Review Article: A Brief Review on Applications of a Lignin

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ABSTRACT

Fossil fuels are used increasingly day by day everywhere on the globe and related to environmental issues like the environmental problems and heating. During this time, attempts are made to seek out sustainable different energy source which is affiliated with fossil material. The foremost important fossil material is plant biomass, especially wood, of the premise of cellulose percentage. However, those materials constituent of lignin have a content of 18-30%. Lignin is mainly used for fuel and has many valuable applications nanoparticles synthesis, like, polycarboxylic acid. supercapacitor electrode, photocatalyst, photovoltaic, etc. Recently, researchers highlighted more sustainable bioenergy production technologies. This review paper focused on different categories application of lignin within the industrial sector which could be a totally sustainable energy conversion.



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1. Introduction

ignin consists of methoxylates of phenylpropane units and derivatives, a three-dimensional amorphous polymer. In the development of bio-renovation materials, lignin is a natural amorphous polymer that has a great potential as a building block. It accounts for approximately 15–35% by weight for lignocellulosic biomass and can help in the production of fuels and chemicals as a significant renewable resource [1-4]. Large amounts of lignin are currently produced and processed in the pulp, paper, and lignin volumes with the continued development of biorefineries are anticipated to increase substantially. There are millions of tons of lignin from the paper industry and a limited quantity of lignin extracted annually through the direct mining of lignin from plants [5]. Several excellent review papers have documented and summarized various lignin converting attempts, including gasification, pyrolysis, and selective depolymerization [6-15]. Lignin constitutes a significant biomass with cellulose component, along and hemicellulose, providing 40% of the total energy for lignocellulosic biomass [16]. In a biorefinery, the lignin processing is still a difficult task, partly because of structural change during pretreatment with biomass [17-22]. There is general further formation of new C-C connections, causing problems to depolymerize and use the resulting lignin [23]. The use of industrial lignin is still very limited, leading to waste of resource and pollution [24].

In recent paper industry and as a feedstock for bio-ethanol production cellulose and other carbohydrates from plant biomass are used sccessfully. Just 2% of lignin produced as a byproduct of the pulp and fuel ethanol production is used commercially of 50 million tons of lignin produced by the pulp and paper industry in 2010 [25]. In the bio-refinery configuration, all of the components extracted from the processing complex are utilized in the most efficient manner. Lignin utilization is therefore a worldwide bio-economic activity in the manufacture of value-added goods. The amorphous lignin biopolymer primarily consists of three major monolignols: pcoumaryl (P), coniferyl (C), and sinapyl (S) spirits with a varying ratio of ether and carbonic bonds [26]. Lignin that was obtained from plant biomass is distinct from natural lignin as by-products. The aromatic structure of lignin's and the existence of large amounts (phenolic, aliphatic and carboxylic) of OH groups, makes it possible to alter technical lignin's by reacting to the epichlorohydrin reaction of OH groups [27].

Lignin is a sustainable ingredient for the processing of a variety of products such as carbon fiber, phenolic compounds, various oxidized products, multifunctional hydrocarbons, and petroleum-based syngasses. In addition, compared with its oil-derived counterparts, lignin derived materials, and fuels provide better environmental efficiency, are of low weight, fuel efficient, and more significant can reduce costs. Lignin has a different type of application in many important sectors such as the adsorption of heavy metal ions in water, nanoparticle synthesis, super capacitor electrode, photo-catalyst, photovoltaic, water flocculation, etc. Here, lignin was modified of different type of compound and showed a better characteristic for acting active sector (25, 26).

This paper presents various type of application of lignin, described the modified compound which is developed the characteristic of lignin, and also described most important application of lignin in our industrial sector with a great contribution of our economic part. It is believed that such investigations would be quite useful to develop a new environmentally friendly lignin modification compound which is greatly the contribution of energy sector and industrial sector.

2. Major sources of lignin

Lignin is present for the cellulose in abundance in the naturally occurring polymers in all vascular plants since lignin is produced through photosynthesis as is the case with many other biomass components (**Figure 1**).

The production of renewable lignin on earth is estimated to be between 5-36, 10, and 8 tons per year. The lignin content is between 15 and 40 percent of wood plants from gymnosperms and phylums of the angiosperms and less than 15 percent of lignin's in herbs [12, 29, 30]. In annual plants, the low content of lignin is also typically found. As a source of cellulose fibers for the production of paper and board products, many softwood and hardwood species, along with certain varieties of annual plants, have commercial significance. Thus, the massive

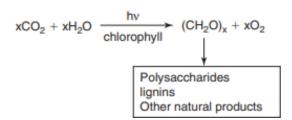


Figure 1. The fixation of carbon dioxide in nature through the photosynthesis reaction [28]

amounts of lignin as alkaline lignin and lignosulfonates are dissolved, respectively, in specific fiber liberation processes such as alkaline or sulfite pulping, while this lignin's is never isolated, but burned together with other wood components released into the liquor pulp to create the required steam for processing, subject to few exceptions. Compared with the original lignin, lignin is structurally altered in industrial pulping processes and emerging processes, including wood hydrolysis in biofuel processing. Often with a high degree of polydispersion, these forms of lignin may generally be defined as the heterogeneous molecular mass Polyphenols of 100-2000. Lignin is an essential part of cell walls in developing plants, on the other hand, and has chemical links to all forms of polysaccharide components. For sprucewood, the main part of lignin was shown to be covalently associated with the hemicelluloses (i.e. xylan and glucomannan), with cellulose being associated in a minor quantity [31]. However, the lignin concentration is not uniformly distributed in the cell wall, and despite the high amount of lignin in the middle lamella, because of its large relative thickness, the predominant portion is in the secondary wall layer S2 [32]. A detailed study included the lignin distribution among two plants, one softwood and one hardwood. Any effort to separate lignin from wood or other forms of biomass should be followed by a mechanical breakdown of the material. Intensive material milling is typically used to remove the structural integrity (i.e. the cell types), the cell layers, and any macromolecular inhomogeneities and from such materials, it is only possible to achieve an average lignin structure. Despite these inconveniences, almost the knowledge of the lignin structure is based on a thorough fraying, followed by solvent extraction with dioxan and (sometimes) further purification, to achieve low to moderate lignin vields. In most isolation procedures, the lignin contains minor impurities of carbohydrates.

3. Lignin Isolation Process

Separating lignin from other biomasscontaining polymers is recorded in several

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isolation procedures [33]. The predominant isolation is sulfate and sulphite processes that generate more than 90% of industrial lignin. Kraft lignin and lignosulfonates are produced as a by-product of wood processing during these processes. Kraft lignin is separated from the other components during a sulfate process under strongly alkaline circumstances which splits the lignin into smaller chains making it soluble in water and alkaline solutions [34]. Sulfur compounds like sodium sulfide create lignin's with the aliphatic thiol groups hydrophobic. Lignosulfonate is obtained similarly to Kraft lignin in the sulfite pulping process. However, the alkaline medium is substituted with an acidic solution. The LS is sulfide-like, but it is sulfonate-like (SO_3) . Other methods are formed in pilot plants and laboratory sizes to isolate organosolv lignin, soda 160 lignin, and ionic liquid lignin. This is made from acidic or alcohol solutions (organosolv lignin), heavy alkaline conditions (soda lignin), and liquid salts (ionic fluids) [34]. The ligning are obtained by the pulping of nonwood products. Organosolv and soda lignins are considered for example the purest lignins since they are free of sulfur and have a low level of impurities, and thus they are regarded as the most natural structure of these ligninstructures. Neither organosolv nor soda lignin has become sufficiently effective to be commercially used, while organosolv lignin is being investigated significantly to increase its use. LS is the most studied lignin, folded down by solid lines and sulfur-free lignin's, in terms of its applications (Figure 2). These forms of lignins are more interesting than other LS antiflocculant properties for energy storage applications. Sulfonates of lingo with hydrophobic and hydrophilic components as well as the high water solubility are amphiphilic molecules. For example, the hydrophilic SO₃anions are absorbed on the plum particle surface in pluma-acid batteries, leading to an increase in repulsion potential, preventing coalescence, or sintering of particles [31].

4. Application Point Details

4.1 Adsorption of heavy metal ions in wate



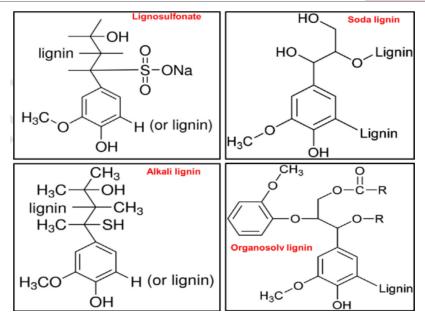


Figure 2. The simplified chemical structure of sulfur-containing and sulfur-free lignin, Organosolv, and soda lignin [35].

Lignin is inactivated because of its poor adsorption potential and unspecified range for some forms of the heavy metal ions. As already mentioned, lignin is not appropriate for practical use. The lignin modification by adding the required properties therefore represents a key issue for the adaptation and stability of the unique physicochemical properties of lignin. New lignin based adsorbents are prepared for the formulation, cross-linking, hybridization, network creation of hvdrogen bonding. copolymerization. condensation, and The reactivity of the primary phenol hydroxyl groups and the active hydrogen atom in paraand orthosites, in close contact with the phenol groups, the alcohol hydroxyl groups and the side-chains can easily change the lignin. Different active groups are able to graft by various chemical methods, for instance, by acvlation. alkylation, carboxymethylation, eradication. esterification, association, condensation, and copolymerization through graft [36, 37]. Based on the literature review, the main and key function groups of binding the heavy metal ions may be categorized into the groups containing oxygen, nitrogen, and sulfur with free valence electrons in these groupings, which can promote the binding of metal ions, but some other functional groups may be incorporated into lignin matrix, for [38] have

shown that the maximal adsorption value of Cr(VI) for H_3PO_4 -aktivated lignin was low at 29.1 mg/g. In addition, new exciting alternatives to conventional materials used for industrial applications are now emerging from composites. The key functional groups for modification of lignin and lignin composites are therefore discussed in this section of the paper.

4.2 Nanoparticle synthesis

Auto-structure Lignin is a key to understanding the chemical basis of xylogenesis in plant cell walls and synthesis of nanostructures and, thus, any discussion on autostructure of lignin is incomplete without xylogenesis. The task is still in place in the supra-molecular organization of cell walls to consider the plant's system of coordination and deposition of phenolic (hydrofobe) and carbohydrate (hydrophilic) biopolymers [39, 40]. From a developmental viewpoint, sites which initiate lignification should be present in xylems prior to the lignification process. These sites should be Carich (needed for H_2O_2 production by using superoxide radicals formed in enzymes), which are essential to polymerise coniferyl alcohol [41]. The pattern "externally in" of the deposition of lignin in a maturing cell wall, which includes polysaccharides and proteins,

(dispersal and absorption of the molecule into

restricts the structures lignin can adopt. In aqueous environments, the self-assembly mechanism of lignin deposition is driven by non-covalent interactions between monomers and conducting protein [42, 43]. The substratum effects (line-carbohydrate, ligninprotein interactions) and their role in selfassembly are another essential element of xylogenis and the lignin assembly. In some studies. the relationship between the hydrodynamic and the fractal characteristics of lignin has already elucidated a supra-molecular structure [44, 45], based on the fractal method. The fractal properties of lignin on a topological and supra-molecular level are attributable to non-linear self-assembling and are connected to the dynamic mode of fractal strange attractors [42, 46]. As demonstrated in theoretical studies, the fractal theory can then be used to describe lignin biosynthesis, polymerization, molecular, and supramoleculic assembly, if monolignols are presumed to be diffused on the site of lignification [43]. Dynamic self-organization in monolignols in *in vitro* lignin biosynthesis was documented in the enzymatic dehydrogenation polymerization, used in the analysis of the Belousov-Zhabotinski method. Furthermore. softwood lignin macromolecular parameters follow the universal fractal class Witten-Sander. On the other hand, the structure of a softwood lignin is connected to a star-like structure, which has linear branch topology as a basis for its scaling parameters [42]. The strengths and mechanisms involved in the formation of lignin-nanoparticulars are consistent with the above-mentioned selfassociative properties in the field of solvent, nature, lignin source, and the temperature used in the analysis. The forces involved in building and stabilizing unmodified lignin-based nanostructuring fulfill their function in two stages: nuculation and development. When an antisolvent precipitation is used, the nucleation rate of a nano-article depends on the degree of super-saturation during a solvent and antisolvent mixing phase. This degree of supersaturation shifts locally up to the end of the mixing phase [47]. The primary nucleation rate depends on certain parameters and a number of equations describe it. Following nucleation, particles are condensed and coagulated

the particle's surface) [47]. The coagulation influences the condensation rate negatively by reducing the total number of particles and hence the surface area. The nucleation rate leads directly to the development of fine particles, in particular if the particle growth rate can be regulated. The solvent-anti-solvent method mentioned for formation of lignin nanoparticles can be understood as a similar mechanism [48, 49]. These findings were similar to the one observed for the development of a single drop one particle hypothesis based on *D*-lignin (dioxane soluble fraction of Kraft lignin) [50]. This was based on our observations. We have been able to synthesize mono-disperse lignin nanoparticles with aerosol-assisted self-assembly in our nonreported sample. This is contrary to our published study in which a significant amount of polydiparty was observed in dioxane soluble fraction of alkaline lignin [50]. The role of homogenization as a supplementary power to help hydrophilic-lipophilic interactions in organosolv lignin nucleation residue nanoparticles [51]. The morphology analysis was made possible by the variation of temperature and rate of solvent-anti-solvent interactions for enzymatic hydrolytic lignin in an [52, 53] and 4 mL/m of anti-solvent concentration for solid particles, but 25°C and 2 mL/min for the individual hole particles. The position of α -T and hydrophobe interactions for the formation of the particles was also suggested. Their research used deionized water as a solvent, a requirement for hydrophobic interactions. The recent studies have shown the synthesis of lignin nanostructure, the hydrogen binding, the hydrophobic interaction, automatic self-assembly layer-by-layer, and solventinduced β interactions as possible mechanisms behind molecular and supermolecular lignin self-assembly [54], [55] a nano-emulsion-based soft template mechanism. They suggested the phase separation and formation, at the interface of THF and water, of membrane layers leading to water packaging that is subsequently evaporated and resulting in hollow particulate or capsule formation. In this research, the authors proposed a role of hydrophobic interactions in hollow nanosphere formation and stabilization. In another study, the hydrophobic interactions and shell formation were encouraged bv ultrasonographic treatment. The underlying phenomena have been described as ultrasoundaided cavitation, radical generation and emulsified [55]. In our research, the peripheral precipitation was suggested as a responsible factor for hollow particle formation because of variations in the time of diffusion and freezing of a solvent. Furthermore, the role of hydrophobic activity was ruled out as the whole process occurred in a non-aquatic environment. The difference in lignin dynamics on the time of freezing and diffusion in a droplet was important [50].

4.3 Super-capacitor electrode

The electrochemical output of the supercapacitors was investigated with a MnO₂ deposited CNFM. There was no binder and 1 M Na₂SO₄ used as an electrolyte. A coin-cella symmetric super-capacitor was made with MnO₂-CNFM₄ for positive and negative electrodes. The symmetrical super-capacitor in the coin cell model demonstrated excellent electrochemical conduct and condenser efficiency, as depicted in the Figure 5. The symmetric super-capacitor cV curve of the coin cell form is rectangular over the complete scans from 2-50 mVs⁻¹ for a possible 0–0.8 V range, showing the ideal supra-capacitor behavior. It was noteworthy that both the low and high scan rates of a MnO₂-CNFM₄ coin cell showed a strong profile CV. This indicated a low inner resistance and the strong capacitive properties for the super-capacitor. Image of 5b displays the MnO₂-CNFM₄-based coin cell supercapacitor's galvanostatic load/discharge profiles. The almost identical and symmetric charging and discharge curves indicate the contribution of the standard dual layer power and high columbic efficiency. An electrode content, such as its electrical Conductance and io-trane capacity, can determine the internal resistance of an appliance [56]. In the charge/unload curves of the MnO₂-CNFM₄ coin cell super-capacitor, there was a very small iR drop I and R respectively reflect current and resistance. The slight ohmic decrease of the

MnO₂-CNFM₄ electromagnetic part (0.037V at specific current of 0.3 Ag⁻¹) may have been the product of the small resistance relation and the strong ionic potential of CNFM substrate. The defined current was increased from 0.1 up to 0.3 Ag⁻¹ when no substantial improvement in the relevant capacitance occurred. The presence of connected highly porous MnO₂ crystals and CNFs, that shorten the paths of diffusion and facilitated the transfer of electrons and ions, enhance the redox faradaic response can be attributed to its high ability. deposited CNFM electrode The was comparatively greater than traditional CNTbased electrochemical micro capacitors [57], with a particular capacity and energy density. Displays a reasonable current of 0.5 Ag⁻¹ for 1000 cycles, cycling output on the MnO₂-CNFM₄ coin cell condenser. The retention capacity rate is around 98.95%, which suggests strong cycling stability. In addition, the cell shows excellent output and good impedance. In the high frequency area a semi-cycle is included in the MnO₂-CNFM₄ impedance spectra of symmetric electrode. In the low frequency field, the almost vertical line implies a perfect capacitive behavior. The interfacial charge transmission resistance (Rct) can be due to the semicircle and parallel connections of dual layer capacitance [56]. The Rct may be caused mainly by the interfacial resistance of electrical double-layer formation at electrode-electrolyte interfaces adsorption/deorption to of electrolyte ion [58]. The radious of semicircles that showed the Rct remained nearly the same prior and after 1000 cycles in the highfrequency region, which seems to suggest that variations in the Rct of the coin were insignificant prior and after 1000 cycles. This is showing the internal intensity (also known as the equivalent series resistor, SSR) of the substrate of the electrode and the electrolyte used [56]. The Nyquist plots intercept the actual axis at a high frequency. In the precedent and after 1000 cycles, the ESR for the coin's symmetrical electrodes (MnO₂-CNFM₄) was calculated, respectively, to be \sim 8.6 and \sim 7.3 µl, due to the relatively low conductivity of the MnO₂ deposited on the CNFM surface [59]. Although the resistance of the coin cell before and after 1000 cycles was relatively high as

opposed to those of the other electrodes of hybrid condensers. These results demonstrated that the ionic and electronic transport properties of the MnO₂-CNFM₄ electrode remained almost constant during long-term cycling, confirming that the MnO₂-CNFM₄ electrode may be a promising electrode material for electrochemical energy storage applications.

4.4 Photo-catalyst and photovoltaic

The recent creation of pore carbon-based materials based on ecologically friendly renewable biomass resources has been a topic of considerable attention [60]. The carbonbased materials derived from biochar used in a wide variety of applications for semiconductors such as wood, cellulose, lignin, hemicellulose, and biochar [61]. The introduction of carbonbased material as a doping agent plays a key role in changing the photocatalyst through changes in photocatalyst visibility [62, 63]. Photocatalyse can increase the adsorption and change the mechanism of the photochemical reaction by means of high surface, electrical conductivity, and porosity of carbon materials. photo-catalytic degradation The of the environmental contaminants and the photocatalytic output and photocurrent generation due to its high electro-conductivity are enhanced by this synergistic effect generated by carbon materials [64]. Several attempts for the use of carbon-based materials have been developed, such as activated carbon and biochar for composite manufacturing. The photo-catalytic material, because of its ability to enhance the interface charge transfer rate and reduce the electron's recovery time, is considered to have the capacity of activated biomass-derived CO_2 . In the case of gas and water repair, it has demonstrated promising properties as TiO_2 help. In addition, the heterojunction between the part results in electrons being inoculated between TiO₂ and activated carbon [65]. Similarly, TiO₂ has shown an improved photo-catalytic activity for selective oxidation by the methanol to methyl methanol and phenol degradation in combination with biochar (a pore-rich solid byproduct of thermal decomposition of organic

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waste), obtained from Miscanthus straw pellets and soft wood pellets. Cellulose was widely used for the manufacture of hybrid photocatalyst among different biomass fractions [66, 67]. Composite TiO₂ flakes are highly successful for photo-catalytic degradation of concentrated phenol accredited to TiO₂ assembly void formation and the hydroxyl immobilization [68]. Carbon photo-catalysts will improve the photo-catalytic method, which finally paves the way to understand the reaction mechanism of the material synthesis, based on its structure and composition, by using well-defended physicochemical features such as basic surface area, pore length, microstructure, solubility, etc. Further research is also needed to understand the kinetics and mechanism of the reaction. interphases, and compound leaching. The use of solar energy for the power generation is another key mode of photovoltaics. Due to the high demand for electricity, it is very important to produce renewable resources energy conversion devices according to the green chemistry principles. The earth is intercepted from the sun by approximately 1.8 × 11011 MW of electricity, far higher than the actual average energy consumption rate [69]. The field of photovoltaics offers significant opportunities for the use of electricity of renewable solar energy. To boost power conversion and decrease the cost to manufacture by using organic molecules or chemically formulated polymers, steady progress was made in photovoltaics [70]. Photovoltaic systems should be cost-effective and eco-friendly. The main focus is on the application of toxic and costly inorganic chemicals [71] such as CdTe and GaAs [72]. The current photovoltaic systems include the possible alternative to inorganic semiconductive material in the photovoltaic field is semiconductors derived from organic polymers. The most important characteristics for their use in photovoltaics are the low cost, renewability, and conjugated structures of organic polymers [73]. Natural polymers can be understood in the importance of photovoltaic products by the working principle. A photovoltaic cell consists of a layered structure in which the luminous layer is stored by two different electrode types, as illustrated. One is made up of Indium-tinoxide ITO, while the other is mostly made up of

metals such as aluminum, calcium-magnesium, gold, etc. When the electrons residing in the higher occupied molecular orbital (HOMO) have been exposed to the light, they absorb a certain wavelength and have passed to the lowest unoccupied molecular orbital (LUMO), causing exciton to form. Free electrons and holes formed by the excitone separation move towards Al and ITO, respectively. The electric current induces electrical activity in the external circuit. The electrical field needed to recombination prevent through the asymmetrical electrodes ionization energy or working functions. This asymmetry is responsible for the flowing of electrons from the low working function region to the high working function region. For in-organic materials based semiconductors, HOMOs and LUMOs interact in adjoining molecules and contribute to conductivity and the valence band. While, the transition of load between the localized states is achieved by hopping for semiconductors based on organic coloration instead of bands. The related structure between organic dyes and inorganic semiconductors is present in polymers [73]. Nano-cellulose was used in photovoltaic and the solar cell processing as а substratum [74]. Carboxymethylenedioxythiophene (PEDOT:PSs), poly(3-hexylthiophene), and [75] phenyl C61-butyphenic acid (PCBM) were used substratum on а poly(3,4as а ethylenedioxythexyethiophene) system. The photo conversion efficiency of the device was not very good (0,2%), as a result of the high ITO resistance [76]. The dye-sensitized solar cell has the potential to optimize the power conversion efficiency by 11% [77] and operates on the concept of an oxidizing/reduction response. For the dye-sensitized solar cell, microcrystalline cellulose is the gel electrolyte. By controlling the cellulose concentration and the ionic volumetric volume ratio, the photovoltaic performance of the cellulosebased solar cell can be optimized. The photoconversion efficiencies hit 3.33 percent by the use, with more than eight hours stimulation under solar radiation, of a gel consisting of LiI

(2 wt percent), iodine (10 wt percent over

weight of iodide), microcellulose (5% by

weight), and 4 *tert*-butylpyridine (10% by weight).

4.5 Lignin-based hydrogels

For the production of lignine-based hydrogels for biosensor applications, copolymerization of kraft lignin, organosolv lignin and lignosulfonite was used with poly (propylene oxide) and combined with multiwall carbon nanotube. The hydrogel can easily be prepared as an all-solid state for high conductivity and stability. Instead of all alkalis, alkali earth, and transition metal cations, the bio-sensor was sensitive to Cr(VI) [78] only. The responsive hydrogel for detection of Cr(VI), known as an extreme water pollution, may be used as a biosensor. The similar approaches were made to prepare hydrogel electrodes based on lignin, which cross-link silicate, lignin and cellulose into hydrogel. Lignin has been chemically altered to form cationic lignin groups with ethyl-trimethyl ammonium chloride [79]. This cationic lignin and water-dispersed clay anions were used to prepare a saponite hydrogel. This process allowed the galleries to open and swell. A conductive web that does not reduce the electrically active surface area of the graphene network significantly was created by this new lignin composite hydrogel. Graphene was used to form a biocompatible platinum electrode film to enhance its conductivity. These calculated redox pitches were used to prepare the Cottrell plots to determine each hydrogel-graph composite's electroactive surface area. This conductivity network remained under research as the fundamental mechanism [80]. The graphene and lignosulfonate hydrogels were used to build a super metal-free supercapacitor that had similar performance with the recorded pseudo-capacitors made of transition addition. metals. In this hvdrogel graphene/lignosulfonate was twice conductive as much as the hydrogel of pure graphene, as a result of the reversible redox charge transfer of quinone groups in lignin [81]. A gel-like electrolyte was made with the addition of fluid electrolyte to a dried lignin membrane and a lignin-based hydrogel electrode. Lithium anode compatibility was developed with the polymer electrolyte. Lignin based gel polymer

electrolvte showed higher temperature conductivity (not weighing before 100 °C) and improved electrochemical stability compared with the typical gel electrolyte polymer polymers, higher room temperature, etc. Lignin as a possible gel polymer electrolyte was assured by excellent performance in lithium ion batteries of high quality [82]. Casting lignin and poly(N-vinylimidazole)-co-poly(poly(ethylene glycol)methacrylate) was used to create a stand-alone lignin-based film. The prepared film performed better electrochemically such as the excellent lithium-ion number and the ability to inhibit lithium dendrites growth. This excellent resulted in the long-cycle performance at room temperature and concentrations of the lignin-based electrolyte / Li cell, which were much higher than those used for cells with an advertisement separator [83]. Flexible supercapacitors (FSC), as electrodes and as electrolyte separators, were assembled with lignosulfonate / single wall nanotuben pressure-sensitive hydrogels. At current densities of 0,5 AP, an excellent rate of performance, and an outstanding power density of 17,1 Wh/kg at a power density of 324 W/kg the assembled biomass-based fSCs showed a high specific capacitance (292 F/G). Moreover, even with a total of 1000 bending cycles the FSC provided excellent electrochemical stability [84].

4.6 Water flocculation

The "grafting to" technique synthesized a highly lignin-cationic successful polyacrylamide flocculent (L-CPA). Second, free radical polymerization by using Acrylamide (AM) or Methodiacryloyloxyethanyl *tri*-methyl ammonium chloride (DMC) as monomers and 4-chloromethyl styrene as a chain transfer compound has been achieved with the linear prepolymer of cationic polyacrylamide (PT) with chlorinated chain ends [85]. In addition, chlorine and hydroxyl phenolic groups grafted the CPA prepolymer into lignin enzyme hydrolysis (EHL) through the reaction of lignin molecules. In the conditions of poor acid, neutral, or alkalescent conditions (pH=5-9), the *L*-CPA displayed an excellent flocculation capacity to provide high turbidity kaolin suspension. The *L*-CPA synthesized via "grafting" to" strategy required a minimum dosage compared with the other lignin-derived flocculants, showing the best flocculation performance. L-CPA was shown to selfassemble in water into octopus-like hydrophilic micelles with water-based CPA segments and core lignin skeletons which enhanced L-CPA with excellent flocculation performance. It could be mounted with water in a potato-like micelle. For the flocculation mechanism of L-CPA, the charge neutralization and bridging effect were suggested. Lignin is a biological macromolecular, and in this work lignin plays a crucial role in blocking the L-CPA grafted component. The main technique for the flocculation performances of L-CPA lies in the hyper-branched amphiphilic lignin structure allowing the *L*-CPA to auto assemble hydrophilic micels in water like octopus. The octopus-like *L*-CPA has an enormous prospect waste water treatment as of an environmentally friendly, inexpensive, nontoxic, and technically viable flocculent [85].

4.7 Excellent UV aging resistance

A new lignin/titanium dioxide compound (QAL/TiO_2) was synthesized by using a simple hydro-thermal process through lignin and butyl titanate with a normal microstructure and synergically increased properties of the UV absorption. The prepared QAL/TiO₂ composite is a hybrid structure with a uniform embedding of lignin, TiO₂, and a strong chemical bonding power [86]. For doping modified waterborne (WPU), polyurethanes with good interfacial stability and dispersibility in WPU, QAL/TiO₂ hybrid composite particles were used. The WPU QAL/TiO₂ film is obtained with the excellent UV safety and good mechanical characteristics, tensile strength, and elongation in break compared with pure WPU film. Likewise, the mechanical efficiency remains largely unchanged after 96 hours of the high power ultraviolet irradiation and also has the excellent anti-UV aging properties. This kind of lignin/TiO₂ hybrid composite is of great importance to use highly valued biomass tools,

with a strong dispersion and excellent optical properties [86].

4.8 Methylene blue, a prevalent cationic type dye

Lignin-derived porous biochar was chemically treated with different oxidation number manganese compounds as a promising adsorbent. The research suggests that making adsorbent from a byproduct of the bio-refinery process could be a promising technique to remove methylene blue from wastewater.

The elimination rate of methylene blue by BC- MnO_2 was 99.73 percent. The pseudo-secondorder kinetics and Langmuir isotherm models could be used to describe the adsorption of MnO_2 modified biochar to methylene blue in aqueous solution. According to the findings, using manganese compounds to modify ligninderived adsorbents is a promising technique for methylene blue in industrial effluents.

This study outlines a method for converting waste lignin into a high-quality methylene blue adsorbent. The lignin-derived material has a high adsorption capability, indicating that it might be used to make an adsorbent for methylene blue in sewage treatment [87].

4.9 LLDPE/lignin films

In the development of LLDPE/lignin films for agricultural mulch applications, Kraft lignins were used. To increase the compatibility and processability of LLDPE/hardwood lignin blends by extrusion, the chemical modification of the lignin via esterification reaction with acetic anhydride was also explored. Spectroscopic, thermal, and morphological studies were used to characterize the blends.

The non-modified softwood lignin (SW) and hardwood lignin modified by esterification were used to create processable mixes (HWE). The flexible films were blown extruded from LLDPE pellets containing (2.5 percent, 5 percent, and 10%) lignin with particle sizes ranging from 38 to 75 micrometers. The temperature difference between the Tg of lignin and the melting temperature of LLPDE in processable extrusion blends was less than 20 °C. The ductility of films made from neat LLPDE and with 2.5 percent HWE and up to 5 percent SW was statistically equal (349 percent). As a sustainable economic and environmental alternative to LLDPE films, lignin-based polyethylene mulch films with better opacity, thermal and biodegradability features, and superior mechanical and water absorption performance were developed. The lignin structure and its interaction with LLDPE determine the film's properties [88].

4.10 Lignin-based hydrogel

A lignin-based hydrogel is made from lignin alkali polymers and poly(ethylene glycol) diglycidyl ether (PEGDGE) in an adjusted alkali (NaOH) solution as a natural plant-based water absorbent. The effective synthesis of a ligninbased hydrogel that is non-toxic, and has good swelling capacity in both non-saline and saline solutions described in this preliminary investigation. The lignin-based hydrogel is a suitable option for usage in agricultural soils because of its favorable qualities, and it has the capacity to retain water in non-saline, saline, and sodic soils. Although the lignin-based hydrogel's swelling capacity (34 g g⁻¹ Hydrogel) is less than that of commercial acrylate-based hydrogels (more than 100 g g⁻¹ Hydrogels) water retention occurred in dry, saline soils lignin-based hydrogel as using а an environmentally beneficial addition. It has several advantages, including: (i) it is made from a low-cost, renewable feedstock (lignin alkali) using small amounts of non-toxic chemicals (1.5 m NaOH, 0.5 mmol PEGDGE g-1 lignin), which is in line with green synthesis principles (ii) it is non-toxic and biodegradable, so it poses no risk to crop production or soil health and (iii) it functions in saline conditions. making it suitable for use in drought impacted saline or sodic soils [89].

4.11 Lignin modified asphalts and virgin asphalt

The goal of this research was to use lignin as a bio-additive to change the base asphalt and compare the rheological properties of lignin modified asphalts virgin asphalt at high temperatures. The virgin asphalt in this investigation was PG 58-28, and four contents

of the total binder by weight of lignin were integrated in the base binder: 2%, 4%, 6%, and 8% of the total binder by weight of lignin. The addition of lignin increased the viscosity of virgin asphalt at various rotating speeds, according to the findings. Fresh asphalt, the activation energy rose as the lignin content increased. Meanwhile, regardless of the lignin level, including lignin into the asphalt binder increased the elastic components and improved the asphalt binder's resistance to permanent deformation. As a green and environmentally acceptable bio-additive, lignin has a lot of potential to change the properties of petroleum-based asphalt [90].

4.12 Biochemicals

Catalytic thermochemical techniques to biomass conversion yield considerable amounts of various platform chemicals such as furfural, 5-hydroxymethylfurfural, levulinic acid, and other furan or non-furan-based compounds. These chemicals are essential in the production of fuel-based materials that can effectively substitute petroleum-based chemicals and fuels. Various homogeneous and heterogeneous catalysts can be used to catalytically transform lignocellulosic biomass and its monomeric sugars into platform chemicals. Mineral acids,

silica materials. zeolites. mesoporous metalorganic frameworks, metal oxides, and ionic liquids are some of the interesting catalysts identified in this review paper for refining to create biochemicals. pre-treatment to enhance bioconversion is achievable using a variety of methods. Acids, bases, or organic solvents are used in the chemical pretreatment process. Various pretreatment greener technologies. such as grinding, milling, ultrasound, microwave, and steam explosion, have been proven to significantly improve biomass hydrolysis. Platform biochemicals produced from lignocellulosic biomass are listed below.

5-Cellobiose, glucose, fructose, hydroxymethylfurfural, levulinic acid, lactic acid, and sorbitol are only a few of the sugars and biochemicals made from cellulose. Hemicellulose, on the other hand, can produce sugars and biochemicals like xylose, xylulose, furfural, furfuryl alcohol, and xylitol (Figure 3). Phenols, catechol, and vanillin are the fundamental biochemicals produced by lignin. The economy is expected to be dominated by the production of biofuel platform chemicals from various integral units of lignocellulosic biomasses. A thermochemical or metabolic

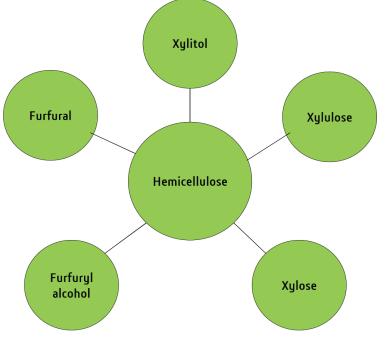


Figure 3. Extraction of chemicals from hemicellulose

route can be used to convert biomass into platform chemicals. The biochemical route is completely green, but it is more expensive and produces lower yields, necessitating extensive scientific research and development to improve the process's competency. The thermochemical method, which employs homogeneous and heterogeneous catalysts, has been effectively applied to platform chemicals. The use of homogeneous mineral acids as a catalyst for this bioconversion is the most commonly commercialized, but the toxicity of these mineral acids has led to the development of more ecologically friendly heterogeneous catalysts [91].

4.13 Derived Kraft lignin

The goal of this study was to see how kraft lignin grafted with poly vinyl pyrrolidone as a microbial carrier affected the vield of biogas/methane produced in anaerobic codigestion of WAF and raw sewage sludge (SS). Waste wafers are a viable substrate for biogas production due to their high carbohydrate content. According to the findings, lignin grafted with PVP improved the anaerobic codigestion of waste wafers and sewage sludge. The porous PVP-coated material boosted cell adherence and increased cell growth and activity. In the WAF SS variation with the carrier, cell count increased by 46 percent, while enzyme activity increased by 43 percent. There was a natural increase in the amount of produced biogas/methane as the microbiological and biochemical parameters WAF+SS+lignin improved. The sample produced 846 m³ mg⁻¹ VS of biogas, including $50_2 \text{ m}^3 \text{ mg}^{-1} \text{ VS}$ of methane, while the WAF + SS co-substrate system produced 722 m³ mg⁻¹ VS of biogas, comprising 428 m³ mg⁻¹ VS of methane. According to the findings, lignin can be used as a very effective microbial transporter in anaerobic digestion (AD). The combination of food waste from the confectionery industry with sewage sludge has a lot of practical possibilities. Lignin was a fascinating approach that can be used to generate renewable energy. It gives novel substrates for agricultural biogas plants while also being environmentally friendly [92].

4.14 Derived anaerobic co-digestion testing

The goal of this study was to see how lignin grafted with poly vinyl pyrrolidone as a microbial carrier affected the yield of biogas/methane produced in anaerobic codigestion of WAF and raw sewage sludge (SS). Wafers are a viable substrate for biogas production due to their high carbohydrate content.

According to the findings, kraft lignin grafted with PVP improved the anaerobic co-digestion of waste wafers and sewage sludge. The PVPcoated material boosted cell adherence and increased cell growth and activity. In the WAF + SS variation with the carrier, cell count increased by 46 percent, while enzyme activity increased by 43 percent. There was a natural increase in the amount of biogas/methane produced microbiological as the and biochemical parameters improved. The WAF + SS + lignin sample produced 846 m³ mg⁻¹ VS of biogas, including 50₂ m³ mg⁻¹ VS of methane, while the WAF + SS co-substrate system produced 722 m³ mg⁻¹ VS of biogas, comprising 428 m³ mg⁻¹ VS of methane. According to the findings, lignin can be used as a very effective microbial transporter in anaerobic digestion (AD). The combination of food waste from the confectionery industry with sewage sludge has a lot of practical possibilities. It was a fascinating approach that can be used to generate renewable energy. It gives novel substrates for agricultural biogas plants while also being environmentally friendly [93].

4.15 Derived PAN-lignin blend

The blending and solution casting used to create polyacrylonitrile (PAN) and lignin blends with three different lignin types. One type of lignin was chosen from three types, and varied blend concentrations were created and cast. PAN can be replaced with lignin to generate an outstanding polymer blend without affecting the mechanical capabilities of PAN, according to this early investigation. SEM, FTIR, and TGA measurements were used to observe the interaction between PAN with lignin. The beginning stages for the PAN and carbon fiber industries were demonstrated with this study with a homo-PAN. This research may also be done with PAN, a carbon fiber precursor, and that polymer blend can be spun into fiber and converted into carbon fiber using carbonization techniques.

In this study, a novel precursor material was created by combining PAN and lignin the cost of the precursor, improve the mechanical properties of the precursor, and discover new uses for lignin, which is an undervalued product to create a sustainable, renewable material. This research revealed a new application for lignin, which is the second most prevalent substance on earth after cellulose. The most significant result of this study was the discovery of a partial replacement of PAN with a renewable resource and the development of a greener PAN precursor technology to benefit the global environment [94].

4.16 Derived sustainable construction

The focus of this analysis is on the most recent methodologies to value lignin and its derivatives in sustainable construction. Lignin and lignin composites allow for the partial substitution of petroleum products, resulting in more sustainable end materials and the construction industry as a whole. Lignin and its derivatives are used in sustainable building as cement composite additives, raw material for rigid polyurethane foams, anti-corrosive, coatings, resins, and a bitumen alternative in asphalt manufacture, among other things [95].

4.17 Urea fertilizer

For the preparation of slow release urea fertilizer, lignin and poly(vinyl acetate) (PVAc) used as coating materials. Coated urea granules were made by mixing polymeric emulsions with urea granules at polymer:urea mass ratios of 1:9, 1:6, and 1:3, respectively, corresponding to polymer concentrations of 10, 15, and 25 wt percent. Compared with pure polymers, a 75:25 blend of PVAc and lignin improved the properties of the produced film and increased the nitrogen release time. As a coating material for creating slow release fertilizers, a mixture of PVAc and lignin at a ratio of 25 wt% lignin to 75 wt% PVAc is suggested.

The nitrogen release time of urea granules coated by biofilms made of pure and blended PVAc and lignin was investigated in this study. The PVAc-coated urea had a dense outer surface, but the lignin-coated urea had minor fissures. The homogeneity of the covering film on urea granules was not harmed by adding lignin to the PVAc emulsion up to 25% by weight. Although covering urea granules with pure PVAc improved nitrogen release time, the lignin-PVAc covered urea with 25 wt% lignin and 75 wt% PVAc had the fastest nitrogen release time. To improve agricultural output while avoiding an environmental and economic difficulties associated with present fertilizer applications, controlled or slow release fertilizers have been advocated [96].

4.18 Flocculants, adsorbents, and dispersants

Although promising results for lignin modification and application as flocculants, adsorbents, and dispersants were published, the modification techniques appeared to be industrially undesirable, as they primarily used solvent-based systems.

Flocculants have been widely utilized to remove colloidal particles from solutions and suspensions in the treatment of wastewater effluents. The heavy metals are present in waste water from mining activities, fossil fuel burning, metal plating, and tanneries posing environmental hazards. The lignin use to adsorb these heavy metals from solutions has proven to be extremely effective. Dispersants are commonly employed in cosmetics, paints, medicines, drilling mud, cement, and ceramic applications to suspend colloidal particles [97].

4.19 Derived dual lignin-derived polymeric systems

In an acidic aqueous suspension solution, kraft lignin (KL) was polymerized with [2-(methacryloyloxy)ethyl] trimethylammonium methyl sulfate (METAM) or acrylic acid (AA) to form cationic and anionic water-soluble lignin polymers with large molecular weights. [2-(methacryloyloxy)ethyl] trimethylammonium methyl sulfate (METAM) and acrylic acid (AA) were used to polymerize lignin to make cationic and anionic lignin polymers in this study. The goal of this study is to use anionic/cationic lignin polymers in single and dual polymer systems to treat synthetic wastewater models with ionic compositions (e.g., ZnCl₂, CuCl₂, and KCl). Because many elements are present in many real wastewater treatment systems, the adsorption and destabilization performance of lignin-based polymers was also tested in a mixture of selected constituents (ZnCl₂, CuCl₂, KCl).

The dual polymer systems of KL-AA/KL-METAM were more successful in removing ions than KL-METAM/KL-AA based on adsorption, sedimentation, and aggregate size measurements. Because Zn^{2+} has a higher reactivity for interacting with other elements than Cu^{2+} and K⁺, it reacted more successfully with polymers in all cases.

Various situations for the removal of heavy metal ions using lignin derivative polymers were investigated. Because of the stronger electrostatic attraction, cation-interaction, and chelation/complexation mechanism generated between the polymer and ions, KL-AA was more efficient than KL-METAM in removing ions from the solution. When KL-AA was introduced as the first polymer followed by KL-METAM, the dual polymer system had a larger adsorption capacity for ions than the single polymer system because KL-AA had a stronger affinity to adsorb ions and then KL-METAM could create bridges to entrap the unattached ions. Furthermore, compared with the single polymer system, the ions diffusion into the voids of polymer aggregates improved the aggregation efficiency of the dual system, as greater seen bv the aggregate size. Functionalization of lignin derivatives for the

ion removal is a promising way to speed up their utilization in the industrial waste water treatment [98].

4.20 Nanoparticles

The kraft lignin nanoparticles were used for the entrapment of bluish anthocyanin-derived pigments (PD and P) to improve their stability and solubility in the aqueous systems. By using nano-precipitation and dialysis methods, lignin nanoparticles (LNP) loaded with pyranoanthocyanin dimers (PD) and portisins (P) were created. LNP and P-LNP had an average size of 150 nm and a polydispersity index of 0.2 when prepared by using the nanoprecipitation method. However, regardless of the presence or absence of the pigment, lignin nanoparticles created by using the dialysis approach produced nanoparticles with an average size of roughly 200 nm and a polydispersity index of less than 0.2. The generated nanoparticles had an average size of roughly 200 nm, an extremely narrow size distribution (PDI 0.2), and a z-potential of -40 mV. The dispersions of lignin nanoparticles were shown to be stable for at least 7 days at pH 5, although aggregation was seen at pH 4. This natural polymer, which is a waste product of the pulping paper process, can be utilized to stabilize the color of natural bluish dyes and improve their solubility in aqueous systems, with potential applications in food and cosmetics [99].

4.21 Other important applications of lignin

For decades, research has been ongoing and its applications. Many studies have shown that lignin can be used as a high-value commodity. However, the industrial scale has still not met these applications. **Table 1** represented possible applications with lignin-modified compound.

Application	Lignin modified compound	Reference
Photovoltaic	Nano-ZnO	16
Reusable catalyst	Ru/SiC	20
Cured epoxy resins	DMSO	27
Nanoparticle synthesis	N.A	46
Water flocculation (cationic	polyacrylamide (cationic)	85
polyacrylamide)		
UV aging resistance	TiO ₂	86
Application in epoxy asphalt	oil	89
Adsorption of heavy metal ions in	–NH ₂ groups	100
water		
Application of renewable energy	N.A	101
Application of super capacitor	mudstone	102
electrode		
Application of lignin-stabilized	stabilized soils	103
silty soil in highway subgrade		
Application of lignin-derived	NaOCl solution	104
polycarboxylic acids		
Electro-fenton process for azo dye	Polypyrrole	105
removal		
Gaicling the preparation of lignin-	lotion	106
colored lignin in micromorphology		
Application in lignin-based	N.A	107
hydrogels		
Application in 3D printing	-	108
electrodes	MnO ₂	109
Application of nanoparticle	Cr(VI)	110
modification	N	
Filter	MgO	111
polyurethane foam for oil	Polyurethane	112
adsorption	X A	112
Application in effluent treatment	N.A	113
from the textile industry	al circa ta	114
Hydrogel synthesis based on lignin	alginate	114
use for agriculture	N.A	115
Microstructure analysis		
High performance sustainable polymeric materials	N.A	116
	Overgon nitrogon with corbon	117
membrane via air plasma for energy storage	Oxygen, nitrogen with carbon nano fiber	11/
Alternative use for petroleum	N.A	118
based polymers	IV.A	110
Application of lignosulfonates and	Sulfuric acid	119
sulfonatedlignin	Summer actu	117
Antioxidant activity for biomedical	lactide	120
application	incluc	120
In paper making	N.A	121
In polyimine thermosets	Levulinic acid	122
High performance super-	Activated carbon	122
capacitors		
apaolioio		1

Table 1. Lignin application and modified compound

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As a dispersant for kaolin suspensions	Hydrogen Peroxide	124
Application in oral drug delivery	dodecyl benzenesulfonate	125
In flame retardant	-	126
Application for the removal of potentially toxic metals from aqueous solution	Magnesium Hydroxide Nanocomposite	127
Formed carbon fibers	-	128
As a adsorbent for oil spill clean- ups and recovery	graphene oxide	129
Application in controlled release of avermectin	dodecyl benzenesulfonate	130
Application to phenolic resins	Halogen Acids	131
Stabilized soils	-	132
Enzymatic saccharification of lignocelluloses	glycol	133
Surfactants with antioxidant and anti-UV properties	Ozone	134
Application as electrodes	MnO ₂	135
Cellulose adsorbent	phenolic hydroxyl (Ph-OH)	136
Transparent polyurethane coating	ZnO hybride nanocomposite	137
Green wood adhesive	-	138
Thermosetting resins	bisphenols	139
Anticorrosive water borne epoxy coatings	Grapheme	140
Pervaporation dehydration	-	141
Adsorption isotherms		142
Poly lactic acid film as active food packaging material		143
Application in oil/water separation	aerogel	144
Aqueous polyurethane coatings	TiO ₂ nanocomposite	145

5. Future Prospect of Lignin

The use of ethanol fuel from biomass around the world is expected to increase by billions of dollars [146]. The developing countries of the world are playing a significant role in ethanol production from food grains and unused biomass. There are many feed stocks in Canada providing the greater biofuel production that impact technology-based industries. However, the proper utilization of biomass can be done through ethanol production by producing lignocellulosic waste. Ethanol needs to be produced from lignocellulosic biomass at low cost through innovation of new technology. The application of lignin should be increased through advanced research and the addition of some modified compounds to lignin that could

lead to the biological application of a new technology (**figure 4**).

D-lightment is one of the new technologies helping in the bioethanol development. The proper use of lignocellulose can be successfully achieved at the industrial level by developing and using appropriate catalysts. There is currently a lot of research being done on lignin and more research is being done on how to increase its proper use. There are many applications such as adsorption of the heavy metal ions in water, lignin acts for depolymerization due to the removal of nanoparticle. In the case of lignin obtained from hydrolysis by lignocellulose biomass, the hydrolysis method needs to be improved. Lignin used should be increased by keeping catalyst ratio and choosing the right catalyst.

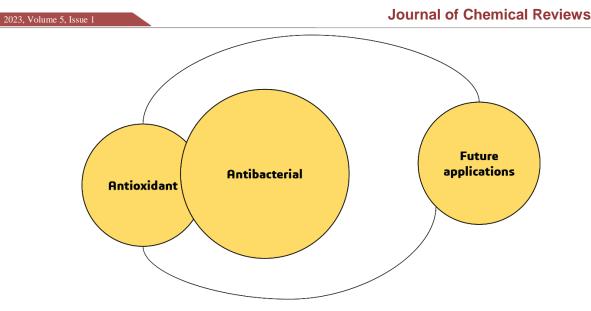


Figure 4. Biological applications of lignin

Some parameters such as temperature, pressure and condition need to be determined through proper exploration for the development of lignocellulose application technology. Researches are also needed to reduce fuel consumption and pollution caused by this technology. Lignin can be modified of different type of compound and showed better characteristic for acting active sector [147,148]. In the future, lignin will make a significant contribution to various research and energy fields. Research needs to be stepped up for new applications and the government needs to play a role through the necessary steps. Biomass will play a major role in demonstrating the sustainability of the second generation, using the right energy and creating an environment that will lead to major changes in technology and industry in the future.

6. Conclusion

Lignin is one of the second generation bio refineries that produce the large quantities in the pulp and paper industry. Producers need to use lignin in various economic industries, including new revolutions in research based on chemical composition. The evaluation of lignin has resulted in different type sustainable products, including the currently available fuels and chemicals. Much research is underway to develop suitable products by adding suitable modifier compounds to the production of useful compounds from lignin. The market perceptions need to be improved in research to

accelerate the development of lignin-based products. Based on the proper use of lignin produced in the industry and proper application of the environment, the lignin biorefinery will make a significant contribution to the industry and economy.

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