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Chapter

Composition and Role of Lignin in Biochemicals

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Abstract

The term lignin is derived from lignum, which means plant wood. Plant wood are mainly composed of extractives, hemicellulose, cellulose, and lignin. The lignin is a cross-linked polymer, made of three phenylpropanoid precursors, *p*-coumaryl, synapyl, and conniferyl alcohols. It is the most abundant polymer in plant world and act mechanically as a natural glue to bind hemicellulose and cellulose. Lignin is amorphous, soluble in alkali, condenses with phenol and has high melting temperature. The function of lignin is to protect the carbohydrates of the biomass from degradation, thus provide stability. The chapter includes information on types of lignin, structure, isolation, degradation, and transformation in to market value chemicals. The application of lignin and lignin base monomers for synthesis of plastic, hydrogels, adhesives, chemicals, fuels and other value added materials at industrial scale.

Keywords: lignin, plant biomass, polymer, pretreatment, biorefinery

1. Introduction

In organic biomass, particularly in the plant biomass, lignin is one of the rich carbon matter. Lignin is part of plant cell wall, which provides a mechanical muscle to keep herbs, plants and large tree standing. The process of synthesis of lignin inside plant biomass is known as lignification. The lignin is a long amorphous polymer containing three major synapyl, *p*coumaryl alcohols and conniferyl phenylpropanoid monomers. Due to this aromatic polymeric nature, lignin supports the other carbohydrates components like cellulose and hemicellulose in lignocellulosic plant biomass. So its acts like a binder for the carbohydrates of plant biomass to make a strong cross link and bond between hemicellulose and cellulose [1].

An estimated quantity of 5 to 36×10^8 tons of lignin is reported annually in natural organic biomass [2]. The uppermost 26–45% of dry matter lignin part is naturally observed in softwood whereas 15–25% a lower amount of lignin in hardwoods biomass [3]. The value of lignin in grasses and straw is relatively low from the softwood range between 15 and 27%, and a small percentage in algae and mosses. As an evolutionary perception, the development of aromatic lignin structure in plant cell wall, is for fast water transportation inside the tracheid plant cell structure [2]. This is an important material of organic carbon polymer incorporation in plant biomass for possible growth in dry land. The lignin makes the biomass rigid and hard, possibly can decrease the water loss in dry and drought condition.

1.1 Significance of biomasses

The word biomass means organic substance made of plants materials. This could be a forest wood, cereal crops, seaweed and leftover substrates from agriculture biomass. Other sources of biomass are human, animals, household and industrial waste. These biomasses contain chemical energy trapped directly from sun through photosynthesis. Photosynthesis converts carbon dioxide and water with the help of sun energy into sugars units, that's make different carbohydrates in fruits, vegetables, and other crops plants. Biomasses for example straw, food like potato, cassava, corn starch, sorghum, wastewaters and other agro-industrial residues are a good source of sugars (glucose, xylose, arabinose, starch, sucrose, cellulosic, and reducing sugars) that can be recycle for multiple products at commercial level. Biomasses (softwood, hardwood, herbs, straw and grasses) are also a good source of organic carbohydrates materials. On the basis of high organic contents, these biomass are favourite food for most of the living species on the globe. Besides, food purpose, the left over residue and waste biomass can also contribute about 7–10% to the global energy stream. These agriculture biomasses, softwood, hardwood, herbs, straw and grasses contained high carbon and water content, thus considered a significant input carbon for production of renewable energy like biodiesel, bioethanol, biogas, biohydrogen. Currently, 8–15% of the overall energy stream is reported in industrial zones of developed countries, while a low amount in developing countries as well [4, 5]. Besides, renewable energy, most of the countries practiced to burn these biomass either in the field or for cooking in stoves, thus a massive amount of carbohydrates biomass containing useful carbon (lignin, cellulose and hemicellulose) is destroyed on low price [6]. Food waste and waste lignocellulosic biomass are of potential interest, which includes utilization for bio-methane, ethanol, butanol, biomaterials, and bio-based products [7, 8]. Food waste is easily digestible in fermentation process for biofuel production [9], however, lignocellulosic biomass like grasses, waste paper, wood residues, and crop residues are difficult to convert directly into fuel. Because the lignocellulosic biomass is comprised of mainly three basic molecules, 20–40% lignin, and 60–70% hemicellulose, cellulose and other extractives in collectively [10]. The composition of carbohydrates varies depending on the growth and nature of the biomass. There is a big barrier in utilization of lignocellulosic biomass containing high lignin content, due to strong crosslinking of ether and ester bonds around polysaccharides (cellulose and hemicellulose) which confers hydrolytic stability, resist degradation and structural recalcitrance [5]. Therefore, to utilize these lignin containing biomasses, pretreatment process is necessary to make them digestible in the fermentation process and synthesis of value added materials.

Energy is the eventual source need for each operation through the globe. More than 25% of the World population is suffering the lack of energy for cooking, lighting, power generation and transportation fuel. The consumption of the energy is higher than the production percentage [11]. The demand for extra energy production builds an energy crisis throughout the world. The details reports released by the European Environment Agency and International Energy Agency (IEA), Energy Information Administration (EIA), oil usage and cost is mounting constantly. The published reports indicated some problems and hurdles in future for energy production and emphasized on potential alternate resolutions. The estimated amount of energy used for heat and power from oil 31.0%, natural gas 21.5%, nuclear 5%, coal 29.0%, hydro 3%, biofuels and waste 10.0%, and 'other' 4%. The electricity generation estimated data was natural gas 22%, oil 31.1%, coal 28.9%, nuclear 12%, hydro 13%, biofuels and waste 10.2%, and 'other' 6% as shown in the (**Figure 1**). These values specify that

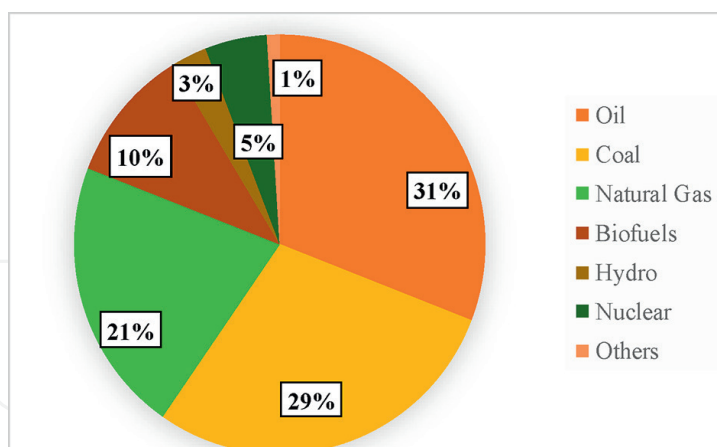


Figure 1.
The results shown here is reflecting the energy production percentage around the globe with less attention for biofuels from waste biomass.

generation of energy from alternative sources like biofuels and bioenergy are receiving more attention instead of fossil fuels [12, 13]. Consumption of waste biomasses (agribiomass and municipal solid waste) for biofuels could meet a rational demand of energy percentage in the future.

To solve the problems of energy crises, production of renewable energy from waste biomass sources is getting more interest instead of fuel generation from fossil sources. Waste biomass especially lignocellulosic biomass residue along other biomass is a good waste reserve that could be reuse for important products [14]. So, utilizing the waste biomass can produce clean bioenergy and has a benefit of to efficiently manage solid waste to reduce environmental pollution. The agriculture waste and waste residue which is about 60–70% around the world can be a cheap carbon material for biofuel and bioenergy production. The cellulose and hemicellulose are carbon source which can be transformed in to varieties of fuels, which includes ethanol, butanol, bio-methane and biohydrogen [1, 15]. However, lignin is an aromatic component, cross link both cellulose and hemicellulose of the lignocellulosic biomass which makes it recalcitrant and harder, so decrease the yield of energy production [16]. Therefore, pretreatment process are carried out to remove the lignin, cellulose and hemicellulose for the biofuel production. The separated lignin is also a good source of fine chemicals and industrially relevant materials discussed in details below.

For the improvement of effective anaerobic fermentation processes, the choice of waste biomass, nature and chemistry of biomass is mainly essential factors. The lignin percentage and quantity of water are the next important properties in picking substrates for the fermentation reaction. While the total organic carbon TOC is the most critical concern factor in the conversion of the waste carbon biomass [17, 18]. The efficiency of the microbial hydrolysis of the biomass in anaerobic fermentation reaction is linked to the biodegradability of biomass [19, 20].

2. Biomass components

The organic constituents in agricultural biomass have a recalcitrant structured cell wall which is called “lignocellulose” [21]. It is evident that the three components cellulose, lignin and hemicellulose are primary components as shown in the (Figure 2 and Table 1). The highest composition is of cellulose in plant cell wall, whereas the

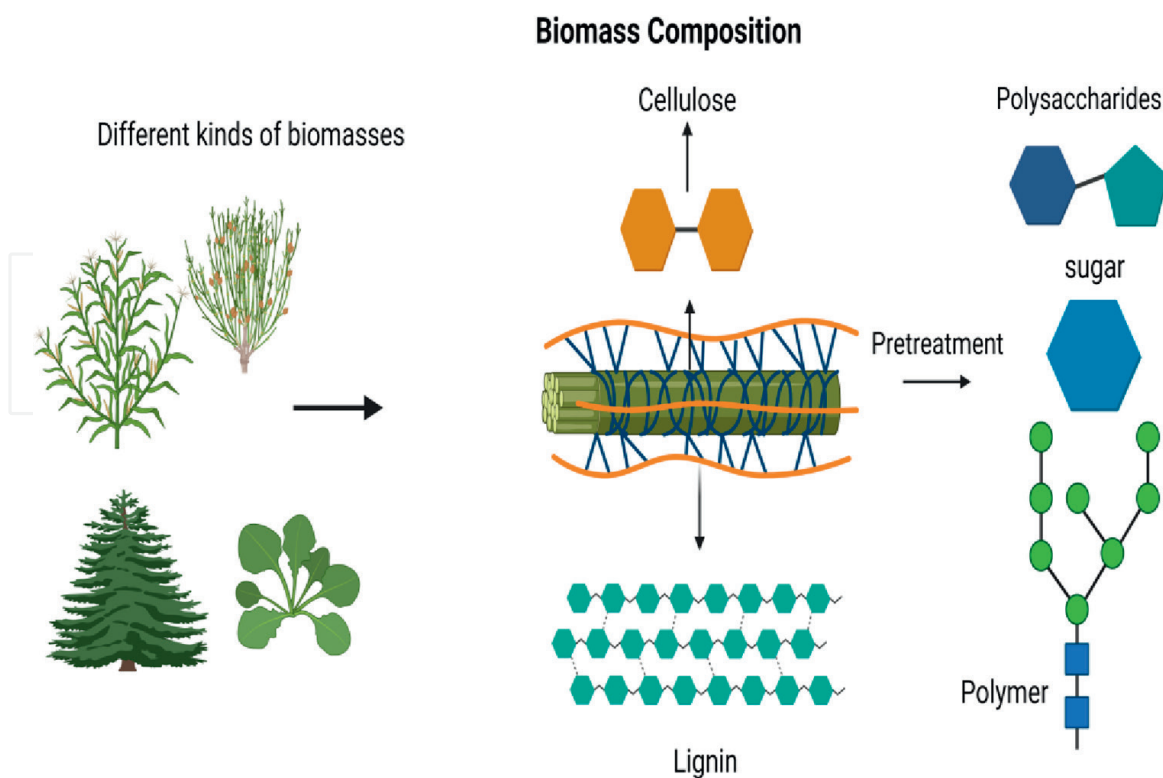


Figure 2.
An overview of the general components of plant biomasses.

Substrates	Cellulose	Hemicellulose	Lignin
Softwoods	45–50	25–35	25–35
Bamboo	41–49	24–28	24–26
Hardwoods	40–55	24–40	18–25
Paper	40–55	25–35	15–20
Corn cob	40–50	20–35	15–17
Peanut	40–45	15–17	20–30
Corn straw	38–45	26–34	17–20
Para grass	35–45	25–30	15–20
Corn stalk	34–36	26–27	16–21
Wheat straw	30–40	30–50	15–16
Sweet sorghum	27–38	21–25	11–17
Grasses	25–40	35–50	10–30
Switch grass	45	31.4	12
Rice straw	38	19	13
Barley straw	37	24	16
Sugarcane bagasse	33	23	5
Arundo donax	31	30	21
Lawn grass	30	43	3–5

Table 1.
Biomass main components and their percent value.

second copolymer is hemicellulose and the third one is aromatic protective polymer is of lignin. The components are discussed in the details separately.

2.1 Cellulose

Cellulose is a homopolyme of long chain basic units of 4-O- β -D-glucopyranosyl-D-glucose and cellubiose. On hydrolysis of cellulosic polymer of most of biomasses is usually of glucose molecule. Chemically, the cellulose has a long chain of $(C_6H_{10}O_5)_n$ units in the polymer. The number of units in cellulose polymer is about 700–1000 glucose units. These glucose units are bonded together with β -1,4 glucosidic bond between the two connecting glucose in a long chain. The glucose units have strong hydrogen bonds in parrallel position to support further the strength between the molecules [22]. Cellulose has crystalline and non-crystalline structure, sorrunded by microfibrils to form fibers. Cellulose has the capacity to absorb about 7–15% water, and is not soluble in diluted acid and water under normal temperature. On increasing the temperature, acid concentration can increase solubility, whereas alkali solution separate, decrease degree of polymerization and swells the cellulose crystalline structure [10].

2.2 Hemicellulose

Hemicellulose is the second highest heterogeneous polymer comprises of various sugars molecules i.e. galactans, glucuronoxylan, glucomannan, and low amounts of other polysaccharides. The other sugars molecules are glucans, xylans, galactans, arabinans and mannans exist in the hemicellulose molecule. The glucans, galactans, arabinans and mannans are linked together with β -1,4 linked backbone. In the hemicellulose polymer, xylan contains 1–4 linkages of xylopyranosyl units attached with α -4-O-methyl-D-glucuronopyranosyl branch chain of glucose connected to other xylose carbon sugar monomers [23]. Notably at ordinary temperature, the hemicellulose is also insoluble in water. It is soluble in acidic solution, and the solubility increase with concnetration of acid and temperature. Naturally, hemicellulose has various size, shape, low polymerization in structure and is not crystalline owing acetyl groups in the polymer. The hemicellulose make a strong backbon in plant biomass by crosslinkg with non-covalent bonds cellulose micro-fibril chains [23].

2.3 Lignin

Lignin is different than the hemicellulose and cellulose because it comprise of aromatic heterogeneous polymer phenyl-propane units. The long phenyl-propane units are attached together by ether bonds. The main function of lignin is to strongly drag hemicellulose and cellulose in complex structure of lignin like a glue to seal each gap in plant biomass. Therefore, this lignin make it harder for the degradation. The concentration of lignin is depending on the size, growth, nature and properties of plants biomass [24]. It is soluble in varios solvents, dioxane, pyridine, dimethyl sulfoxide, acetone, and in high concentration of acidic solution at high temperature. Notably, the lignin is easily soluble in alkaline solutions at both low and high temperature [25]. In a general thermal temperature heating of range 150–300°C degrade hemicellulose, 315–400°C degrade cellulose and 250–500°C degrade lignin from plant biomass. In lignin structure, three aromatic phenolic components coniferyl (G), p-coumaryl (H), and sinapyl (S) are the major monomers (**Figure 3**).

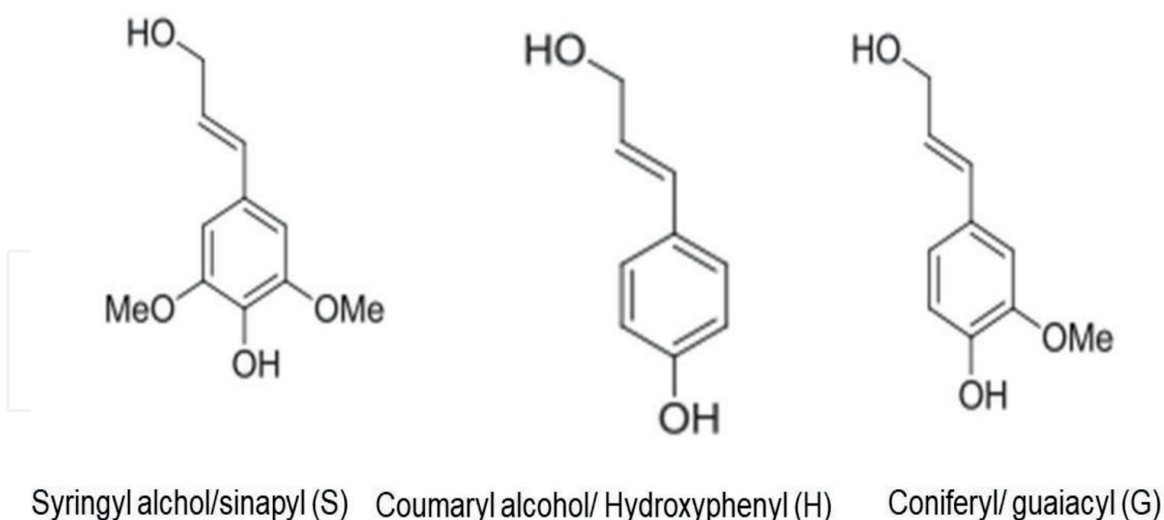


Figure 3.
Three main components in lignin structure.

Generally phenolic hydroxyl, methoxyl, and terminal aldehyde groups are present in the lignin. Softwoods lignin comprise of guaiacyl units, while in hardwoods the lignin contain guaiacyl-syringyl, whereas *p*-coumaryl alcohol units are found in Gramineaceous lignin. In lignin synthesis, alcoholic hydroxyl and carbonyl groups are

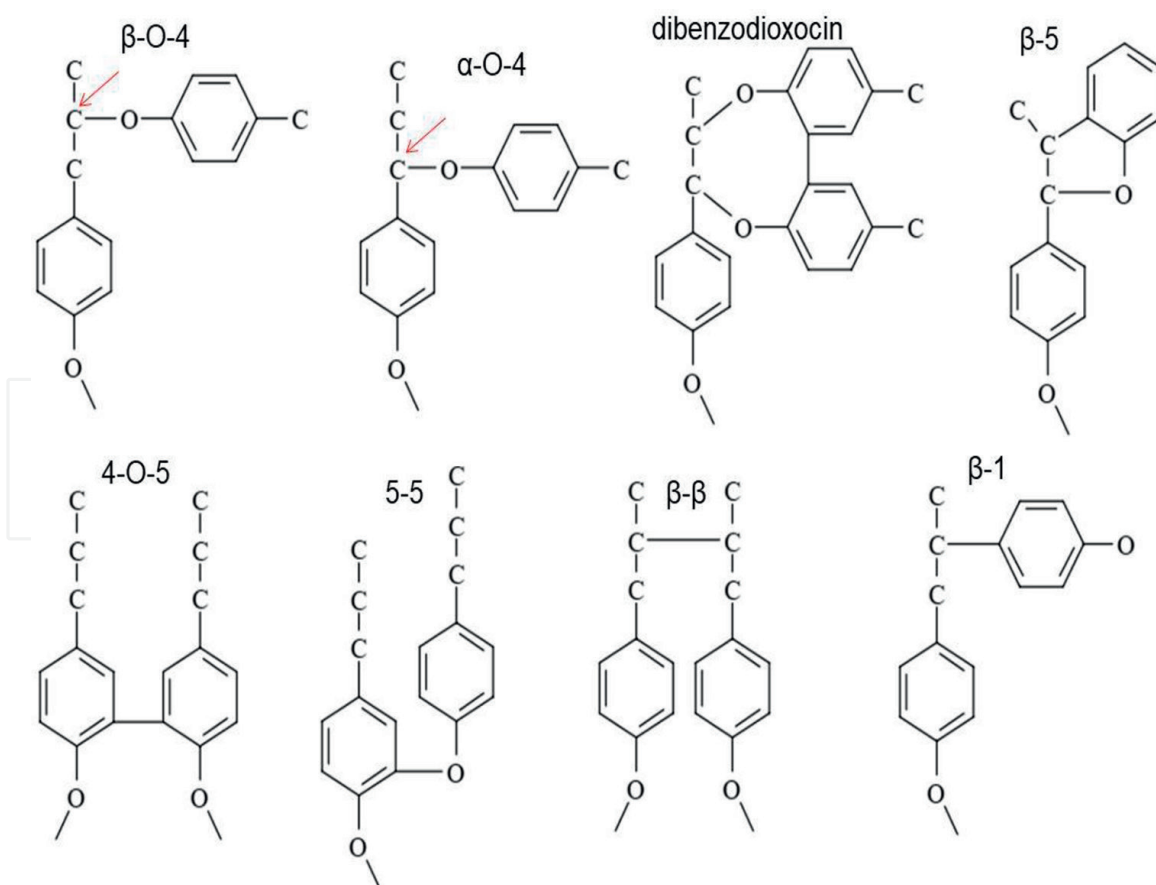


Figure 4.
Basic phenylpropane linkages in lignin structure.

assimilated into the structure of lignin during enzymatic dehydrogenation. Lignin structure has some mutual functional groups and common linkages between the aromatic phenolic components. Few of them are, β -O-4, α -O-4, dibenzodioxocin, β -5, 5-5, 4-O-5, β - β , and β -1 linkages. The density of the lignin structure is from the monomers ratio, compositions pattern and due to a number of linkages options between lignin monomers. Some of the common bonds arrange in carbon-carbon bonds (β -1, β - β , 5-5') carbon-oxygen bonds (α -O-4, β -O-4, and 4-O-5), carbon-oxygen and carbon-carbon bonds (β -5'/ α -O-4, β - β '/ α -O- γ). One the prominent 60% of total is ether β -O-4 linkage present in the polymer. (Figure 4) [26].

3. Chemical groups in biomass

Plant biomass has various functional groups i.e. phenolic and furfural compounds, among them the important groups are listed in the (Table 2). Among cellulose, hemicellulose and lignin, highest different functional groups are present in lignin polymer. Hydrogen and ether glucosidic bonds are common in cellulose. Thus cellulose can be easily transformed and fractionated into sugars monomers. Kirk-Otmer [27] defined the alteration, substitutions and transformations in functional groups. In lignin chlorine and nitro groups are added in the substitution reactions of chlorination and nitration. Reaction like, acidic solutions change hydroxyl group to allylic or aryl ether in lignin and make it water soluble. The glucosidic linkage in sugars is the most important bond in ether groups, in lignin polymer. Removal of this ether bond distort the chain in lignin and start separation of lignin from the rest of plant biomass. Condition of alkaline solution remove aromatic rings, whereas, solvolytic reaction split ether bond, and acidic reaction transform ether bond into hydroxyl and carboxyl prior fragmented into C3 or C2 molecules.

In hemicellulose, the common bond is hydrogen or ester bond with a hydroxyl chain. In long chain of hemicellulos polysaccharides, the ester bond connect to either carboxyl or hydroxyl groups but the position is not fixed between the cross linking of hemicellulose-lignin, and hemicellulose-cellulose [22]. The glucose monomer are connected by hydrogen bonds, oxygen atom and a hydroxyl group in hemicellulose and cellulose polymer chains. These bonding makes the polysaccharides in plant biomass rigid and only harsh conditions of high temperatures acids and alkali can break bonding of the polymer structure of the biomass [28].

Group	Cellulose	Hemicellulose	Lignin
Hydroxyl group	X	X	√
Carbon to carbon linkage	X	X	√
Ester bond	X	√	X
Hydrogen bond	√	√	X
Ether (glucosidic linkage)	√	√	√
Aromatic ring	X	X	√

Table 2.
 Basic functional groups in plant biomass.

4. Lignin types, isolation and pretreatment methods

Base on the isolation and pulping process, lignin products is termed with five different names

1. Technical lignin = which is made of paper, pulp and cellulose at industrial level
2. Kraft lignin = containing sulfate after pulping process
3. Lignosulfonate = containing sulfite groups in pulping process
4. Alkali lignin = lignin isolated from biomass using different alkali
5. Organosolv lignin = isolated with organic solvents treatment

As it known to us that the lignocellulosic biomass has three major components i.e. lignin, hemicellulose and cellulose that are linked together through different linkages and bonds between them. The details components and linkages are shown in the **Figures 3 and 4**. The isolation of lignin requires to disrupt the covalent, ether and hydrogen bonds between lignin and other fraction. The efficacy of the process arises from the yield, purity, and the degree of transformation in lignin structure. In each isolation process, either full or partial cleavage of bonds and functional groups are targeted. During the isolation method, the lignin linkages can be exposed to changes such as ether, carbon-carbon, oxygen-carbon bonds alteration and other than degradation to small fractions. Different kinds of pretreatment methods (**Figure 5**) are tested to effectively separate out the main components of plant biomasses. The methods tested includes physicals, biologicals and chemicals to degrade and hydrolyze

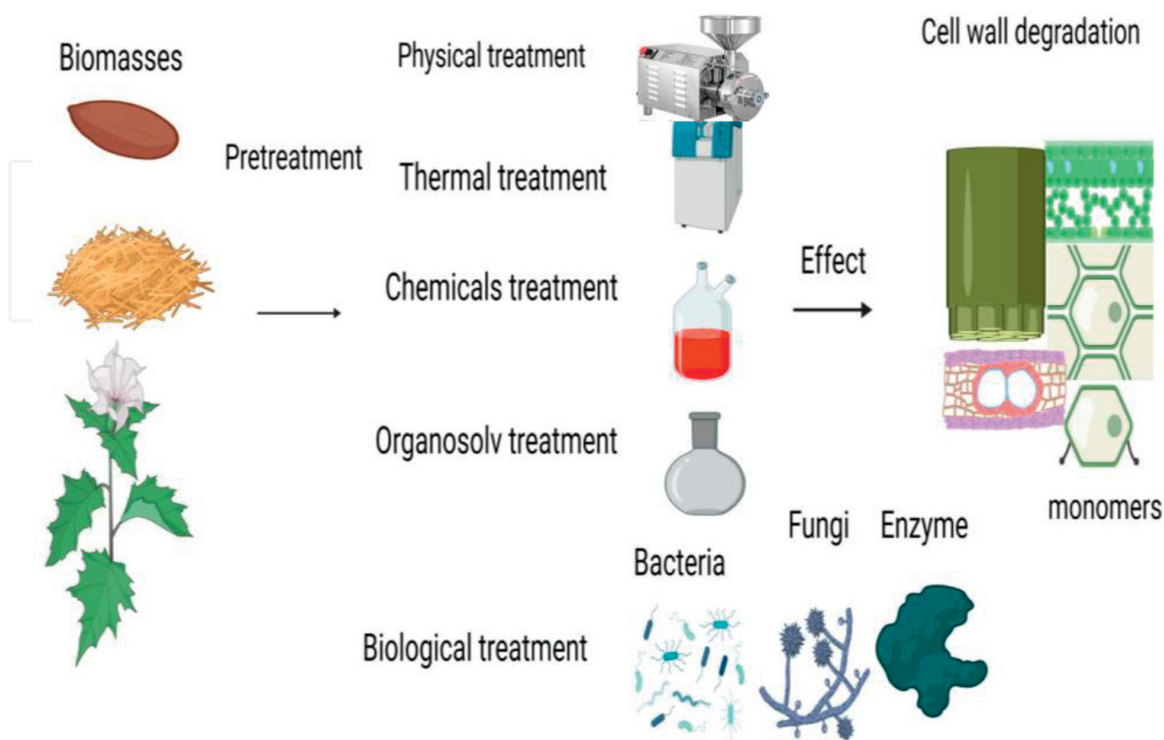


Figure 5.
Pretreatment methods and their effect on biomass.

the targeted biomasses into its monomers. The pretreatments are necessary to remove lignin, one of the toughest structure that act as an obstacle for its utilization purposes. Thus lignin is considered to be remove from the biomasses and makes the cellulosic component expose for the transformation into usable materials [29].

The preeminent approach must have characteristics like (a) minimum chemicals uses (b) high carbohydrates reclamation (c) narrow quantities of by-products (d) economical far-reaching applications (e) appropriate for diverse biomasses and (f) decrease the concentration of enzymes used in hydrolysis of biomasses [30]. So far none of a single pretreatment method has all the good properties as supposed above, but in broad-spectrum, this section will concisely focus on the common methods reported for different biomass hydrolysis.

4.1 Mechanical treatment

Mechanical method change the solid fragments of the biomass into granular shape, improve the precise surface area and degrade into lesser particles, remove water content, decrease the needs high amount of energy consumption in further pre-treatment reaction. Various mechanical methods like high-pressure homogenizer, piston press, bead mill, grinding and sonication are reported.

4.2 Thermal method

A high temperature utilization is also applied at commercial scale that's disintegrate the plant biomass and direct conversion of biomasses into polysaccharides and carbon materials. The thermal treatment scale depends on the plant biomass materials and conversion into target molecules. Low thermal temperature ranges from 120 to 180°C are uses for proteins, carbohydrates and other sugars molecules solubilization. Whereas, high thermal treatment are applied for prouction of volatile organics, carbons and gases from biomass. Thermal heating in autoclave uses steam heat under high pressure on lignocellulosic biomass results in a considerable break in lignin linkages in biomass [31]. Electromagnetic radiation from microwaves with a frequency range of 250–300 MHz energy induced molecular vibration and is showed more efficient and less time consuming pretreatment method compared to conventional heating [32]. The microwave heating combine with acid, alkali and organic solvents has high impact than alone thermal treatment method [33]. So thermal treatment with any technology can be use to disintegrate the plant biomass into its components.

4.3 Lignosulfonate process

The isolation of lignin using sulfite and bisulfite anions at industrial scale. In this process, sulfur dioxide reacts with water with control oxygen supply in sulfur combustion and produce sulfurous acid for making pulping liquor. This reaction use alkali base or carbonates for pH (1–6) adjustment, and temperature adjustment of 140–160°C. The final product lignosulfonate polymer is water soluble and comprises of 5% sulfur and carbohydrate impurities.

4.4 Kraft process

The Kraft process is a universal delignification method used in paper and pulp industry for lignin removal. In this process sodium sulfide (Na₂S) and sodium

hydroxide NaOH are used to disassociate lignin linkages in substrates to separate out cellulose. The addition of these alkali solutions at high temperature of 150–170°C for about 100–120 minutes, results a brown liquid and solid pulp. The lignin is precipitated through acidification from dark liquor and purified while cellulose and other carbohydrate residues and inorganic impurities are left aside. Purified Kraft lignin is then used to energy purpose through combustion in paper mills.

4.5 Chemical method

Chemical method with thermal heating is commonly used for fractionation of biomass into lignin cellulose, and hemicellulose. The function of acids in low concentration break the outer surface and release bulk of extratives and hemicellulose of the biomass. Whereas, the concentrated acids at high thermal treatment disassociate the firm structure of the biomass. This treatment release both lignin and hemicellulose sugars of the biomass simultaneously. Sulfuric acid, hydrochloric acid, and nitric acid with (1–10% w/v) are mostly reported in the acid chemical treatment method [34]. The alkaline solutions particularly of sodium hydroxide, potassium hydroxide, and calcium hydroxide specific target linkages bonds in lignin and has very less penetration power for the cellulose of biomass. The alkaline solution with thermal heating pretreatment makes the biomass digestible for enzymes saccharification into sugars [35] allowing maximum entrance to hemicellulose and cellulose molecules [36]. It is hard to classify the most appropriate pre-treatment process for different kinds of biomasses [37]. But, the right choice pre-treatment process needs to enhance porosity of the biomass and reduce the inhibitors generation [37]. Ideally, low acids and alkali concentration has revealed optimum separation of lignin, hemicellulose and cellulose of the biomass without addition of inhibitors [38]. Further, dilute acids and alkali pre-treatment can be economical for bioenergy and biochemicals production from biomass polysaccharides at large scale. Potassium hydroxide, calcium hydroxide and sodium hydroxide are the highly esteemed alkalis for lignocellulose degradation, however, sodium hydroxide has a greater potential reaction rate compare to other alkalies [39]. Whereas, in cost perspective, calcium hydroxide has less cost per kg than the other and could prove to be the inexpensive pretreatment of biomass [40]. Therefore, for industrial scale process, it is better to select the inexpensive acids and alkali with optimum thermal process for yield of polysaccharides and biofuels production from pretreated biomass through anaerobic fermentation.

4.6 Organosolv method

Organosolv extraction method include, an organic solvent dissolved in water at high hydrothermal condition for biomass hydrolysis to remove a pure sulfur-free lignin. Common tested solvents have very low boiling point and can be simply recycle back after the pretreatment process. The subsequent lignin structure has small changes related to the native lignin. The organosolv treatments in fact chop favorably the bonds between carbohydrate-lignin molecules separating a partially modified lignin. Due to this characteristic, lignin obtained with organosolv treatments is a best monomer for making polymers, such as bio-based polymers, polyesters, polyurethanes, and phenolformaldehyde resins. The most universal organic solvents are acetone, ethanol, methanol, or a mixture thereof. The purified lignin is recuperated after the precipitation process using water.

4.7 Biotreatment

Biotreatment is basically biological pretreatment method applying either bacteria, fungi or yeast cells in single culture or mix microbial communities composition. Additionally, specific enzymes in as a single entity or mixed enzymes solution has also been used in biotreatment system. The nature and function of enzymes and microbial culture could be different but the overall target is to fractionate the biomass into separate polysaccharides molecules. A number of enzymes such as lignin peroxidases, laccases, xylanases, endoglucanases, peptidases, esterase and hydrolases has been applied in biomass saccharification process. Beside enzymes, a number of fungal strains *Phanerochaete chrysosporium*, *Trametes versicolor*, *Pleurotus ostreatus*, *Ceriporiopsis subvermispora*, and bacterial species particularly *Clostridium* sp. *Pseudomonas* sp. LD002 [41], actinomycetes [42], *Streptomyces viridosporus* T7A [43], *Rhodococcus jostii* RHA 1 and *Pseudomonas putida* [44, 45], *Bacillus* sp. strains [20–23], and thermophile *anaerocellum thermophilum* are reported for oxidative hydrolysis of lignin from biomass. [46, 47]. Fungi like white and brown-rot fungi has the ability to hydrolyze both lignin and cellulose [48]. Such strains has the enzymes machinery of lignin peroxidase, manganese peroxidase, versatile peroxidase, laccase and cellulases [49]. The efficiency and percentage of lignin degradation depends on the enzymes and growth of the microorganisms like *Stereum hirsutum* (white-rot fungi) has 14.5% degradation of the lignin from the wood biomass [49]. Whereas, *Coniochaet ligniaria* fungus reported upto 75% of lignin degradation from pepper plant, likewise, *Pleurotus Florida* with 45–50% degradation of lignin from corn straw [50]. The importance of biological treatment method is consumption of low energy, safe for environment and has no involvement of toxic chemicals. However, the problems that needs to be adjusted is sluggish growth, optimum conditions of enzymes, products inhibition, pretreatment time, enzymes purification, economical approach, feasible for the degradation of diverse agriculture biomasses [51]. However, all of these studies proposed that biological treatment is economical pre-treatment method among the all for inexpensive biofuels productions.

5. Lignin applications

Isolated lignin through any pretreatment methods can be use directly as unmodified crude lignin or pure lignin with further modification reactions in the applied field. This section will briefly describe the main applications of both native lignin and modified lignin.

5.1 Native lignin

Lignin has many applications; one of them is direct combustion of lignin as black liquor as a fuel and power in paper and wood pulping industry. Also the native lignin increase combustion heat to bio-fire made of propane-1,3-diol and cellulose. In view of its binding stuffs, it is commonly used as a stabilizer in coal briquettes in which it raises the boiling speed and strength in packing paper material. Regardless of the importance of lignin for power generation, it has many other uses like as toluene or benzene, non-toxic binder in pelleted feeds, nonhazardous chelating agent, transporter of nutrients as lignosulfonate for the plants to discharge them gradually in the soil. Lignin can also

be use as a sequestrant of heavy metals (e.g. zinc, nickel, cadmium and mercury) for purification of polluted water due to chelating property [26, 52].

5.1.1 Polymers from native lignin

Native lignin can be an outstanding preparatory material for making of polymer composites with other molecules through covalent bonds. Additionally, as an additive the native lignin can protect polymers from high temperature, light and oxidation. The most essential linkages are the hydroxyl groups in polymerization. Remarkably, the steric interruption decrease the reactivity of lignin and due to fairly small amount of free active hydroxyls, still the use of lignin in polymer materials has been successful. For example, in the reaction between phenol and formaldehyde for production of phenol-formaldehyde adhesives of chipboards, plywood etc., lignin is convenient as a substitute for phenol binding reagent. Similarly, lignin can be blended in polyethylene, polypropylene, to change its mechanical properties and improving the oxidative resistance. Kraft-lignin as an unmodified material used in polyesters as a reaction monomer has been reacted with sebacoyl chloride, increased the recycling of subsequent polymer. Native lignin has many other applications also, it can react with polyethylene glycol (PEG) and methylene diphenyl isocyanate to make polyurethanes, biodegradable foam, cheap composites, bioplastic materials mixed with cellulose fibers, cellulose-lignin based hydrogel, medical devices or controlled drug release exercises [26, 52].

5.2 Modified lignin

Lignin reaction can be change and modified to add new functionalities with aim for fine chemicals production.

5.2.1 Adding new function

Amination, a reaction to add reactive amino group to lignin to synthesize aminated lignin hat has significant application as a slow-release mediator for fertilizers and flocculant to remove anionic dyes from water solutions [26].

5.2.2 Synthesis of polymers

The native lignin can be used for synthesis of several polymers. To do this, changes in the reactive sites such as phenol and hydroxyl groups like lignin-phenolation is the mostly used process. Lignin-phenolation is carried out using methanol or ethanol in acidic medium, with a boiling point temperature of the tested solvent to make phenol-formaldehyde (PF) resins. Similarly, sulfur-mediated demethylation is a process to remove the methyl from the hydroxyl groups in lignin is economical and most significant reaction to synthesize phenol-formaldehyde resins [26].

5.2.3 Catalytic reactions

There are feasibly many catalytic reactions for lignin modification; but the three important of them are oxidation, hydrogenolysis, and hydrodeoxygenation.

5.2.4 Oxidation

In oxidation, ether bonds are sliced of the hydroxyl-benzyl group of the lignin structure, resulting to a combination of aromatic ketones and aldehydes that are valuable predecessors to fine chemicals. For example, in an alkaline medium, lignin is oxidized under high-pressure of oxygen for vanillin synthesis. Further, catalysts like Pd/Al₂O₃ speed up the selective oxygenation of lignin for high yield of vanillin and syringaldehyde [26].

5.2.5 Hydrogenolysis

Hydrogenolysis is a reaction that breaks ether bonds in lignin at high temperature and hydrogen in the presence of a catalyst. For example, in the presence of Ni, lignin is converted into aromatics compounds such as dihydroconiferyl alcohol, dihydroxysinapyl alcohol, guaiacol, and 4-propylsyringol. In hydrogenolysis, the selective reaction on specific bonds of the lignin towards valuable chemicals, identification and separation of the specific product from the complex mixture of aromatics is a challenging task [26].

5.2.6 Hydrodeoxygenation

Hydrodeoxygenation is a degradation reaction that gives rise to aromatics with low oxygen content. In hydrodeoxygenation, under strict temperature and pressure using a catalyst, the lignin can be converted into benzene, cycloalkanes and hydrogenated bio-oil as a fuel [26]. A list of lignin base products synthesized through different reaction process are given below in **Table 3**.

The high abundance and availability of lignin has a great market potential for industrial use. In future the efficient utilization of the isolation process and chemical conversion reaction with new technologies may have significant contributions

Product	Lignin or Lignin Monomers Reaction
Feruloyl and p-coumaryl	Conversion of ferulate and coumarate by Acyl-CoA synthetase (HcaC) of <i>Acinetobacter baylyi</i> , <i>Cupriavidus necator</i> JMP134
Vanillin	Conversion of feruloyl-by Acyl-CoA hydratase (HcaA) of <i>A. baylyi</i>
Phydroxybenzaldehyde	onversion of p-hydroxybenzaldehyde by Dehydrogenase (HcaB) of <i>A. baylyi</i> ,
Guaiacol	Vanillate by Decarboxylases (VdcB, C, D) of <i>Streptomyces</i> sp. D7
Formaldehyde	Methyl-THF by O-Demethylase systems (MetF) of <i>Acetobacterium dehalogenans</i> , <i>Sphingobium</i> sp. SYK-6
Methanol and C8–C9 alkanes	Conversion of Birch wood sawdust at 200/250°C, 40 bar, Ru/C, Pd/C, Rh/C, Pt/C
Sugars	Wood flours from Japanese beech (<i>Fagus crenata</i>) using catalyst 1 ethyl-3-methylimidazolium chloride at 90–120°C
Phenol	Sugarcane bagasse lignin using Raney Ni and β -zeolite at 2 h at 160 °C; 2 h at 240°C conditions
Plywood and fiber board binder	Making of binder of through phenolation that condense lignin aromatics monomers with phenol

Product	Lignin or Lignin Monomers Reaction
Adhesives	Reaction of lignin with phenolic resin to make phenol-formaldehyde (PF) adhesive
Asphalt	Bitumen in asphalt can be substituted by lignin to make epoxy concrete or epoxy-cement.
Bio-sourced battery	In lithium-ion batteries for enhanced electrical systems lignin can bind cathode, electrolyte, and anode as a bio-sourced polymer
Lignosulfonates	lignosulfonates of sulfite spent liquors (SSL), calcium, and sodium can produce wood adhesives
Medical/healthcare devices	plant-based adhesive hydrogel using Ag-Lignin nanoparticles (NPs), The hydrogels is made of a solution of poly (ethylene glycol), acrylic acid (AA), pectin, ammonium persulfate, Ag-Lignin NPs solution, and diacrylate.
Biocomposites	treatment of cotton fiber or polylactic acid (PLA) as a matrix for the composites with native lignin extracted from biomass
Leather skeleton	Lignin coated leather can replace using azobenzene in dyeing industries
Lignin coating polymer	Klason lignin treatment with hexamethoxy methyl melamine, p-toluene sulfonic acid goes for self-polyesterification with sodium hypophosphite (NaHP) to produced polymer

Table 3.
Examples of few important lignin base products [26, 52].

for chemicals, materials and fuels from raw lignocellulosic biomass. The successful application of novel process will build a sustainable route in future bioeconomy. In brief the lignin can be used to be converted through the reactions described in to many chemicals products. The lignin has valuable raw materials for several applications. The potential products from lignin for the market are

- Syngas products (Dimethyl ether, Methanol, Ethanol, C1–C7 gases)
- Hydrocarbons (Benzene, toluene, xylene, higher alkylates, cyclohexane, styrenes, biphenyls)
- Phenols (Phenol, catechols, cresols, resorcinols, syringols, coniferols, guaiacol)s
- Oxidized products (Vanillin, vanillic acid, syringaldehyde, syringic acid, aliphatic acids, cyclohexanol/al, β -keto adipate)
- Macromolecules (Carbon fibers, polymer alloys, composites, adhesives, binders, preservatives, polyols)

6. Conclusion

As global fossil resources are immensely diminishing and high utilization of it causing climate pollution due to discharging of harmful gases. Lignin was assumed as useless materials in plant biomasses and same for other waste residue of lignocellulosic substrates. So a huge amount of beneficial carbon materials vanished either burning in the field or for cooking purpose. This chapter highlights that plant biomass

contains cellulose, hemicellulose and lignin. All of the three main components can be converted into industrially valuable products. This chapter described the accessibility of huge amount of lignin along with cellulose and hemicellulose carbons, separation methods of polysaccharides and conversion of these usable carbons to high value chemicals production. This brief information about lignin has the possibility to be extended for better depolymerization of lignin base biomasses, and a knowledge source for efficient reaction to new aromatic catabolic chemicals in the future.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work.

Notes/thanks/other declarations

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