A review on lignin, a sustainable raw material

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ABSTRACT

Lignin is one of the main components of lignocellulosic biomass. It is an abundant aromatic macromolecule in nature with potential for production in various products. However, the high number of C-C and C-O bonds makes its deconstruction difficult, necessitating the application of pretreatment methods for its removal from plant biomass. Chemical pretreatment is one of several types of treatments that can be used, aiming to deconstruct the lignocellulosic structure through chemical agents. After depolymerization, lignin and its derivatives can be useful as substrates for bacterial strains tolerant to high concentrations of aromatic compounds. These strains can even perform bioconversion of these compounds as a detoxification response to high-value-added fine chemicals, such as 4-vinyl derivatives. These molecules have various industrial applications, making the exploration of lignin and its derivatives very promising for sustainable production by bacteria.

Keywords: Lignin, Pretreatments, Bioconversion.

INTRODUCTION

Lignin is the second most abundant natural polymer on Earth and is associated with other compounds in the lignocellulosic complex, such as cellulose and hemicellulose, playing structural roles by providing strength and rigidity to the plant cell wall [1]. Lignin is primarily composed of phenylpropane (C6-C3) units derived from the dehydrogenative polymerization of p-coumaryl, coniferyl, and sinapyl alcohols, resulting in various phenolic compounds [2].

The diversity of aromatic compounds derived from lignin offers the possibility of producing a wide range of products through its chemical or biological conversion, such as biofuels, pharmaceuticals, and food additives, among other high-value-added products [3].

However, lignin is more difficult to deconstruct compared to other components of lignocellulosic biomass due to its natural recalcitrance, a characteristic that provides plants with advantages such as defense against herbivory and microbial attacks [4]. This property, however, hinders the utilization of lignin, necessitating the use of techniques that initially deconstruct this structure, a process called pretreatment [5].

For decades, pretreatment methods have aimed exclusively at obtaining fermentable sugars, considering lignin an obstacle to the valorization of polysaccharides, usually being underutilized in the process [6]. These fractionation processes are applied in the production of pulp and second-generation bioethanol, with the goal of removing lignin from plant biomass [7]. However, for biorefinery industries to be more economically efficient, extracting value from lignin is essential, as it represents 15% to 25% of the biomass used in these processes [8].

About 98% of the lignin produced in pulp and paper mills is inefficiently used for burning to produce energy or is discarded in landfills. These destinations are environmentally harmful and exacerbate the release of atmospheric pollutants. Therefore, the development of economically viable biotechnologies is essential for the ecological utilization of lignin in biorefineries [9].

MAIN TYPES OF LIGNIN

There are different pretreatment techniques aimed at deconstructing the lignocellulosic matrix, where the selection of the method influences the characteristics of the final product. The methods used can be chemical, physical, or biological, each with distinct advantages and disadvantages [10]. The main procedures include common pulping methods, such as sulfite, kraft, and soda pulping. These processes alter the structure of lignin, aiming to prepare the biomass for subsequent conversion processes. In addition to pulping, other methods stand out, such as oxidative pretreatments, organosolv, and others [7].

From sulfite pulping, lignosulfonates are extracted, a process in which sulfite is used to break down the biomass over a wide pH range. In kraft pulping, lignin dissociation occurs through the ionization of phenolic groups due to the alkaline pH. This process uses a mixture of hot water, sodium hydroxide (NaOH), and sodium sulfide

(Na_2S). In soda pulping, heating the biomass combined with the use of a strong alkali results in a lower-quality pulp, as this process leads to cellulose degradation [11 12].

The applicability of different types of lignin presents an efficient way to increase the productivity and profitability of industries that produce it as a byproduct, in addition to offering an alternative to the consumption of fossil fuels as an energy source and raw material. Lignosulfonates stand out as binders, while the main applications of kraft lignin are as dispersing and emulsifying agents. Soda lignin derivatives are applied in the field of animal feed and nutrition [13].

In general, the valorization of different types of lignin can be achieved through various applications, such as deriving aromatic compounds from the phenolics present in its structure, acting as a binder useful in cement production; converting it into BTX aromatics (benzene, toluene, and xylene) used in the production of rubber, fibers, dyes, and other fine chemicals; or using it in the synthesis of carbon fiber, among other applications [9].

CHALLENGES IN THE UTILIZATION AND VALORIZATION OF LIGNIN COMPOUNDS

Plants have various secondary metabolites that perform multiple functions and exhibit high chemical variability. One of the molecules resulting from the secondary metabolism of plants are the phenolic compounds that constitute lignin, which have one or more hydroxyl groups directly attached to an aromatic ring. Among these subunits, the hydroxycinnamic acids [14] stand out, including ferulic acid, p-coumaric acid, caffeic acid, and sinapic acid, which have antioxidant and antimicrobial properties. The antimicrobial action of hydroxycinnamic acids involves cell membrane permeability and binding to the DNA of microorganisms, resulting in increased sensitivity to osmotic pressure and deleterious mutations [15].

Despite exhibiting bactericidal action that hinders microbial growth, some tolerant strains can deconstruct lignin derivatives, i.e., perform their bioconversion into less toxic aromatic compounds. This characteristic is attractive from the perspective of exploiting the organic synthesis of high-value-added aromatic molecules [15].

The metabolic pathways of hydroxycinnamic bioconversion are catalyzed by bacteria that possess enzymes promoting non-oxidative decarboxylation in a cofactor-independent manner. An advantage of using bacteria for the biodegradation of lignin derivatives is their adaptation to different environments, making them more tolerant to abiotic variations. However, the intracellular location of these enzymes presents a challenge for their biotechnological utilization [16 17].

There are several classes of hydroxycinnamic derivatives, among them the 4-vinylphenols, which are functionalized styrenes notable for their application as flavoring agents used in the cosmetic, perfume, feed, food, and beverage industries. The industrial demand for 4-vinylphenols is not met by natural sources, making production by microorganisms/enzymes from plant biomass interesting18. For this purpose, microbial bioprospecting methods enable the discovery of ligninolytic strains relevant to this goal [15].

The decarboxylation of ferulic acid results in 4-vinylguaiacol, while the decarboxylation of p-coumaric acid results in 4-vinylphenol. The catalysis of these substrates is carried out by various phenolic acid decarboxylase enzymes with a certain degree of promiscuity, meaning they catalyze different substrates as previously discussed. 4-vinyl derivatives are useful in various industrial sectors, mainly as flavoring agents with an aroma/flavor similar to cloves, used in the production of beers, wines, wine vinegars, and soy sauce due to the added sensory effect [6].

In summary, the production of 4-vinyl derivatives from hydroxycinnamics is interesting due to their various applications as flavoring agents and the production of bioactive molecules. However, for bioconversion to be efficient, it is essential to develop methods that allow bacterial growth and the production of target enzymes, overcoming the toxicity of these molecules and their intermediates. In addition to these challenges, various extraction and purification processes for the 4-vinyl derivatives after bioconversion are also necessary, making production more costly. Thus, it is concluded that the development of studies related to the valorization process of hydroxycinnamics is necessary, aiming for greater profitability and feasibility of production.

METHODOLOGY

To obtain the articles used in the review, the academic databases "PubMed," "Elsevier," "Google Scholar," and "NCBI" were used. A review of the last 5 years on the topic of "lignocellulosic materials" was conducted. The articles obtained through this screening were subjected to a critical reading to evaluate their relevance for the text's preparation. The main terms searched were "lignin," "lignin bioconversion," "phenolic compounds," and "p-coumaric acid."

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