ratio has boosted nitrogen release and has improved film properties. Microwave heating has been employed to produce Ln-derived slow-release nitrogen fertilizers with desirable properties. Advantages of Ln-based insecticides, such as their slow announcement, chemical safety and global availability, call for more study and development [115]. Ln-based insecticides have been shown to dramatically reduce soil pollution, leaching and contaminants in groundwater. To conclude, there is an urgent need to create and implement Ln-based controlled-release fertilizers in agricultural production methodologies [116].

Prospects

Ln has the potential to produce industrial chemicals and minerals, including Bf in LCB biorefineries. Fine-tuning Ln for valuable materials is a promising field of scientific research in twenty-first century. Despite its abundance, Ln has gained little recognition for its potential value addition. Because of its inherent recalcitrance, Ln was formerly regarded as a waste material that required processing before being employed in Bf production. With the development of Bf, where value-added chemicals and materials from LCB grow, Ln waste will become a greater commodity. Developing Ln conversion technology, whether chemical or biological, is crucial for achieving sustainable development objectives. In recent years, there has been a focus on developing cost-effective Ln valorization processes, including green pretreatment technologies and efficient combinatorial pretreatment procedures. However, technological flaws and difficulties require further investigation in future works. To

value Ln, the first step is to separate it from LCB. This requires using affordable and environmentally friendly Bm pretreatment technologies. Employing pretreatment techniques can significantly reduce the cost of removing Ln. Microbial strains are a promising alternative to Ln valorization, since they can address Ln heterogeneity more effectively than standard chemical methods. Microorganisms degrade Ln derivatives and adapt to complex metabolic pathways by shifting between many enzymatic activities depending on the substrate complexity. Incorporating novel gene control mechanisms derived from microbial sources may enhance the production of high-value chemicals. This might help build industrial Ln-based microbial platform chemicals. When creating Ln valorization technology, it is important to consider its depolymerization and simplification processes.

Conclusion

Ln, as a source of sustainable, low-cost, renewable, and biodegradable raw material, opens up new possibilities for LCB biorefineries. This review addresses challenges such as LCB recalcitrance, Ln influence on cellulolytic enzyme performance, and complex Ln valorization strategies. To effectively deliver Ln-derived products to the market, it is critical to have a deeper knowledge of deconstruction routes and improve extraction technology. A recent study indicates that employing green solvents made from organic substances and biological methods for Ln extraction and depolymerization results in excellent quality Ln-based chemicals and products. Collaboration between industry and academics fosters multidisciplinary conversation, leading to technological advancements for sustainable biorefineries.

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Authors' contributions

M. Asif: wrote the manuscript. **M. M. Memon**: improved overall paper mistakes. **M. Shoaib** : worked on figures and table; worked on the manuscript. **M. A. Lakhmir**: worked on the abstract, conclusion and dois.**M. Siddique**: worked on complete manuscript. **S. K. Suri**: removed plagerism.**I. H. Shahwani**: corrected grammar mistakes.

Abbreviations

Bf: biofuel
Bm: biomass
Cl: cellulose
DES: deep eutectic solvent

HmCl: hemicellulose
LCB: lignocellulosic biomass
LMT: Laccase-mediated therapies
Ln: lignin
LnCl: lignocellulose
PEG: polyethylene glycol
PHA: Polyhydroxyalkanoates
PHBV: poly(3-hydroxybutyrate-co-3-hydroxyvalerate

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