LIGNIN, A COMPLEX HETEROPOLYMER AND ITS POSSIBILITIES OF USE: COMPARISON OF CHEMICAL AND BIOLOGICAL TREATMENTS

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ABSTRACT

Lignin, the second most abundant polymer in nature, provides rigidity and impermeability to plant cells, contributing to their mechanical strength. Its amorphous nature lubricates connective tissue and acts as a barrier against microorganisms. Apart from being a crucial by-product in the pulp and paper industry, lignin holds promise in biofuels, chemicals, and materials production. It enhances the properties of concrete, adhesives, paints, and coatings. Recent studies explore its potential as a sustainable alternative for bioplastics and biodegradable materials. Lignin can be converted into high-value chemicals and serves as a source for biofuel production in biorefinery processes. Structurally, lignin comprises phenylpropanoid units derived from monomers – p-coumaric, coniferyl, and sinapyl alcohol – forming diverse phenolic substructures. The distribution of these monomers varies with plant origin. Ether bonds within lignin resist degradation, with monomer proportions differing between angiosperms and gymnosperms.

Keywords: Lignin. Pre treatments. Chemical cleavage. Biological cleavage. Bioprocess.

1 INTRODUCTION

Lignin is a complex polymer and the second most abundant in nature, after cellulose, found in several terrestrial plants, such as trees, shrubs, grasses and other vascular plants. Lignin is composed of phenylpropanoid units, being responsible for providing rigidity and impermeability to plant cells, as well as contributing to their mechanical resistance[1]. Furthermore, it is an amorphous substance that makes up the extracellular environment of connective tissue, and its function is to lubricate and provide a barrier to the penetration of invading microorganisms[2].

Lignin has various applications due to its unique properties. It is an essential by-product in the pulp and paper industry, apart from this, recent research has investigated its biofuels, chemicals and innovative materials production potential, even though it is yet commonly burned to generate energy. Furthermore, this polymer is used as an additive in concrete, adhesives, paints and coatings, improving their resistance, durability and insulation properties. Contemporary studies have also explored lignin as a sustainable alternative for bioplastics and biodegradable materials manufacturing, aiming to reduce dependence on conventional plastics derived from fossil fuels[3]. Its ability to be converted into high-value chemicals such as vanillin, phenols, aromatic acids and other relevant chemical industry compounds, highlights its versatile potential. Additionally, lignin is a promising source for biofuel production, ethanol and biodiesel, as part of biorefinery processes that aim to transform biomass into renewable energy sources.

Lignin chemical structure is composed of phenylpropanoid units that originate from three aromatic alcohol precursors, known as monomers, p-coumaric, coniferyl and sinapyl. These monomers form phenolic substructures, including p-hydroxyphenyl, coniferyl alcohol-derived guaiacyl, and sinapyl alcohol-derived syringyl units, contributing to lignin's chemical composition diversity[4]. The distribution and proportion of lignin monomers follow the phylogenetic origin of each plant. The ether bonds resist many types of hydrolytic agents and enzymatic degradation systems. The relative amount of each monomer varies significantly depending on where this lignin originates, whether from angiosperms or gymnosperms[5].

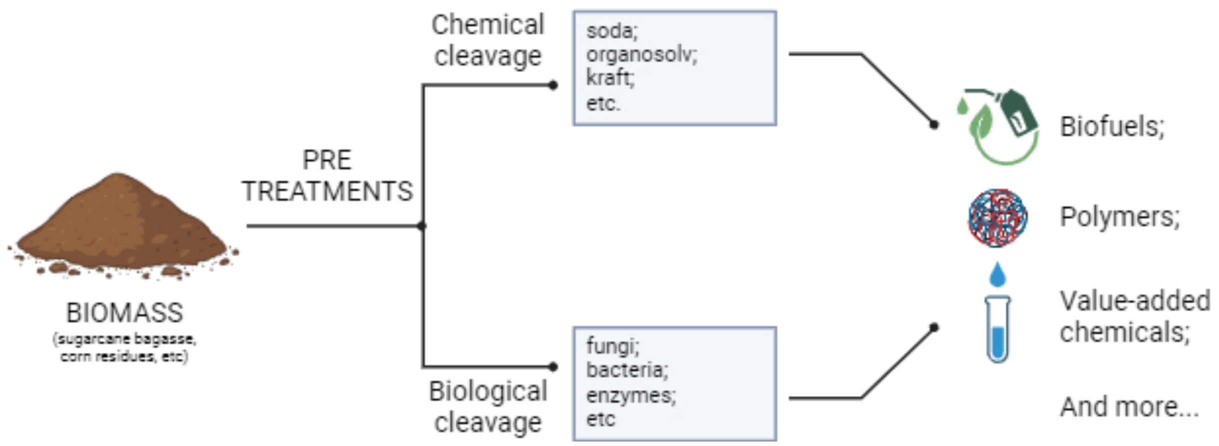

Figure 1 Biomass processing and possible applications. Created with Biorender.com

2 TYPES OF LIGNIN

There are different techniques to extract lignin from the lignocellulosic matrix, and the selection of the method, together with the plant source, influences the characteristics of the final product. The kraft, sulfite, soda and organosolv methods stand out due to the quantity produced, quality and characteristics of the resulting product. Each of these methods results in lignins with specific properties, which influence their potential applications and market value[6].

Kraft lignin is a by-product of the kraft process in the pulp and paper industry, obtained by reacting small pieces of wood with sodium hydroxide (NaOH) and sodium sulfite (Na_2S). This method dissolves lignin, allowing the separation of cellulose fibers, and is responsible for more than 90% of cellulosic pulp production by chemical means. This type of lignin is characterised by being rich in resistant carbon bonds and phenolic units, but it also contains impurities such as carbohydrates, fatty acids and sulfur (1.5% to 3%). The presence of sulfur can limit its application in thermochemical processes due to the formation of hydrogen sulfide gas. Although it is widely used in energy generation, kraft lignin has several potential applications, including its use as a dispersant for dyes, agrochemicals, concrete additives, asphalt emulsifiers, sunscreens and aromatic chemical intermediates. Sulfonated lignin is another by-product of lignin that has unique properties due to the presence of sulfonate groups in the chain, which makes it soluble in water and transforms it into anionic polyelectrolytes[7].

These characteristics give lignosulfonates special properties, making them useful as stabilisers, dispersing agents, surfactants and adhesives. While organosolv lignin is obtained through the organosolv pulping process, using a mixture of organic solvents and water, such as ethanol and methanol, with acid catalysts such as acetic acid and formic acid[8]. This method is used to extract carbohydrates for the production of second-generation ethanol, which is relevant for biorefineries.

3 CHEMICAL CLEAVAGE

The cleavage of lignin, which consists of breaking its structure into smaller components, can be carried out through various chemical modification processes. Some ordinary methods to accomplish this cleavage include oxidation, esterification, etherification, and urethanization. In the oxidation of lignin, several oxidants, such as nitrobenzene, metal oxides, air and oxygen, are used to preserve the aromatic rings of lignin and produce aldehydes and phenolic acids, such as vanillin, vanillic acid and syringic acid. This process can be conducted with or without catalysts, such as copper (II) and cobalt (II)[7].

Esterification involves the reaction of lignin with acids or acid anhydrides to form esters, thus modifying its properties and allowing its use in different applications. Etherification is another method of reacting lignin with alkylating agents to form ethers, which can change its structure and create new functional groups. Urethanization involves the reaction of lignin with isocyanates to form urethanes, resulting in the modification of lignin and the incorporation of urethane groups into its structure.

The choice of the appropriate method will depend on the type of modification desired and the final properties intended for the modified lignin. Each chemical modification method offers unique opportunities to transform lignin into products with new properties and applications[3,9].

4 BIOLOGICAL CLEAVAGE

The cleavage of lignin biologically can be carried out through organisms such as fungi, bacteria and specific enzymes. These biological methods involve different strategies to degrade lignin into smaller components. Certain fungi, such as *Phanerochaete chrysosporium* and *Trametes versicolor*, can degrade lignin through ligninolytic enzymes, such as peroxidases and laccases, which act to break their bonds[10,11].

Some bacteria, such as *Rhodococcus* and *Pseudomonas*, also have enzymes capable of degrading lignin, such as ligninases and peroxidases, contributing to cleavage. In addition to organisms, isolated enzymes, such as laccases and peroxidases, can be used to cleave lignin in a controlled and efficient way, being produced in the laboratory or by genetically modified organisms. The advantages of the biological lignin cleavage process include selectivity, low environmental impact, efficiency and biorefinery potential. These characteristics make biological lignin cleavage a promising approach for valuing lignin as a renewable resource.

However, biological processes are generally slower compared to chemical methods of lignin cleavage, due to the time required for the growth and metabolism of the organisms involved. Some ligninolytic organisms and enzymes require specific environmental conditions such as pH, temperature and nutrients to be effective, which can increase the complexity of the process[12]. Furthermore, biological lignin cleavage can be more difficult to control compared with chemical methods due to the influence of variable biological factors such as enzymatic activity and the response of microorganisms to the environment. The large-scale implementation of biological processes for lignin cleavage can be challenging due to cost, time and operational complexity[8].

5 DERIVATIVES COMPOUNDS

Lignin can be chemically processed to yield a variety of valuable chemical compounds. One such compound is vanillin, used extensively as a flavouring agent in the food industry, adding a distinctive vanilla taste to numerous products. Guaiacol and syringaldehyde are aromatic compounds also derived from lignin, finding applications in pharmaceuticals, agrochemicals, and fragrances, where they contribute unique scents and flavours. Acetovanillone, derived from lignin through acetylation of vanillin, finds applications as a flavouring agent in food products and contributes to scents and flavours in cosmetics, perfumes, and pharmaceuticals[13,14].

Coniferyl alcohol is a precursor for resins, adhesives and polymers production, offering versatility in various industrial applications. Lignosulfonates, obtained from lignin through sulfite pulping processes, exhibit excellent dispersing and binding properties, making them valuable additives in the construction, agriculture and ceramics industries. Furfural, produced from lignocellulosic biomass, is used as a chemical platform for solvents, plastics and pharmaceuticals synthesis, contributing to the development of sustainable biorefineries. Levulinic acid finds applications as a solvent, plasticizer, and additive in various industrial processes, as well as a precursor for pharmaceuticals and agrochemicals synthesis[15].

Other examples are eugenol, which has a spicy, clove-like odour and is used in fragrances, flavours, and pharmaceuticals; guaifenesin, commonly used as an expectorant in cough medications[16]; sinapyl alcohol, a precursor for lignin-based polymers and natural antioxidants; syringyl acetate, valued for its sweet, floral aroma in perfumes and personal care products; vanillic acid, used as a flavouring agent and antioxidant in food, cosmetics, and pharmaceuticals; p-coumaric acid, a precursor for various natural products with applications in pharmaceuticals and cosmetics; lignin-based adhesives, offering a renewable alternative for wood products and construction materials[17]; and lignin-based carbon fibers, utilized for their strength and sustainability in aerospace, automotive, and sporting goods industries[18,19].

These lignin-derived compounds showcase the potential of lignocellulosic biomass as a renewable feedstock for high-value chemical production, contributing to the advancement of sustainable and environmentally friendly industrial practices.

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ACKNOWLEDGEMENTS

We thank CAPES and FAPESP for the resources and financial support. To the professor Dra Eleni Gomes for the opportunity and assistance during the research. Also thank UNESP, as well as the Institute of Bioscience, Humanities and Exact Sciences for the infrastructure.