

Effect of Green Logistics Management on Biodegradability Studies of Lignin-Based Materials with Sustainable Environment

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How to cite this article: Apeksha Garg, Sudha Vemaraju (2024) Effect of Green Logistics Management on Biodegradability Studies of Lignin-Based Materials with Sustainable Environment. *Library Progress International*, 44(3), 10268-10299.

ABSTRACT

In today's era, bioplastic is too important for renewability. For this purpose, green logistic management is an important part of biodegradability for the green environment. There has been a rise in demand for biodegradable, ecologically benign, and sustainable alternatives. Although various biopolymers, including polylactic acid, cellulose, starch, and plant proteins, have been combined to create bioplastics, further research and development are still needed to ensure that the materials can be used for a broad range of purposes. For multinational corporations, infrastructure, and commitments to environmental, social, and governance (ESG) responsibilities are becoming more crucial action items. In addition to satisfying global compliance requirements and stakeholders who are motivated by values, these policies seek to safeguard the environment and all its inhabitants in the long run. Lignin, the world's second most prevalent natural biopolymer, acts as a matrix for cellulose and hemicellulose in plant cell walls, giving biofibers their mechanical strength. These bio-renewable polymers have emerged as a viable alternative to traditional metallic and organic materials for a wide range of applications. This is due to its biocompatibility, biodegradability, and inexpensive manufacturing costs. In this chapter, the biodegradability of lignin-based composites is compared with that of conventional composites. This chapter will give an encyclopedic view of research used to assess biodegradability. This chapter will also attempt to link biodegradation to structure and raw materials, focusing on the biodegradation of lignin-based healthcare products. The chapter covers the basic introduction of lignin, various biological degradation mechanisms of linings in-depth, different microbes responsible for biodegradation, and factors affecting lignin degradation.

12.1 Introduction

Sustainable substitutes for synthetic plastics and other materials created from fossil fuels are goods based on biomass. One of the most promising renewable material precursors for smart materials that may react to a range of stimuli is lignin, an aromatic plant polymer. One of the most viable strategies for reducing the exploitation of fossil fuels—which has been connected to rising greenhouse gas emissions and climate change—is the use of sustainable methods to create products from renewable resources [1]. With the growing environmental effect of the fossil fuel sector, the search for internationally accessible, clean alternative resources has taken on more significance. Utilizing lignocellulosic acid-rich biomass products can aid in lowering dependency on petrochemical resources. Agricultural waste is often burned to produce energy, but lignocellulosic biomass develops on top of it, as the literature clearly demonstrates [2]. There are severe environmental consequences from this behavior. Because lignocellulosic materials are readily available, bio renewable, and do not compete with food, they have garnered significant attention from researchers recently. They have shown to be useful raw materials for the manufacturing of goods with substantial added value, both economically and environmentally [3]. Non-biodegradable plastic waste made from petroleum has detrimental effects on people and the environment, making it a global problem that needs immediate attention. In the context of environmental concerns supporting the use of circular economy principles in materials science, lignin is a feasible, underutilized, and environmentally benign building material [4].

Lignin was discovered by Swiss botanist A.P. de Candolle in 1813, who characterized it as a fibrous, tasteless substance that is soluble in mild alkaline solutions and maybe precipitated (to create something) from solution using acid. The solution was given the name "lignine" by A.P.de Candolle, which comes from the Latin word "lignum," which means "wood." Lignin makes up a quarter to a third of the dry mass of wood and accounts for 30% of non-fossil organic carbon. Depending on the species, lignin has a different chemical makeup. Lignin is a waterproof polymer that is present in schlerenchymatic tissues. Both lignin and cellulose can be found in the wood. Before utilizing it, separate it into lignin-rich and sugar-rich streams. Once they've separated the sugar-rich stream, they may make several things with it. Ethanol and other platform chemicals, as well as lignin, have all been burnt to create energy in the past, but there has been a slew of new research on the utilization of lignin since 2010 [5]. This is due to two factors:

- The more applications salono's can discover, the more lignin will be generated, making the entire process more sustainable and cost-effective.
- It's not only that lignin is abundant; it's also that it's the most energy-dense molecule in the material.

How to utilize it?

Lignin is a big and complicated protein. So, if cellinos and split cellulose into one component, glucose, and 100 with lignin, researchers can feed these chemicals to bacteria and funnel them to a few intermediates from which many goods may be made. The intricacy of lignin can be reduced by using the bio funnel. Lignin is a polymer of strongly ramified aromatic, phenolic alcohols (monolignols) [6]. Despite its unknown structure and its insolubility in water and most organic solvents, it is the second most prevalent polymer. Lignin creates interconnections with polymers that enhance the mechanical strength and rigidity of lignified wood stem. It decreases the digestibility of the connected polymers, as it is difficult for herbivores to digest them (cellulose). The most common polymer is cellulose. Lignin protects Plants from herbivores, which renders them indigestible (animals that only eat grass and plants). Lignin and phenolic compounds combine to produce a fungal penetration site, which inhibits the pace of cell wall breakdown (fungal entry). It shields the cell from harm [7]. Figure:1 shows wood-lignin: supply, extraction processes, and use as bio-based material.

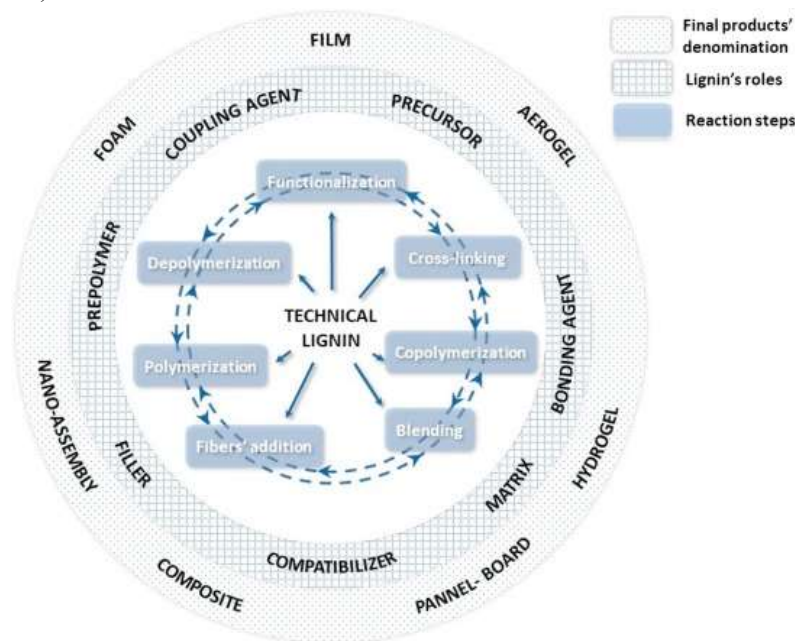


Figure:1 Lignin from wood: sources, extraction, and bio-based uses [8]. **Reproduced from Maarouf et al. [2019], with permission from Elsevier.**

12.1.1 Biological Function

Lignin fills gaps in xylem tracheid, vessel elements, and sclereid cell walls between the cellulose, hemicellulose, and pectin. It binds different polysaccharides of plants because it has hemicellulose covalently bonded (a carbohydrate e.g., cellulose, starch, and glycogen whose molecules consist of several sugar molecules bonded

together). Compression wood is not common in reaction wood-like tension wood, but unusual (with considerable concentrations). The conductivity of water in plant stalks is lignin-dependent [9]. The polysaccharide components of the plant cell wall are hydrophilic (love to mingle with them) and therefore water-permeable (fail to mix with water). Water absorption to the cell membrane is problematic due to the crosslinking of polysaccharides by lignin. As a result, lignin aids the appropriate transfer of water by the plant's vascular (vein-containing) tissue [10]. Except for bryophytes (a tiny flowerless green plant), lignin is found in all vascular plants, implying that its initial role was limited to water transport. However, lignin-containing red algae suggest that, on the other hand, the original job of lignin is restricted to water transport by red algae. Lignin is a common ancestor of lignin-generating plants and red algae. Its initial job was structural because it maintains links in the calibration of red algae between calcified segments (callithron is a genus including two species of thaloid intertidal algae). Another theory is that lignin has been developed separately from a common ancestor, red algae, and plants [11]. Figure:2 shows composites with lignin functionalization.

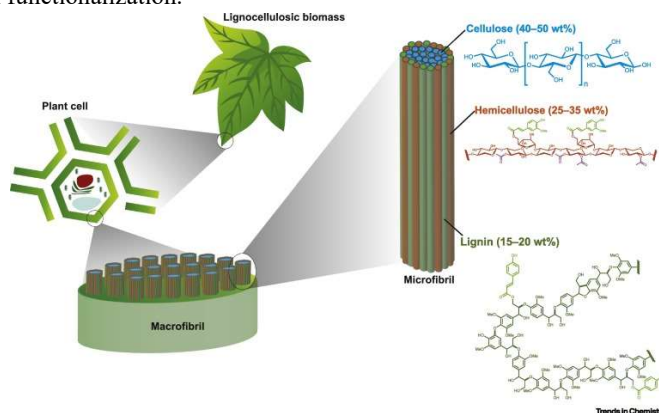


Figure:2 Composites with Lignin Functionalization [12]. Reproduced from Stefania et al. [2020], with permission from Elsevier.

Ecological Function

For the carbon cycle, lignin is vital because it sequesters (or hides) atmospheric carbon from woody permanent plant tissues [13]. Lignin (all the plants that perished in certain regions) is one of the slowest degrading components of dead vegetation, representing a large volume of humus-formant material. The resulting soil humus (a substance made from dead plants and leaves placed in the ground to help plants grow) is increasing the photosynthetic productivity of plant populations growing on-site by providing increased cation availability in the site as a result of the transition from disturbed mineral soil through ecological succession [14].

Economic Significance

Highly lignified wood is a durable raw material that can be used in various ways. It is also a very good fuel source, as lignin produces more energy than cellulose when burned [15]. Most Lignin found in wood can be found in the pulp used in newsprint mechanical or high yield (a cheap, low-quality paper used to print newspapers). Lignin is what makes them yellow with time in newspapers. Lignin must be removed from the pulp before a high-quality bleached paper (a soft material made specifically by pressing something) can be formed. Sulfite pulping removes lignin from wood pulp as sulfonates (a salt of sulfuric acid containing the anion SO_3^{2-}) (a salt or ester of sulphuric acid). There are various applications for these lignosulfonates [16]:

- It is employed in high-performance cement applications, in water treatment formulas, and textile dyes (a liquid or gas used to disperse small particles into a medium).
- The additive is used in oil fields, and agricultural chemicals are used to list some uses. Vanillin dimethyl sulfoxide (DMSO), ethanol, sugar xylitol, and humic acid are produced in this raw material—environmentally safe roadway dust removal agent [17].
- Marathon Cooperation, a paper business located in Rothschild, Wisconsin, claimed the first commercial use of lignin research in 1923. Leather tanning chemicals were the first category to fall short of

expectations. Marathon Chemicals was the name of the lignin chemical division of Marathon for many years.

- The lignin removed during the Kraft (a type of strong, smooth brown wrapping paper) process is often burned to provide electricity for the mill's operations.
- In 1988, Tecnar, a German business, created a technology for converting lignin into "Aboform," a plastics-like material that is used in many applications for injection molding. If an object survives, it can be disposed of in the same manner as wood.
- Shrubby willow lignin (a tree with long, thin branches that hang down and grows near water) was effectively utilized to make expanded polyurethane foam in 2007. Carbon fiber might be made from lignin rather than fossil fuels, according to research published in 2012.
- The Flemish Institute for Biotechnology oversaw an experiment in which 448 poplar trees (a tall straight tree with softwood) were genetically engineered to produce less lignin, making them better suitable for biofuel conversion.

The global commercial lignin supply has been significantly impacted by the papermaking industry. In 1988, global paper production surpassed 220 million tonnes. The fiber content of a paper is around one-third lignin and two-thirds cellulose [18]. In the papermaking process, lignin is an obstacle because it turns yellow when exposed to air, weakening the paper. After being extracted from cellulose, it is burned as fuel. Due to the quality being less of a factor in low-volume applications, only a small percentage of the material is used. A considerable amount of the lignin initially present in the wood is retained in the newsprint, which is created from the mechanical or high-yield pulp. The lignin in newsprint is what causes the yellowing over time. To make high-quality paper, lignin must be removed from the pulp. A substantial source of pollution is generated by paper industry delignification procedures, although these methods are vital [19]. Lignosulfonates, which are formed when lignin is removed from wood pulp by sulfite pulping, have a wide range of possible uses because of their versatility. They're used as a dispersion, humectant, emulsion stabilizer, and sequestrant (for water treatment). lignosulfonate was another water reducer or superplasticizer in 1930s concrete, which decreased the water-cement ratio, which is one of the most important factors affecting concrete porosity and therefore its mechanical strength as well its diffusivity and hydraulic conductivity, all of which are critical for the long-term durability of concrete. It can be used as an environmentally benign and effective dust suppressant on highways. Lignin extraction can be used in the production of biodegradable plastic with cellulose as an alternative to hydrocarbon-made plastics, as long as the method is more environmentally friendly than generic plastic production [20].

Biosynthesis

The development of amino acid phenylalanine glycosylated monolignols in the cytosol (a watery component of a cell cytoplasm) (the production of complex chemicals within living organisms or cells). These early reactions also occur in the course of phenyl propanol. It is water-soluble and less harmful as it is linked to glucose [21]. After the transport of glucose to the cell membrane and polymerization processes start, the glucose is removed from the apoplast. Oxidation enzymes catalyze the radical coupling stage of the polymerization process. Peroxidases (an enzyme oxidizing hydroquinone into quinones (any compound that has a ring structure) and cuprocoating enzymes (a compound that oxidizes hydroquinone into quinones) are found in plant cell walls, but it is unknown whether one or both of these categories are involved in polymerization [22].

Low molecular oxidants can be used to produce monolignol radicals in oxidative enzyme catalysts. Although the theory (a viable explanation that has yet to be proved) was recently put into question, although it has been generally assumed that these radicals undertake an uncatalyzed coupling to produce a lignin polymer. The biodegradation of lignin by a fungus such as brown-red, soft red, or white red (to go bad) causes loss of wood forest floors as well as structures constructed by human beings such as closed and wooden structures [23]. However, before plant raw materials produce biofuel, lignin biodegradation is necessary (it must occur before anything else can occur).

The enhanced breakdown of lignin would increase the amount of the digestible or degradable biofuel component [24]. Improvements in the breakdown of lignin would result in improved biofuel processing profit or efficiency factor. Lignin cannot be digested using mammalian enzymes but can be biodegraded by fungal and bacterial ligninases. Biodegradation remains a mystery, with various paths according to the type of wood rot [25].

Coupled with the other components of a well, lignin reduces access to microbial enzymes such as cellobiose dehydrogenase by cellulose and hemicellulose. Lignin has thus been associated with a decrease in the overall digestive of plant biomass that supports illness and resistance to insects. Microorganisms such as fungi and bacteria cause lignin breakdown. Coupled with the other components of lignin reduces access to microbial enzymes such as cellobiose dehydrogenase by cellulose and hemicellulose. Lignin has thus been associated with a decrease in the overall digestive of plant biomass that supports illness and resistance to insects. Microorganisms such as fungi and bacteria cause lignin breakdown [26].

Detection

Lignin is also detected using a solution of hydrochloric acid and phloroglucinol. Due to the presence of significant groups in the lignin, a bright red hue arises [27].

Literature Review

- **Ian et al. [1995]** A polymer present in woody plants; lignin is an aromatic polymer that provides the tissue with a high degree of rigidity while also being resistant to organic breakdown. Lignin is a challenging substrate for enzyme depolymerization because it is insoluble, chemically complicated, and devoid of hydrolyzable connections, all of which make it difficult to depolymerize. White-red fungi can mineralize lignin, but brown-red fungi only alter lignin when digesting wood carbon, which is why mushrooms, particularly basidiomycetes, can biodegrade lignin to a significant level [28].
- **Tuomela, M., et al. [2000]** When it comes to getting rid of municipal solid waste, composting is becoming increasingly popular. In addition to herbal trash, compostable household garbage contains a range of papers and boards. Composting, as an alternative to standard package recycling in the European Union, will most likely benefit biodegradable packaging such as paper and board, according to the European Commission. Composted organic matter is broken down by microorganisms, which release carbon dioxide, humus, and heat in the process. A major component of humus is lignin, which is considered to be the most significant component. As a result, lignin does not mineralize entirely throughout the composting process [29].
- **Li, Yan et al. [2003]** Lignins are rarely listed in biodegradable polymeric compound compendia. Regardless, lignin derivatives are plentiful in plants and quickly biodegradable (although slowly). Indeed, significant (85%) industrial by-product lignin content in thermoplastics was first identified in 19971, and a US patent² has since been filed in response to the finding of plasticizers for simple derivatives of the same type of raw materials. The current study explores the philosophical foundations for the paradigm change in the lignin-based thermoplastic formulation [30].
- **Amar K. Mohanty et al. [2011]** Composites consisting of polybutylene succinate (PBS) and lignin-based natural material have been produced using melting methods. The effects on lignin and polymer diphenyl diisocyanate composite material (PMDI). Lignin and PMDI have been added to virgin plastic heat flush temperature (HDT). Interface adhesion to suitable composites has improved in SEM micrographs [31].
- **Joana S., et al. [2012]** Optical and scanning microscopy electron (SEM) have been utilized to investigate changes in the shape of RPU foams and to analyses structural alterations using FTIR spectroscopy. After 90 days of treatment, the two lignin-based foams displayed morphological changes in the surface (cell wall), which suggested an increased effect on the microorganisms. Following the respirometry trials, the chemical structure of the polymer was changed due to a microbe assault, as proven by FTIR spectra [32].
- **Grzegorz, et al. [2017]** In light of substantial scientific work to characterize wood degradation, the microorganisms have evolved several enzyme-organisms and non-enzymatic methods for exploiting this rich plant material. This study investigates the development of competitive and reciprocal wood damage and survival strategies between distinct fungal and bacterial species under various ecological circumstances. To clarify different wood breakup forms, the investigation of the enzyme mechanisms involved in wood degradation, which generally was based on ecological niches of one organism. A thorough description of low

molecular chemical products is also provided which is a new revolutionary alternative to the combustion of enzymes and that not only assists these bodies in the process of decay but is also a new evolutionary alternative to the combustion of enzymes [33].

- **Figueredo, Patricia, et al. [2018]** Bio regenerated polymers have been identified in a variety of applications as a feasible alternative to standard metals and organic components. It is biocompatible, biodegradable, and has a little cost of manufacture. Many chemical approaches are used to modify lignin after removal. Chemical changes include: deploying or fragmenting lignin, modification of the manufacture of new chemical sites, changes in hydroxyl groups in chemical products, and the development of lignin graft copolymers. Lignin offers a broad range of industrial and medical uses for nanoparticles for the supply of medicinal products, including biofuels, chemicals, and polymers. However, their uses rely on lignin supply, chemical modifications, and physicochemical characteristics [34].
- **Siracusa, Valentina. et al. [2019]** The capacity to employ renewable resources while reducing dependency on petroleum resources, on the other hand, may serve as a motivator to accelerate their future growth. The potential to be transformed into chemical intermediates and polymers that are utilized to replace fossil fuel feedstock are oils, maize, and pulp starch, cellulose of paint and wood, and other waste in the industry. The adoption of these new goods might have a major influence on long-term sustainable development. On the other hand, it is no longer guaranteed the use of renewable resources and the manufacture of bioplastics with the lowest environmental repercussions [35].
- **Yern Chee Ching et al. [2019]** The two most valuable natural sources on the earth are lignin and lignocellulosic fibers. They can decrease consumption/contamination of energy while enhancing biodegradability by replacing bioplastic synthetic fibers. The fiber matrix's compatibility has a significant influence on the bioplastic features. Lignin is removed from most surface treatments that improve the effects of lignocellulosic fibers. Lignocellulosic fibers are becoming more popular in bioplastics due to environmental contamination and the cost of modifying cellulose. In addition, the success of lignin-reinforced bioplastics varies. These applications demonstrate, from a technical viewpoint, that lignin from lignocellulosic fibers does not need to be removed before producing bioplastics [36].
- **Sibeko, M. A., et al. [2019]** non-biodegradable polymers, particularly packaging, have been widely utilized in several applications for decades. On the other side, the nature of polymers has caused worry about their influence on the environment. To tackle these difficulties, scientists have developed nanocomposites that are biodegradable, recyclable and sustainable, composite materials. By mixing biodegradable polymers with biodegradable fillers, bio-nano composites are produced; as both are biodegradable, the final biological-nanocomposite components should be biodegradable [37].
- **Moreno et al. [2020]** Synthetic polymers and other fossil-based commodities are gradually being replaced by biomass-derived products. Lignin is a fragrant plant polymer that might be used as a renewable material precursor for smart materials that respond to a variety of stimuli. The author addresses the applications of lignin-based smart materials like sensors, biological systems, and shape-programmable materials, as well as the necessary processing and chemical production procedures [38].
- **Asada, Chika et al. [2020]** In the culinary, aviation, automotive, and electronics sectors, epoxy resin is often employed as a coating agent. These, on the other hand, are environmentally detrimental and the petrochemical industry is responsible for this. In this instance, the treatment has been proposed for ecological epoxy resins consisting of biodegradable natural polymers. Lignin is a biodegradable plant biomass (agricultural waste or by-product) polymer with less bioethanol production potential than cellulose, resulting from under-used plant biomass [39].
- **Kateřina, et al. [2020]** A stage termed flotation comprises the process of mineral separation. Xanthates are the most popular collectors for sulfide ores to extract Cu, Ni, and Zn. Xanthates are environmentally damaging

as they are manufactured from fossil fuels, on the other hand. This research aimed to determine if lignin nanoparticles and microparticles might be employed for ecologically sound and durable collectors [40].

- **Shao-Jun, et al. [2020]** In the previous 70 years over 8 billion tonnes have been created, much of which do not completely biodegrade, leaving shields across the biosphere, including live animals. The combination of poly (Butylene adipate-co-terephthalate) with technical lignin using a dual-screw extrusion method generated a range of biodegradable composites. Researchers have developed two techniques for improving the mechanical properties of compounded polybutylene adipate-co-terephthalate (PBAT) /lignin: i) to decrease the hydrogen bonding between OH groups by the use of methylating lignin, and ii) to ensure the compatibility between male anhydride graft PBAT and lignin intermolecular interactions [41].

- **Parvathy, G., et al. [2020]** Because bio-based nanocomposites are important to the present environmental setting, the production and modification of lignin-based nanocomposites will get future focus. Lignin, a linked biopolymer and a major renewable resource with antioxidant characteristics, thermal stability, biodegradability, and ability to absorb UV, is the potential for application in several applications. When extra functionality is added to lignin, this produces a valuable composite material. The main goal of this project is to raise awareness about the environmentally beneficial use of waste lignin by emphasizing lignin nanoparticle production methods, functionalization, and applications, as well as lignin-based nanocomposites [42].

- **Diana, et al. [2020]** Due to their cheap manufacturing costs, biocompatibility, and biodegradability, biomass-based polymers are a potential alternative to petro-based polymers. The second most prevalent biopolymer in plants is lignin. Lignin has crosslinked polymers, including hydroxyls, carbonyls, and methoxyl, and it is very promising to be used in biologically degradable hydrogels, which have a large number of functions in biomedicine, soil and water, and agriculture. This study discusses the best-documented ways in recent years for producing lignin-based hydrogels which have been employed in hydrogel formulations through chemical and/or physical interactions with polymers [43].

- **Emma MN, et al. [2020]** The large volumes of fossil-based plastics created and squandered in recent decades are replacing biodegradable plastics made of naturally occurring biopolymers or biological polymers (manufactured). This study is compared to the unmodified biopolymers, starch, cellulose, and lignin-based lignin from which these bioplastics are generated, the speeds and processes of thermoplastic starch, and celluloacetate. This knowledge is significant since it is likely to affect future bioplastics research and development as well as assessments and controls of bioplastic wastes. On the upper level of the structure, such as thermoplastic starch, the biodegradation process was only minimally modified. When a polymer changes its chemical structure like cellulose acetate, biodegradation involves numerous bacteria and enzymes [44].

- **Appukuttan Saritha et al. [2020]** describe that the current environmental framework, the progression of bio mastic nanocomposite products, and modification of lignin-based nanocomposites are growing. Lignin comes from timber debris that is created as an unwanted by-product of ethanol and paper manufacture. Lignin may be used with antioxidant, high-temperature stability, biodegradability, and UV absorption for several applications in cross-link biopolymers. By integrating multiple functionalities in lignin, it is converted into a desired composite material. To raise the consciousness on the environmental usage of waste lignin, the main purpose of this study is the synthesis and functionality methods of lignin nanoparticles and the use of lignin-based nano-composites [45].

- **Diego A. Bonilla. et al. [2021]** The loss of indigenous and ecosystem-disrupting plant species is the most important environmental problem posed by invasive plants, which has implications for human health and the global economy. The results of the reaction were compared using two different extraction methods: base/acid extraction and solvent-based extraction. Fourier-transformation infrasound spectroscopy was used to extract and polymerize compounds in the laboratory setting. A unique biopolymer was tested using differential calorimetry and a soil burial test, and the thermal and stability properties of the novel biopolymer were investigated using thermogravimetry [46].

Problem Statement

Due to the intricacy of lignin's structure, researchers are moving closer to nano lignin by manufacturing it, as illustrated in Figure:3.

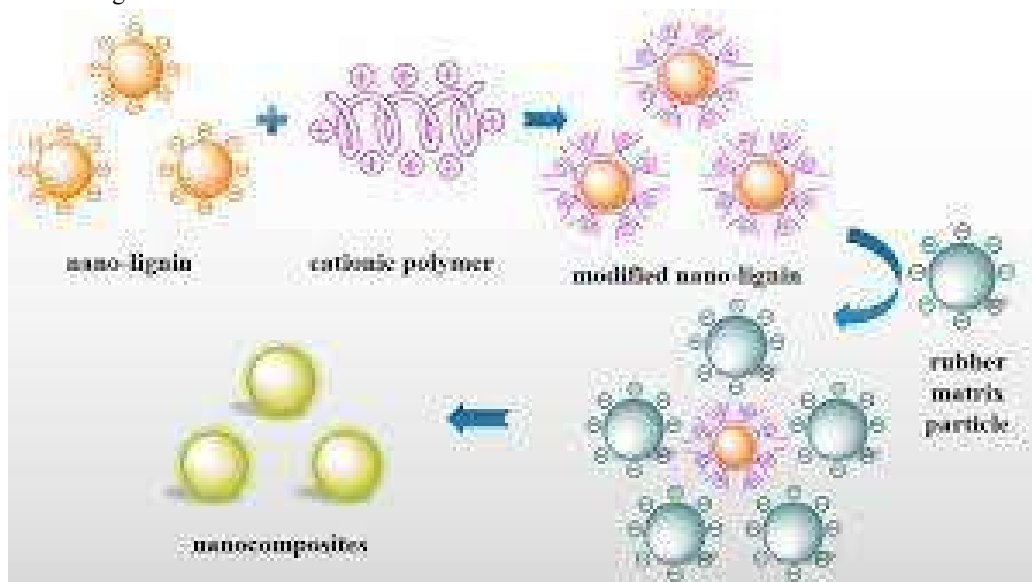


Figure:3 Structure of lignin [47]. Reproduced from Zhao Zhang et al. [2021] under the terms of the Creative Commons Attribution License (CC BY 4.0). <http://creativecommons.org/licenses/by/4.0/>.

Synthesis of Lignin Nanoparticles

Biodegradable nanoparticles (NPs) are being employed in various applications, including farming, and are made from renewable resources [48]. The use of biopolymers such as cellulose, lignin, and other biopolymers in manufacturing nanoparticles for composite reinforcement is possible [49]. Lignin nanoparticles in nanotechnology and biotechnology are widely employed nowadays in the world. The study showed that the pH stability of lignin nanoparticles produced using the conventional way was higher than those made using a green method [50]. The lignin nanoparticles (LNPs) created by both processes are electrostatically stable, as they contain negative charges on their surfaces; nevertheless, modifying surface charges and joining surfaces can further boost stability. Figure: 4 shows a synthesis of lignin nanoparticles.

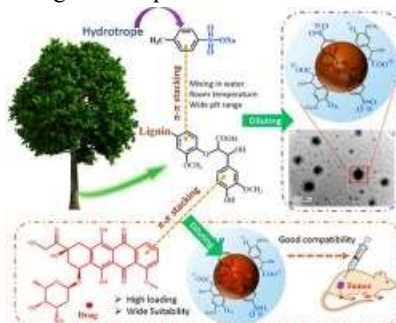


Figure: 4 Synthesis of lignin nanoparticles [51]. Reproduced from Liheng et al. [2018], with permission from Elsevier.

12.1.1 Structures of lignin

As our sensitivity to environmental contamination and shortage of resources increases [52], the regenerative and degradable qualities of biomass materials are recognized further. In recent years, lignin, the second most prevalent natural polymer after cellulose, has been the subject of a great deal of investigation. Given their biocompatibility and biodegradability, lignin-based products are an important component of any complete biorefining strategy, particularly in the pharmaceutical industry. It contributes to product and market diversity, garbage recycling, and long-term economic growth by reducing waste and increasing recycling. But with only a 5 percent worldwide

market share for high-value development, there are substantial difficulties and possibilities for novel lignin research and development to be explored. It has working groups that are aliphatic, hydroxyl, and aromatic, among other things [53]. Efficient utilization of biomass is closely associated with efficient cellulose, hemicellulose, and lignin extraction and extraction is closely associated with efficient utilization of biomass. Lignin has a variety of structural and functional properties that vary depending on the extraction process and pulp operation used [54]. These differences influence the future development and application of lignin. Among the most popular procedures for separating and extracting lignin include grinding, acid/alkaline/thioacid hydrolysis, enzymolysis of cellulose, organic solvent extraction, and ionic liquid extraction. Organic solvent pulping removes the need for alkali or inorganic acids, which are often used in the pulping process. The extraction of lignin from cellulose can be accomplished by the use of organic solvents such as alcohols, esters, and amines to dissolve it in the starting materials [55]. Biological enzymes are responsible for the selective breakdown of cellulose and the extraction of lignin. Lignin is separated using a biological method that has minimal influence on the structure and chemical characteristics of the protein [56]. Therefore, it is important to pick appropriate and effective extraction techniques that do not interfere with the lignin structure of a variety of source materials to get the best results. Lignin attachment and separation are highly dependent on ionic strength in the solution, which may be measured by measuring the presence of various types of ions in the solution [57]. Lignin's macromolecular and colloidal properties may be investigated using self-aggregation kinetics in specific solutions. To understand its physicochemical properties, further research into lignin solutions/colloidal behavior, associative/dissociative processes, and associative/dissociative processes is required. A large amount of research is being done on lignin for composite materials and the generation of biological products from lignin breakdown [58]. However, due to a variety of undesirable by-products, the high-value application of lignin cannot be completely realized. The structural complexity and diversity of lignin resources make investigating potential applications of lignin both fascinating and challenging [59]. The development of lignin-based nanomaterials will extend the range of high-value lignin uses. The goal of creating lignin nanoparticles is to generate new desired characteristics that can only be acquired when a substance is structured on a nanoscale, similar to what other materials and biopolymers like cellulose and chitosan can do. Figure:5 shows three main lignin monolignols structures.

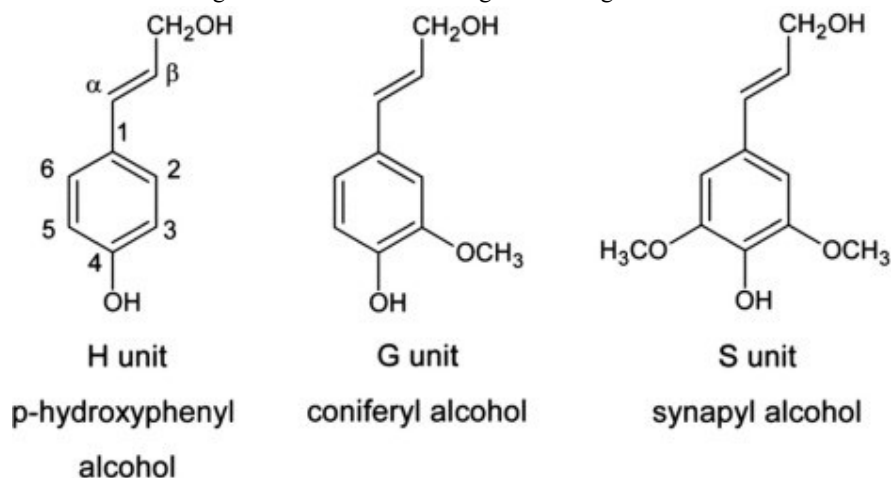


Figure:5 Three Main Lignin Monolignols Structure [60]. Reproduced from Antoine et al. [2014], with permission from Elsevier.

12.1.2 Lignin-based smart materials

Lignin polymers, oligomers, dimers/monomers, and dimers/monomers may be generated from plant biomass in a variety of ways and then transformed into intelligent material via a variety of methods. During the polymerization process, interconnections with aryl ether (β -O-4') account for more than half of the bonds formed, and they might result in low molecular weight phenolic compounds of lignin [61]. Several other linkages are far more difficult to break down, including resinol (β - β), phenylcoumaran (β -5'), biphenyl (5-5'), diphenyl ether (4-O-5'), and diphenylmethane (β -1). Intricate links exist between the chemical structure of lignin and the genesis and separation of plants; recent advancements in analytical technology have made researching chemical linkages more straightforward. The pulp and paper industries are the primary producers of technical lignin [62]. When it comes

to creating well-defined lignin-based polymers for a variety of applications ranging from biobased composites to gene delivery systems, different polymerization grafts, atomic transfer radical polymerization (ATRP), and ring-opening polymerization were regarded as the most successful methods of doing so. The ring-opening polymerization (ROP) method, in particular, was regarded as the most successful method of doing so. It is possible to attach a previously synthesized polymer chain to the lignin core and use it as the site of reaction to lignin in a "grafting to" process, which is described in a functional chain end group [63]. This approach has numerous advantages, including the ability to modify the length of the grafted chains before grafting and the ability to conduct a comprehensive characterization of the grafted chains before grafting, among others. Lignin recalcitrance, which is generated by pulping operations, is the most difficult barrier to overcome in the production of aromatic compounds [64]. Although it requires the use of expensive metal catalytic agents that are difficult to recover from heterogeneous reaction mixtures, catalytic fragmentation using so-called "line first" concepts has demonstrated significantly better results and aromatic chemical selectivity [65], compared to other methods.

Lignin-based smart materials: applications and materials chemistry

Smart lignin material may sense environmental stimuli and transform them, depending on physiochemical changes, into visible responses. A wide range of stimuli, including pH, temperature, mechanical and electrical energy are accessible [66].

Biosensing and Sensor Applications

Sensors are a form of self-integrated device capable of receiving specific inputs from their surroundings into output signals that can be readable. A biosensor is a means that biological species of interest can be identified even if it is surrounded by other species [67]. Lignin-based sensors have been very interested in their ability to detect and produce detectable signals from complex species combinations (Table 1) and Figure:6 shows lignin-based smart material.

Table 1 Smart Lignin-Based Sensing Materials

Ref.	Field of application	Type of lignin material	Type of sensor
[68]	Hg ²⁺ and Ni ²⁺ detection	lignin-silver nanoparticles (Ag LNPs)	chemical sensor
[69]	Formaldehyde detection	lignin nanoparticles	chemical sensor
[70]	Heavy metal ion detection	lignin-porphyrin polymer	chemical sensor
[71]	Organic imagery and labeling	lignin-rhodamine polymer	biosensor
[72]	Chromate ion detection	lignin-based polymeric composite	chemical sensor
[73]	Moisture detection	graphene oxide-lignin composite	humidity sensor
[74]	Pulse and muscle movement detection	polydimethylsiloxane-lignin composite	pressure sensor
[75]	Glucose detection	magnetite/lignin hybrid electrode	biocatalytic sensor
[76]	Glucose detection	silica/lignin hybrid electrode	biocatalytic sensor
[77]	Antibody detection (Ab)	lignin/peptide-based gold electrode	immunosensor
[78]	H ₂ O ₂ Detection and bioimaging of metal ions	lignin-derived graphene quantum dots (LGQDs)	chemical sensor
[79]	Fe ³⁺ Bioimaging and detection	Lignin-based carbon quantum dots (LCQDs)	chemical sensor
[80]	Release of drugs and bioimages	LCQDs	chemical sensor
[81]	Biological imaging and etiquette	LCQDs	biosensor
[82,83]	Heavy metal ion detection	LCQDs	biosensor



Figure:6 lignin-based smart material [84]. Reproduced from Wisnu et al. [2020], with permission from Elsevier.

Quantum dots of carbon and graphene based on lignin for sensing applications

Lignin-based carbon quantum dots (LCQDs) have developed as a unique form of material in a variety of applications, including metal ion sensors, bio-imaging, and biosensors, among others. Most LCQD sensors are used to quench or prevent LCQDs, but their low production costs and competitive use of non-food and relatively simple production processes when compared to carbon-quantum dots (CQDs) based on precursors such as citric acid, gelatin, and others are perhaps their most appealing characteristics [85].

Lignin as a Biosensor Precursor

Because of its inexpensive cost and high matrix compatibility, lignin was used to make more biosensor electrodes. Lignin-based biosensors are composites that include biomolecules such as enzymes or proteins. Biomolecules collected from biological (e.g., glucose) samples induce changes in system macroscopic characteristics such as pH, temperature, and electrical conductivity [86].

Lignin-based Nanomaterials and Composites for Sensing

In particular, the stiff polyaromatic structure of lignin, as well as the presence of a range of functional cationic chemicals, such as carboxylic acid and phenolic hydroxyl groups, is fascinating [87]. In this application, it was observed that the presence of sulfonic acids, kraft, and organosolv lignin had a more sensitive effect on the existence of lignosulfonate than the absence of these compounds. The uncontrolled nature of polycondensation reactions, which normally result in partially interconnected materials that are difficult to recycle, is one of the most significant disadvantages of using such materials as potential precursors in the production of selective membranes. One of the most significant disadvantages of using such materials as possible precursors in the production of selective membranes is the lack of control and reproducibility over the final morphological material. Figure:7 illustrates the production and uses of lignin-based nano-composites.

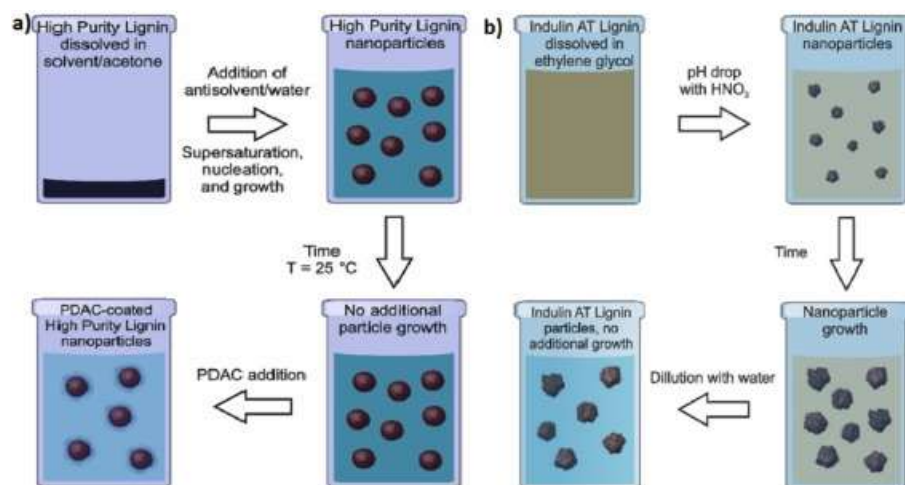


Figure:7 Production and Uses of Lignin-based Nano-Composites [88]. Reproduced from Parvathy et al. [2021], with permission from Elsevier.

Sensing applications employ lignin nanoparticles as a platform

Because of their inexpensive cost and functional characteristics, lignin nanoparticles (LNP) have been utilized to load and release active substances (antioxidant and UV- barrier properties). LNP are being used as sensors in addition to loading and unloading chemical payloads. The feasibility of using cellulolytic enzyme lignin (CEL) nanoparticles (CEL-NPs) as a formaldehyde sensor. The method is based on the phenomenon of aggregation-induced emissions [89], which results in the emission of CEL-NP fluorescence. Figure:8 shows lignin nanoparticles: a novel eco-friendly tool.

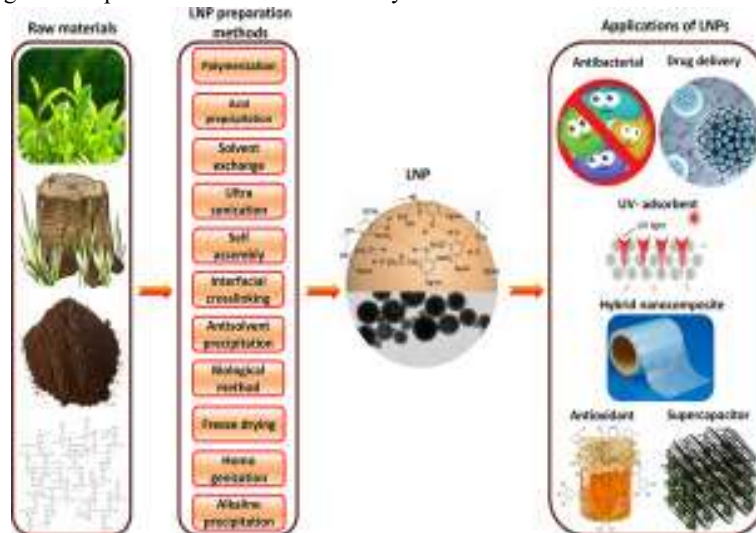


Figure:8 Lignin nanoparticles: A novel eco-friendly tool [90]. Reproduced from Prakram et al. [2020], with permission from Elsevier.

Biomedical Applications

Lignin-based intelligent materials have been mainly constructed on biological lignin-based polymers. The two most well-known and well-studied reactions in organic systems are temperature and pH, which means that grafting polymer is selected to respond. Lignins with a lower critical solution temperature (LCST) are those that have a structure that incorporates the belt-globe transition mechanism, which is the lowest boundary for mixing when using the belt-globe transition mechanism to mix. Because of mostly hydrogen bond interactions between polymers and water, polymer chains persist below the LCST in the form of random coils [91]. This results in a homogeneously mixed phase. Figure 9 illustrates the use of lignin in pharmaceutical and biological products.

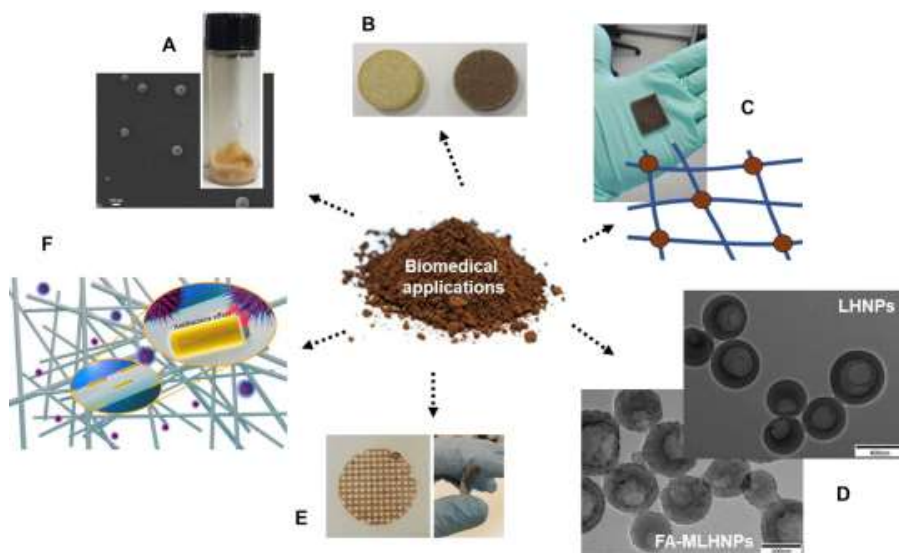


Figure:9 Lignin in Pharmaceutical and Biological Products [92]. Reproduced from Juan et al. [2020], with permission from Elsevier.

Nano/microparticles and capsules made of lignin

Advanced nanomaterials, particularly those capable of encapsulating and releasing molecules in response to specific stimuli, have lately piqued the interest of researchers in a variety of fields, including medicine. It has been decided that stimulating polymers should be the subject of discussion because of their capacity to carry chemicals of importance to specific places. Recently, lignin has been established as a feasible option for load release applications because of its low toxicity, high biodegradability, high stability, and pH-dependent solubility, among other characteristics [93].

Smart hydrogels based on lignin

Its porous texture is similar to that of the extracellular biological matrix, and its capacity to expand in response to stimuli is important for the administration of medicines. The two most common impulses used in biomaterial and biomedical applications were lignin-based hydrogels as intelligent biomaterials that respond to pH and temperature, and lignin-based hydrogels as intelligent biomaterials that respond to pH and temperature. Using thermal lignin-based hydrogels, it is possible to achieve phase transitions at temperatures close to body temperature by grafting temperature-sensitive monomers to the core of the lignin [94].

Lignin-based smart materials for biological applications face technical hurdles

While the results of the foregoing research indicate that lignin may be utilized in the creation of biological materials, there are still several issues to be resolved. Alternative lignins, such as cellulolytic enzyme lignin (CEL), will help to relieve the issue, but they will not eliminate the problem. The purity of the original compounds must be improved, and the reactivity of the compounds must be understood, regulate the cytotoxicity of these lignin-based compounds. It is also possible to make improvements to the method for manufacturing lignin nanoparticles (LNPs) [95]. To begin dealing with this problem, researchers have suggested using ethanol instead of other solvents. Ethyl lactate, for example, might be made from biomass-derived solvents like ethanol in the future. Lignin nanoparticles biodegradability is an important issue that is often disregarded. The biodegradability of these compounds is poorly understood, although many studies focus primarily on their cytotoxicity and biocompatibility. When it comes to smart materials, although enzymes are capable of degrading lignin to a certain extent, this can present issues with degradability. There are many different examples, but materials constructed of cross-linked lignin are expected to deteriorate more slowly than those manufactured from other materials since they don't have as much protection against degradation from phenolic hydroxyl groups. There is therefore a need for more research into lignin-based smart materials' biodegradability, particularly about their breakdown products.

Elastomeric and thermoplastic elastomer materials based on lignin

The development of elastomeric and thermoplastic polymers based on lignin in recent years has resulted in the development of adjustable form memory properties. During a phase transition or conformation shift, one of the two phases acts as a "switch," allowing the material to "remember" its previous shape while the other remains static. The glass transition between grafted polymers with lignin, the reversible dissociation between the auto-complementary non-covalent bond (e.g., hydrogen bonding), and the regulation of cross-linking density were all used to program the temperature sensitivity of most of these lignin-based compounds [96].

When combined with stimuli-responsive behavior, lignin-based thermoplastic elastomers (Lig-TPEs) exhibit shape memory behavior, as well as thermoplastic and elastomeric qualities. Lignin crosslinking with acrylonitrile butadiene rubber (NBR) via a thermal compounding technique, produces Lig-TPEs, which are made from ABL (acrylonitrile–butadiene–lignin) composites with high lignin content. Chemical cross-links in the inherent structure of NBR and the intrinsic networked structures of lignin, which complimented physical cross-links created by hydrogen bonds within lignin and nitrile rubber molecules, resulted in good shape memory behavior in the ABL materials. Additionally, the authors found that silver (Ag) nanoparticles deposited on the surface of an ABL specimen served as a programmable and switchable conducting material. After the external force was removed, the shape-programmed sample returned to its original shape and resistance, indicating a reversible disruption in particle percolation. Developing new motion sensors like human motion tracking sensors could benefit from these novel shape-programmable conductive materials, which can sense resistance changes caused by applied stress. Importantly, the final products still showed good shape memory qualities, indicating that this method might be used to better adjust the thermomechanical properties of Lig-TPEs and make them more useful in a variety of contexts. Shape-memory Lig-TPEs combine the features of thermoplastic and elastomeric materials with the response to stimuli. In a thermal compounding technique, a lignin-rich NBR is crosslinked with lignin to form Lig-TPEs using shape memory. Chemical cross-links in the inherent structure of NBR and lignin's intrinsic networked structures in ABL materials with good shape memory behavior complimented physical cross-links created by hydrogen bonds inside lignin and nitrile rubber molecules. Silver nanoparticles placed on the surface of an ABL specimen were also identified by the scientists as a programmable and switchable conducting material. To show that particle percolation might be disturbed reversibly, researchers applied an external force to the shape-programmed sample and then withdrew it. Shape-programmable conductive materials, such as human motion tracking sensors, can detect resistance changes caused by an applied stress and could aid in the creation of new motion sensors. Because the Lig-TPEs' shape memory was unaffected by the oxidation process, this method could be useful for fine-tuning their thermomechanical properties and making them more adaptable.

12.2.1. Microorganisms during composting

Composter bacteria break down organic matter, producing CO₂, H₂, and humus, an organic end product with good stability. Depending on the conditions, the composting process can take anywhere from a few days to several months [97]. Upon establishing proper environmental conditions for composting, the procedure is divided into three stages: a mesophilic (moderate temperature) phase, a thermophilic (high temperature) phase, and maturation and cooling phase. At each stage of the composting process, a different microbial community takes control. As a result of the heat they generate, the temperature of the compost soon increases to dangerous levels. When exposed to high temperatures, the structural components of a plant, such as cellulose and hemicellulose (which are the most prevalent in thermophilic plants), break down. Mesophilic bacteria take over for the final step of "curing" or maturation of the organic matter that has remained to break down after the high-energy molecules have exhausted their energy reserves. The temperature of the compost will soon begin to drop [98].

Actinomycetes

Mushroom-like Actinomycetes, which are filamentous bacteria, are to blame for soil's distinctive earthy smell [99]. Instead of nuclei, they produce multicellular filaments that resemble fungus. Composter microorganisms are essential in the process of composting since it involves the breakdown of complex organic materials such as cellulose, lignin, chitin, and proteins. Enzymes can chemically break down tough materials such as woody stems, bark, and paper [100]. Humus is formed by the most resistant chemicals remaining after the thermophilic and

cooling curing phases. Compost-stretching grey spider webs are resembling the long, branching filaments produced by Actinomycetes.

12.2.2 Compost environment: Bacteria, Fungi, and Enzymes

Composting is a process in which microorganisms break down organic waste, releasing CO₂, biomass, heat, and a humus-like end product in the process. The vast majority of organic substrates, bulking agents, and composting additives are derived from plants in some form. Carbohydrates (for example, cellulose), proteins, lipids, and lignin are the primary constituents of organic matter, according to [101]. When it comes to the capacity of microbes to absorb organic molecules, the enzymes they create for the breakdown of the substrates play a crucial role. As the intricacy of the substrate rises, so does the size and complexity of the enzyme system required to break it down. Nitrogen, Phosphorus, and Potassium-fixing microorganisms, for example, require a carbon source as well as certain trace elements to thrive. Microorganisms obtain the majority of their energy from carbon sources, with just a small proportion of carbon found within their cells [102]. Some of the energy produced is needed for microbial metabolism, while the remainder is converted to heat. Figure: 10 depicts the breakdown of lignin by enzymes.

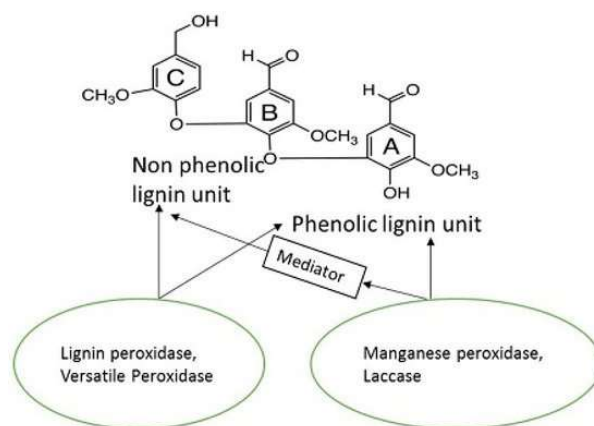


Figure:10 Enzymatic Degradation of Lignin [103]. Reproduced from Datta et al. [2017] under the terms of the Creative Commons Attribution License (CC BY 4.0). <http://creativecommons.org/licenses/by/4.0/>.

Bacteria

Bacteria, due to their tiny size, have a high surface-to-volume ratio, which allows them to transport soluble substrates into the cell in a short period. As a result, bacteria are typically found in considerably greater numbers than bigger fungal species in the environment [104]. For example, *Bacillus* spp. may form highly heat, radiation, and chemical disinfection resistant, thick-walled endospores (Haug, 1993). Bacteria play a big role in compost breakdown and heat output. They use a wide range of enzymes to chemically break down a wide range of organic components since they are the most nutrient-diverse compost organisms [105]. Rod-shaped bacilli, sphere cocci, and spiral-shaped spirilla are frequent structural types in bacteria and other microbes. Many of them can move wherever they desire because they are mobile. The soil contains fungus, which accounts for the vast majority of these organisms. All over the place and ready to play whenever the situation necessitates, these creatures can be counted on [106]. Even at extremely high temperatures, compost contains bacteria of the genus *Thermus*. Figure: 11 shows bacterial enzymes that degrade lignin.

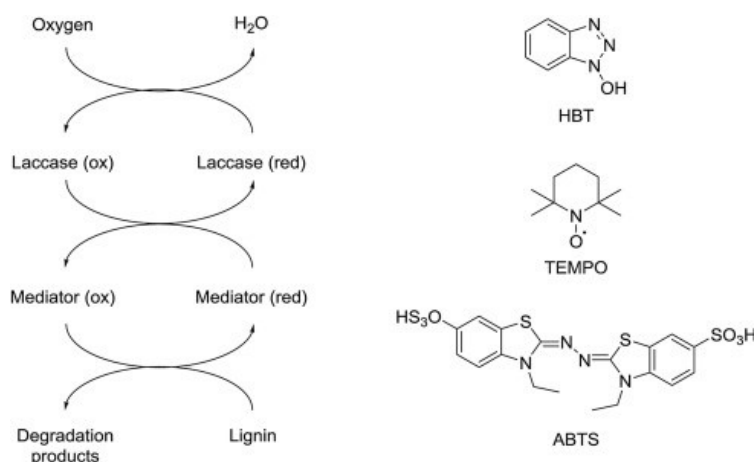


Figure: 11 Bacterial enzymes that degrade lignin [107]. **Reproduced from Gonzalo et al. [2016] under the terms of the Creative Commons Attribution License (CC BY 4.0).**
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Fungi

When it comes to fungus development, temperature is one of the most crucial elements to consider. Carbon, nitrogen, and pH availability are all important factors to consider [108]. Some fungal products, such as wood-rotting fungus, may, on the other hand, thrive at lower levels of nitrogen, while others, such as mushrooms, may require very high levels of nitrogen. The breakdown of lignin is generally hampered by a deficiency in necessary nitrogen. Molds and yeasts are members of the fungus family, and they play an important part in the decomposition of compost and the degradation of soil by degrading different plant polymers. Molds break down difficult materials in the compost, but after the cellulose in the material has been entirely digested, bacteria can take over and continue the breakdown process [109]. They may break down organic wastes that are too dry, acidic, or nitrogen-deficient for bacteria to break down due to the development of numerous cells and filaments. As saprophytes, the majority of fungus derive their energy from decomposing organic substances found in disintegrating sources of living matter (fungi that feed on dead or dying materials). Fungi reproduce at a high rate during the mesophilic and thermophilic phases of the composting process, respectively. When the temperature in the compost pile is high, the exterior layer of the compost pile transforms into a fungal refuge [110].

12.3 Steps of lignin degradation

Microorganism involved in lignin degradation

- The biological breakdown of lignin is one of the most crucial phases in the carbon and oxygen biosphere cycle [111]. **Figure:12** describes the microbiology of lignin degradation and the purification of useful compounds are little known, although the majority of the plant-biotype lignin biosynthesized is mineralized and returned to the environment as carbon dioxide (CO₂).

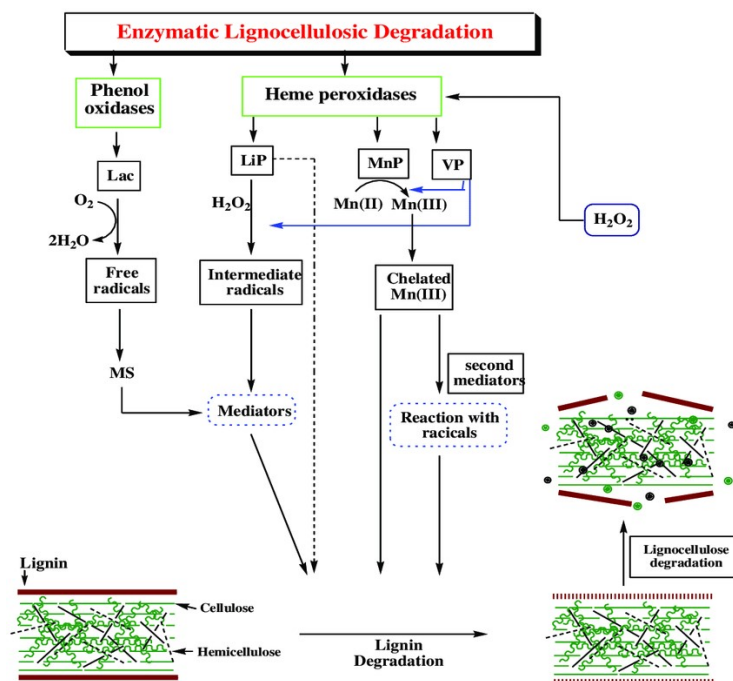


Figure: 12 Processes for Degrading Lignin and Purifying Valued Products [112]. Reproduced from Rehman et al. [2019] under the terms of the Creative Commons Attribution License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>.

- A wide range of fungus and bacteria is included in the list of micro-organisms currently breaking down the lignin.
- In addition, degrade of lignin is known to micro-organisms such as cyanobacteria and actinomycetes, although depending on the microbe, the degree of degradation is different.
- Because of the breakdown and processing of lignocellulose wastes, the metabolism of the indigenous microorganisms is responsible.
- Diverse microbes predominate and have different functions at various phases of the organic matter disintegration process.

12.3.1 Depolymerization

The first phase in lignin degradation is the depolymerization of aryl and biaryl composites such -aryl ether. This is a non-specific process conducted outside of the cell by a range of bacterial and fungal enzymes [113]. The breakdown of the β -O-4 ether link, representing approximately half or more of the total lignin connections, leads to depolymerization. In this phase the lignin polymer length is shortened, leading to dimeric or oligomeric units that may then be broken down into smaller molecules. In many bacteria, different lignin-degrading enzymes are present, such as peroxidases and phenol oxidases [114]. These enzymes target lignin randomly and then turn the phenolic group into free radicals which depolymerize lignin as shown in figure:13.

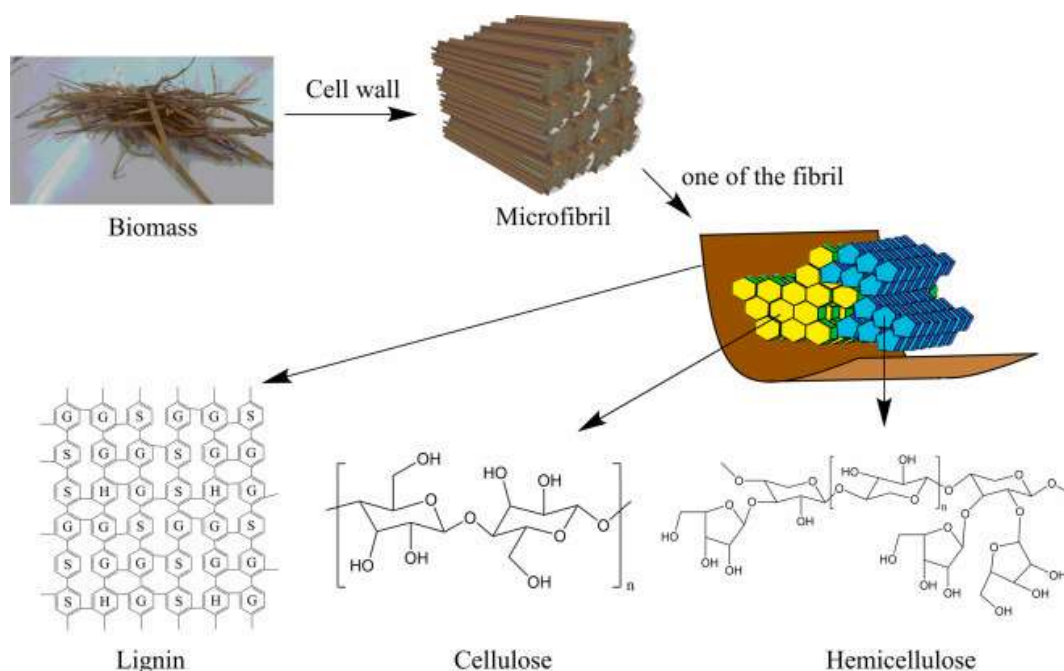


Figure: 13 Lignin Depolymerization [115]. Reproduced from Chonlong et al. [2019], with permission from Elsevier.

Lignin Depolymerization Catalyzed by a Base

It was a straightforward process to extract phenols and phenol derivatives from lignin utilizing a high-temperature water solution for sodium hydroxide. Gas chromatographic and mass spectrometric (GC-MS) detected 26 compounds after the procedure, most of which were guaiacol, catechol, and vanillin [116]. However, this investigation showed that the addition of boric acid to further treatment of the base catalytic products improved the production of the phenols. The primary products were syringol, hydroxy acetophenone, and catechol. In the treatment of kraft lignin, Beauchet employed similar methods [117].

All methods of degradation aim to simplify the natural lignin molecule, reduce its molecular weight, and increase the chemical reactivity of the degradation products as a side effect. Liquid oil, oligomers (also known as tar fraction), and higher polymeric lignin species (also known as char) are the three fractions created. Formic acid, acetic acid, methanol, and carbon dioxide are all byproducts. When weak phenolic connections break off during the lignin molecule's cleavage, radical production is initiated. Once radical moieties recombine, additional types of carbon-carbon bonds may form, leading to oligomers and more complex condensed structures known as char. By breaking it down into its mono- and di-phenolic components, as well as its carbon dioxide monomer and dimer, lignin can be converted into an array of degradation products that include aliphatic alcohols (methanol, formic acid, and acetic acid).

Breaking of bonds and creation of products is mediated by the following mechanisms: Alkaline water dissolves lignin, while alkaline or earth alkaline metal ions polarize the ether bond. It is known that under reaction conditions, bond breaking occurs most frequently at bonds such as those between the aryl glyceryl and the aryl ether (O4) and the diaryl ether (O5), which are among the weakest in lignin. The ideal technique would provide high yields in monomers while also cleaving virtually all of the lignin molecule's aryl-ether linkages. Depending on the method used for separation, these chemicals build up in the liquid product. The oligomeric polyphenols, highly condensed structures, and unreacted lignin are all found in the base-catalyzed depolymerization (BCD)-oligomer fraction. The reaction produces short-chain acids, which neutralize the base and slow down hydrolysis. This can cause phenolates to precipitate and clog up the reactor, or worse, the pH can drop so low that the reactor becomes blocked.

Depolymerization of Lignin Catalyzed by Acid

Lignin can be used for treatment in the 1940s with acid. By processing maple wood meal with different combinations of acids and alcohol, including HCl/ethanol and formal acid/ethylene glycol, Hewson and Hibbert separated lignin into water-soluble and water-insoluble materials, respectively. An acid-catalyzed technique has been studied recently at a higher temperature range to depolymerize lignin. In combination with metals catalyst enhancers, other experiments employed a mixture of acid-ethanol solution. An acid-catalyzed method was recently explored across a wider temperature range to depolymerize lignin. A different ratio of formic acid to ethanol solution was used in the reaction with wheat straw lignin. Methoxyphenol, catechol, and phenol were the primary ingredients when the reaction temperature was elevated. Other investigations made use of metallic catalyst enhancers in addition to acid/ethanol solution systems. The acid-catalyzed depolymerization, which also attacked lignin's β -O-4 link, finished the reaction. Formic acid or other acids were utilized as hydrogen sources in the hydrolysis to create H_3O^+ on the β -O-4 bond or cationic aromatic rings, respectively. When employed in conjunction with a primary catalyst, co-catalysts can improve selectivity. According to the research, neither palladium nor platinum decreased the activation energy required for depolymerization. A harsh reaction environment is required for acid-catalyzed depolymerization [118].

Lignin Depolymerization Catalyzed by Metals

The lignin depolymerization selectivity was improved with metallic catalysts. In the case of NiCl_2 or FeCl_3 in the procedure, Hepditch and Thring observed cell-generated lignin. A Si-Al catalyst was used initially in an H_2O /butanol medium to treat the kraft lignin before reacting it with a $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-FeO}_x$ catalyst to maximize phenol recovery. In the treatment of organosolv switchgrass lignin, a Pt/C catalyst was utilized with formic acid and ethanol to improve the production of the low-molecular-weight fraction. In the presence of metallic enhancers, the yield of guaiacol derivatives significantly increased. The formic acid-catalyzed system is once again being optimized by the use of phosphoric acid. Varying pretreatment procedures for lignin resulted in slightly different guaiacol, pyrocatechol, and resorcinol yields. A lower temperature depolymerization method than simple acid-catalyzed depolymerization was used, however, no difference in activation energy was found. The mechanism and function of metallic enhancers in acid-catalyzed lignin depolymerization must be clarified in future research. Cracking facilitated by base- or acid-catalyzed reactions were typically carried out at extremely high temperatures. However, to carry out lignin depolymerization under mild conditions, attempts were made to reduce the reaction activation energy. Depolymerization of lignosulfonate by nickel compound accelerated depolymerization into guaiacols. Propenylsyringol was found to be selectively produced by nickel catalyst treatment of birch wood lignin, with conversion rates above 50%. In the treatment of lignin isolated from organosolv olive tree pruning lignin, nickel, palladium, platinum, and ruthenium nanoparticles are supported by mesoporous Al-SBA-15 and microwaves help. The depolymerization activation energy was greatly reduced with the use of metallic catalysts, resulting in a moderate reaction condition. In the presence of hydrogen sources like ethanol or water, metallic catalysis continued to target lignin's C-O and C-C cleavages. Solid catalysts such as nickel or other metals supplied chemical reaction sites on the exterior surface where the depolymerization process took place [119].

Lignin Depolymerization by Ionic Liquids-Assisted

Using ionic liquid for lignin and cellulose extraction from raw lignocellulosic materials was discovered. Ionic liquid combined with ionic salt showed excellent selectivity for both lignin and the model chemicals. The researchers found cleavages in the alkyl-aryl ether bond. Lignin in different ionic liquids, a series of experiments were carried out in which 1-H-3-methylimidazolium chloride depolymerized both guaiacylglycerol—guaiacyl ether and veratrylglycerol—guaiacyl ether model compounds to generate the chemical molecule known as Guaiacol. Model compounds of acylglycerol—guaiacyl ether were depolymerized in the presence of 1-H-3-methylimidazolium chloride methylsulfate, and guanyl was detected. Some ionic liquids have been proven to be suitable solvents for the dissolving of lignin, according to recent research. In the past, hydrogen sources were thought to be generated by a catalyst found in ionic liquids like Brønsted acid. Although expensive, the ionic liquids could only be used on small amounts of lignin depolymerization due to their high cost. Due to the high cost of ionic liquid, recycling is essential. Ionic liquid and aromatic moieties interact in an incompatible way, making it difficult to separate the liquid from the lignin-derived compounds. Lignin depolymerization may have a restricted role in the usage of ionic liquid [120].

12.3.2 Solubilization and Mineralization in Lignin by White Rot Fungi

Different microorganisms collect and perform several conversions using different in vivo enzymes from the smaller molecules created during depolymerization. Most lignin molecular linkages have their metabolic processes for cleaving them. The mineralization and solubilization of oligomers and monomers that can be utilized by organisms involve the formation of CO₂ and other essential molecules [121].

When the white-rot fungus breaks down lignin, water-soluble chemicals and CO₂ are likely generated as well. There is more evidence to show that the two develop differently due to differences in metabolism. Soluble chemicals are used to make carbon dioxide, and when those chemical emissions are reduced, it should cause the soluble compounds to accumulate. Enzyme feedback inhibition, for example, can prevent or not further solubilization. Solubilization conditions that decrease CO₂ production also slow the production of other greenhouse gases, albeit more slowly over time. There is some evidence to suggest the participation of these enzymes when comparing their effects on enzyme activity with the degradation process itself. LiP and MnP synthesis in *Phanerochaete chrysosporium* are suppressed by dietary nitrogen, which also prevents the formation of the chemicals responsible for lignin breakdown. When manganese (Mn²⁺) is present, the activity of MnP is higher than that of LiP. Reduces the rate of degradation of lignin, which is by LiP's function as a process rate limiter. However, it is not known if the LiP, MnP, or laccase function during the first attack on lignin or during subsequent degradation phases. Depending on the species, degradation may be more effective at a certain pH. Degradation mechanisms used by various species of mushrooms may differ, or environmental factors may affect fungal development, as seen by these differences. The effects of a new composition can be mitigated by changing the medium regularly. Although fungal growth may be quantified quantitatively, this does not allow for differences in fungus development to be corrected.

12.4 Mechanisms of microbial degradation of lignin

The microbial breakdown of lignin, resulting in various processes, may require different types of enzymes. In in vitro depolymerization of bigger lignin molecules, Laccases and lignin peroxidases are two important enzymes [122]. In bacteria, the solubility of lignin to even smaller usable molecules is engaged through various processes. Figure:14 shows microbial degradation of lignin.

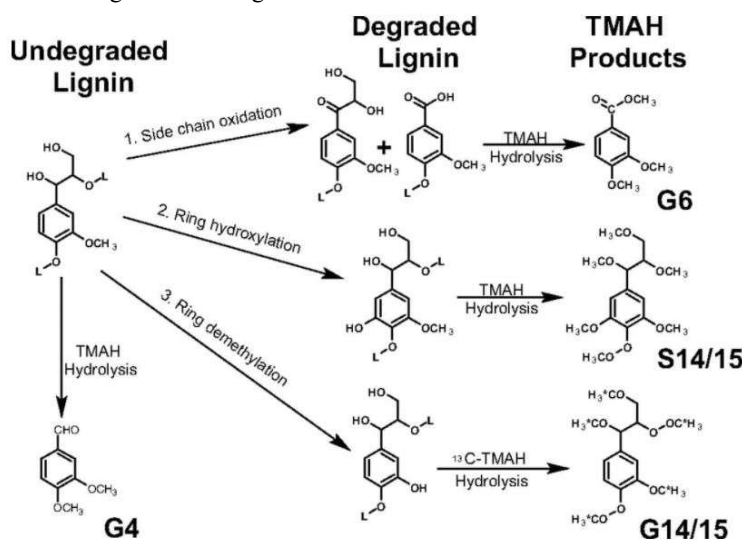


Figure:14 Microbial degradation of lignin [123]. Reproduced from Scott et al. [2008] under the terms of the Creative Commons Attribution License (CC BY 4.0). <http://creativecommons.org/licenses/by/4.0/>.

12.4.1 In vitro degradation

12.4.1.1. Biodegradation of lignin with laccase

Lignin biodegradation in the laccase enzyme system is an oxidative process involving radical reactions that are aided by the mediator and enzyme catalyst. This process destroys both phenolic and non-phenolic lignin aromatic

structures, as well as lignin aromatic structures [124]. First of all, the phenolic movement is attacked and non-phenolic benzyl structures are destroyed. The initial assault releases phenol residues with oxidized side chains. This allows the enzyme to enter and act as natural mediators in the bulk lignin polymer, which enables non-phenolic portions to be oxidized. The C-C division of non-phenolic sites in lignin results in lignin fragments being solubilized by the development of lignin-mediation hydrophilic complexes. This is responsible for the three mechanisms of oxidation, electron transfer, radical transfer of hydrogen atom, or ionic mechanism [125].

12.4.1.2. Biodegradation of lignin-by-lignin peroxidase

The catalytic cycle for lignin peroxidase-like manganese peroxidase starts with the synthesis of an iron-peroxide complex following H_2O_2 . The complicated cleavage causes Mn^{2+} to Mn^{3+} to oxidize. Mn^{3+} chelates with carboxylic acids cause 1-electron oxidation of various substrates (e.g., oxalate, malonate, malate). The elimination of hydrogen products from phenolic and amino-aromatic compounds results in the formation of phenoxyl and amino radicals [126]. These radicals are the sources of peroxide produced in the absence of an external H_2O_2 via autocatalytic processes in the absence of an external H_2O_2 source. The initial one-electron oxidation of the substratum with Mn^{3+} generated enzymes result in an intermediate phenoxyl radical reaction, which is the primary mechanism for the breakdown of lignin and is described in detail below. This radical is further oxidized by Mn^{3+} , resulting in the formation of a carbon cation. The ketone dimer is formed as a result of the proton loss [127].

12.4.2 In vivo degradation

12.4.2.1. β -O-4 ether degradation

The breaking of the β -O-4 ether bond is a key step in the depolymerization of lignin since it accounts for around half of all lignin connections. The first enzyme in the course of the breakdown of β -O-4 is the C-dehydrogenase, LigD. The β -etherase LigE or LigF cleaves the etheric bond with β -O-4 and produces vanillin and glutathionyl- β -hydroxypropiovanillone (GS-HPV) as intermediary after the hydroxy group oxidizes in C position LigD. Finally, the GS-HPV is oxidized by LigG, glutathione S-transferase. Glutathione is clamped and vanillin may be further oxidized by the β -hydroxypropiovanillone that remains [128].

12.4.2.2. Bi-phenyl degradation pathway

The biphenyl connection is 10% of all connections in softwood lignin. When 5, 5' dehydrodivanillate (DDVA) is inserted in the body LigX, a DDVA-o-demethylase, demethylates one of the methoxy groups and changes them into hydroxyl. LigZ is a product of the OH-DDVA dioxygenase substrate for oxidative meta-cleavage. Hydrolyzing further the LigZ product, LigY hydrolyses OH-DDVA meta-cleavage molecule. Finally, LigY cleavage generated 4-carboxy-2-hydroxypentadienoic acid, the latter metabolized in vanillate, one of its major components [129].

12.5 Fungal degradation of lignin: Mechanism of lignin biodegradation

The litter degrading fungus *Agaricus bisporus* produces laccases and manganese peroxidases and is a characteristic blue red fungus because it degrades cellulose and lignin [130]. Figure: 15 shows fungal degradations of lignin.

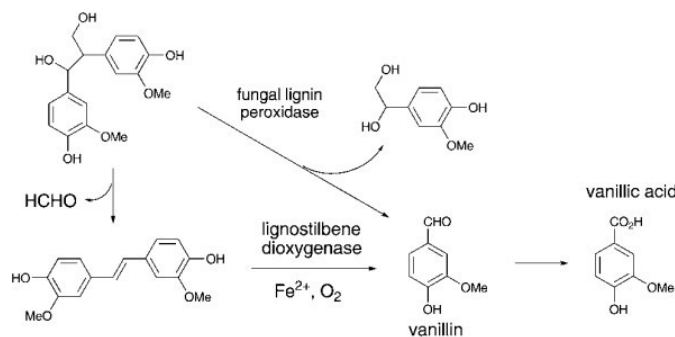


Figure: 15 Fungal degradations of lignin [131]. Reproduced from Bugg et al. [2011], with permission from the Royal Society of Chemistry.

12.6 Bacterial degradation of lignin: Mechanism of lignin biodegradation

- Bacterial wood deterioration is occurring slowly, and bacteria often infiltrate wood cells in surfaces with high moisture content at the same time as fungi because of the lack of penetration capacity [132]. Figure: 16 shows bacterial degradations of lignin.

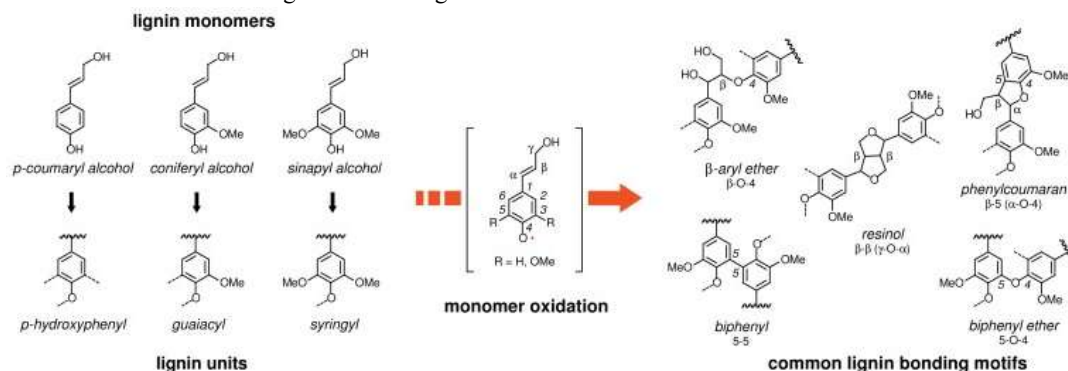


Figure: 16 Bacterial degradations of lignin [133]. Reproduced from Margaret et al. [2014], with permission from Elsevier.

- The bacteria are significantly degraded by plant fiber cell walls, and by bacteria that occur in the area of bacteria such as *Mycobacterium tuberculosis*, *Mycobacterium avium*, *Pseudomonas syringae*.

12.7 Lignin-degrading Actinomycetes

- The actinomycetes were long assumed to have a role in the destruction of lignocelluloses, but the scale and strategies used are less well understood [134].

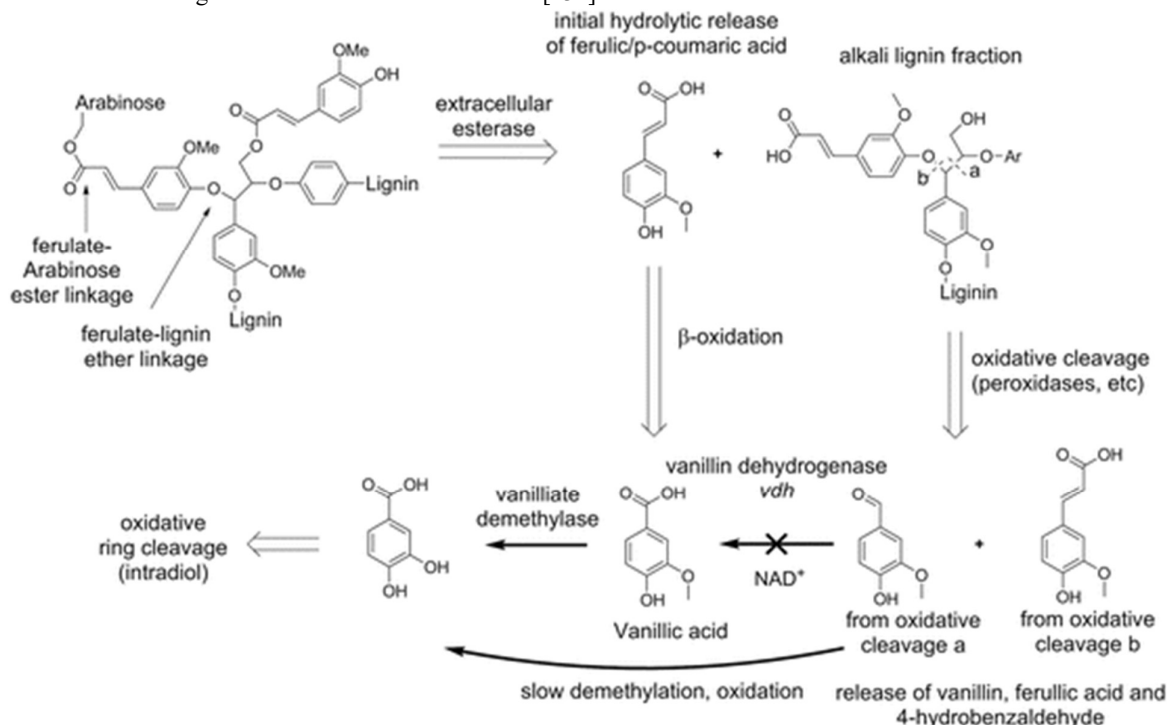


Figure: 17 Biodegradation of Lignin using Fungi, Bacteria, and Enzymes to Produce Chemicals and Improve Process [135]. Reproduced from Lionel et al. [2016], with permission from the Royal Society of Chemistry

- This study discovered that lignin-degrading organisms may be protected from a variety of environmental factors such as soil and extreme temperatures.
- It also discovered that the activity of peroxidase and polyphenol oxidase was increased in both thermophilic and mesophilic *Streptomyces* isolates. Lignin biodegradation using fungus, bacteria, and enzymes is depicted in figure:17 to generate chemicals and boost process efficiency.

12.8 Lignin-degrading enzymes: Lignin peroxidase, Manganese peroxidase, Laccase, Celllobiose: quinone oxidoreductase (CBQase), Other enzymes, Enzyme access to lignin

- The enzymes that break them down need to be oxidative since lignin has no hydrolyzable linkages [136].
- Lignin is a stereo-irregular molecule, meaning it is more unspecifically attacked by enzymes than other natural polymers.
- Lignin division is mediated principally by three enzymes: peroxidase of manganese (MnP), peroxidase of lignine (LiP), and laccases. On the other hand, several other enzymes are involved in the degradation of lignin [137].

12.8.1 Manganese peroxidases (MnP)

- The lignin-reducing capacity for Mn^{2+} is an extracellular heme peroxidase that requires Mn^{2+} as a decreasing substrate [138].
- The majority of wood-decaying fungus and many litter-decomposing fungi produce manganese peroxidase, which is one of the most frequent lignin-degrading peroxidases.
- These enzymes are glycosylated proteins in their structure including iron protoporphyrin IX (heme).
- Towards Mn^{2+} , the enzyme is oxidized into Mn^{3+} and phenoxyl radicals are then oxidized by the enzyme. Mn^{3+} is a very reactive metal that makes complicated organic acids such as oxalate and malate chelating.
- Towards the oxidation of the phenolic substrates, the MnP-Mn complex exhibits a reduced redox potential as compared to the lignin peroxidase.
- The produced phenoxyl radicals can continue to react and release CO_2 . The generation of phenoxyl radicals may then split C-C or alkyl-phenyl bond, leading to depolymerization and smaller intermediates such quinones and quinines of hydroxylating.

1.1.

12.8.2 Laccases

- Laccases of the N-glycosylated extracellular blue oxidizes are lignin-degrading enzymes with four copper atoms spread among binding sites in the active place [139].
- Plant laccases catalyze the oxidation of several aromatic hydrogen donors, followed by oxygen decreases to water, and also decarboxylate to attack phenolic acid methoxy lateral chains or groups.
- Several fungal laccases, such as 1-(3,4)-dimethoxyphenyl)-2, (2-methoxyphenyl)-propane-1,3-diol (I), and phenolic lignin compounds such as phenol Red have been studied for the oxidation of the molecules in the presence of redox mediators.
- The refractory chemicals many are oxidized by laccases, including chlorophenols, polycyclic, aromatic hydrocarbons (PAHs), structures linked to the lignins, and organophosphorus compounds. Figure:18 shows a comparison of lignin degradation by laccase and peroxidases manganese peroxidase (MnP), versatile peroxidase (VP), lignin peroxidase (LiP).

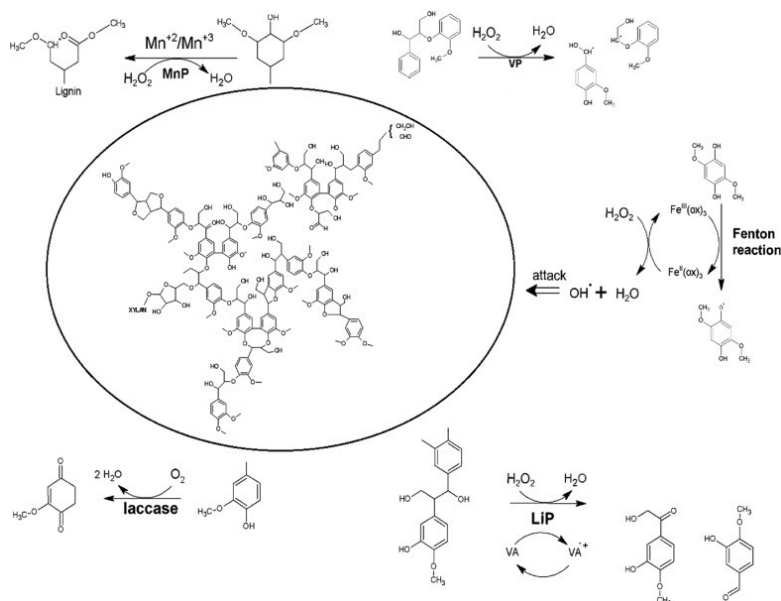


Figure:18 Comparison of lignin degradation by laccase and peroxidases manganese peroxidase (MnP), versatile peroxidase (VP), lignin peroxidase (LiP) [140]. Reproduced from Adarsh et al. [2020], with permission from Elsevier.

12.9 Lignin degradation by Pseudomonas

- Pseudomonas metabolizes different lipids contained in the biomass of lignocellulose in low molecular weight [141]. Figure: 19 shows pseudomonas degradation of lignin.
- It creates the benzaldehyde lyase, which blends 1,2-diarylethene and benzoin with the acyloin connection.
- The enzyme is very selective, cleaving anison exclusively and benzoin.
- Even protocatechuate-4,5-Dioxygenase can create some Pseudomonas species which catalyzes protocatechuate and 3-methyl-gallic acid ring-fission.

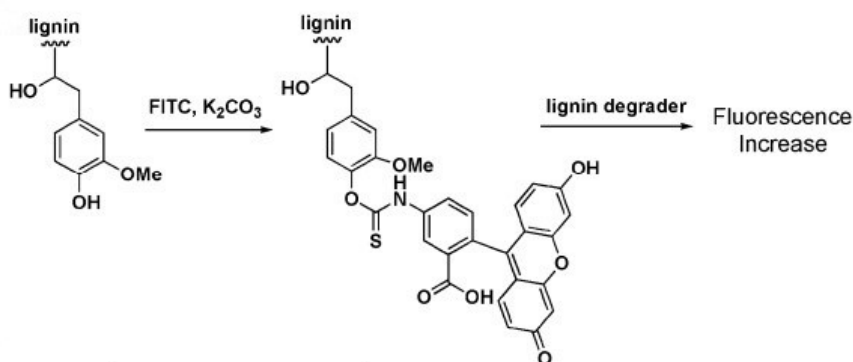


Figure: 19 Pseudomonas degradation of lignin [142]. Reproduced from Ahmad et al. [2010], with permission from the Royal Society of Chemistry.

12.10 Genomes Analysis and Evolution

Genomic, it appears from white-red fungi that brown rot developed. Brown rot usually lacks a carbohydrate-binding module 1 (CBM1) domain for ligninolytic class II peroxidase and cellobiohydrolase-producing genes throughout time [143]. In addition, GH74 xyloglucanase and GH10 endo-xylanase, and GH79 β -glucuronidase are more common in white red fungi, compared to brown-red basidiomycetes, and CE15 glucuronoyl methylesterase is common. The only brown-red fungus that has been shown to support Fenton's chemistry is quinone reductase activity, but its gene homologs were detected in white-red fungi. *Fistulina hepatica* (brown rot)

still has genes associated with a typically plesiomorphic cellulose breakdown and is shared with white red predecessors [144]. Some Coniophora and Serpula species can digest cellulose similarly to white reddish species. The genes that code DyP and HTP are less than white red fungi, although there are several general peroxidase genes in brown-red genomes that have low redox potential and cannot degrade lignin [145].

Fungal growth is thought to coincide with rapid fungal development and diversity times in particular with biostratigraphic levels. Using evolutionary genomics in conjunction with evolutionary and ecological engineering and the assessment of fossils, researchers determined the oldest fungal ancestor — a shape similar to a cyrtid [146]. Data obtained utilizing fossilized fungus from the molecular clock show that terrestrial fungi differ from Chytridiomycota. Bayesian relaxed molecular clock analysis, which indicated the mean age of Agaricomycetes, to locate the genesis of lignin degradation in the context of geological time [147]. Figure:20 shows a comparative genome analysis of lignin biosynthesis gene families.

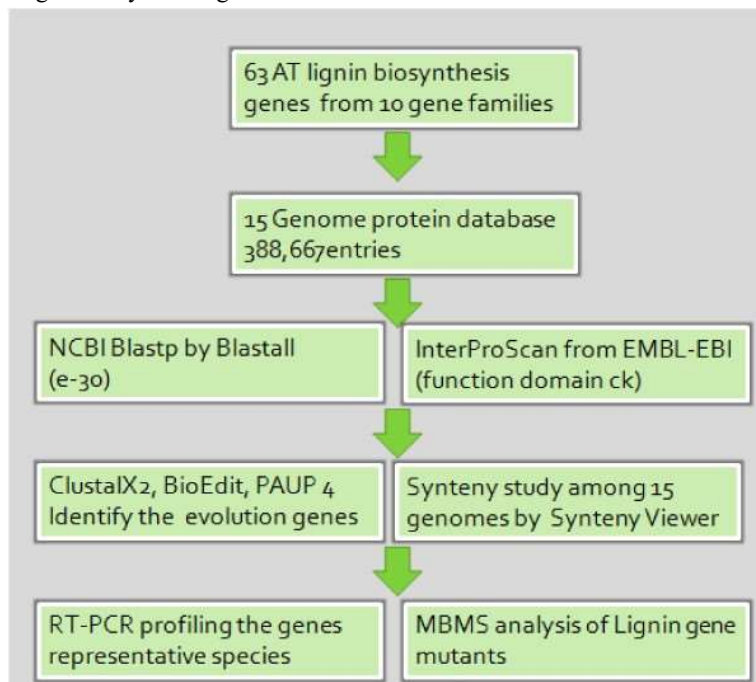


Figure:20 Comparative genome analysis of lignin biosynthesis gene families [148]. Reproduced from Zhangyou et al. [2009] under the terms of the Creative Commons Attribution License (CC BY 4.0). <http://creativecommons.org/licenses/by/4.0/>.

The Ascomycota and Basidiomycota saprophytic were developed in line with the initial emergence of the primitive earth plants. The higher Ascomycetes, the Pezizomycotina, are expected to diversify, corresponding with vascular plant diversification, as evidenced by the fossil record. Further analysis of molecular clocks showed that Pezizomycotina and Agaricomycetes are 400 and 300 million years old.

12.12 Conclusions

Multinational corporations' social and environmental sustainability strategies include a sustainable supply chain as a key objective. The tiered-chain hypothesis states that decisions made at the top of the chain can spread to other organizations, promoting adoption and enhancing sustainability on a larger scale in the social, environmental, and economic spheres. This paper concludes that green logistic management is important to lignin and makes our green environment eco-friendly. This chapter concludes that lignin is the second most abundant polymer due to the biodegradability of lignin-based materials, which are most relevant today. This chapter covers a brief introduction to lignin, utilization of lignin, biological function, ecological function, economic function, economic significance, biosynthesis, detection, a small literature review from 1995 to 2021, problem statement and synthesis of lignin nanoparticles, and then the structure of lignin as because it makes a different covalent bond with different polymers. Moreover, this chapter covers lignin-based smart materials such as material chemistry, biosensing, and sensor application, quantum dots of carbon and graphene-based on lignin for sensing applications,

use of lignin as a precursor in the production of biosensors, synthesis of lignin-based smart nanomaterials, and composites for sensing applications, sensing applications employ lignin nanoparticles as a platform, biomedical application, nano/microparticles and capsules made of lignin, smart hydrogels based on lignin, lignin-based smart materials for biological application face technical hurdles, and elastomeric and thermoplastic elastomer materials based on lignin, microorganism during composite having a description of actinomycetes, compost environment; bacteria, fungi and enzymes having a description of bacteria and fungi. The chapter also covers steps of lignin degradation which describe microorganisms involved in lignin degradation, depolymerization, lignin depolymerization, catalyzed by a base, depolymerization of lignin catalyzed by acid, lignin depolymerization catalyzed of metals, solubilization, and mineralization. Apart from it, the chapter has a description of the mechanism of microbial degradation of lignin which has a description of Vitro degradation (biodegradation of lignin with laccase, the biodegradability of lignin-by-lignin peroxidase), Vivo degradation (β -O-4 ether degradation and Bi-phenyl degradation pathway). Furthermore, the chapter covers fungal degradation of lignin, bacterial degradation of lignin, lignin-degrading actinomycetes, lignin-degrading enzymes such as lignin peroxidase, manganese peroxidase, laccase, cellobiose (quinone oxidoreductase, other enzymes, enzyme access to lignin), lignin degradation by pseudomonas, genomes analysis and evolution and factors affecting lignin degradation such as moisture content, added nitrogen, added glucose, and aeration.

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