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Recent advances in transforming agricultural biorefinery lignins into value-added products

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ABSTRACT

Each year, agricultural residues such as stalks, husks, and pits/nutshells from food crop harvesting are available on a gigatonne scale worldwide. While biorefinery routes have been used convert agricultural residue carbohydrates into value-added products (e.g., bioethanol, biochemicals), the lignin, comprising 20–50% of the dry mass of agricultural residues, remains largely underutilized. Therefore, there is an urgent need to explore the utilization of agricultural biorefinery lignins for value-added products. In this review, we briefly introduce the origins of agricultural lignins, discuss their structural differences, and compare them with the more commonly studied wood lignins. We highlight in greater detail the recent advances in using agricultural lignins as macromonomers/fillers for polymer syntheses that include epoxies and polyurethanes. The use of agricultural lignins as carbon-rich precursors for the preparation of carbon fibers, supercapacitor electrodes, and carbon foams are also discussed, as well as their use for other applications such as additives for fertilizer release control and UV-shielding. Altogether, this review provides key developments in the progress made to date for agricultural lignin utilization that may help promote future innovation in the field.

1. Introduction

The world's population reached 7.9 billion in 2021, and is expected to grow to 9 billion by 2050 and 11 billion by 2100 [1]. To meet the food supply crisis brought on by rapid population growth, most countries are vigorously developing their agricultural systems to increase production, which inevitably will result in even a larger volume of agricultural residues as an underutilized biomass resource. Agricultural residues are primarily comprised of biomass that is generally not collected during the harvesting of crops; examples include sugar cane bagasse, corn stover (stalks, leaves, husks, and cobs), wheat straw, rice straw, rice hulls, nut hulls, barley straw, sweet sorghum bagasse, etc. [2]. The total production of agricultural residues across the world is currently projected to be 2.8 to 3.8 billion tonnes per year [3]. Despite a series of biorefinery routes that can convert carbohydrates fractions from these residues into value-added products (e.g., bioethanol, biochemicals), the lignin fraction that remains as a byproduct can range from 20 to 50% of the dry mass of most agricultural residues.

Lignin is primarily composed of randomly crosslinked phenylpropanoid units *via* various C–O and C–C linkages, as shown in Fig. 1 [4]. Three types of phenylpropanoid units are found in lignin; wood lignins have mostly syringyl (S) and guaiacyl (G) units while grass (or herbaceous plant) lignins also have a significant proportion of the *p*-hydroxyphenyl (H) unit. In comparison with S and G units, the H unit has no methoxyl groups on the meta positions (i.e., 3 or 5) of the aromatic rings. This not only lowers the steric hindrance of the phenolic hydroxyls in chemical reactions, but it also provides extra reaction sites (i.e., 3 and 5) on aromatic ring, thereby providing greater reactivity for polymer syntheses (e.g., epoxy and phenolic resins) [5,6].

Owing to its aromatic structure, and thus a high carbon density, lignin carbonization/pyrolysis yields 1–3 times more solid carbon than that obtained from either cellulose or the hemicelluloses [7]. This makes lignin an ideal candidate for the development of value-added carbon products such as carbon fiber, battery electrodes, supercapacitors, etc.

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[8,9]. Moreover, the lignin's aromatic macromolecular structure and abundant reactive hydroxyl groups also allow it to be used as absorbents for environmental remediation [10], as polyols for polyurethanes [11,12], and as UV-absorbers for shielding composites [13,14].

To date, several articles have reviewed the research progress towards the utilization of lignins for value-added applications [15–17]; however, these articles have all focused on wood lignins. Herein, we provide what appears to be the first review article focusing on the development of products based on agricultural biorefinery lignins. With the increasing demands for circular economies, the conversion and utilization of agricultural residues are becoming increasingly important [18]. Agricultural biorefinery lignins are increasing in their availability [19] and their valorization continues to gain interest. The main contribution of this review is to provide an overview of the current research on the conversion of agricultural residue lignins into value-added products along with both the challenges and prospects for success.

2. Lignin-based polymer products

2.1. Epoxy resins

Among the thermosetting polymers, epoxies are among the most versatile and valuable, having both good thermal resistance and superior mechanical properties [21,22], making them widely suitable for electronic laminates, coatings, adhesives, automotive applications, etc. Worldwide, around 90% of the commercially available epoxy resins come from the reaction between bisphenol A (BPA) and epichlorohydrin [23]. Unfortunately, these chemicals are produced from petroleum resources, thus hindering the sustainability of epoxy resin production [24]. Furthermore, BPA is known to be an endocrine disruptor that has both detrimental effects on human health and the environment [25]. Hence, there is an urgent need to seek a sustainable and less hazardous substitute for BPA for the synthesis of epoxy resins.

Owing to the presence of phenolic hydroxyl groups in its structure, lignin is an excellent substitute for BPA for epoxy resin synthesis. Compared with wood lignins, agricultural residue lignins contain up to 35% of H units [26], which reduces steric hindrance and improves the reactivity of the phenolic hydroxyl groups. It is of great interest to use unmodified lignin directly as a BPA replacement in epoxy resin formulation. Nikafshar et al. evaluated the reactivities of thirteen commercially available lignins toward epichlorohydrin for epoxy resin synthesis [27]. Among all tested lignins, the organosolv corn stover lignin was the best candidate for epoxy resin formulations because of its low ash content, low molecular weight, and low polydispersity. These characteristics led to the powdered lignin-based epoxy resin having the highest epoxy content. However, due to unfavorable lignin condensation and polymerization reactions during the epoxidation, the resulting powdered epoxy resin suffered from both a high molecular weight and a low solubility to regular solvents (e.g., acetone, ethanol, methanol). This limited its practical applications in coatings and adhesives. In another study, Xue et al. synthesized lignin-based epoxy vitrimers (LEVs) with high tensile strengths (up to 46.8 MPa) using epoxidized corncob lignin [104] (Fig. 2). The LEVs exhibit excellent self-healing, reprocessing, and shape memory properties. The crack widths of the vitrimers were reduced by over 80% in just 5 min at 160 °C; the tensile strength can reach up to 97% healing efficiency after being reprocessed with heat.

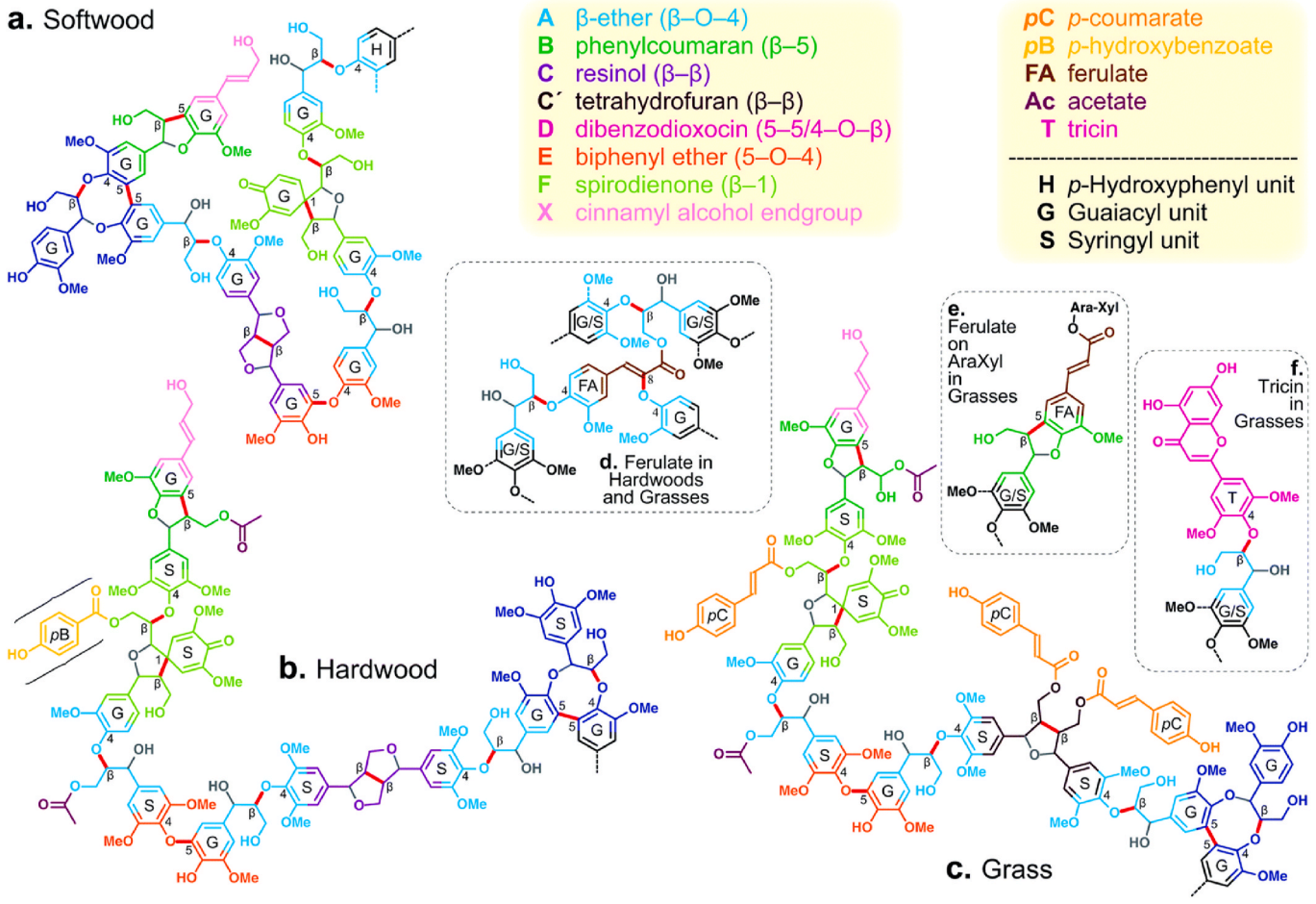

Fig. 1. Model lignin structures containing 11 primary units each as follows: (a) softwood lignin with H and G units, (b) hardwood lignin with G and S units, and (c) grass lignin with G, S units along with *p*-coumarates [20].

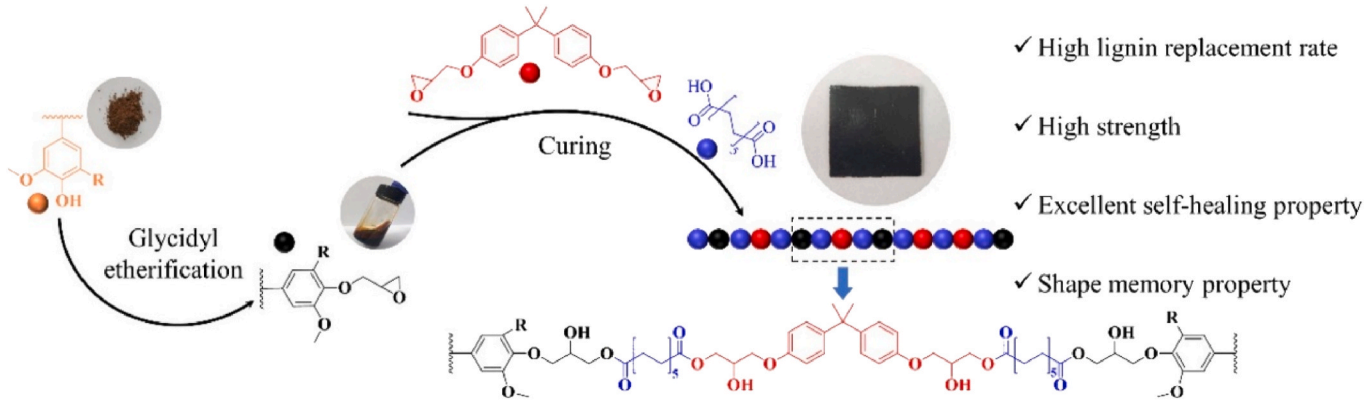

Fig. 2. Preparation of lignin-based epoxy vitrimers [104].

The direct utilization of lignin for epoxy resin synthesis still poses significant challenges due to the inherent structural heterogeneity of the lignin. The irregular and complex chemical structures result in poor compatibility and dispersibility of lignin [28]. Furthermore, various electronic constraints and steric hindrance effects arise from a highly branched molecular structure, making the lignin phenolic hydroxyls less reactive than BPA for epoxidation [29]. Lignin pretreatment before epoxy resin synthesis can alleviate these issues. To improve lignin's reactivity, Ding et al. modified straw lignin with formaldehyde and diethanolamine through the Mannich reaction [30]. They studied the chemical addition method on the reactivity of lignin-based epoxy resins. In comparison to adding formaldehyde into the lignin and diethanolamine mixture solution, adding formaldehyde and diethanolamine mixture into the lignin solution produced a lignin-based epoxy resin with higher epoxy content and reactivity. This was because the latter method prevented the over reactions between formaldehyde and lignin. Zhang et al. compared the effect of lignin pretreatments (i.e., demethylation, phenolation, and hydroxymethylation) on the synthesis of organosolv straw lignin-based epoxy resins [31]. Demethylation, phenolation, and hydroxymethylation increased the total hydroxyl group content by 10%, 25%, and 51%, respectively, which enhanced the potential reactivity of these modified lignins towards the lignin-based epoxy resin. Furthermore, the hydrolysis process effectively reduced the molecular weight and significantly increased the total hydroxyl content, thus improving the dispersibility and the reactivity of the lignin concurrently [32].

In addition to chemical modification, lignin fractionation is an effective and simple refinement technology used to resolve the lignin heterogeneity issue so that relatively homogeneous lignin fractions with well-defined characteristics (e.g., lower molecule weight and narrower molecular weight distribution) can be obtained [33–35]. Tang et al. regulated the molecular weight and phenolic hydroxyl content of a corncob lignin through fractionation, and prepared various LEVs from fractionated lignins [36]. They found the fractionated lignin with lower molecular weights and S/G ratios improved the self-repairing and reprocessing performances of the LEVs. Wang et al. obtained a low molecular weight corn stover-based enzymatic hydrolysis lignin through bioethanol fractionation, which could be directly dissolved into epichlorohydrin for lignin-based epoxy resin (LEp) synthesis [37] (Fig. 3). Moreover, LEp can be fully dissolved into acetone, making it readily used for adhesive and coating applications. When incorporated with the polyamide curing agent, the obtained lignin-based anticorrosive epoxy coatings demonstrating good performance for steel protection.

2.2. Polyurethanes

Polyurethane (PU), produced by the polyaddition reaction of diisocyanates with polyols, has been widely used in various products, including coatings, adhesives, foams, and elastomers [38]. Most of the commercial PUs heavily depend on non-renewable petroleum resources at present [39]. Lignin is a polyphenol existing in plant resources that can provide aromatic groups in a rigid structure to reinforce polymers. Avelino et al. synthesized PUs through a three-component system formed by coconut shell ethanosolv lignin (CSEL, without modifications as co-polyol), polyethylene glycol 400, and toluene diisocyanate (TDI) by a solvent-free polymerization route [40]. CSEL-based PUs showed superior thermal and thermo-oxidative stabilities to PU without CSEL.

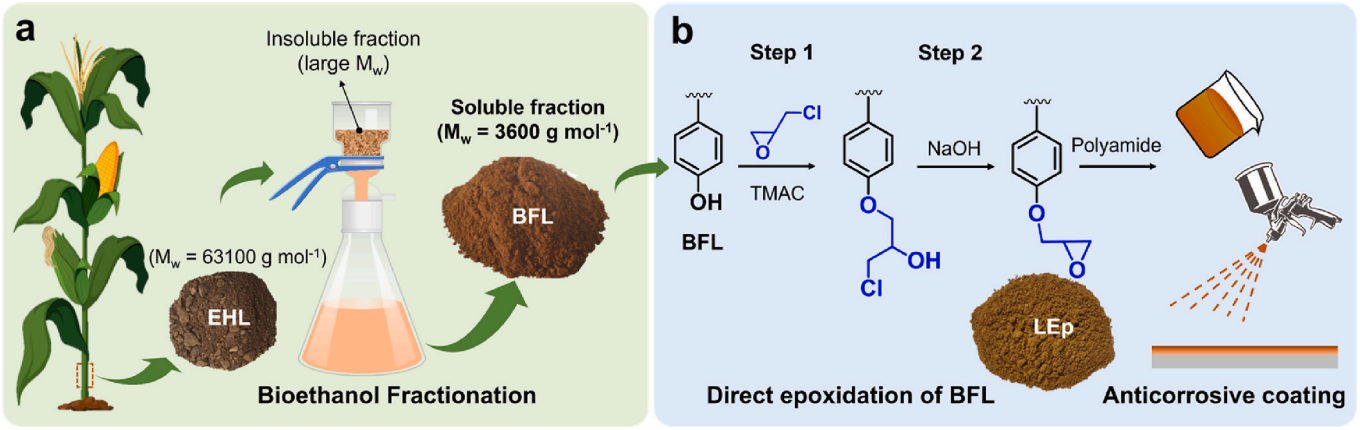

Fig. 3. Preparation of lignin-based epoxy resin (LEp) and anticorrosive coating [37]. EHL and BFL represent the enzymatic hydrolysis lignin and fractionated lignin, respectively.

The use of high CSEL contents in the PU formulations produced materials with poor mechanical properties (brittleness), reflected in their inability to undergo compression. Cao et al. prepared lignin samples from the alkaline black liquor of corn stover by gradient acid precipitation and applied them in the preparation of semi-rigid polyurethane (PU) foams [41] (Fig. 4a). Results showed that a higher hydroxyl group content in lignin largely improved the compressive strength and led to the reduction of the apparent density. In addition, the foam with higher β-O-4 bond content exhibited a lower thermal conductivity.

Although unmodified macromolecular lignin is rich in hydroxyl groups, most of them are phenolic hydroxyl groups, and its large spatial site resistance results in low reactivity with isocyanates. Pretreatment of lignin is therefore required to enhance its reactivity with isocyanates. He et al. pretreated bamboo acetic acid lignin (AAL) using mild hydrolytic degradation combined with hydroxylation modification; H_2O_2 and Fe $(OH)_3$ were employed as the hydroxylation reagent and the catalyst, respectively [42]. The modified AAL-based polyols, with a reduction in the number average molecular weight (Mn) from 2923 to 684 g·mol ^{1}, and an increase in the hydroxyl content from 5.21 to 9.13 mmol·g ^{1}, showed improved reactivity and compatibility with a diisocyanate, along with significantly enhanced toughness and tensile strength of the AAL-based polyurethane elastomers.

Chen et al. modified a bagasse AAL by hydroxymethylation with formaldehyde to improve its reactivity with isocyanate during the preparation of PU adhesives [43]. The hydroxyl content was increased by 189.11% compared with the original AAL and reached 2.92 mmol·g ^{1}. In the polymerization of PU adhesives, the hydroxymethylated lignin with a higher aliphatic hydroxyl content formed a more compact three-dimensional urethane cross-linking network with isocyanate. Chen also effectively enhanced the reactivity of AAL by demethylation with a hydrobromic acid solution under heating conditions [44]. The hydroxyl content of lignin under demethylation was increased by 36.5% and reached 5.25 mmol·g ^{1}. Alternatively, Wang et al. proposed a two-step approach for structure homogenization of biorefinery corn stover lignin, i.e., ethanol fractionation (step 1) to lower lignin's MW and narrow its polydispersity index (Đ), and oxyalkylation (step 2) to convert lignin's phenolic and carboxylic hydroxyls to aliphatic hydroxyls (ethylene carbonate as the oxyalkylation agent) [45] (Fig. 4b). The obtained structure-homogenized lignin had good compatibility and crosslinking with hexamethylene diisocyanate for PU coating synthesis. Moreover, PU coatings prepared from structure-homogenized lignin displayed a defect-free microscopic structure and showed better corrosion resistance than coatings prepared from the raw lignin.

3. Lignin-based carbon fiber

Carbon fiber is a high-value material with broad applications in the sporting equipment, automotive, wind turbine, and aerospace industries. Currently, more than 90% of carbon fiber is produced using petroleum-derived polyacrylonitrile (PAN) due to its uniform structure which that gives defect-free carbon fibers with superior mechanical properties (>6 GPa of tensile strength) [46]. The high cost of PAN has also driven the exploration of more affordable alternatives with comparable performance.

Lignin, with its high carbon content and aromatic structure, has received significant attention to replace PAN polymer with sustainable

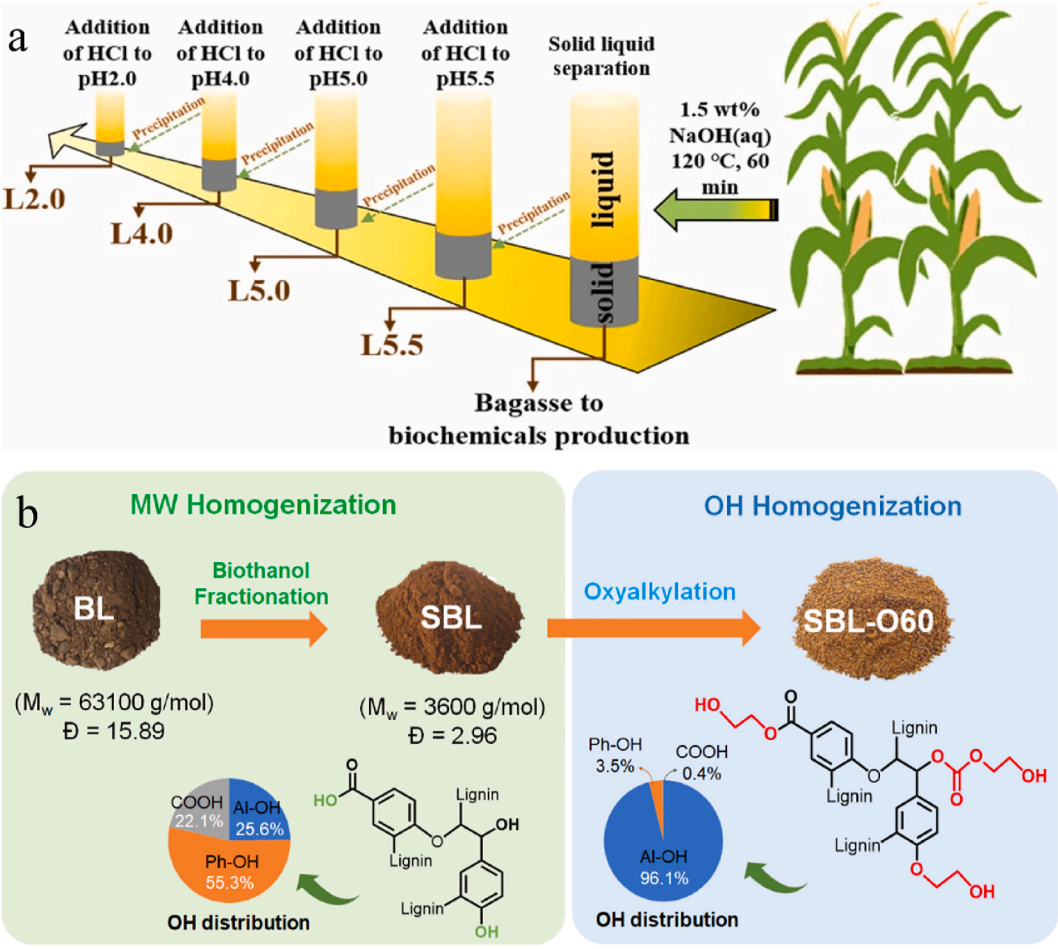

Fig. 4. (a) Flow chart of lignin specimens that precipitated from the black liquor of corn stover; (b) Lignin structure homogenization for PU coating preparation [45]. BL, SBL, and SBL-O60 represent the original corn stover lignin, fractionated lignin, and oxyalkylated SBL, respectively.

and cost-effective biopolymer without severely compromising carbon fiber performance. As such, lignins from various sources have been compared to correlate their molecular structures to the properties of the resulting carbon fibers. Most investigations have focused on wood lignins (i.e., softwood, hardwood) and bamboo lignins, while their agricultural counterparts have more recently received some attention.

Table 1 summarizes all published studies we found to report the preparation of carbon fibers with agriculturally sourced lignins over the past 10 years. The agricultural feedstocks used for lignin production include switchgrass, wheat straw, sugarcane bagasse, sorghum, corn stalk, and spent coffee grounds [47–53]. Compared to wood lignins, agricultural lignins have significant proportions of *p*-hydroxyphenyl (H) units [54] which have unoccupied C3 and C5 sites on the aromatic rings. The lignin characteristics that have important impacts on the final carbon fiber properties include its molecular weight and polydispersity, structure uniformity, content, purity, as well as composition (H/S/G ratio) [55,56]. Indeed, all these characteristics are correlated to some extent as discussed below.

The lignin molecular weight and polydispersity are dominant factors that define carbon fiber mechanical performance. The polydispersity is closely connected to the crystallite content and size of pre-graphitic turbostratic carbon. Significant correlations between the polydispersity, crystallite size and degree of defect of the pre-graphitic turbostratic carbon were recently reported [52]. Narrow polydispersity is favorable and coincides with a marked molecular uniformity of the lignin, thereby producing carbon fibers with greater performance [52]. Lignin structure uniformity, especially the high frequency of β-O-4 linkages, appears to improve the mechanical, and electroconductive properties, as well as increase the crystallite size and content of the pre-graphitic turbostratic carbon structure in the carbon fibers [51]. The mechanistic explanation is that lignin with more β-O-4 linkages could form more linear structures and thus be more flexible [56], resulting in better-aligned polymer orientations under stretching forces loaded on the precursor fibers during melt-spinning. The better-aligned lignin fibers contribute to higher frequencies of the pre-graphitic turbostratic structure and a more uniform microstructure of the resultant carbon

Table 1
Summary of carbon fiber fabrication methods and major findings related to studies using agricultural lignins.

Lignin source	Preparation of lignin	Carbon fiber fabrication	Results	Ref
Sorghum	Extraction by acetic acid + acid precipitation	Wet spinning: lignin + PAN Thermostabilization: RT to 250 °C, 1 °C·min ^{1}, 1 h Carbonization: RT to 1000 °C, 5 °C·min ^{1}, 1 h	The molecular uniformity of lignin defined the microstructures and the carbon fiber mechanical performances, while molecular weight, lignin content, and S/G ratio may not be the main factors.	[57]
Hardwood-sugar maple; softwood-red cedar, loblolly pine; Herbaceous plants-switchgrass, corn stover	Extraction by acetic acid	Wet spinning: lignin + PAN Thermostabilization: RT to 250 °C, 1 °C·min ^{1}, 1 h Carbonization:1000 °C, 5 °C·min ^{1}, 1 h, N_2	The β-O-4 linkages in lignin were significantly linear correlated with the crystallite structure and the MOE and tensile strength of lignin-based carbon fibers.	[58]
Corn residues	Extraction by acetic acid + acid precipitation	1. Electrospinning: lignin + PAN 2. Iodine-treated lignin-based precursor fibers 3. Thermostabilization: RT to 220 °C, 0.2/2 °C·min ^{1}, 1 h 4. Carbonization:1400 °C, 4 °C·min ^{1}, 2 h, N_2	Iodination of lignin-based carbon fibers resulted in better tensile strength (89 MPa) than that of PAN carbon fibers produced by electrospinning.	[59]
Alamo switchgrass; Yellow poplar chips	Organosolv fractionation	Melt spinning: yellow poplar + switchgrass lignins Thermostabilization: RT to 250 °C, 0.05/0.1/0.2/0.5 °C·min ^{1}, 30 min Carbonization: 600 °C, 3 °C·min ^{1}, 5 min, 600–1000 °C, 5 °C·min ^{1}, 15 min,	Higher switchgrass content enables thermostabilization of fibers at high rates without fusing, whereas lower switchgrass content rendered higher mechanical properties of carbon fibers.	[60]
Corn stalk refining residues	Sequential acidification at different pH levels (10, 8, 6, 4, and 2)	Electrospinning: lignin + PAN Thermostabilization: RT to 220 °C, 0.5 °C·min ^{1}, 12 h Carbonization: 1000 °C, 4 °C·min ^{1}, 4 h, N_2	A fractionated lignin with a large molecular weight, low PDI, and strong thermal stability can produce carbon fibers with excellent spinnability, high crystallization, and mechanical strength.	[61]
Corn stover	Organosolv process	1. Organosolv lignin treatment by butyric anhydride (BL) 2. Electrospinning: BL + PAN 3. Thermostabilization: RT to 200 °C, 0.2 °C·min, 12 h 4. Carbonization:1000 °C, 5 °C·min ^{1}, 0.5 h, N_2	Butylation decreased the intermolecular interaction of lignin/PAN. A 50-50 blending ratio of BL/PAN fibers resulted in the best inter-fiber bonding during oxidative thermostabilization.	[62]
Switchgrass; Yellow poplar wood	Organosolv process	Melt spinning Thermostabilization: RT to 250 °C, 0.05/0.1/0.2/0.5 °C·min ^{1}, 30 min Carbonization: 600 °C, 3 °C·min ^{1}, 5 min, 600–1000 °C, 5 °C·min ^{1}, 15 min	Higher fractionation severity resulted in fewer impurities, higher content of phenolic hydroxyl groups, and more condensed structures due to the cleavage of aryl ether linkages. High severity also decreased thermostabilization time and increased tensile strength and modulus of carbon fibers. The low temperature generated volatiles, leaving pores on the surface of switchgrass fibers.	[63]
Spent coffee grounds	Fractionation by ethanol/water at different temperatures	Electrospinning: lignin + PAN Thermostabilization: RT to 220 °C, 2 °C·min ^{1}, 2 h Carbonization: 900 °C, 2 °C·min ^{1}, 2 h	The linear structure of SCG lignin with large molecular weight and low PDI was favorable to fabricating carbon fibers with great performance.	[64]

Note: RT: room temperature, PDI: Polydispersity index, SCG: Spent coffee grounds.

fibers.

The purity of lignin precursor can also influence the carbon fiber properties. High purity is required since impurities can limit the precursor fusibility, resulting in a poor spinning performance with defects (such as voids) in carbon fibers [65]. Therefore, various fractionation strategies have been proposed to improve the purity of lignin precursors, such as the manipulation of pH value, solvent composition, temperature, etc. [47,48,56]. Lignin processed through a step-wise fractionation can result in lignin with high molecular weight, narrow polydispersity, and uniform linear structure, which is beneficial for the fabrication of high-quality carbon fibers [48].

The H/S/G ratio of lignin also affects the structure of carbon fibers. For example, the higher amount of the H unit in agricultural lignins may negatively affect melt-spinning performance due to more unoccupied sites in the aromatic rings resulting in higher cross-linking and intermolecular hydrogen bonds, that in turn, leads to less thermal mobility and fusibility within the agricultural lignin fibers. In addition, more aliphatic hydroxyl groups rendered more volatile components and thus voids in fibers during the carbonization process [65]. In other studies, H and G units were suggested to have a positive effect, facilitating the formation of a more condensed structure, thus faster thermostabilization time of agricultural lignin fibers [54,65]. Note that there is always a trade-off between spinning temperature and thermostabilization time.

To fabricate better quality carbon fibers, the blending of agricultural lignin with wood lignins was proposed to take advantage of their respective strengths [54]. For example, blending yellow poplar lignin with switchgrass lignin not only solved the poor spinnability issue of switchgrass lignin, but also reduced the thermostabilization time of pure yellow poplar spun fibers [54]. A more common approach with agricultural lignins is to mix them with PAN polymers. The objective here is to replace as much PAN as possible without severely compromising the carbon fiber properties. When blending lignin with PAN, the number of hydrophilic hydroxyl groups needs to be lowered to reduce the polarity of lignin; a lignin fraction of up to 50% in the lignin-PAN mixture can be achieved [53,66]. Future studies should be directed to improve the miscibility of these mixtures, lower the processing temperature, and increase efficiency. Modifying the lignin precursors by esterifying the aliphatic and aromatic hydroxyl groups with anhydrides was studied to reduce intermolecular/intramolecular interactions between molecules and increase structure uniformity [66]; results showed that thermal mobility was improved, making the spinning and processing of carbon fibers easier.

Apart from manipulations of lignin precursor properties, an alternative approach was to locate specific plants with unique lignin precursors. A new lignin precursor, poly-(caffeyl alcohol) (also known as "C-lignin," which essentially is a G unit lacking the methyl group on the C3-oxygen) was found in vanilla orchid (*Vanilla planifolia*) and Brazilian cactus (*Melocactus salvadorensis*) [50]. Compared to typical wood and grass lignins, the C-lignin is mostly comprised of caffeyl alcohol monomers, which are linked head to tail into benzodioxane chains via "endwise" radical coupling reactions. The outstanding merit of the C-lignin is the linear polymer structure that resulted in narrow molecular weight polydispersity, repulsion between the precursors, high purity carbon equivalent to PAN, and a highly ordered graphitic structure that ultimately gave high quality carbon fibers. Although research has been done to investigate the relationships between lignin precursor structure and carbon fiber properties, there are still many of unknowns that need to be unraveled. For example, given the remarkable molecular differences in the lignins from various plant sources, selecting these plants by their lignin structure may give carbon fibers with specific properties. Notwithstanding, it has yet to be investigated if genetic modifications of crop plants would increase lignin structure uniformity enough to give noticeable improvements lignin precursor performance during spinning, stabilization, and carbonization.

4. Lignin-based energy storage materials

4.1. Supercapacitor electrodes

Porous carbons derived from lignin are of interest for use as electrodes in supercapacitors, such as electrical double-layer capacitors and pseudo-capacitors, due to their low cost, tunable surface properties, and eco-friendly nature [67]. The energy storage of an electrical double-layer capacitor (EDLC) relies on ion adsorption-desorption at the surface, interface, or internal pores of electrode materials, thus the electrode material's pore characteristics (i.e., pore volume and size distribution) are critical. Pseudo-capacitors store energy through reversible redox or faradaic reactions between the electrodes and electrolyte; their energy storage performance is determined by the type and amount of oxygen-containing functional groups of electrodes [68]. Lignin has been utilized to produce both EDLC and pseudo-capacitors via various materials design strategies.

Through physical or chemical activations, lignin can be converted into porous carbon electrodes. In a typical activation process, as the lignin is heated to transform it into a solid carbon, active agents such as oxidizing gases (e.g., CO_2 or O_2) and chemicals (e.g., KOH, $ZnCl_2$, KCO_3, $NaCO_3$) etch the lignin carbons and convert them to porous carbons with the desired surface and pore characteristics [67,69]. Despite the high specific surface area (SSA) of porous carbon being essential for EDLC electrodes, the well-regulated pore size distribution is more important. In particular, hierarchical porous carbons (HPCs) with micro (<2 nm), meso (2–50 nm), and macro (>50 nm) pores are desired for EDLC electrodes because they can provide multilevel diffusion paths for electrolytes. For example, macropores have a high buffering capacity for electrolyte ions, mesoporous channels are conducive to the rapid transport of ions, and the micropores can further increase the ion-accessible surface area of the construction of an electrical double layer [67,69]. The combined features can endow EDLS with superior electrochemical performance.

To produce HPCs with optimal porous structure from agricultural lignins, multi-step treatment/activation processes are usually needed. The recent advances in agricultural lignin activation strategies and the resultant HPC properties, as well as the energy storage performance of EDLCs, are listed in Table 2. Wan et al. prepared HPCs from corn stover lignin through a pre-oxidation step followed by KOH activation [70]. The obtained carbon reached the maximum specific surface area of 3094 $m^2 \cdot g^{-1}$, pore volume of 1.72 $cm^3 \cdot g^{-1}$, and the appropriate pore size distribution (0.5–6 nm). When HPCs were employed as the supercapacitor electrode, a maximum specific capacitance of 352.85 $F \cdot g^{-1}$ at 0.5 $A \cdot g^{-1}$ was achieved. Moreover, outstanding capacitance retention of 88.46% after 5000 cycles of charge/discharge was also achieved. The pre-oxidation step is believed to be critical because it produces oxidized lignin with low molecular weight and abundant oxygen-containing function, and that benefits the formation of hierarchical pores. In another study, Guo et al. prepared HPCs from corn straw through a hydrothermal treatment step followed by KOH activation; the derived HPCs demonstrated an SSA of up to 1660 $m^2 \cdot g^{-1}$ [71] (Fig. 5a). When HPCs were used as a supercapacitor electrode, a superior specific capacitance of 420 $F \cdot g^{-1}$ at 0.1 $A \cdot g^{-1}$ was achieved. The HPC-based electrode also showed good structural stability. This was evidenced by the high capacitance retention of 99% after 10,000 cycles of charge/discharge at 5 $A \cdot g^{-1}$.

To avoid the use of corrosive activation chemicals, Zhang et al. established a green bacterial activation approach that converts corn stover lignin to HPCs [72] (Fig. 5b). Notably, bacterial activities disrupt lignin's β-O-4, β - β, and β-5 bonds, thereby decreasing its molecular weight which enhances pore formation during lignin carbonization [72]. As a result, the supercapacitor's specific capacitance reached 428 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$ in 6 M KOH. In the ionic liquid system, the symmetric supercapacitor also showed a high energy density of 66.18 $Wh \cdot kg^{-1}$ at a power density of 312 $W \cdot kg^{-1}$. Moreover, the

Table 2
The recent advances in agricultural lignin activation strategies and the energy storage performance of electrical double-layer capacitors.

Lignin	Synthesis conditions	Elemental Composition	Structural Properties	Electrolyte type	Specific capacitance (F g ^{1})	Cycle stability	Ref
Corn Stover/ H_3PO_4 and H_2O_2 Oxidized lignin	1. Activated by KOH and 2. Carbonization (800 °C)	C-94.5% O-3.7% N-1.40% P-0.4%	S_T: 3094 $m^2.g^{1}$ S_{micro}:1421 $m^2.g^{1}$ V_T: 1.72 $cm^3.g^{1}$ V_T: 0.62 $cm^3.g^{1}$	3E/6 M KOH	E 274.0 [0.1 A·g ^{1}]	88.46% after 5000 cycles at 5 A·g ^{1}	[86]
Corncob/NaOH treated lignin	1 Spray drying 2 Carbonization (1000 °C)	–	S_T: 1261.7 $m^2.g^{1}$	–	–	64.2% after 5000 cycles at a sweep rate of 50 mV·s ^{1}	[73]
Corn stalk/ EHL lignin	Phenolic resin+20% Lignin 1 Spray drying 2. Pre- carbonization (800 °C) 3. KOH Activation (850 °C)	–	S_T: 1899.45 $m^2.g^{1}$ V_T: 1.059 $cm^2.g^{1}$	3E/6 KOH	E 217.3 [0.5 A·g ^{1}]	95.34% after 5000 cycles at 20 A·g ^{1}	[87]
Wheat grass/ alkali lignin	Ionic liquid + Lignin (microwave assisted dissolution) 1. Pre-oxidation (200 °C) 2. Carbonization (750 °C)	C-80.7% O-15.68% N-2.28% P-1.23% S-0.11%	S_T: 938.1 $m^2.g^{1}$ V_T:0.64 $cm^2.g^{1}$	3E/1 M H_2SO4	E 338.2 [0.8 A·g ^{1}] SC-194 [1 A·g ^{1}]	97.3% after 5000 cycles at 2 A·g ^{1}	[76]
Corn stalk	1 Carbonization (350 °C) 2 KOH Activation (650 °C)	C-83.03% O-32.20% S-0.2% N-1.0%	S_T:1228.93 $m^2.g^{1}$ V_t:0.68 $cm^3.g^{1}$	3E/	E 280 [0.5 A·g ^{1}]	96% after 10000 cycles at 1 A·g ^{1}	[88]
Cherry stones	1 .Lignin dissolution by alkali treatment and precipitation. 2 N doping (melamine) 3 Na2CO3–K2CO3 Activation	C- 86.5% O-11% N-2.5%	S_T:1681 $m^2.g^{1}$ S_{meso}: 1519 $m^2.g^{1}$ S_{micro}:161 $m^2.g^{1}$ V_T: 0.86 $cm^3.g^{1}$ V_{micro}:0.57 $cm^3.g^{1}$ V_{meso}:0.12 $cm^3.g^{1}$	3E/6 M KOH	E 370.5 [0.5 A·g ^{1}] S-203.1 [0.2 A·g ^{1}]	99.1% after 5000 cycles at 20.0 A·g ^{1}	[89]
Corn straw/ alkaline lignin	1 Bacterial Activation 2 Carbonization (900 °C)	–	S_T: 1831 $m^2.g^{1}$ V_T: 1.53 $m^2.g^{1}$ V_{micro}: 0.77 $cm^3.g^{1}$ V_{meso}: 0.76 $cm^3.g^{1}$	2/6 M KOH	E 428 [1 A·g ^{1}] SC-289 [1 A·g ^{1}]	E 96.7% after 10000 cycles at 5 A·g ^{1} SC-92% after 5000 cycles at 1 A·g ^{1}	[90]
Corn straw/EHL lignin	1 Hydrothermal Carbonization with 5% H2SO4 (180 °C) 2. KOH activation (800 °C)	C-90.1% O-8.6%	S_T:1660 $m^2.g^{1}$ V_T: 0.78 $cm^3.g^{1}$ V_{micro}: 0.66 $cm^3.g^{1}$ V_{meso}: 0.10 $cm^3.g^{1}$	2E/6 M KOH	E 420 [0.1 A·g ^{1}]	E 99% after 10000 at 5 A·g ^{1}	[91]
wheat straw	1 Lignin urea formaldehyde resin 2 Carbonization (500 °C)	C-88.64% O-9.01% N-2.35%	S_T:3342 $m^2.g^{1}$ V_T: 2.96 $cm^3.g^{1}$ V_{micro}: 0.49 $cm^3.g^{1}$ V_{meso}:2.47 $cm^3.g^{1}$	/1 M H_2SO_4	SC-305 [5 mV·s ^{1}]	96.3% after 10000 at 5 mV·s ^{1}	[74]

Note: The capacitance of a three-electrode system is generally two to three times greater than that of a two-electrode system. *ST -Specific surface area calculated using BET method; *Smicro: Specific micropore surface area; *Smeso: Specific mesopore surface area; *VT: Total pore volume; *Vmicro: Micro pore volume; *Vmeso: Meso pore volume; * E Electrode; * SC- Supper capacitor; *TEABF4-tetraethylammonium tetrafluoroboratecarbon, *2E/3E represents two electrode systems and three electrode electrochemical testing configuration.

supercapacitor's capacitance retention was up to 96.7% after 10,000 cycles of charge/discharge at 5 A·g ^{1}. In another study, Pan et al. prepared hollow carbon spheres with micro- and mesopores from corncob waste-derived lignin through a one-step NaOH activation process [73]. Despite no lignin pretreatment step being used, they employed a spray drying method to produce a lignin-NaOH dry mixture from lignin-NaOH solution before activation. This spray-drying step was critical for the formation of hollow carbon spheres during carbonization. When the hollow carbon spheres are used as an electrode for supercapacitors, the cavity of carbon spheres acts as a reservoir for the electrolyte, and

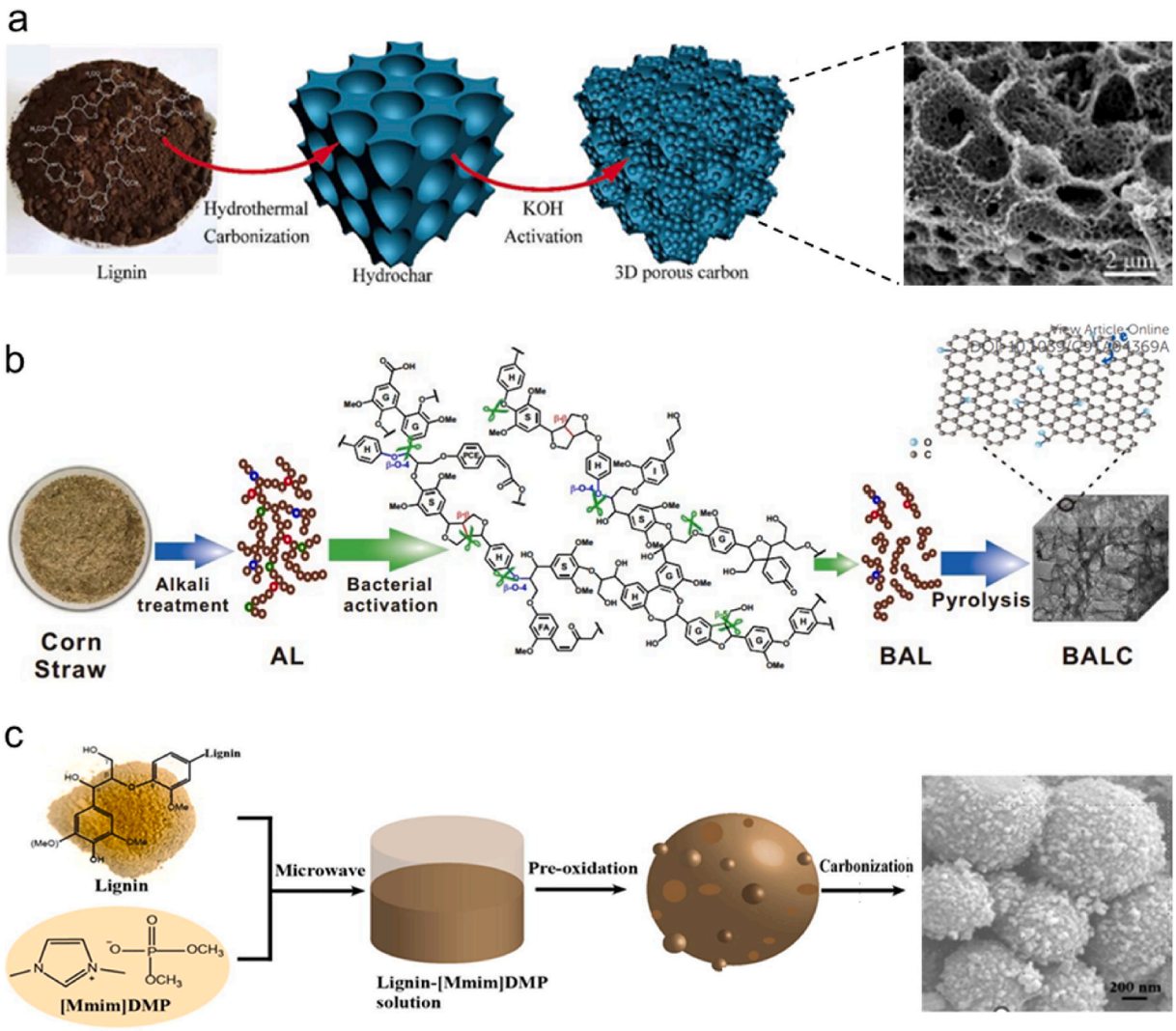

Fig. 5. Schematic illustration for the a) transformation of lignin into 3D hierarchical porous carbons [71]; b) mechanism diagram of bacterial activation [72]; c) synthesis process of carbon microspheres from [Mmim]DMP-lignin solution for supercapacitors [76].

mesopores provide fast-ion-diffusion channels, while micropores serve as the sites for ion storage. This structure thus leads to a high-rate capability (capacity retention of 64.2%, the capacity at a sweep rate of 1000 mV· s ^{1} to that of 2 mV·s ^{1}).

In addition to all lignin-based supercapacitor electrodes, agricultural lignin has been incorporated with petroleum-based resins for electrode synthesis. For instance, Qi et al. prepared the activated carbon microspheres (ACMs) from wheat straw lignin–urea–formaldehyde resin through NaOH activation [74]. The use of lignin and urea brought in oxygen- and nitrogen-containing groups, respectively, resulting in carbon electrodes with excellent electrochemical performance. The ACMs exhibited a high SSA of up to 3342 m^2·g ^{1} and a mesopore ratio of up to 83%. As a result, the ACM-based supercapacitor showed a specific capacitance of up to 290 F·g ^{1} at a current density of 0.5 A·g ^{1}. Moreover, the capacitance retention was maintained at 96.3% after 10,000 cycles. Most recently, Li et al. produced cage-like mesoporous carbon from corn stalk lignin [75]. In their study, lignin was first mixed with phenolic resin followed by spray drying to form a lignin-based phenolic resin (LPR). Then, LPR was pre-carbonized, KOH blended, and finally activated to obtain the cage-like mesoporous carbon. The specific capacitance of such carbon-based supercapacitors was up to 217.3 F·g ^{1}at 0.5 A·g ^{1}, which was higher than that of lignin-free mesoporous carbon (122.6 F·g ^{1}).

Finally, innovative modifications of porous carbon, such as heteroatom doping, have gained attention to improve electrochemical performance, especially in pseudo-capacitors. Liu et al. generated the N and P dual-doped lignin-based carbon microspheres (MLCM) using a simple two-step pre-oxidation and carbonization technique without needing high-pressure equipment or a templating agent, which may be easily scaled up for supercapacitor electrode manufacture [76] (Fig. 5c). In this work, they employed an ionic liquid ([Mmim]DMP) to dissolve lignin, and a variety of cation-anion combinations that allow for porosity and morphological control of target products. Meanwhile, it adds N and P to the carbon microspheres, increasing chemical affinity and pseudo-capacitance, which could significantly enhance the electrical conductivity of carbon materials. An abundance of quinone functional groups in lignin also facilitates redox activity, facilitating charge transfer processes between the electrode surface and soluble species. Altogether, MLCM materials demonstrated superior electrochemical performance at a current density of 0.8 A·g ^{1}; the maximum specific capacitance was 338.2 F·g ^{1}. The MLCM was formed into a symmetrical supercapacitor with a specific capacitance of 194 F·g ^{1} at 1A·g ^{1}, outstanding cycle stability after 5000 charging and discharging cycles at 2 A·g ^{1}, and a capacitance retention rate of 97.3%. In addition, the device's energy density was 7.81 Wh·kg ^{1} when its power density was 62.5 W·kg ^{1}.

4.2. Lithium battery and hydrogen storage materials

In addition to supercapacitor electrodes, agricultural lignins were also used as the cathode slurry to fabricate electrodes for lithium battery and hydrogen storage materials [77–82]. For example, Gnedenkov et al. developed a cathode for primary lithium batteries using buckwheat husk lignins [79]. In their study, 75 wt% of lignin powder, was blended with 15 wt% carbon black (to ensure electronic conductivity), and 10 wt% polytetrafluoroethylenes (binder) followed by drying under pressure (12 MPa) and then thermally treated at 250 °C for 2 h. The fabricated lithium battery had a specific capacity of 600 mAh·g ^{1} at a current density of 75 μA·cm ^{2}. In another study, the same group also developed a sunflower husk lignin-based cathode for lithium batteries, which had a specific capacity of 380 mAh·g ^{1} at a current density of 25 mA·g ^{1} [80]. The high oxygen content and rich oxygen-containing functional groups were the main reasons for selecting lignin for cathode fabrication.

Xi et al. produced highly graphitized and porous carbons from maize stalk lignin through K_2CO_3, KOH, K_3PO_4, or $K_3C_2O_4$ activation, and used them as battery electrodes [83,84]. They found K_2CO_3 outperformed other activators for lignin activation, which yielded a lignin-based carbon with a multilayer lamellar structure, a higher SSA, and a larger pore volume. The produced electrode exhibited a desired reversible capacity of 520 mAh·g ^{1} at a current density of 200 mA·g ^{1} over 200 cycles. Later, the same group produced HPC from corn stalk lignin through gas exfoliation and in-situ template technology using $ZnCO_3$ as an activator [85]. Compared to the porous lignin carbon prepared by $ZnCl_2$ and K_2CO_3, the HPC prepared by $ZnCO_3$ demonstrated superior lithium storage performance. It offered an extraordinary volume/mass specific capacity (730 mAh·cm ^{3}; 550 mAh·g ^{1} after 200 cycles at 0.2 A·g^{-1}) and cycling performance (99% retention after 10,000 cycles). This was attributable to its multi-stage pore distribution, which facilitates lithium-ion and electron transfer and provides more active sites for lithium-ion storage.

Hydrogen storage is another use that adds value to the carbon precursor of agricultural lignin. Recently, Rowlandson et al. prepared activated carbons using organosolv lignins extracted from hemp hurds, eucalyptus chips, flax straw, and rice husk [82]. The activation was conducted at 1000 °C using CO_2 as the activator. Activated carbons produced from the study displayed an SSA of 1060–1260 m^2·g ^{1} and has a hydrogen absorption of up to 1.8 wt % at 1 bar and 196 °C.

5. Lignin-based carbon foams

Carbon foams are solid materials characterized by their high carbon content, monolithic pore structure, and low density [92]. Depending on the feedstock and production process, carbon foams may exhibit favorable characteristics such as high strength, thermal stability, chemical inertness, and tailorable thermal and electrical conductivities. Carbon foams are currently commercially produced from coal- and petroleum-derived feedstocks, and to date, have not found widespread commercial utilization due at least in part to the high cost of production [93]. Few studies have demonstrated the production of carbon foams directly from biomass-derived feedstocks [94].

Specific to agricultural lignins, Vannarath and Thalla produced an organosolv lignin from Arecanut husk and used it prepare an irregular shape porous carbon for oil uptake in oil-water separations [95]. Despite the porous carbon being three-dimensional (3D) and lightweight (i.e., density was 0.0294 g·cm ^{3}), it's hard to be considered as carbon foam because its shape cannot be regulated. Nevertheless, this 3D porous carbon exhibited an oil sorption capacity (i.e., 7842.71 mg·g ^{1} for diesel oil) because of its hydrophobicity and high porosity. Most recently, Liang et al. directly converted fractionated corncob lignin into shapeable carbon foams by a two-step pyrolysis (stabilization and carbonization) process [96]. Upon heating, the formation of carbon foam depended on the interplays of lignin melting, thermal decomposition, and cross-linking. They found foam shape, density, and mechanical strength can be tailored by manipulating lignin molecular weight, stabilization temperature, and temperature ramping rate. For example, high molecular weight lignin fractions yielded a high-density carbon foam with a more regular shape, higher density, and higher compressive strength.

6. Lignin-based products for agricultural applications

In recent years, irregular and indiscriminate applications of chemical fertilizers have led to the degradation of soil fertility and environmental pollution. Using the adsorption capacities and/or specific functional groups in lignin, researchers have used lignin, and its derivatives, in a variety of slow-release fertilizer formulations. In general, lignin-based slow-release fertilizers can be classified into two major categories: physically impeded (e.g. coatings) and chemically modified (e.g., ammoxidation, Mannich, and chelation reactions) [97].

Due to the poor film-forming properties and low water resistance, the slow-release capacity of lignin-based coatings is typically limited [98]. Therefore, to obtain a better slow-release effect, a double-coating technology with a modified agricultural lignin was developed [99–101]. Fertahi et al. reported a new coating material based on lignin extracted from olive pomace with polysaccharides; the coating, applied to water-soluble triple superphosphate (TSP) fertilizer, had both good interaction and adhesion with the mineral fertilizer surface [102]. The results showed that compared to >95% of P being released from uncoated TSP within 48 h (and all P being released within 72 h), the release of P with the lignin-polysaccharide coated TSP decreased to approximately 60% within 72 h using a TSP/polymer ratio of 5/1.

With respect to the use of chemically modified lignins as slow-release fertilizers, direct/indirect chemical reactions have been used to incorporate the nutrient element into the lignin. Currently, most studies are mainly focused on introducing nitrogen into the structure of lignin [103]. Ammoxidation and Mannich reaction modifications are the two most common methods for preparing lignin-based slow-release fertilizers. Focusing on the agricultural lignins, Jiao et al. prepared corn cob lignin enriched with nitrogen using the Mannich reaction following a phenolation pretreatment [98]. The amounts of active sites in lignin for nitrogen incorporation were significantly increased to 8.26 mmol·g ^{1} from the original 2.91 mmol·g ^{1} by phenolation. The aminated lignin, with a high nitrogen content (10.13%), and low C/N ratio (6.08), had a favorable nitrogen release behavior in soil.

7. Summary and future research

Lignin is an abundant and sustainable polymer resource that can be isolated from biomass; it has a one-of-a-kind aromatic structure and a high carbon content. Above all, its production does not compete with food supply chains and its valorization allows for use of an ever-increasing volumes of agricultural residues. Over the years, many innovative applications have been proposed, opening the door for the utilization of lignin as a candidate material to replace non-renewable petroleum-based polymers. However, progress in all these applications can only be sustained by the continuous supply of high-quality lignin, as its properties are strongly dependent on the source and extraction method. This calls for the development of versatile processing routes and the provision of industrial scale biorefineries to possibly produce predefined lignin chemical structures with the aid of artificial intelligence and machine learning. This may help in the elucidation of structure/property/function relationships of lignin precursors and the tailoring of their products for specific applications.

Data availability

Data will be made available on request.

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