Review:

Recent Advancement and Emerging Applications of Lignin

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Abstract: *Lignin is a significant renewable natural energy resource these days, used as an environmentally acceptable and sustainable alternative fossil fuel feedstock in a huge possibility of value-added products. Lignin is a polymeric molecule that possesses an aromatic unit structure, together with cellulose, and is a main component of the cell walls of plants. It is the byproduct of agriculture residues and biorefinery products and can be extracted from paper-pulp industries. Properties of lignin may differ depending on the extraction method and source and also on an aromatic ring as the main constituent of lignin in the structure. This rare composition of lignin makes it more valuable, allowing for value-added applications such as in the field of storage devices and energy harvesters. This review focuses on derivatives of lignin, structure and composition sources and characteristics, and its sustainable emerging application in various fields are discussed.*

Keywords: *lignin-biopolymer; biofuel; renewable energy; sensors*

■ INTRODUCTION

Utilization of alternate energy sources, such as renewable energy, is the best way out due to the world's increasing energy demand. Renewable energy sources are divided into many categories. However, biomass is the always widely available source of renewable energy worldwide [1]. The biorefinery techniques that convert indigestible biomass into biofuel must be upgraded to flourish sustainably. In this line of research, lignocellulose biomass, composed of lignin, hemicellulose, and cellulose, is a promising context for the production of biofuel [2].

Lignocellulosic biomass is a commonly available, indigestible biomass resource that will be renewed globally in considerable quantity every year. However, the maximum of the biorefinery processes at present concentrates on the utilization of cellulose material (carbohydrate fractions), leaving lignin, which is the subsequent most profuse terrestrial polymer, underutilized. Therefore, resourceful valorization and utilization of lignin in biofuel as a value-added product is mandatory for the industry scale [3]. Lignocellulosic biomass is found in the range of 45% by energy and 15–30% by dry weight as the only large-volume renewable bioresource.

Lignin has greater density, which makes it a promising candidate for biofuel and aromatic production, for example phenol, benzene, and toluene [4]. Only some of the efforts can be profitable commercially due to the low yield and quality of the final product, even though thorough studies have focused on the conversion of lignin into value-added products, mainly complexity and obstinacy in the lignin's structure attributed to the difficulties in the vaporization process of lignin and degradation of lignin fraction with many condensation reactions. In addition, the desired products of lignin are associated with several problems, such as fractionation, characterization of lignin derivatives, product upgrading, and depolymerization. A good fractionation method must be needed for the attainment of high purity and yield of lignin. The final structure of lignin and its isolation efficiency can be affected by different factors, which include resources of biomass and method of fractionation [5]. The characterization is quite difficult for native lignin due to its heterogeneous and irregular structure. Meanwhile, due to the high molecular weight of the lignin and for the transformation into fuel of chemical compounds, the depolymerization step is usually mandatory [6]. Henceforth, the direct production of lignin compounds is challenging due to its heterogeneous and irregular structure. To handle the complex nature of native lignin, advanced processes are needed. In recent years, to deal with this problem, extensive research has been done to use lignin in biorefinery or as biofuel. This article intends to give an instantaneous of recent research on the current applications of lignin to products having valuable efficiency. Challenges, prospects, and opportunities are also presented.

■ DERIVATIVES OF LIGNIN

Lignocellulosic material derivative from natural biomass comprises three elementary components: approximately 5–30% lignin, 35–50% cellulose, and 20–35% hemicellulose by weight [7]. After cellulose, lignin is considered the second most abundant naturally occurring substance [8-10]. It is calculated that the total amount of 20% biomass is lignin, though it depends on the extraction process [11]. Lignin derivatives can be used to get high-value-added products such as synthesis gas, phenolic compounds, oxidized products, various hydrocarbons, and biofuels [12]. Lignin quantifies as a unique natural resource due to its numerous properties such as biodegradability, structure integrity, antimicrobial and antioxidant behavior, abundance, enzymatic stability, resistance to UV/fire, hydrophobic/hydrophilic properties, which depend upon the lignin's source [13]. In addition, as compared to cellulose and hemicellulose, lignin possesses excellent physiochemical properties, rheological behavior, and good compatibility [14-16]. Utilization of lignin at an industrial scale is still difficult, despite the said excellent properties primarily due to its delicate structure and chemical reactivity [17-19]. Lignin is classified into several categories depending mainly on its isolation method. The most general type of lignin is Kraft lignin, lignosulphonate lignin, soda lignin, organoslov lignin, isolated lignin, and degraded lignin [20].

■ STRUCTURE AND COMPOSITION OF LIGNIN

Lignin is considered the second most abundant polymer in the group of lignocellulosic materials. Lignin is found in the cells of the plant, which can form the secondary cell wall. The major role of lignin is to provide a diffusion barrier in the plant's roots and to provide mechanical strength. A complex heteropolymer lignin consists of three standard monomers: (i) *p*-coumarin (H), (ii) coniferyl (G), and (iii) sinapyl (S) monomers. Different degrees of methoxylation of the aromatic ring at the ortho, meta, and para positions, respectively, are given differently with all these monomers of lignin. In the biosynthesis of lignin, phenylalanine is found to be an important substrate. Mainly, the structure and composition of lignin depend upon (i) monomer accessibility and (ii) bond formation during the polymerization process. Also, the availability of monomer is responsible for the formation of condensed and no condensed bonds and reactive ends present in the lignin. In general, the synthesis procedure of lignin uses several enzymes and transporters. Phenol oxidases have been used for the determination of the composition of the polymer [21]. The monomer the native structure of the polymer is completely broken down into respective monomers during the compositional and structural analysis. For the compositional analysis of lignin, destructive methods like oxidation, and reduction, hydrolysis are employed. Several techniques have been utilized for the characterization of end products, such as proton-nuclear magnetic resonance spectroscopy (^{1}H-NMR), mass spectroscopy, and gas chromatography [22]. The solubilization and quantification of lignin at a specific absorbance value (280 nm) for acetyl bromide and thioglycolic acid are significantly used. The thermal gravimetric analysis (TGA) method has been used for the formation of benzyl–OH groups as thioesters in the lignin for the solubilization of lignin in an alkali. For the formation of acetyl derivatives in non-substituted –OH groups, the acetyl bromide (ACBR) method is used to complete the solubilization of lignin in acidic reactions. Klason lignin method, a gravimetric assay, has been used to quantify the amount of lignin.

NMR spectroscopy is another non-destructive technique for the analysis of lignin structure. The biosynthesized chemistry of lignin is identified by this analytical method. Pyrolysis molecular beam mass spectrometry (py-MBMS) is a fast characterization technique that deals with the heating of lignin samples at very high temperatures (500 °C) and in an inert atmosphere. In this way, the chemical structure of lignin is retained so that it is easy to analyze the complex molecular structure present in lignin.

Characteristics and Sources of Lignin

The approximate production of lignin annually occurs within a window of $5–36 \times 10^8$ tons, generated through photosynthesis. It is found in woody plants such as angiosperms and gymnosperms (about 15–40%), herbs (15%), and also in a very small amount in annual plants [23-24]. Lignin is chemically linked to several polysaccharides and is a major essential of cell walls in plants. For example, lignin is linked with hemicellulose via covalent bonds in the case of spruce wood, and a small part is attached to the cellulose.

For the separation of lignin from a variety of biomass, mechanical disintegration is required which result from inhomogeneity at the macromolecular structure level and isolation of lignin may be achieved. Based on the current knowledge of lignin structure, comprehensive milling of the material and solvent extraction with the help of dioxane followed by purification will give a low reasonable yield with some chances of carbohydrate impurities [25-26].

There are more voids in computing a precise understanding of the macromolecular and structural characteristics of the product due to insufficient information being present regarding the fundamental analysis and characterization of lignin. Many advancements have been made in modern analytical techniques, which help in elucidating the other types of lignin, like native lignin, and changes in the structure of lignin during kraft pulping, organosolv, and sulfite pulping. It has been reported that the content of sulfur in lignosulphonates is around 4–8% [27]. Generally, sulfur exists in the form of sulphonate in lignin; thus, they show their solubility characteristics in water and organic solvents. The molecular weight, processing, and purity of lignosulphonates mainly depend upon the quantity of other functional groups in lignosulphonates, such as aromatic hydroxyl, aliphatic hydroxyl, and carbonyl.

Biofuel Conversion of Lignin

Lignocellulosic biomass is a potential candidate to be a valuable resource for the manufacture of biofuels. However, the presence of lignin hindered the conversion of biomass into useful products [28]. Lignin is a complex polymer that is difficult to degrade; it needs to be modified and pre-treated before it can be used for the production of biofuel production. For the improvement in the biofuel conversion from lignocellulosic biomass, modification and pre-treatment is mandatory. The digestibility of lignocellulosic biomass by breaking down the complex polymeric structure of lignin, thus allowing the release of valuable compounds by the pre-treatment procedure of lignin [29].

The treatment of lignin involves the use of acids and bases to break down the structure of lignin; enzymatic, alkaline, and acidic hydrolysis techniques are used. Enzymatic hydrolysis involves the use of enzymes for the degradation of lignin [30]. For the conversion of lignocellulosic biomass into useful products, pre-treatment can have a significant impact on the economics of biofuel production and is also helpful for improving the efficiency of biofuel. The cost of pre-treatment is directly related to the amount of lignocellulosic biomass that needs to be converted. Additionally, to maximize the biofuel production from lignocellulosic biomass, it is necessary to understand the different strategies of pre-treatment and, eventually their impact on biofuel conversion [31]. Lignocellulosic biomass could pave the pathway for emerging applications in energy storage devices, water treatment, and hydrogels in drug delivery. Fig. 1 presents the steps to treat lignocellulose biomass to produce new materials for any purpose.

■ EMERGING APPLICATIONS OF LIGNIN

Prospective applications and research on advanced lignin material have been under study for decades. The

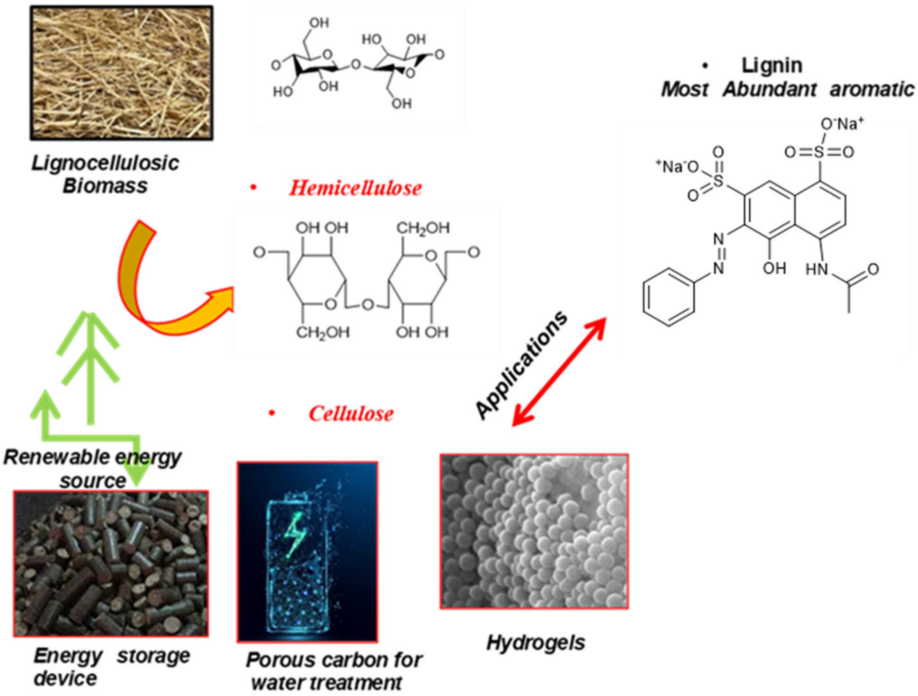

Fig 1. Renewable energy source applications of lignin

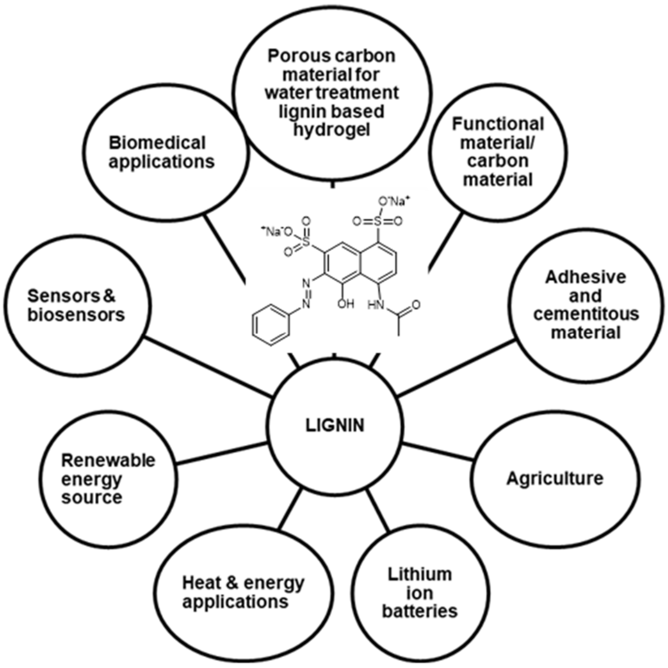

Fig 2. Recent advances and emerging applications of lignin

possible use of lignin as a high-value product has been reported by many researchers [32-34]. Different methods have been intensive on the depolymerization and synthesis of chemically active sites, functionalization of hydroxyl groups, and production of copolymers that were grafted with lignin. Some novel applications of lignin, such as oxidized products, carbon fibers, and phenol, have been reported in many studies [35-37]. In addition, lignin has been used in many emerging applications such as biomedical engineering, tissue engineering, energy storage devices, nanocomposites, heavy metal ion detectors, and drug delivery. Extensive research work could pave the path underway to derive more valued lignin products and competent progressions of lignin in various fields Fig. 2. However, the applications of lignin have not been reached at an industrial scale due to its restricted use and an inadequate number of low-value uses. In this chapter, the major highlights are the application of advanced biopolymer lignin in the energy sector as a biofuel.

Energy Sector

Lignin biopolymer is a promising and environmentally friendly candidate in the sector of energy and storage. Lignin helps increase the efficiency of energy storage devices and also in the context of environmental sustainability and cost-effectiveness. It has been reported that lignin could be used as an additive in lead-acid batteries in the form of a negative paste to increase its efficiency and durability in various charge and discharge cycles and cycle life [38]. In the recent studies, lignin has been proposed as a potential component used in environmentally safe capacitors and supercapacitors. Also, lignin phenol has been used as conducting polymers for fuel cells and solar cells. In conventional lithium batteries, a lithium-based anode has been used, which contains inorganic compounds, an electrolyte that is non-renewable, toxic, and costly. Klason lignin has been studied for the development of low-cost cathode active material extracted from the buck-wheat husk and sunflower husk termed [39-41].

The 3D hierarchical porous carbon, carbon nanofibers, and fiber mats have been prepared using lignin as a raw material to reduce the manufacturing time and cost of lithium-ion batteries. Superconductors have many advantages and have received much attention over batteries, such as fast charge/discharge capability, high power density, and durability. Superconductors made by lignin have drawn much attention because activated carbon derived from renewable and abundant sources can be obtained by green and sustainable processes and at low cost [42]. Lignin has been used to improve alternative photosensitizers of polymer solar cells and dye-sensitized solar cells.

Lignin as Binder

In the pigment printing industry, water-soluble lignin is particularly used as a binder. A commonly used form of lignin as a lignin sulfate has been used as a binder in ceramics and coal briquettes. Particle boards and plywood (mineral dust and wood material) have been used for briquette formation [43-46]. Particularly in lithium-ion batteries, lignin-derived binders are used as a silicon anode and for next-generation devices. Lignin has changed its volume during the extraction procedure; this is considered as a primary challenge for using lignin as a binder. Consequently, specific attention has been specified to the lignin improvement as a binder.

Lignin in Cementitious Material

In several studies, the economical use of lignin in cement material has been reported widely. To get a high-yield and high-performance concrete, a low level of lignin and modified lignin has been used. Lignin-based cement material improves strength and ease of grinding. Additionally, lignin can be used as a binder selectively for the improvement in the compressive strength of cement material. The sulfonation process of lignin helps to attach sulfate groups to lignin due to the high value of zeta potential, which makes lignin a good dispersant in the matrix of cement. A high charge value of zeta potential caused the electrostatic repulsion in between the cement particles and increased its property [47].

Lignin-Based Smart Materials for Sensing Applications

A biosensor is an analytical device that consists of a bio-receptor that identifies and communicates with the analyte to give off a biological signal. In biosensors, the encapsulation of the biological component can either be done utilizing a semipermeable barrier, such as a dialysis membrane or a hydrogel, or a 3D polymer matrix. Biosensors can be classified into electrochemical, optical, thermal, and piezoelectric biosensors, depending on the transducer. Lignin exhibits strong compatibility with carbon-based materials and effective adsorption onto sp^2-hybridized carbon surfaces due to the abundance of aromatic subunits. Lignin is also capable of acting as a stabilizing agent for nanoparticles, including silver. In combination with its biocompatible property, lignin presents itself as a suitable material for bio-sensing and bio-imaging.

Biosensors can provide cost-effective, easy-to-use, sensitive, and highly accurate detection devices in a variety of research and commercial applications. Several types of lignin materials help sense different fields of application. A lignin/peptide-based gold electrode is used to detect antibodies and is called an immune sensor [48]. The amount of glucose is detected by biocatalytic sensors based on a silica/lignin hybrid electrode or magnetite/lignin hybrid electrode [49-51]. Chemical sensors are widely used in many applications based on a variety of lignin materials such as lignin-based carbon quantum dots (LCQDs) for metal-ion detection, lignin-based polymeric composite for the detection of chromate ions, lignin nanoparticles for the detection of formaldehyde, and lignin-porphyrin polymer for heavy metal-ion detection [52-55]. Biosensors are of great interest for bioimaging and biological labeling.

Commercialized Lignin-Driven Products with Environmental Benefits

In the twenty-first century, climate change is one of the biggest environmental concerns. Over the past centuries, countries around the world have been endorsing programs and policies to encourage a shift from non-renewable fossil fuels to renewable energy sources and industry. Lignin-derived products could play an important role in renewable energy sources producing heat, electricity, and fuel [56]. Lignin has reduced the dependency on fossil fuel as an energy resource for the on-site combustion of biorefinery. Combustion of lignin in cellulosic ethanol can reduce the lifecycle of biorefinery. However, in this approach, lignin releases carbon content into the atmosphere, so it may not be the most sustainable use of lignin in the long-term use [57]. The advancement of lignin byproduct in higher value chemicals will additionally improve the overall environmental effect on biorefineries with higher profit facilities. Likewise, syn gas production by gasification and the production of bio-oil by pyrolysis of lignin reduces greenhouse and toxic gas emissions in comparison with petroleum-based products [58]. In addition, the implementation of lignin-derived carbon fiber in automobile industries and potentially replacement fuel in transportation can reduce the weight of vehicles and will improve fuel economy, thus lowering the transportation sector's carbon footprint.

Lignin-Based Hydrogels

Cross-linked hydrophilic polymers whose intrinsic ability exhibits the ability to adsorb water up to a thousand times their dry weights are called hydrogels. Hydrogel exhibits characteristics in different fields, such as adsorption, drug delivery, tissue engineering, and provides promising options and applications [59]. Even though hydrogels have been used commercially, hydrogels are mainly prepared from petroleum-based chemicals such as polyvinyl pyrrolidones, acrylic acid, and polyvinyl alcohol commercially. Nowadays, hydrogels are being prepared using bio-based materials, lignin, and other renewable bio-based materials, which include chitosan, starch, and pectin cellulose [60-62].

Lignin-Based Porous Carbon Material for Adsorption of Water Pollutants

In recent times, porous carbon made of lignin as an adsorbent has received much attention in wastewater treatment from pollutants [63]. The characteristic mechanism involved in the adsorption process is pore filling, hydrogen bonding, hydrophobic, and electrostatic interactions [64]. Porous carbon derived from lignosulphonate comprises substantial acidic surface sites and achieves considerable efficiency for the removal of metal ions and is thus the best promising tool for water treatment [65]. Studies on chemical modification of porous carbon promote anion adsorption have been reported lately. Lignin-based biochar functionalized with MgO by using the hydrothermal carbonization method has high pollutant removal efficiency and high adsorption capacity at very low concentrations (2 mg P/L) [66].

Lignin Base Porous Carbon

In the adsorption of contaminants from wastewater, catalytic degradation of pollutants using porous carbon materials gives promising opportunities and applications. Lignin-based carbon has been used as a supporting platform for catalytic deposition. With the help of a catalytic process, highly toxic metal ions could be reduced to less toxic metal ions such as Cr(VI) and reduced to Cr(III). This method has been considered a simple and cost-effective method for the reduction of toxic metal ions [67]. Magnetic porous carbon with the doping of nitrogen was synthesized from black lignin liquor [68]. The results revealed that for the adsorption and removal of Cr(VI) - 130.5 mg/g due to the presence of a high number of nitrogen-containing functional groups, this nitrogen-doped lignin has a high adsorption capacity. In addition, it could be easily separated under the external magnetic field. Lignin and red mud co-pyrolysis have also been employed as functionalized porous biochar. This combination of lignin red mud composite possesses more capabilities for adsorbing Cr(IV), and the reduction removal efficiency has been achieved by up to 70% [69]. Metal oxide semiconductors such as ZnO and TiO_2 are mostly considered the conventional photocatalysts for the water treatment and degradation of water pollutants. However, improvements are still required in current photocatalytic systems due to their low quantum efficiency and high rate of charge carrier recombination [70]. Fascinatingly, due to the presence of a large number of sp^2 hybridized carbon atoms, porous carbon possesses superior mobility and electron conductivity. In addition, the range of optical absorption will extend due to the interface electronic interaction between photocatalyst and carbon-based material. Consequently, porous carbon, which is based on lignin and its composites with semiconductor metal oxides, can act as an electron transfer platform for the enhancement of catalytic performance. Alkali lignin-based porous carbon, such as porous carbon-ZnO hybrid composite, has been used for the degradation of an anionic dye such as methyl orange as well as cationic dye such as rhodamine B.

■ CHALLENGES AND PERSPECTIVES ON LIGNIN VALORIZATION

Challenges

Tremendous effort has been put into unlocking the potential of lignin for the production of value-added products; lignin utilization faces several challenges, even though considerable progress has been made in the field of lignin valorization and utilization. The basic structure of lignin has been investigated, even though it remains unclear. Isolation of lignin from analytical methods is the major challenge associated with its extraction. Isolation and purification procedures cause modification in the molecular structure of lignin, and thus, it is a challenge to determine the basic structure of lignin. To obtain a high concentration yield of lignin, less condensation and low-temperature conditions are required in the conversion procedure.

In the paper and pulp industry, traditional extraction methods have been employed for the extraction of lignin. In these methods, lignin possesses more impurities and a highly condensed structure, which is responsible for the further conversion reactions of lignin. Nowadays, biorefineries focus on the carbohydrate conversion process, which results from an alteration in the structure of technical lignin. Some procedures have been investigated and developed for the isolation of lignin with a basic structure. It is believed that lignin extracted from the dioxane/water process is known as Bjorkman lignin; it signifies an example of pure lignin. However, the energy consumption is high, and the yield of lignin is low < 30%. However, in the cellulosic enzyme hydrolysis method, the purity of extracted lignin is very low, but the yield could be relatively high. In lignin, hydrodeoxygenation conversion negative on carbohydrate impurities has a significant negative effect.

Continuous efforts have been made on the pre-treatment of biomass for efficient fractionate lignocellulosic biomass to lignin. Considerable challenges, such as the heterogeneous structure of lignin, affect the selective conversion of lignin. Different types of lignin structure are also depending upon the pre-treatment methods and different feedstock. Also, selective depolymerization of lignin is hindered by C–O and C–C linkages with wide dissociation energy. In addition, another difficulty in the selective conversion of lignin and its impact on the reactivity of lignin is the presence of different functional groups such as phenolic hydroxyl group, methoxy group, and terminal aldehydes. High molecular weight and amorphous structure are other difficulties associated with lignin, which is responsible for the limited solubility of lignin in common solvents at ambient temperature conditions. Lignin intermediate is prone to side reactions due to a high degradation rate, making it difficult in the high yield production of lignin in desired products. Besides, extensive research has been reported in this area, but so far, for the determination of lignin structure and theoretical conversion of technical lignin in high yield, no method has been reported to date.

Prospects and Opportunities

Lignin could be used as a renewable energy feedstock in biorefineries for fuel production. Due to its intrinsic aromatic structure and its high energy density, lignin has been used as a functional material and value-added chemical. The article gives a summary of the major applications of lignin. In thermal power plants for power production, lignin has been used and burned directly. To increase the affordability of biorefineries and to achieve renewable energy goals, advanced lignin fuel is a promising candidate. The use of chemicals such as xylene, benzene, phenols, and toluene is the topmost challenge in the application of lignin. Meanwhile, lignin is a biopolymer based on phenol in the process of petrochemical as a macromolecule. Lignin has also been used as a promising candidate to produce value-added material of lignin, including activated carbon, carbon fiber, and composite materials [71]. This value-added material has been extensively used in the field of energy storage, pollutant removal, and catalysis. The selective conversion of lignin is an effective catalyst for the fulfillment of value-added products with high efficacy rates. Extraction of lignin monomer with the help of acid or base is futile for the reason of the production of intermediates, which are prone to degrade the condensation and depolymerization reaction. The methods involved could be used to overcome this issue by the use of trapping agents such as phenol, boric acid, and 2-naphthol diols for the stabilization of reactive species and reduction in char formation. Suitable solvents such as formic acid and alcohol can also improve the yield of the product and act as a hydrogen donating agent to give better solubility of lignin. Another wide attempt approach for more active catalysts, bimetallic and bifunctional allows conversion of lignin and degradation under mild temperature. Moreover, the multi-phase reaction is also beneficial for the production of lignin monomers. Generally, several factors, such as catalysts, solvents, and multi-phase reaction systems, are reasons for the successful conversion of lignin biomass into value-added products and should be addressed.

■ CONCLUSION

Lignin biopolymer is an abundant resource on earth in the form of biomass, and it is also found as a coproduct of biorefineries. Lignin derived from biomass could be applied for better environmental applications and high profit in industries. Sustainable products of lignin obtained by the valorization technique have been discussed. Many research efforts have been done in developing processes that could produce value-added products of lignin. Lignin-derived products have shown the potential to significantly reduce the harmful impacts on the environment. For the industrial development of lignin-derived products, a continued investigation of cost-effective vaporization of lignin technologies is required. This review emphasized the current advances and applications of lignin-based advanced functional material, which includes porous material, lignin-based hydrogel porous carbon, and material. The applications of lignin in heat and energy, lignin as a binder and cementitious material, sensor, biosensor, and biomedical applications have also been reviewed and analyzed.

■ AUTHOR CONTRIBUTIONS

Mohit Kumar Goel edited and rephrased the sentences in the manuscript. Rishi Kant and Yogesh Bhalla rewrote and edited the references. All the co-authors reviewed and approved the final version of the manuscript.

■ REFERENCES

[1] Chen, Z., Ragauskas, A., and Wan, C., 2020, Lignin extraction and upgrading using deep eutectic solvents, *Ind. Crops Prod.*, 147, 112241.

[2] Rinaldi, R., Jastrzebski, R., Clough, M.T., Ralph, J., Kennema, M., Bruijnincx, P.C.A., and Weckhuysen, B.M., 2016, Paving the way for lignin valorisation: Recent advances in bioengineering, biorefining and catalysis, *Angew. Chem., Int. Ed.*, 55 (29), 8164–8215.

[3] Lupoi, J.S., Singh, S., Parthasarathi, R., Simmons, B.A., and Henry, R.J., 2015, Recent innovations in analytical methods for the qualitative and quantitative assessment of lignin, *Renewable Sustainable Energy Rev.*, 49, 871–906.

[4] Hassanpour, M., Abbasabadi, M., Gebbie, L., Te'o, V.S.J., O'Hara, I.M., and Zhang, Z., 2020, Acid-catalyzed glycerol pretreatment of sugarcane bagasse: Understanding the properties of lignin and its effects on enzymatic hydrolysis, *ACS Sustainable Chem. Eng.*, 8 (28), 10380–10388.

[5] Saratale, R.G., Saratale, G.D., Shin, H.S., Jacob, J.M., Pugazhendhi, A., Bhaisare, M., and Kumar, G., 2018, New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: Current knowledge, their agricultural and environmental applications, *Environ. Sci. Pollut. Res.*, 25 (11), 10164–10183.

[6] Ma, R., Guo, M., and Zhang, X., 2018, Recent advances in oxidative valorization of lignin, *Catal. Today*, 302, 50–60.

[7] Borges, C.S.P., Akhavan-Safar, A., Marques, E.A.S., Carbas, R.J.C., Ueffing, C., Weißgraeber, P., and da Silva, L.F., 2021, Effect of water ingress on the mechanical and chemical properties of polybutylene terephthalate reinforced with glass fibers, *Materials*, 14 (5), 1261.

[8] Saha, K., Dwibedi, P., Ghosh, A., Sikder, J., Chakraborty, S., and Curcio, S., 2018 Extraction of lignin, structural characterization and bioconversion of sugarcane bagasse after ionic liquid assisted pretreatment, *3 Biotech*, 8 (8), 374.

[9] Qiu, Z., Aita, G.M., and Walker, M.S., 2012, Effect of ionic liquid pretreatment on the chemical composition, structure and enzymatic hydrolysis of energy cane bagasse, *Bioresour. Technol.*, 117, 251–256.

[10] Moghaddam, L., Zhang, Z., Wellard, R.M., Bartley, J.P., O'Hara, I.M., and Doherty, W.O., 2014, Characterisation of lignins isolated from sugarcane bagasse pretreated with acidified ethylene glycol and ionic liquids, *Biomass Bioenergy*, 70, 498–512.

[11] Li, Y., Li, F., Yang, Y., Ge, B., and Meng, F., 2021, Research and application progress of lignin-based composite membrane, *J. Polym. Eng.*, 41 (4), 245–258.

[12] Norgren, M., and Edlund, H., 2014, Lignin: Recent advances and emerging applications, *Curr. Opin. Colloid Interface Sci.*, 19 (5), 409–416.

[13] Wu, X., Jiang, J., Wang, C., Liu, J., Pu, Y., Ragauskas, A., Li, S., and Yang, B., 2020, Lignin-derived electrochemical energy materials and systems, *Biofuels, Bioprod. Biorefin.*, 14 (3), 650–672.

[14] Zhu, J., Yan, C., Zhang, X., Yang, C., Jiang, M., and Zhang, X., 2020, A sustainable platform of lignin: From bioresources to materials and their applications in rechargeable batteries and supercapacitors, *Prog. Energy Combust. Sci.*, 76, 100788.

[15] Liu, H., Xu, T., Liu, K., Zhang, M., Liu, W., Li, H., Du, H., and Si, C., 2021, Lignin-based electrodes for energy storage application, *Ind. Crops Prod.*, 165, 113425.

[16] Chaleawlert-umpon, S., Berthold, T., Wang, X., Antonietti, M., and Liedel, C., 2017, Kraft lignin as electrode material for sustainable electrochemical energy storage, *Adv. Mater. Interfaces*, 4 (23), 1700698.

[17] Khan, N., Ali, S., Latif, S., and Mehmood, A., 2022, Biological synthesis of nanoparticles and their applications in sustainable agriculture production, *Nat. Sci.*, 14 (6), 226–234.

[18] Hernández-Díaz, J.A., Garza-García, J.J.O., Zamudio-Ojeda, A., León-Morales, J.M., López-Velázquez, J.C., and García-Morales, S., 2021, Plant-mediated synthesis of nanoparticles and their antimicrobial activity against phytopathogens, *J. Sci. Food Agric.*, 101 (4), 1270–1287.

[19] Lee, S.C., Yoo, E., Lee, S.H., and Won, K., 2020, Preparation and application of light-colored lignin nanoparticles for broad-spectrum sunscreens, *Polymers*, 12 (3), 699.

[20] Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, A., and Jeelani, S., 2015, Extraction and characterization of lignin from different biomass resources, *J. Mater. Res. Technol.*, 4 (1), 26–32.

[21] Weng, J.K., and Chapple, C., 2010, The origin and evolution of lignin biosynthesis, *New Phytol.*, 187 (2), 273–285.

[22] Sharma, A., Kaur, P., Singh, G., and Arya, S.K., 2021, Economical concerns of lignin in the energy sector, *Cleaner Eng. Technol.*, 4, 100258.

[23] Zhao, Y., Shakeel, U., Saif Ur Rehman, M., Li, H., Xu, X., and Xu, J., 2020, Lignin-carbohydrate complexes (LCCs) and its role in biorefinery, *J. Cleaner Prod.*, 253, 120076.

[24] Du, X., Gellerstedt, G., and Li, J., 2013, Universal fractionation of lignin–carbohydrate complexes

(LCC s) from lignocellulosic biomass: An example using spruce wood, *Plant J.*, 74 (2), 328–338.

[25] Melro, E., Filipe, A., Sousa, D., Medronho, B., and Romano, A., 2021, Revisiting lignin: A tour through its structural features, characterization methods and applications, *New J. Chem.*, 45 (16), 6986–7013.

[26] Komisarz, K., Majka, T.M., and Pielichowski, K., 2022, Chemical and physical modification of lignin for green polymeric composite materials, *Materials*, 16 (1), 16.

[27] Ralph, J., Lapierre, C., and Boerjan, W., 2019, Lignin structure and its engineering, *Curr. Opin. Biotechnol.*, 56, 240–249.

[28] Zhang, K., Xu, R., Abomohra, A.E.F., Xie, S., Yu, Z., Guo, Q., Liu, P., Peng, L., and Li, X., 2019, A sustainable approach for efficient conversion of lignin into biodiesel accompanied by biological pretreatment of corn straw, *Energy Convers. Manage.*, 199, 111928.

[29] Kocaturk, E., Salan, T., Ozcelik, O., Alma, M.H., and Candan, Z., 2023, Recent advances in lignin-based biofuel production, *Energies*, 16 (8), 3382.

[30] Figueiredo, P., Lintinen, K., Hirvonen, J.T., Kostiainen, M.A., and Santos, H.A., 2018, Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications, *Prog. Mater. Sci.*, 93, 233–269.

[31] Kim, K.H., and Yoo, C.G., 2021, Challenges and perspective of recent biomass pretreatment solvents, *Front. Chem. Eng.*, 3, 785709.

[32] Stewart, D., 2008, Lignin as a base material for materials applications: Chemistry, application and economics, *Ind. Crops Prod.*, 27 (2), 202–207.

[33] Beaucamp, A., Muddasar, M., Amiinu, I.S., Moraes Leite, M., Culebras, M., Latha, K., Gutiérrez, M.C., Rodriguez-Padron, D., del Monte, F., Kennedy, T., Ryan, K.M., Luque, R., Titirici, M.M., and Collins, M.N., 2022, Lignin for energy applications–state of the art, life cycle, technoeconomic analysis and future trends, *Green Chem.*, 24 (21), 8193–8226.

[34] Bruijnincx, P.C.A., Rinaldi, R., and Weckhuysen, B.M., 2015, Unlocking the potential of a sleeping giant: Lignins as sustainable raw materials for renewable fuels, chemicals and materials, *Green Chem.*, 17 (11), 4860–4861.

[35] Fang, W., Yang, S., Wang, X.L., Yuan, T.Q., and Sun, R.C., 2017, Manufacture and application of lignin-based carbon fibers (LCFs) and lignin-based carbon nanofibers (LCNFs), *Green Chem.*, 19 (8), 1794–1827.

[36] Li, Q., Xie, S., Serem, W.K., Naik, M.T., Liu, L., and Yuan, J.S., 2017, Quality carbon fibers from fractionated lignin, *Green Chem.*, 19 (7), 1628–1634.

[37] Zhang, R., Du, Q., Wang, L., Zheng, Z., Guo, L., Zhang, X., Yang, X., and Yu, H., 2019, Unlocking the response of lignin structure for improved carbon fiber production and mechanical strength, *Green Chem.*, 21 (18), 4981–4987.

[38] Akao, Y., Seki, N., Nakagawa, Y., Yi, H., Matsumoto, K., Ito, Y., Ito, K., Funaoka, M., Maruyama, W., Naoi, M., and Nozawa, Y., 2004, A highly bioactive lignophenol derivative from bamboo lignin exhibits a potent activity to suppress apoptosis induced by oxidative stress in human neuroblastoma SH-SY5Y cells, *Bioorg. Med. Chem.*, 12 (18), 4791–4801.

[39] Abe, M.M., Martins, J.R., Sanvezzo, P.B., Macedo, J.V., Branciforti, M.C., Halley, P., Botaro, V.R., and Brienzo, M., 2021, Advantages and disadvantages of bioplastics production from starch and lignocellulosic components, *Polymers*, 13 (15), 2484.

[40] Chong, T.Y., Law, M.C., and Chan, Y.S., 2021, The potentials of corn waste lignocellulosic fibre as an improved reinforced bioplastic composites, *J. Polym. Environ.*, 29 (2), 363–381.

[41] Coppola, G., Gaudio, M.T., Lopresto, C.G., Calabro, V., Curcio, S., and Chakraborty, S., 2021, Bioplastic from renewable biomass: A facile solution for a greener environment, *Earth Syst. Environ.*, 5 (2), 231–251.

[42] Ani, J.U., Akpomie, K.G., Okoro, U.C., Aneke, L.E., Onukwuli, O.D., and Ujam, O.T., 2020, Potentials of activated carbon produced from biomass materials for sequestration of dyes, heavy metals,

and crude oil components from aqueous environment, *Appl. Water Sci.*, 10 (2), 69.

[43] Gadhave, R.V., Srivastava, S., Mahanwar, P.A., and Gadekar, P.T., 2019, Lignin: Renewable raw material for adhesive, *Open J. Polym. Chem.*, 9 (2), 27–38.

[44] Khan, T.A., Lee, J.H., and Kim, H.J., 2019, "Lignin-based adhesives and coatings" in *Lignocellulose for Future Bioeconomy*, Eds. Ariffin, H., Sapuan, S.M., and Hassan, M.A., Elsevier, Amsterdam, Netherlands, 153–206.

[45] Gong, X., Liu, T., Yu, S., Meng, Y., Lu, J., Cheng, Y., and Wang, H., 2020, The preparation and performance of a novel lignin-based adhesive without formaldehyde, *Ind. Crops Prod.*, 153, 112593.

[46] Yang, S., Wu, J.Q., Zhang, Y., Yuan, T.Q., and Sun, R.C., 2015, Preparation of lignin-phenol-formaldehyde resin adhesive based on active sites of technical lignin, *J. Biobased Mater. Bioenergy*, 9 (2), 266–272.

[47] Murase, K., Morrison, K.L., Tam, P.Y., Stafford, R.L., Jurnak, F., and Weiss, G.A., 2003, EF-Tu binding peptides identified, dissected, and affinity optimized by phage display, *Chem. Biol.*, 10 (2), 161–168.

[48] Cerrutti, B.M., Moraes, M.L., Pulcinelli, S.H., and Santilli, C.V., 2015, Lignin as immobilization matrix for HIV p17 peptide used in immunosensing, *Biosens. Bioelectron.*, 71, 420–426.

[49] Budnyak, T.M., Slabon, A., and Sipponen, M.H., 2020, Lignin–inorganic interfaces: Chemistry and applications from adsorbents to catalysts and energy storage materials, *ChemSusChem*, 13 (17), 4344–4355.

[50] Wang, D., Lee, S.H., Kim, J., and Park, C.B., 2020, "Waste to wealth": Lignin as a renewable building block for energy harvesting/storage and environmental remediation, *ChemSusChem*, 13 (11), 2807–2827.

[51] Gale, M., Cai, C.M., and Gilliard-Abdul-Aziz, K.L., 2020, Heterogeneous catalyst design principles for the conversion of lignin into high-value commodity fuels and chemicals, *ChemSusChem*, 13 (8), 1947–1966.

[52] Kärkäs, M.D., Matsuura, B.S., Monos, T.M., Magallanes, G., and Stephenson, C.R.J., 2016, Transition-metal catalyzed valorization of lignin: The key to a sustainable carbon-neutral future, *Org. Biomol. Chem.*, 14 (6), 1853–1914.

[53] Moreno, A., and Sipponen, M.H., 2020, Lignin-based smart materials: A roadmap to processing and synthesis for current and future applications, *Mater. Horiz.*, 7 (9), 2237–2257.

[54] Kai, D., Tan, M.J., Chee, P.L., Chua, Y.K., Yap, Y.L., and Loh, X.J., 2016, Towards lignin-based functional materials in a sustainable world, *Green Chem.*, 18 (5), 1175–1200.

[55] Park, Y., and Lee, J.S., 2017, Flexible multistate data storage devices fabricated using natural lignin at room temperature, *ACS Appl. Mater. Interfaces*, 9 (7), 6207–6212.

[56] Mwithiga, G., 2013, The potential for second generation bio-ethanol production from agro-industrial waste in South Africa, *Afr. J. Biotechnol.*, 2 (9), 871–879.

[57] Kant, R., and Maji, S., 2023, Synthesis, characterization and biological evaluation of piperazine embedded copper complexes, *Inorg. Chim. Acta*, 552, 121515.

[58] Kalidasan, B., Deepika, K., Shankar, R., Pandey, A.K., Shahabuddin, S., Kothari, R., Agarwal, P., and Sharma, K., 2023, Reduction of emission gas concentration from coal based thermal power plant using full combustion and partial oxidation system, *J. Eng. Res.*,11 (1B), 197–211.

[59] Mc Crudden, M.T., Larrañeta, E., Clark, A., Jarrahian, C., Rein-Weston, A., Lachau-Durand, S., Niemeijer, N., Williams, P., Haeck, C., McCarthy, H.O., Zehrung, D., and Donnelly, R.F., 2018, Design, formulation and evaluation of novel dissolving microarray patches containing a long-acting rilpivirine nanosuspension, *J. Controlled Release*, 292, 119–129.

[60] Saravanan, A., Kumar, P.S., and Renita, A.A., 2018, Hybrid synthesis of novel material through acid modification followed ultrasonication to improve adsorption capacity for zinc removal, *J. Cleaner Prod.*, 172, 92–105.

[61] Doshi, B., Ayati, A., Tanhaei, B., Repo, E., and Sillanpää, M., 2018, Partially carboxymethylated

and partially cross-linked surface of chitosan versus the adsorptive removal of dyes and divalent metal ions, *Carbohydr. Polym.*, 197, 586–597.

[62] Farhat, W., Venditti, R., Mignard, N., Taha, M., Becquart, F., and Ayoub, A., 2017, Polysaccharides and lignin based hydrogels with potential pharmaceutical use as a drug delivery system produced by a reactive extrusion process, *Int. J. Biol. Macromol.*, 104, 564–575.

[63] Ma, Q., Yu, Y., Sindoro, M., Fane, A.G., Wang, R., and Zhang, H., 2017, Carbon-based functional materials derived from waste for water remediation and energy storage, *Adv. Mater.*, 29 (13), 1605361.

[64] Xu, K., Li, L., Huang, Z., Tian, Z., and Li, H., 2022, Efficient adsorption of heavy metals from wastewater on nanocomposite beads prepared by chitosan and paper sludge, *Sci. Total Environ.*, 846, 157399.

[65] Zięzio, M., Charmas, B., Jedynak, K., Hawryluk, M., and Kucio, K., 2020, Preparation and characterization of activated carbons obtained from the waste materials impregnated with phosphoric acid(V), *Appl. Nanosci.*, 10 (12), 4703–4716.

[66] Beri, A., Kant, R., Bhalla, Y., Mittal, T., Aggarwal, N., Behal, I., Latchireddi, B., and Dhara, A., 2023, Effect on CMC of sodium dodecyl benzene sulphate (SDBS) in the presence of alcohols and its derivatives at different temperatures, *Eur. Chem. Bull*, 12 (7), 1490–1506.

[67] Zhou, X., Chen, X., Han, W., Han, Y., Guo, M., Peng, Z., Fan, Z., Shi, Y., and Wan, S., 2022, Tetracycline removal by hercynite-biochar from the co-pyrolysis of red mud-steel slag-sludge, *Nanomaterials*, 12 (15), 2595.

[68] Jiang, X., Lu, W.X., Zhao, H.Q., Yang, Q.C., and Yang, Z.P., 2014, Potential ecological risk assessment and prediction of soil heavy-metal pollution around coal gangue dump, *Nat. Hazards Earth Syst. Sci.*, 14 (6), 1599–1610.

[69] Wang, H., Qiu, X., Zhong, R., Fu, F., Qian, Y., and Yang, D., 2017, One-pot *in-situ* preparation of a lignin-based carbon/ZnO nanocomposite with excellent photocatalytic performance, *Mater. Chem. Phys.*, 199, 193–202.

[70] Ibhadon, A.O., and Fitzpatrick, P., 2013, Heterogeneous photocatalysis: Recent advances and applications, *Catalysts*, 3 (1), 189–218.

[71] Zhang, W., Qiu, X., Wang, C., Zhong, L., Fu, F., Zhu, J., Zhang, Z., Qin, Y., Yang, D., and Xu, C.C., 2022, Lignin derived carbon materials: Current status and future trends, *Carbon Res.*, 1 (1), 1–39.