Lignin to Materials: A Focused Review on Recent Novel Lignin Applications

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Abstract: In recent decades, advancements in lignin application include the synthesis of polymers, dyes, adhesives and fertilizers. There has recently been a shift from perceiving lignin as a waste product to viewing lignin as a potential raw material for valuable products. More recently, considerable attention has been placed in sectors, like the medical, electrochemical, and polymer sectors, where lignin can be significantly valorized. Despite some technical challenges in lignin recovery and depolymerization, lignin is viewed as a promising material due to it being biocompatible, cheap, and abundant in nature. In the medical sector, lignins can be used as wound dressings, pharmaceuticals, and drug delivery materials. They can also be used for electrochemical energy materials and 3D printing lignin–plastic composite materials. This review covers the recent research progress in lignin valorization, specifically focusing on medical, electrochemical, and 3D printing applications. The technoeconomic assessment of lignin application is also discussed.

Keywords: lignin valorization; lignin applications; 3D printing; electrochemical material; medical application

1. Introduction

The overdependence on fossil fuels has raised increasing concerns about climate change and an energy crisis, which has warranted research to search for renewable and clean energy alternatives. Lignocellulosic biomass is the most abundant and renewable source of organic carbon on Earth, presenting the best option to achieve a sustainable biorefinery in the future [1]. In recent decades, there has been significant research conducted to convert biomass components into biofuel and value-added products. Although some sectors in biorefineries, including lignocellulosic bioethanol, have been widely researched, the economic feasibility is often discussed when it comes to commercialization. From the technoeconomic perspective, the success of future biorefineries is highly dependent on lignin valorization.

Lignin can be obtained from a variety of natural sources, including woody biomass, agricultural residues, and energy crops. Regardless of the type of lignin, there are typically two pathways for lignin valorization. One pathway uses the lignin as a macro-polymer to produce valuable materials; the other pathway involves the depolymerization of lignin into low-molecular weight monomers [2]. Lignin monomers can undergo derivatization through various chemical processes to be converted into desired products [3].

The world annually produces around 100 million metric tons of lignin, worth approximately 732.7 million USD [3]. Since lignin is a cheap and abundant natural polymer, much research has been spent on valorizing lignin. In recent decades, perspectives on lignin have changed from a waste

product used as a low-grade fuel and animal feed to valuable products such as polymers, adhesives, and others [3–6]. More recently, lignin valorization has received interest in other sectors, like the medical and electrochemical energy materials sectors. The scope of this review will focus on the valorization of technical lignin in advanced materials.

2. Technical Lignins

In nature, lignin is an amorphous phenolic polymer that is randomly branched and crosslinked with cellulose and hemicellulose [7]. To utilize lignin, it needs to be isolated from biomass through various processes, and the extracted lignin is called technical lignin. Since most technical lignins are available in the pulp and paper industries as byproducts, the production of lignin will continue to increase as lignocellulosic ethanol emerges. Considering that the lignin extraction method modifies the native structure of lignin, it is important to understand how the process affects lignin structures to develop effective lignin valorization technologies. There have been many review articles that thoroughly discuss lignin separation methods and their influence on the structures and properties of the extracted lignin [8–11]. The following overview briefly introduces common industrial processes in which lignin is extracted from biomass.

Figure 1 illustrates several processes to extract technical lignins from lignocellulosic biomass. Among the technical processes, Kraft pulping is the major chemical pulping process, accounting for 85% of the total lignin production in the world [12]. The process is performed at a high pH, and about 90–95% of the lignin is dissolved into the black liquor. Kraft lignin is typically precipitated and recovered from black liquor by the addition of acidifying agents. Predominantly, the acidification is carried out by adding either mineral acid (e.g., sulfuric acid) or carbon dioxide, followed by filtering, washing, and drying for the recovery of Kraft lignin. Around 630,000 tons of Kraft lignin are annually produced, and most Kraft lignin is combusted for heat generation, resulting in low-value utilization. The sulfite pulping process is conducted between a pH of 2–12, depending on the cationic composition of the pulping liquor [13]. Lignosulfonates, isolated lignins from the sulfite process, contain significant amounts of sulfur in the form of sulfonate groups. Since lignosulfonates are widely available, lignosulfonates were used in a wide range of applications, such as dispersants, flocculants, concrete additives, and composites [14].
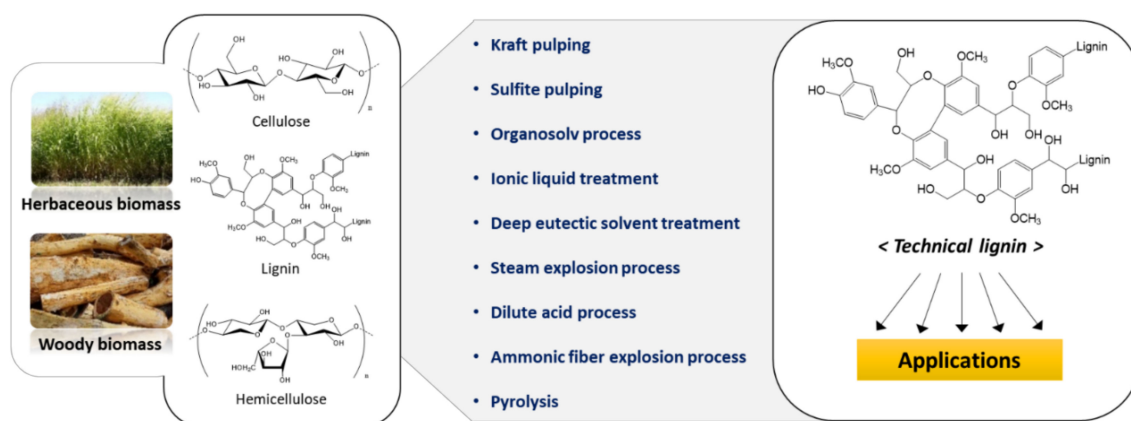
Figure 1. Processes for the extraction of technical lignins.

The organosolv process constitutes the fractionation of biomass components through treatment using an organic solvent, such as ethanol, ethylene glycol, acetone, tetrahydrofuran, and γ-valerolactone [15,16]. Since the organosolv process is conducted in the absence of sulfur, it has recently been utilized more so than Kraft and sulfite pulping. Furthermore, the large-scale production of organosolv lignin is expected from the emerging cellulosic ethanol sectors, which offers significant opportunities for lignin valorization.

In addition to the conventional pulping and biomass pretreatment processes such as steam explosion, dilute acid, and ammonic fiber explosion, there have been significant advances in biomass fractionation to extract high-quality lignin using novel solvents. For example, ionic liquids (ILs) and deep eutectic solvents (DESs) have attracted considerable attention as promising agents for biomass fractionation due to their high solvation capacity in the dissolution of biomass components [17,18]. The technical lignins obtained from ILs and DESs have been found to retain their original structures; the eco-friendly properties of such solvents offer new options for lignin extraction.

3. Medical Applications

3.1. Wound Dressings

Hydrogels are three-dimensional (3D) networks of polymers; their hydrophilic structures make them capable of absorbing and holding large amounts of water in their 3D networks [19,20]. Hydrogels have gained significant attention in biomedical sectors because they can be used for drug delivery, tissue engineering, and antimicrobial materials [21]. Recently, lignin has been viewed as a promising material for the production of hydrogels, because lignin possesses great antioxidant and antibacterial properties [22]. Furthermore, hydrogels have a high absorption capacity, allowing them to effectively remove undesirable metabolites from the wound [23]. Due to lignin's high mechanical strength, the use of lignin in hydrogels helps protect the wound from further injury or contamination [23]. However, due to the relatively low amount of hydroxyl groups and its rigid structure, lignin requires pretreatment for it to be effectively used as a medical material. In this respect, many studies have focused on developing chemical modification strategies of lignin. Such modifications include the introduction of new active sites on lignin by combining other materials and the functionalization of the hydroxyl group to enhance its reactivity.

There are several ways that lignin can be combined with other materials to construct composite wound dressings that are antimicrobial and biocompatible. A study that used a lignin model polymeric compound, dehydrogenate polymer (DHP), in alginate (Alg) hydrogel, determined that the lignin model DHP in hydrogel produced antimicrobial effects against several clinical bacterial strains and did not have toxic effects on human epithelial cells [24]. A stock suspension of 10 mg/mL DHP and 20 mg/mL Alg was used to test for antibacterial properties. The DHP–Alg demonstrated minimum inhibitory concentration values of 0.002–0.90 mg/mL and a minimum bactericidal concentration of 0.004–1.25 mg/mL. Furthermore, DHP–Alg showed higher antibacterial activity against *L. monocytogenes*, *P. aeruginosa*, and *S. Typhimurium* than streptomycin and ampicillin [24]. The mechanism of antibacterial action was speculated to be that DHP in hydrogel interacts with bacterial cell wall synthesis and/or cell wall structure, which could lead to the disorganization of the cell wall. Although more studies need to be conducted on elucidating the antibacterial mechanism of DHP, the results show the potential application of lignin as a wound-healing agent.

Lignin amine and sulfite-pulped lignin can also be used to construct two different wound dressings. Lignin amine can be synthesized from sodium lignosulfonate by a Mannich reaction; the lignin amine can be crosslinked with poly(vinyl alcohol) (PVA) to form a hydrogel. When a solution of silver nitrate was added to the lignin-based hydrogel, the biocompatible hydrogel not only demonstrated enhanced antimicrobial properties against *E. coli* and *S. aureus*, but the hydrogel also exhibited good elasticity [25]. Additionally, the lignin obtained from sulfite pulping can be combined with chitosan dissolved in an acetic acid solution and PVA dissolved in water to form a lignin–chitosan–PVA composite hydrogel. The sulfonate groups in the lignin formed ionic bonds with amino groups in the chitosan; this is what gives the hydrogel a high mechanical strength and high antioxidant activity [23]. The lignin–chitosan–PVA composite hydrogel demonstrated inhibitory effects on *S. aureus* by penetrating its cell membrane. Results from the study suggested that a hydrogel with a greater lignin concentration resulted in an increase in the swelling ratio, hydrophilicity, protein adsorption capacity, tensile strength, and elongation.

Three-dimensional-printed wound dressings can also be constructed from lignin. Poly(lactic acid) (PLA) pellets coated with castor oil can also be combined with a small amount of Kraft lignin (3 wt % or less) and an antibiotic, tetracycline, to create a composite used for 3D printing wound dressings. The printed filament material was treated with the 2,2-diphenyl-1-picrylhydrazyl (DPPH), a free radical standard, to assess its radical scavenging activity, which can potentially be applied in wound care applications [26]. Figure 2 shows photographs of meshes that were 3D-printed from PLA and 2 wt % Kraft lignin. While lignin in the 3D-printing composite provided antioxidant properties to the composite, small amounts of lignin in the composite did not demonstrate antimicrobial properties with *S. aureus*. However, the tetracycline in the composite was what contributed to the composite's antimicrobial properties. More interestingly, the mesh of the PLA–tetracycline–lignin wound dressing can be 3D-printed based on the patients' needs, leading to the possible customization of wound dressings in the future.
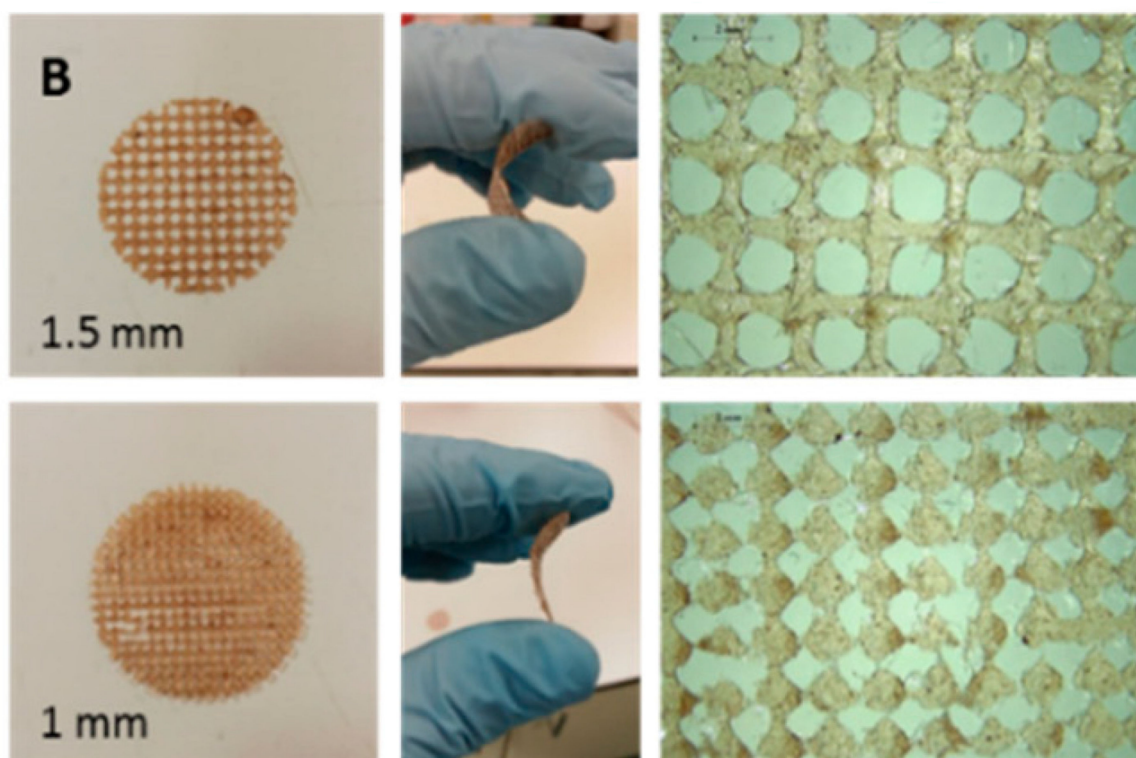
Figure 2. Meshes 3D-printed from poly(lactic acid) (PLA) and 2 wt % lignin with grid sizes of 1.5 mm and 1 mm. The middle column shows the side view of each mesh when slightly bent, while the right column shows the close-ups of each mesh. Reprinted from reference [26], with permission from the MDPI.
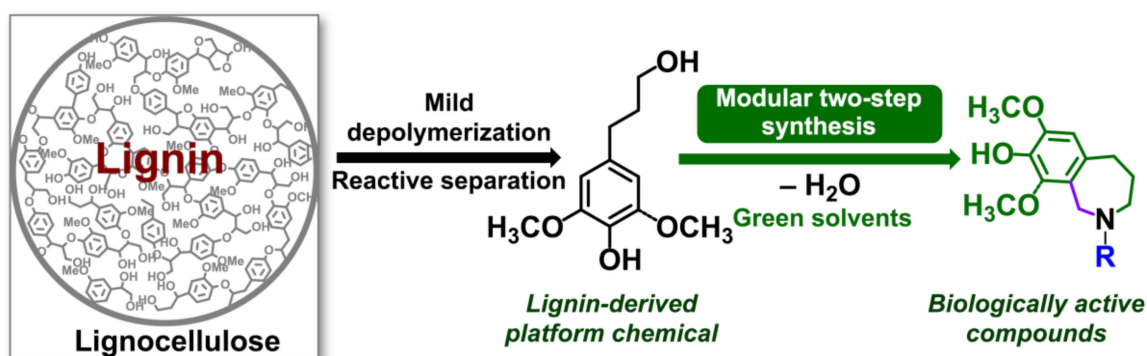
3.2. Pharmaceuticals

There are specific compounds derived from lignin that can not only be used to construct pharmaceuticals to alleviative the symptoms of diseases, but can also be used to construct drug delivery materials. While sulfite and Kraft lignins are more commonly used lignins to synthesize pharmaceutical products, recently lignins obtained from steam explosion and the organosolv process have been investigated for pharmaceutical use. The mechanism commonly employed to utilize lignin is to depolymerize lignin and obtain derivatives to construct biologically active compounds. These biologically active compounds can be used to treat the Herpes simplex virus, influenza virus, and other viruses [27]. Since the toxicity of drugs is an important factor in the drug discovery phase, the cytotoxicity of lignin was studied; findings from a study show that lignins are generally safe to consume and no not disrupt cell viability [27]. When synthesizing pharmaceutical drugs,

the antioxidant property of lignins is highly valued because its hydroxyl functional groups in their phenolic rings neutralize free radicals and protect molecules from oxidation [27]. For instance, lignins isolated from Bagasse, steam explosion lignins, and lignosulfonates have half maximal inhibitory concentrations of 44.9 µg/mL, 74.6 µg/mL, and 133.6 µg/mL, respectively. Compared to a common antioxidant present in tea, epicatechin, which has a half maximal inhibitory concentration of 42.3 µg/mL, these lignins have enhanced antioxidant properties [28].

Lignin-derived components and products, including polyphenols, may help in controlling diseases, like diabetes, coronary heart disease, and Alzheimer's disease. Results of a study suggest that lignosulfonic acid can be taken with glucose to cause a delay in the uptake of glucose to potentially treat diabetes [29]. The study administered a combination of lignosulfonic acid and glucose as well as glucose alone to determine their effects on 2-deoxyglucose uptake in human colorectal adenocarcinoma cells. Since lignosulfonic acid is a non-competitive inhibitor of α-glucosidase, lignosulfonic acid can inhibit α-glucosidase activity and delay the absorption of glucose in the intestines. Lignosulfonic acid was also demonstrated to inhibit human immunodeficiency virus (HIV) and herpes simplex virus (HSV) transmission when tested with human T-cell leukemia cells, human embryonic kidney cells, and peripheral blood mononuclear cells [30]. Furthermore, lignosulfonates have the potential to be developed into drugs that could decrease oxidative activity, thereby boosting the immune system [3]. Lignin may also helpful in controlling obesity. Out of the dietary fiber components, lignin is reported to be the strongest bile acid adsorbent due to the presence of methoxyl and β-carbonyl groups in lignin. When the lignin binds to the bile, micelles are unable to be produced, thereby resulting in decreased lipid absorption [27].

Table 1 summarizes several studies describing the value products that can be synthesized from technical lignins. In a study, lignophenols derived from the native lignin of Japanese cedar were shown to decrease oleate-induced apolipoprotein-B secretion and reduce cholesterol in HepG2 cells (human liver cells), thereby potentially preventing coronary heart disease [31]. These lignophenols were derived using a phase separation process that included cresol and sulfuric acid; lignophenols were then dissolved in dimethyl sulfoxide before being cultured with HepG2 cells. Another study presents three steps in which lignocellulose can be depolymerized to form platform chemicals, which can then be used to synthesize biologically active compounds with the use of a DES [32]. The DES used was a mixture of choline chloride and oxalic acid. Biologically active compounds that can be synthesized include tetrahydro-2-benzazepines. Tetrahydro-2-benzazepines are present in alkaloids, such as galantamine, that could treat Alzheimer's disease. In this three-step process, the only by-product was water. Furthermore, biologically active compounds derived in this study were also shown to be effective against *S. aureus*. Figure 3 summarizes the reaction pathway to synthesize biologically active compounds that likely exhibit antibacterial or anticancer activities.


Figure 3. Summary of the reaction pathway to synthesize the biologically active compounds. Reprinted with permission from [32]. Copyright (2019) American Chemical Society.

Table 1. Summary of the studies on the pharmaceutical applications of lignin.

Product	Usage	Feedstock Lignin	Lignin Content (wt %)	Reaction/Process Condition	Source
Lignophenols	Potentially prevent coronary heart disease	Japanese cedar native lignin	N/A	Phase-separation with cresol and sulfuric acid.	[31]
Tetrahydro-2-benzazepines	Precursor to the drugs that could treat Alzheimer's disease	Pine and poplar lignocellulose	N/A	For depolymerization step, copper-doped porous metal oxides and 40 bar H_2; for synthesis of product, used choline chloride/ oxalic acid DES at 70−80 °C for 20−48 h.	[32]
Drug vehicles	Deliver methotrexate	Sugar cane bagasse	N/A	Lignin soaked in 100 ppm methotrexate solution with intense stirring at 40 °C for 18 h.	[33]
Nanoparticles	Deliver Sorafenib and Benzazulene	LignoBoost™ softwood Kraft lignin	50%	Lignin dissolved in tetrahydrofuran and put in the dialysis bag, iron (III) isopropoxide in tetrahydrofuran for 24 h.	[34]
Hydrogels	Drug delivery system	Kraft lignin	Up to 80%	20 to 200 wt % citric acid, used micro-extruder at 120 °C for 2 or 5 min of recirculation.	[35]
Biosorbent	Adsorb ibuprofen and acetaminophen	Kraft lignin	50%	Kraft lignin and α-chitin powder mixed, following activation with 15% hydrogen peroxide.	[36]
Photocatalyst	Degrade acetaminophen	LignoTech lignin	33%	TiO_2 and NaOH, hydrothermal treatment at 130 °C for 48 h, centrifuged, dried, calcined in N_2 or air.	[37]
Nanofibers	Adsorb fluoxetine	Alkali lignin	30–50%	Aqueous polyvinyl alcohol and distilled water at 80 °C for 60 min, electrospinning fibers.	[38]

Materials containing lignin and lignin derivatives can also be effectively used to deliver drugs inside the human body. Perhaps the largest advantages of lignin-based nanoparticles for delivering drugs are their inexpensive and non-toxic properties. For instance, lignins derived from sugarcane can be used as a drug carrier to deliver methotrexate and treat rheumatoid arthritis [33]. Lignin nanoparticles encapsulating iron oxide could effectively deliver Sorafenib and Benzazulene in alkali media [34]. Hydrogels produced from varying concentrations of starch, Kraft lignin, hemicellulose, and citric acid were tested for their ability to deliver drugs effectively [35]. To characterize the performance of these hydrogels, the swelling capability was analyzed because it indicates the crosslinking density and ultimately the amount of water absorbed in the hydrogel. Based on the experiments testing the diffusion of water into the gel, the hydrogel has the potential to swell to 1380% at a pH of 9 and the potential to swell to 345% at a pH of 4. The pH-dependent swelling behavior is desirable for hydrogels, because the diffusion rates of molecules in and out of the gel can be controlled.

Since pharmaceutical products are a common source of water pollution, lignin can adsorb these pharmaceuticals to alleviate water pollution. Kraft lignin and α-chitin powder from crab shells were mixed with hydrogen peroxide to create a sorbent that adsorbed ibuprofen and acetaminophen, which are commonly used drugs that cause water pollution [36]. Figure 4 summarizes the process to construct the biosorbent with a high removal efficiency of ibuprofen and acetaminophen. Several mechanisms for the adsorption process were proposed. One such mechanism was ion−dipole interactions; there could be electrostatic interaction between pharmaceutical ions and the negatively or positively charged surface of the sorbent surface. Another mechanism could be hydrogen bonds forming between the pharmaceutical drug and the sorbent. Such sorbents can potentially be reused. For instance, ethanol was an effective eluent for ibuprofen with a yield of 82.2%, while methanol was an effective eluent for acetaminophen with a yield of 80.8%.
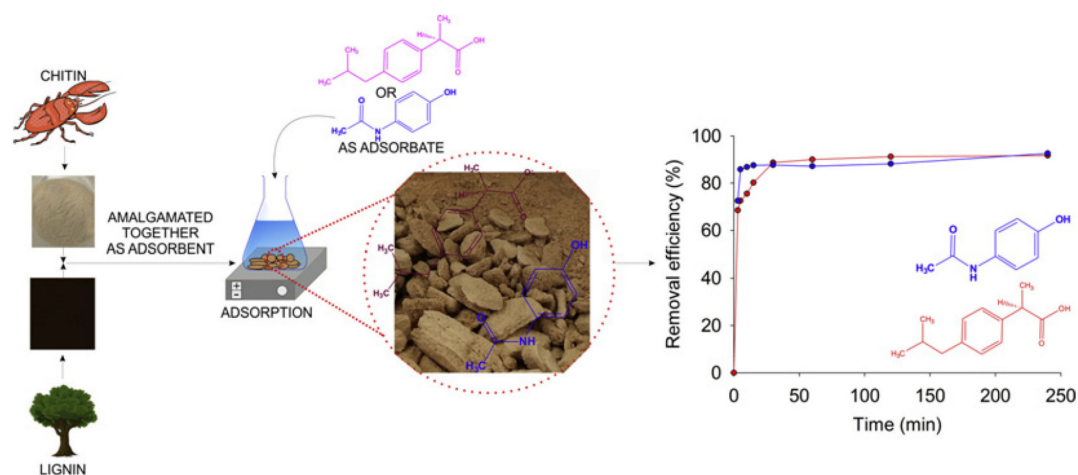
Figure 4. Biosorbent consisting of chitin and lignin removing ibuprofen and acetaminophen with high efficiency. Reprinted from reference [36], with permission from Elsevier.

In another application, lignin was used as a carbonaceous precursor with TiO_2 to form a photocatalyst that degraded acetaminophen, or Tylenol, in one hour of solar radiation [37]. Photocatalysts that experienced thermal treatment in nitrogen rather than in air maintained more carbon from the lignin. This caused a higher light absorption and decreased the photocatalytic efficiency. In another study investigating the use of lignin to adsorb fluoxetine, alkali lignin with low sulfur content and PVA were dissolved to form a solution used for electrospinning [38]. Nanofibers recovered from the electrospinning process then went through a thermostabilization processes and an acidic bath to increase the strength of the fibers. A lignin:PVA ratio of 1:1 resulted in the optimal adsorption capacity; this lignin−PVA nanofibrous membrane adsorbed around 38% of the fluoxetine. The authors

of the study hypothesized the sorption mechanism to be the phenol groups in lignin-forming hydrogen bonds with the amino or Fluor groups of the fluoxetine.

4. Electrochemical Energy Materials

In the past decade, lignin has been increasingly investigated for its potential incorporation in the production of battery materials and supercapacitors for the main advantage of being environmentally friendly. With the increasing manufacturing of lignin in recent years, lignin has been available at a low cost. The relatively low cost of lignin makes it an attractive ingredient for the production of anodes for lithium batteries, gel electrolytes, binders, and sodium batteries [39]. Lignin is also valued for the production of energy materials due to its high carbon content that is greater than 60 wt %. Specific functional groups of lignin, such as benzyl and phenolic groups, act as active reaction sites for ions to be stored in applications to supercapacitors. Additionally, the abundant oxygen atoms in lignin are integral for facilitating electrolyte ion adsorption and redox reactions for supercapacitors. Lignin can be used for porous carbon structures in supercapacitors due to its favorable crosslinked structure [2]. While lignin types like lignosulfonate can act as a sulfur-doped agent in batteries or supercapacitors, alkali lignins have shown to be suitable for electrospinning processes to construct nanomaterials [39]. There are generally two processes commonly employed to derive carbon from lignin for energy material applications. One process utilizes precursor carbonization and carbon activation, while the other process uses chemical activators before carbonization and activation that happen at the same time [2]. Graphene, a promising carbon material for electrochemical energy materials, can be synthesized from lignin by catalytic graphitization, carbonization, or oxidative cleavage along with aromatic refusion [40–42].

The incorporation of lignin results in a high gravimetric capacitance and great cycling durability for energy materials. Table 2 shows the summary of recent studies on the electrochemical applications of technical lignins. In an experiment with electrospun carbon nanofibers produced from alkali lignin−PVA solutions, the capacitance of the supercapacitor reduced by 10% after 6000 cycles of discharging and charging [43]. Furthermore, a higher energy value of 42 W h kg^{-1} and a power density of 91 kW kg^{-1} were reported. The experiment suggested that an increasing amount of lignin in precursor nanofibers resulted in a decreased average pore size, increased pore volume, and increased specific surface area. In another study, electrodes constructed from 75 wt % alkali lignin and 25 wt % 0.5 M sodium sulfate electrolyte resulted in one of the highest specific capacitances for electrodes produced from biopolymers: 205 F g^{-1} [44]. The mesopore range of carbon fibers had a wide pore distribution, which contributed to excellent electrochemical performance. Additionally, hierarchical porous carbons can be derived from steam explosion lignin through the carbonization−activation method. Lignin-based hierarchical porous carbons showed a high capacitance of 286.7 F g^{-1} at 0.2 A g^{-1} [45]. The structure of lignin provided advantages to the electrochemical performance, including accessible ion transportation pathways and a high surface area.

Lignin-derived materials used to construct batteries have performed similarly with commercial graphite and other materials commonly used in the industry. Ball-milled hydrolysis lignin can be used for low-rate power sources. A study investigated the performance of a battery that used hydrolysis lignin as the lithium battery cathode material [46]. The cathode material had 76 wt % hydrolysis lignin, 13 wt % carbon black, and 11 wt % polytetrafluoroethylene (PTFE)-based binder. Lithium batteries using this hydrolysis lignin as a cathode material achieved a high discharge capacity of 450 m A h g^{-1}.

Additionally, acetone was used to extract lignin from a corn stalk lignin precursor; the extracted lignin was used to construct hard carbon materials through stabilization in nitrogen, carbonization in nitrogen, and hydrogen reduction [47]. Figure 5 shows the pyrolysis reaction mechanism that occurred after the lignin was extracted from a precursor with acetone. The hard carbon had an initial discharge capacity of 882.2 m A h g^{-1} at 0.1 °C and retained a charge capacity of 228.8 m A h g^{-1} at 2 °C for 200 cycles. In another study, a blend of lignin, PLA, and elastomeric polyurethane was used to create

carbon nanofibers through electrospinning. These nanofibers led to increased porosity levels and additional lithium storage sites [48].

Table 2. Summary of the studies on the electrochemical applications of lignin.

Product	Feedstock	Lignin Content (wt %)	Reaction/Process Condition	Source
Supercapacitor	Alkali lignin	30–70%	Electrospinning aqueous alkali lignin and PVA, temperature stabilization in the tube furnace ramped from 25 to 220 °C, held at 220 °C for 8 h.	[43]
Supercapacitor	Softwood alkali lignin	75%	Lignin, PVA, and distilled water mixed at 60 °C for 1 h and at room temperature for 4 h, followed by electrospinning.	[44]
Supercapacitor	Steam explosion lignin	17–50%	Carbonization at 500 °C or 800 °C, activation with KOH, post-treatment by washing with hot water and drying at 100 °C overnight.	[45]
Lithium battery cathode material	Hydrolysis lignin	76%	Ball milled to 30 microns, washed with distilled water in centrifuge for 10–12 h, dried at 60 °C for 24 h.	[46]
Lithium battery anode material	Acetone lignin from corn stalks	80%	Stabilized at 300 °C for 2 h in N_2 in tube furnace.	[47]
Lithium battery anode material	Organosolv hardwood lignin	50–80%	Thermoplastic elastomeric polyurethane, dimethylformamide, PLA stirred at 50 °C for 5 min before electrospinning.	[48]
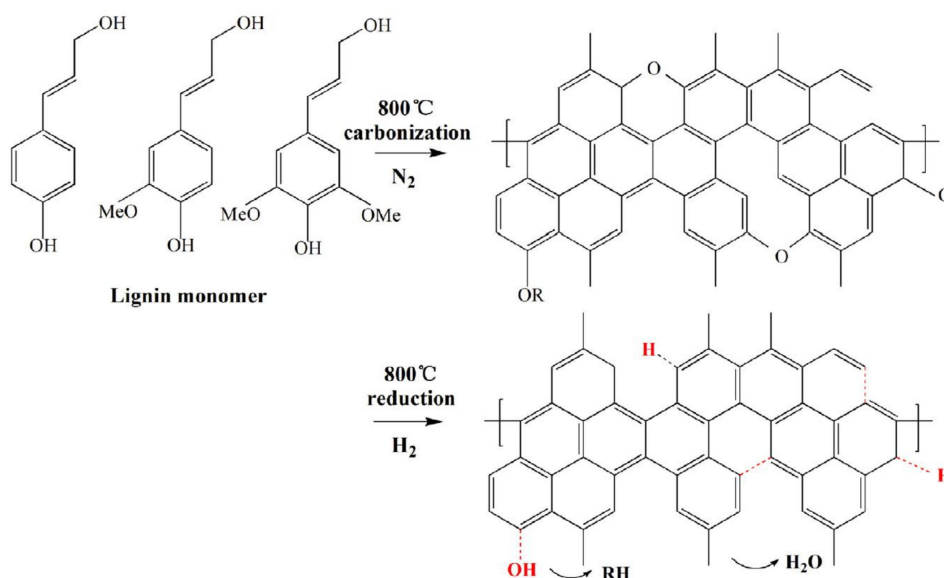
Figure 5. Reaction mechanism using the pyrolysis technology. Reprinted from reference [47], with permission from Elsevier.

5. 3D Printing Lignin−Plastic Composites

Blending lignin with various plastic materials to form 3D printing composites has recently received attention. The ideal 3D printing material has excellent extrudability to ease the process of 3D printing while also being strong so that the final printed material can retain its structure. Lignin has several structures that are advantageous for 3D printing: aliphatic ether groups, β-O-4′ linkages, and oxygenated aromatic bonds [49,50]. Incorporating lignin into plastic materials traditionally used for 3D printing results in composites that can be used for a more environmentally friendly and cost-effective 3D printing process.

There has also been recent discussion with energy sacrificial bonds as a mechanism for strong biomaterials, including lignin. Such sacrificial bonds dissipate energy through rupturing and reform by stretching. In light of this, a study investigated Zn-based coordination bonds between lignin nanoparticles and an elastomer matrix [51]. Such bonds were found to facilitate the dispersion of lignin in the matrix, thereby enhancing the strength of the composite. This study reported that a

lignin loading as high as 30 wt % can increase the strength, ductility, and toughness of thermoplastic elastomers, which can be used for 3D printing.

Several studies show that lignin can enhance structural properties of 3D printing materials. Table 3 summarizes recent studies on the application of technical lignins to 3D printing materials. In a study, when Kraft lignin was blended with acrylonitrile butadiene styrene (ABS), the result was a more brittle structure; this composite demonstrated low tensile energy and strength [49]. However, when 10 wt % acrylonitrile butadiene rubber (NBR41) was added to the composite, the chemical and physical crosslinks between the NBR41 and lignin resulted in the improved mechanical properties of the composite relative to common petroleum-based thermoplastics. This composite containing 40 wt % lignin, 10 wt % NBR41, and 50 wt % ABS showed great 3D-printability.

Table 3. Summary of the studies on the 3D printing applications of lignin.

Lignin Feedstock	Polymer Feedstock	Lignin Content in 3D Printing Composite (wt %)	Source
Kraft lignin	ABS	40%	[49]
Organosolv hardwood lignin	Nylon	40–60%	[50]
Softwood lignin from soda cooking process	PLA	20% and 40%	[52]
Alkali lignin and organosolv lignin	PLA	0.5–20%	[53]
Organosolv lignin	Polymer resins	5–15%	[54]
Softwood lignin from *P. radiata*	Polyhydroxybutyrate	20%	[55]

In an experiment where organosolv hardwood lignin was blended with nylon, the lignin was found to reinforce the thermoplastic matrix by increasing the stiffness of the structure, leading to increased 3D printability [50]. The melt viscosity was also reduced as a result of blending the lignin, which further increases 3D printability. The proposed mechanism for the bonding in the composite was lignin domains forming hydrogen bonds with the thermoplastic matrix. In addition, a study shows that 20–40% lignin can be used with PLA to form a matrix material for 3D printing. In the study, characterization techniques including thermogravimetric analysis, X-ray diffraction, and scanning electron microscope indicated that lignin is a nucleating agent that increases the crystallization of PLA [52]. This composite material resulted in great extrudability and flowability; it was also observed that lignin did not agglomerate. In another study, alkali lignin and organosolv lignin were acetylated to improve the compatibility with PLA to form a composite [53]. Even though the lignin decreased the crystallization behavior of PLA, it drastically improved the thermal stability of PLA and increased the elongation at break. The acetylated lignin was observed to prevent PLA from undergoing hydrolytic degradation.

Besides combining lignin with PLA, other studies have shown the diverse types of plastics that lignin can be blended with to construct effective 3D printing materials. For instance, authors of a study constructed photoactive acrylate resins used for 3D printing from up to 15 wt % acylated organosolv lignin, resin bases, a reactive diluent, and other compounds [54]. Figure 6 shows the reaction used for lignin acylation to construct resins. Even though the resulting lignin resin had decreased thermal stability compared to the commonly available resin, the resin exhibited characteristics that were favorable for 3D printing. The resin had increased ductility and resulted in 3D prints that were uniformly fused, high-resolution, and tough.

Additionally, a study reports that 20 wt % biorefinery lignin from *P. radiata* combined with polyhydroxybutyrate (PHB) improved the surface quality and reduced the shrinkage of the 3D printing material compared to the PHB alone [55]. Figure 7 below is a flow chart depicting how lignin can be extracted from softwood chips and combined with PHB to construct an improved 3D printing material. The presence of lignin was reported to reduce wrapping by values between 38% and 78% when compared to PHB, used as the sole printing material. This reduction of shrinkage was possibly due to the complex bulk lignin structure in addition to the lack of interfacial tension between the lignin and the polymer matrix.
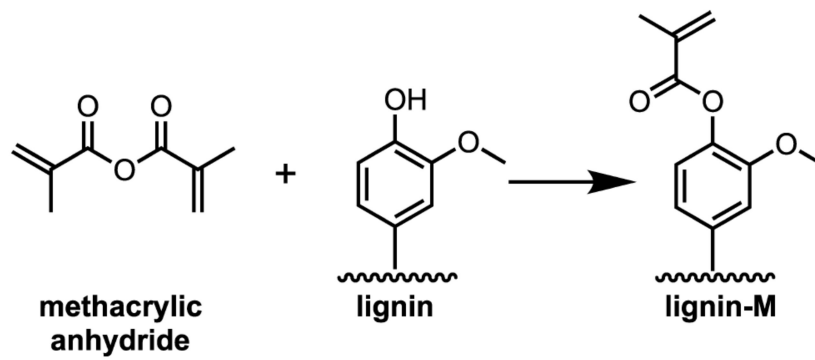
Figure 6. Reaction to synthesize acylated lignin for the construction of resin. Reprinted with permission from [54]. Copyright (2018) American Chemical Society.

Figure 7. Flow chart showing 3D printed product constructed from high-temperature mechanical pretreatment (HTMP)-derived lignin and polyhydroxybutyrate (PHB). Reprinted from reference [55], with permission from Elsevier.

6. Perspectives

In the past decade, there have been more investigations conducted on using lignin to construct medical materials, electrochemical energy materials, and 3D printing composites. From the limited technoeconomic assessments conducted, it is difficult to predict the economic trajectory of lignin valorization. Since lignin valorization is an emerging concept, production costs may be higher than conventional processes [3]. According to a technoeconomic assessment analyzing catechol production from lignin, the lignin depolymerization and product separation stages accounted for a total of 55% [3]. For the production of lignin micro- and nanoparticles, their investment cost was 160 million USD, with an atomizer and separation system costing roughly 65% of the capital investment [56]. Assuming Kraft lignin and lignosulfonates are used, manufacturing costs can vary between 870 and USD 1170 per ton. The production capacity of around 70% of North American Kraft pulp mills is restricted by the operation of recovery boilers. Another challenge is finding the optimal membrane used for the Kraft process that will result in the highest lignin yield and purity [57]. Factors to consider for future scale-up efforts would be the size of the market, price volatility of the desired product [3], and the cost of feedstock in addition to solvents [56]. Lignin commercialization is likely with increased international collaboration, as this will mobilize resources and facilitate the development of innovative pathways [57].

Materials constituting lignin and its derivatives have potential in the medical sector due to their versatility as a wound dressing, pharmaceutical drug, drug delivery system, and drug removal material. However, it is difficult for lignin to be absorbed by the human's small intestine or stomach because of its high molecular weight and polydispersity [27]. There have also been studies suggesting that lignin can adsorb toxins, cholesterol, and surfactants, which can negatively impact human health [27]. Much of the research conducted is still at the proof of concept stage and pharmaceutical drugs will need to go through clinical trials before determining their efficacy. Regulatory bodies, like the US Food and Drug Administration, will need to approve the medical products even before they can be commercialized [58]. Clinical trials are time-consuming and costly; thus, there needs to be sufficient confidence in the research done and the viability of the production process before pursuing clinical trials.

While lignin is cheap and eco-friendly as a feedstock material for battery and 3D printing materials, a significant challenge is that it is hard to control or isolate lignin's complex recalcitrant structures. Even when fractionation is employed to isolate a lignin structure, fractionation often results in a mixture of products [59,60]. The electrochemical performance of bio-based battery materials depends on pore features, surface chemistry, and the structure of the lignin raw material [2]. Even though lignin is a relatively cheap starting material, it is still challenging to produce high performing carbon materials for supercapacitors and batteries. Since some lignins cannot stabilize easily, they convert to carbon nanofibers and consequently their morphologies are difficult to control; this makes high-performing lignin-based electrodes difficult to achieve [61]. Furthermore, lignin reaction mechanisms are not well understood [2].

Incorporating lignin in 3D printing materials decreases the reliance on typical petroleum-based plastic 3D printing materials. Doing so not only makes the 3D printing materials more environmentally friendly, but it also reduces costs as lignin is much cheaper than typical 3D printing materials [62]. Additionally, a myriad of materials can not only be created by 3D printing, but they can also be customized. This is of interest in the medical sector, where wound dressings can be 3D printed and customized to best suit the patients' needs. While lignin and other materials are being developed as 3D printing materials, they will most likely not replace traditional 3D printing materials including plastics [62]. Studies conducted so far in this current review suggest that lignin can be used to enhance the properties of the lignin–plastic composite 3D printing material but will not be the main feedstock material for 3D printing.

Even though the technoeconomic assessments of lignin valorization present several challenges, lignin's versatility has attracted significant efforts to valorize lignin. To illustrate lignin's versatility as a renewable material, Figure 8 shows the number of publications and citations searched in the

Web of Science with the keywords: "lignin application." As presented, the number of publications and citations have substantially increased over the past decade, indicating that significant efforts have been made in lignin valorization. Considering that there has been increased market demand for renewable materials in a wide range of industries, innovative lignin applications will continue to be developed indefinitely.
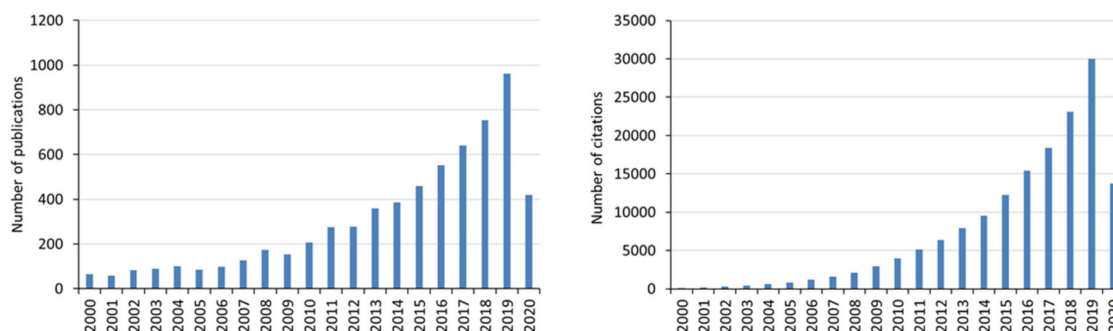
Figure 8. Number of publications (**left**) and citations (**right**) searched in the Web of Science with the keywords "lignin application" (as of May 30th 2020).

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