

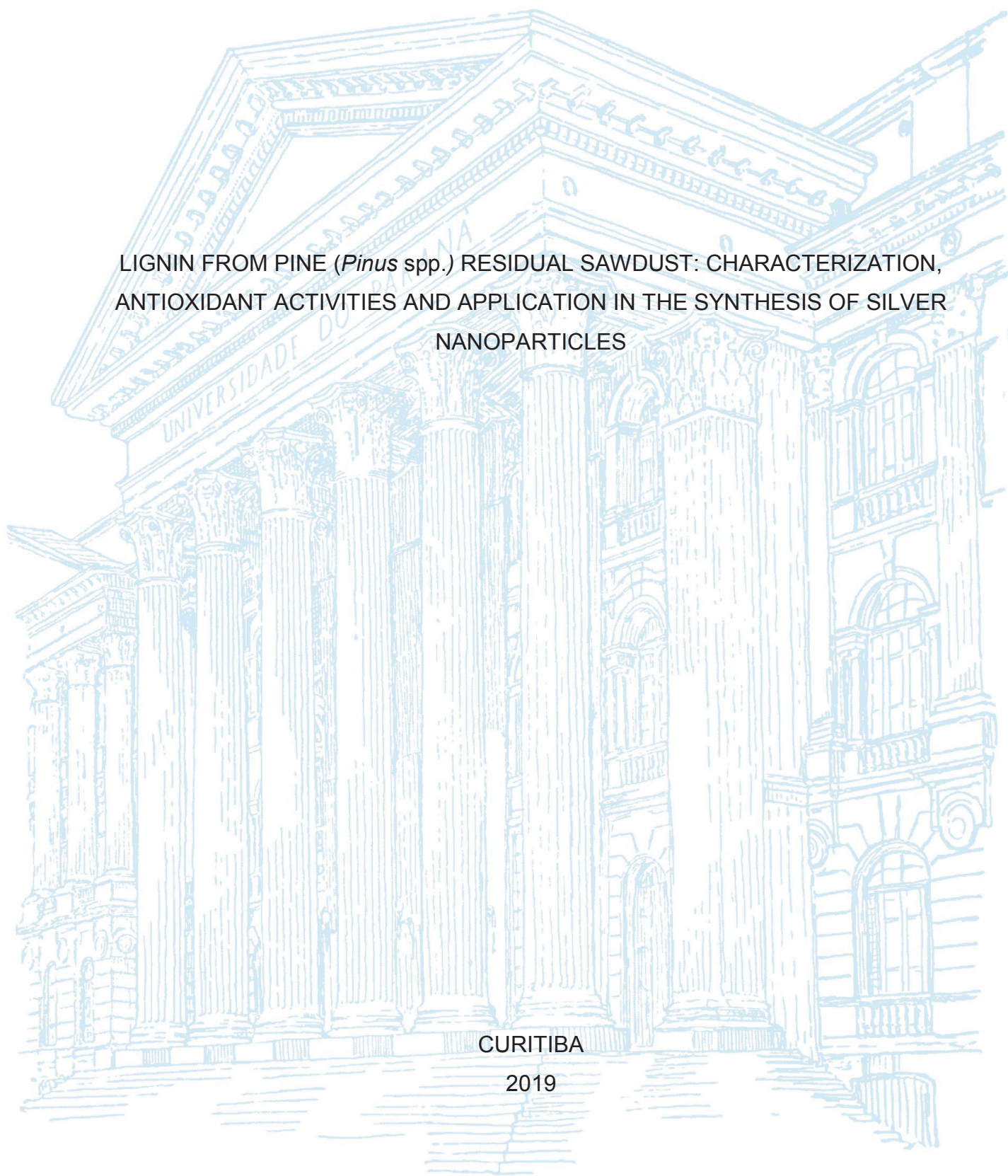
UNIVERSIDADE FEDERAL DO PARANÁ

MATHEUS CAVALI

LIGNIN FROM PINE (*Pinus* spp.) RESIDUAL SAWDUST: CHARACTERIZATION,
ANTIOXIDANT ACTIVITIES AND APPLICATION IN THE SYNTHESIS OF SILVER
NANOPARTICLES

CURITIBA

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NANOPARTICLES

Dissertação apresentada ao curso de Pós-Graduação em Engenharia de Bioprocessos e Biotecnologia, Setor de Tecnologia, Universidade Federal do Paraná, como requisito parcial à obtenção do título de Mestre em Engenharia de Bioprocessos e Biotecnologia.

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Profa. Dra. Adenise Lorenci Woiciechowski

Coorientador:
Prof. Dr. Carlos Ricardo Soccol

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Ao meu pai Lauro e à minha mãe Jeovani.

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“Palavras, palavras, palavras... [...] O resto é silêncio.”

Hamlet – William Shakespeare.

RESUMO

A biomassa é um recurso renovável e amplamente disponível, com grande potencial para fomentar o desenvolvimento da bioeconomia por meio da ideia de biorrefinaria. Dentro do conceito abrangente de biomassa, os materiais lignocelulósicos têm um interesse especial devido à sua estrutura, a qual é composta majoritariamente por celulose, hemicelulose e lignina, podendo ser fracionada para diversas aplicações. Isso, no entanto, requer métodos adequados para recuperar um componente de interesse sem degradar outro. Ao longo do tempo, a pesquisa relacionada ao beneficiamento dos carboidratos lignocelulósicos (celulose e hemicelulose) recebeu muita atenção, enquanto que o interesse pela lignina é recente. Por ser uma fonte de compostos fenólicos, atualmente a lignina tem entusiasmado pesquisas, as quais empregam métodos distintos de recuperação e buscam testar aplicações deste biopolímero como antioxidante e na síntese de nanopartículas, por exemplo. De acordo com o conceito de biorefinaria, os resíduos lignocelulósicos são fontes atrativas de lignina, pois, como um subproduto, demandam um descarte adequado, de modo que a sua utilização em outro processo torna-se conveniente. A indústria brasileira de madeiras, por exemplo, produz abundantes quantidades de serragem, um resíduo proveniente do processamento mecânico realizado nas serrarias, as quais utilizam predominantemente os gêneros *Pinus* e *Eucalyptus*. Frente a esse panorama, o objetivo deste estudo foi recuperar a lignina da serragem residual de pinus (PRS) e avaliá-la como antioxidante e na síntese de nanopartículas de prata (LAgNPs) para utilização como agente antimicrobiano. Porém, os carboidratos hemicelulósicos primeiramente foram extraídos por meio de um pré-tratamento ácido diluído e os sólidos remanescentes foram então submetidos a um tratamento alcalino para a recuperação da lignina em três temperaturas distintas. As ligninas recuperadas em cada temperatura foram caracterizadas por Espectroscopia de Infravermelho com Transformada de Fourier (F-TIR), Ressonância Magnética Nuclear (NMR) e termogravimetria. Também foi avaliado o teor de fenóis totais (TPC) presente em cada lignina, assim como suas respectivas atividades antioxidantes pelos métodos DPPH \cdot e ABTS $^+$. Em seguida as LAgNPs foram sintetizadas e analisadas por F-TIR, espalhamento dinâmico de luz (DLS) e microscopia eletrônica de transmissão (TEM) e utilizadas como agente antimicrobiano com bactérias Gram-positivas (*Staphylococcus aureus* e *Bacillus subtilis*) e Gram-negativas (*Escherichia coli* e *Salmonella typhimurium*). Os resultados encontrados foram satisfatórios, indicando, portanto, algumas possíveis aplicações para a PRSL. Além disso, essa abordagem com a PSR também serve para instigar o desenvolvimento da biorrefinaria na indústria madeireira através do uso dos seus subprodutos de maneira a agregar valor ao referido resíduo.

Palavras-chave: Biomassa. Tratamento ácido-alcálico. Biorefinaria. Nanotecnologia.

ABSTRACT

Biomass is a renewable and widely available resource with great potential to boost the bioeconomy development through the idea of biorefinery. Within the comprehensive concept of biomass, lignocellulosic materials are of particular interest because of their structure, composed mainly of cellulose, hemicellulose and lignin, which can be fractionated for various applications. This, however, requires suitable methods to recover one component of interest without degrading another. Over time, research on the processing of lignocellulosic carbohydrates (cellulose and hemicellulose) has received a lot of attention, while interest in lignin is recent. As a source of phenolic compounds, lignin has been addressed by many studies, which apply different methods of recovering and propose applications for this biopolymer such as natural antioxidant and in the synthesis of nanoparticles. According to the concept of biorefinery, lignocellulosic residues are an attractive source of lignin because, as a by-product, they require an adequate disposal, so that their use in another process becomes convenient. The Brazilian timber industry, for example, produces abundant amounts of sawdust, a residue from the mechanical processing performed at sawmills, in which the genera *Pinus* and *Eucalyptus* are predominantly utilized. In this sense, the aim of this study was to recover lignin from pine residual sawdust (PRS) and evaluate it as an antioxidant and in the synthesis of silver nanoparticle (LAgNPs) for using as antimicrobial agent. First, hemicellulosic carbohydrates were extracted by dilute acid pretreatment and the remaining solids were then subjected to an alkaline treatment in order to recover the lignin at three temperatures. The lignins recovered at each temperature were characterized by Fourier Transform Infrared Spectroscopy (F-IRR), Nuclear Magnetic Resonance (NMR) and thermogravimetry. The total phenol content (TPC) present in each lignin was evaluated as well as their respective antioxidant activities by the DPPH \cdot and ABTS $^+$ methods. Then LAgNPs were synthesized and analyzed by F-TIR, dynamic light scattering (DLS) and transmission electron microscopy (TEM) and used as antimicrobial agent with Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative bacteria (*Escherichia coli* and *Salmonella typhimurium*). The results obtained herein were satisfactory, indicating, therefore, some possible applications for PRSL. In addition, this approach with PSR also serves to instigate the development of biorefinery in the timber industry through the use of its by-products in order to add value to that residue.

Keywords: Biomass. Acid-alkaline treatment. Biorefinery. Nanotechnology.

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**1 LIGNOCELLULOSIC SOFTWOOD BIOMASS: COMPOSITION, DILUTED
ACID PRETREATMENT AND LIGNIN VALORIZATION AS ANTIOXIDANT
AND IN THE SYNTHESIS OF NANOPARTICLES**

Lignocellulosic softwood biomass: composition, diluted acid pretreatment and lignin valorization as antioxidant and in the synthesis of nanoparticles

Abstract: It is well known that biomass as feedstock for various processes can undoubtedly contribute to decrease problems related to greenhouse gas emissions since fossil resources are environmentally harmful and must be replaced for alternatives sources. Biomass has a great potential for that purpose because it is renewable and plenty available, which can boost a bio-based economy by addressing the biorefinery idea. In addition to the comprehensive concept of biomass, lignocellulosic materials have a special interest due to its structure made mainly of cellulose, hemicellulose and lignin that is able to be fractionated for utilizing in several applications. This, however, requires suitable methods in order to extract a desired component without degrading another. In this sense, this chapter aimed to describe the fundamental composition of woody biomass focusing on softwoods (pine residual sawdust – PRS) as well as its fractionation by acid diluted pretreatment and alkaline treatment for hemicellulose removal and lignin recovery, respectively. This aromatic biopolymer named lignin, known by its complexity, is in a strongly entangled association with cellulose and hemicellulose due to its different linkages and can be a great source of organic compounds. According to that, lignin has recently been studied for many uses such as antimicrobial and antioxidant agents and also applied in the nanotechnology field for synthesizing silver nanoparticles. Silver nanoparticles, due to their size, are of great interest because present peculiar properties which are unachieved with the bulk material. These approaches emphasize the great potential of lignin from woody residual biomass as well as its valorization to corroborate with the biorefinery development.

1.1 INTRODUCTION

Bio-based economy focuses on using non-fossil feedstocks as a way to mitigate environment problems, still allowing the economic growth. What incentives this new type of economy is the population increase and their contribution on waste generation and consumption of non-renewable resources, besides global warming due to the utilization of fossil fuels. The use of petroleum is the main cause of carbon dioxide (CO₂) emissions and global climate change is directly related to it. In this regard, biomass along with carbon storage is considered the only route to reduce greenhouse gas emissions (MUSSATO; DRAGONE, 2016; KAUR et al., 2013).

Therefore, renewable raw materials as sources of energy, materials and chemicals are going to expand in the future as a response to demand for fossil fuels. Alternatives raw materials such as plant biomass are less polluting, cheaper and capable of adding economic value to the agroindustrial chains (JAWAID; PARIDAH;

SABA, 2017; ALEKHINA et al., 2015). However, abundant amounts of residues from industrial and agricultural processes are still inadequately utilized as energy sources. Hence, further advances are required in order to establish processes in the context of biorefinery approach, since all fraction of biomass must be properly used.

1.2 BIOMASS

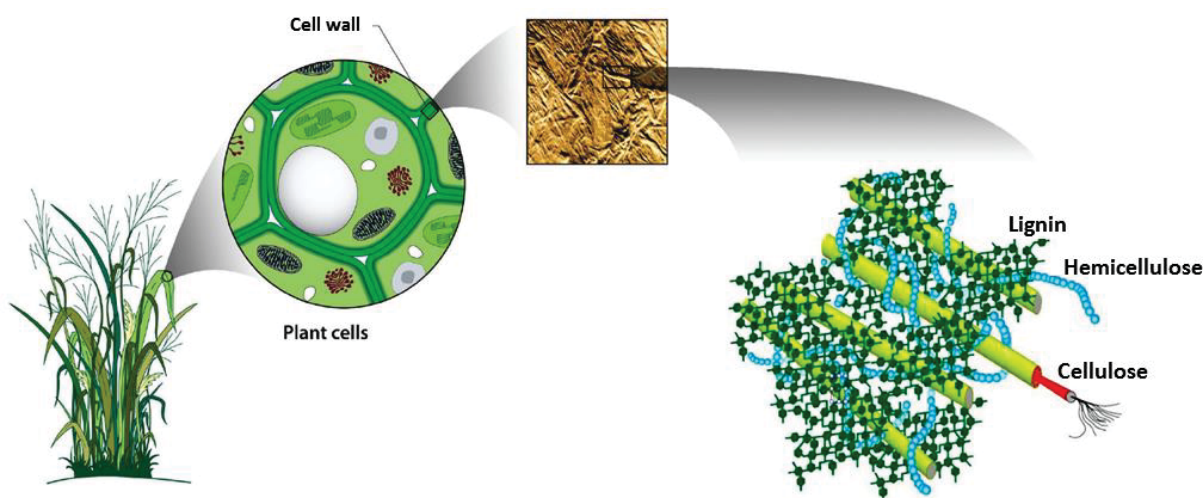
The biomass term comprises all organic matter coming from either animal or plant origin and it is produced directly or indirectly by photosynthesis process. Therefore, biomass can be defined as everything that has an organic matrix consisting of a great variety of materials (BONECHI et al., 2017)

Phytobiomass is a type of biomass and refers to that organic matter originated directly from photosynthesis by solar energy. According to the storage form of its sugars, it is subdivided in saccharides, amylaceous, oleaginous and lignocellulosic. The lignocellulosic phytobiomass has a complex composition, which consist of cellulose, hemicellulose and lignin. Some species also contain a fraction of extractable materials, proteins, lipids, waxes, hydrocarbons and metals. Woody and agroindustrial residues are examples of phytobiomass (WOICIECHOWSKI et al., 2013; JAWAID; PARIDAH; SABA, 2017).

1.2.1 LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass has a heterogeneous structure which becomes its fractionation difficult because cellulose, hemicellulose and lignin are naturally connected in an intricate way, resulting in a recalcitrant material, as shown in FIGURE 1.1. These three main constituents are defined as structural components of biomass, whereas extractives and the moisture are named nonstructural fraction (CASTOLDI et al., 2014; ROMANÍ; GARROTE; PARAJÓ, 2012).

FIGURE 1.1 – RECALCITRANT STRUCTURE OF LIGNOCELLULOSIC PHYTOBIOMASS



SOURCE: Modified from Wang et al. (2017) and Quiroz-Castañeda and Folch-Mallol (2013).

1.2.1.1 Cellulose

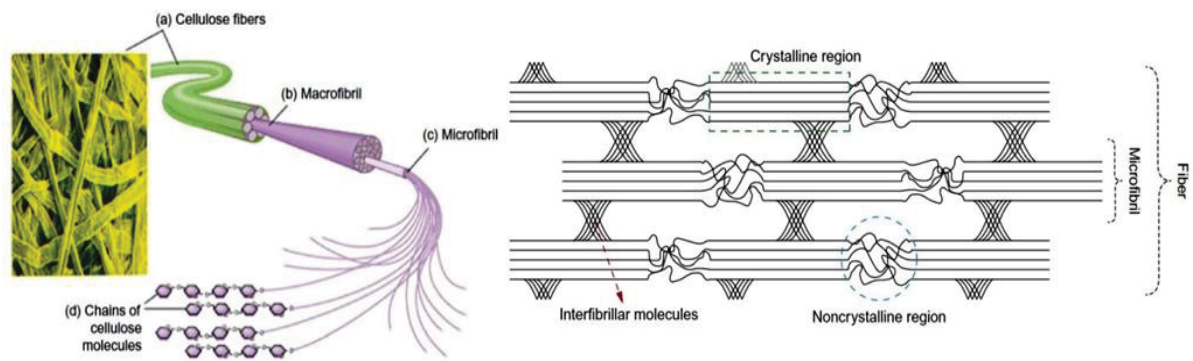
Cellulose, a fibrous, insoluble and very resistant structure, is the most abundant homopolysaccharide in nature; its composition comprises glucose molecules linked together by glycosidic bonds ($\beta - 1,4$). Although cellulose polymer is made up of more than 10.000 units of glucose or, specifically, anidroglucose, the monomeric unit of cellulose is the cellobiose which is a glucose dimer (BRANDT et al., 2013). Additionally, cellulose has great resistance and insolubility due to its chemical properties. The intramolecular hydrogen bonds interactions contribute to the linearity and resistance of the polymer whereas the intermolecular hydrogen bonds interactions packed the cellulose chains creating the microfibril (NAGARAJAN, 2017).

Furthermore, cellulose is an amphiphilic homopolysaccharide since it has hydrophobic and hydrophilic regions. Besides chain linearity, the equatorial orientation of the hydroxyl groups ($-OH$) in the glucose units also confers to cellulose its hydrophilic characteristic. On the other hand, the axial orientation of hydrogen atoms from carbon-hydrogen bonds promotes the polymer hydrophobicity which propitiates the hydrophobic interaction between chains (NAGARAJAN et al., 2017; JONG, 2015; LINDMAN; KARLSTRÖM; STIGSSON, 2010).

This arrangement is responsible for cellulose fiber constitution whose composition comprises microfibrils and macrofibrils in a way that the

former aggregate themselves to produce the latter. Microfibrils have highly ordered (crystalline) and less organized (amorphous) regions, as depicted in FIGURE 1.2 (BONECHI et al., 2017).

FIGURE 1.2 - CELLULOSE FIBERS ARRANGEMENT.



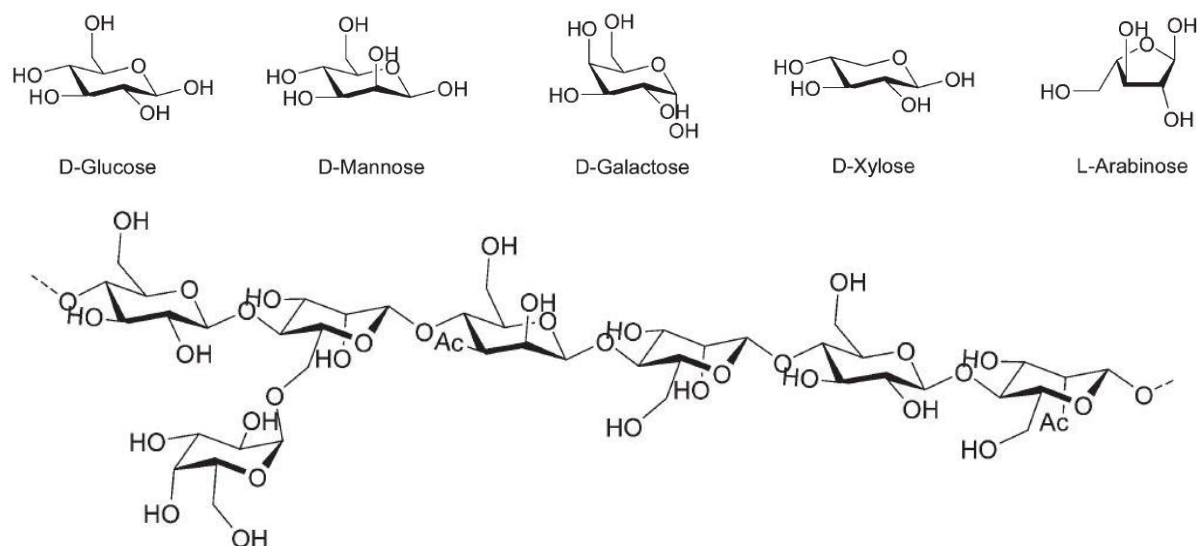
SOURCE: Bonechi et al. (2017).

1.2.1.2 Hemicellulose

Hemicellulose is an amorphous, non-cellulosic and non-starchy polysaccharide that is composed of hexoses (glucose, mannose and galactose), pentoses (xylose and arabinose), uronic acids and deoxyhexoses (rhamnose and fucose) and it has a minor chain compared to cellulose. Due to branched and amorphous structure of hemicellulose, its interaction with cellulose readily occurs and, thus, allows flexibility and stability to lignocellulosic matrix. On the other hand, hemicellulose is degraded first in pretreatment processes (BONECHI et al., 2017; BRANDT et al., 2013; WOICIECHOWSKI et al., 2014).

In softwoods, for example, hemicellulose is made up of galactoglucomans whose monomers are mannose, glucose and galactose. Galactoglucomans have a linear chain of glucose and mannose with branches of galactose distributed laterally. Thereby, when softwood biomass is submitted to a pretreatment the sugars released are mainly glucose and mannose. Other sugar present in the hemicellulose of softwoods is arabinose and xylose; the latter is released in a less amount because of its minor content in the hemicellulose composition. FIGURE 1.3 shows the possible monomers of hemicellulose and galactoglucomann polymer (BRAVO et al., 2017; LIM; LEE, 2013).

FIGURE 1.3 – MONOMERIC COMPONENTS OF HEMICELLULOSE AND GALACTOGLUCOMANNAN POLYMER.



SOURCE: Brandt et al. (2013).

1.2.1.3 Lignin

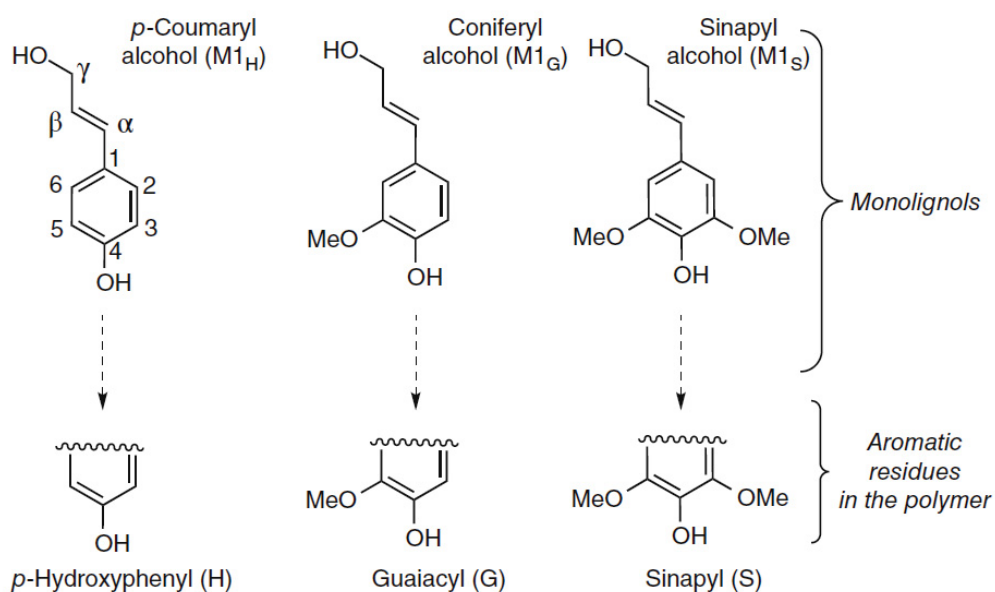
Lignin is another constituent of phytobiomass cell wall and it is a hydrophobic biopolymer that fills the space between cellulose and hemicellulose and gives stiffness to the plants. Lignin is not linear like cellulose but a three-dimensional web; after cellulose, lignin is the most abundant natural polymer ranging between 20 and 30% of lignocellulosic biomass on earth (LIMA et al., 2016).

Although the aim of lignin is to provide stiffness to cell wall and gives support to the plant, it also controls the permeability as well as the chemical and thermal stability of the cell, besides to protect it against microorganism degradation. Its monomeric precursors are made up of an aromatic ring plus a lateral aliphatic chain and this structure is called phenyl-propane. The methylation degree ($-OCH_3$) of the aromatic ring is what distinguishes one monomer from another; the *p*-coumaryl alcohol is not methylated, whereas coniferyl and sinapyl alcohols are methylated once and twice, respectively (HAGHDAN; RENNECKAR; SMITH, 2016).

Therefore, according to the presence of a specific monomer, lignin can be classified as guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H), deriving, respectively, from coniferyl, sinapyl and *p*-coumaryl alcohols, as shown in FIGURE

1.4. Softwoods, for example, present a predominant amount of G lignin, while hardwoods have a G/S lignin ratio that ranges from 1/1 and 1/3 and they can present small portions of H lignin. This latter type of lignin is present in grasses, which have these three monomers in their lignin composition (HENRIKSSON, 2009).

FIGURE 1.4 – MONOMERIC PRECURSORS OF LIGNIN UNITS.



SOURCE: Calvo-Flores et al. (2015).

1.2.1.4 Extractives

Extractives are heterogeneous compounds existing in the wood that can be removed with a solvent by an extraction process. Differently from the structural polymers of wood (cellulose, hemicellulose and lignin), the composition of the extractives varies according to the specie. In addition, they are known as accidental components of the wood since they do not constitute the structural part of the cell wall and the middle lamella. They are present in a small amount, but supply for wood characteristics like smell, color and taste. Besides, extractives play an important role to the tree; while some of them are necessary for the metabolism of living cells, others are produced to protect it against degrading agents such as insects and fungi. Moreover, extractives can be classified according to their chemical composition (phenolic and aliphatic compounds, terpenes and terpenoids) and regarding to the extraction form (soluble in water or organic solvent and volatile material in water

vapor) (CHEN et al., 2014; PENG; BIAN; SUN et al., 2010; JANSSON; NILVEBRANT, 2009).

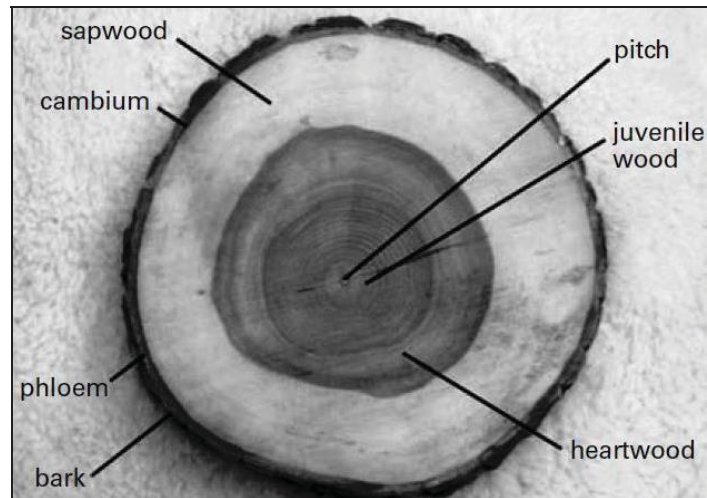
1.2.1.5 Ashes

Besides the majority organic fraction that constitutes the lignocellulosic phytobiomass, there is still a portion of inorganic material generally reported as ashes content. It is the result of complete combustion of the biomass at temperatures ranging from 500 to 600°C in laboratory conditions, in which is present the minerals that aided the plant growth (VASSILEV et al., 2017). These minerals, essential to the development of the plant, are supplied by soil; hence, the ashes composition is distinct for plants from different environments. The woody biomass has minor ash content when compared to herbaceous and agricultural biomass. Ash percentage is higher in the leaves and bark and smaller in the branches and stems. In addition, hardwoods have more ashes in their composition in contrast with softwoods (VASSILEV et al., 2013).

1.3 SOFTWOODS

Wood is a biological structure with great complexity and at a fundamental level it is a composite of many cell types acting together to provide the plant needs. There are some layers from outside to inside as shown in FIGURE 1.5. The bark supplies mechanical protection to the inner bark that is so-called phloem, and it is responsible for transporting the sugars produced by photosynthesis from the leaves to the growing parts of the tree. The layer between phloem and wood is the vascular cambium, responsible for producing phloem and xylem as well. Xylem (sapwood) is the structure that conducts water from the roots to the leaves; it is the active wood and does not have a darker-colored aspect. Unlike, heartwood has its colored characteristic because of the extractives content that are present; all cells in this part of the stem are dead. The juvenile wood is derived from the pitch, which is the plant from the early growth of the trunk before wood is formed (WIEDENHOEFT; MILLER, 2005; HENRIKSSON; BRÄNNVALL; LENNHOLM, 2009).

FIGURE 1.5 – PARTS OF WOOD IN A SCOTS PINE STEM.

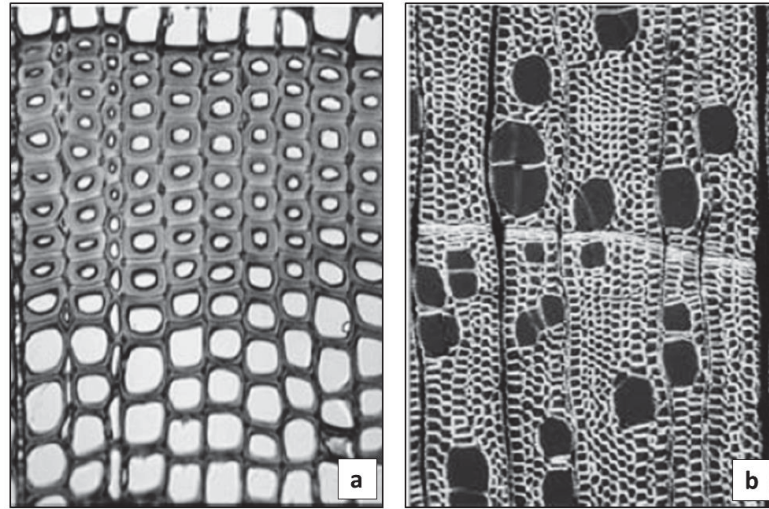


SOURCE: Henriksson; Brännvall; Lennholm (2009).

Coniferous gymnosperm comprises pine, spruce, cypress, fir, redwood hemlock and larch and the wood of them is known as softwood. In Northern Hemisphere large lands are colonized by softwoods since they have a significant economic value for timber and paper production as well as for ecology (HENRIKSSON; BRÄNNVALL; LENNHOLM, 2009; WAGNER; DONALDSON; RALPH, 2012).

Softwoods are constituted by three types of cells named tracheids, parenchyma and epithelial, although the former comprises 90 to 95% of the total cell volume. They are 100 times greater in length than in diameter, oriented in the longitudinal direction of the stem and are connected by openings. Additionally, earlywood tracheids (thin-walled) and latewood tracheids (thick-walled) are responsible for conducting fluids and providing mechanical strength, respectively. Parenchymas are living cells that perform the liquid transport among the rays and axial tracheids, while epithelial cells surround the resin canals in order to secrete the resin transported by them. In contrast, hardwoods have different cells such as vessels, fibers and parenchyma. The vessels are specialized water-conducting cells whereas mechanical strength is provided by fibers that are smaller than softwood tracheids; parenchyma cells storage reserve materials like starch. In FIGURE 1.6 is showed the transversal section for comparing those differences between (a) softwood and (b) hardwood in which the vessels are clearly present (WIEDENHOEFT; MILLER, 2005; DANIEL, 2005; HENRIKSSON; BRÄNNVALL; LENNHOLM, 2009; STOKKE; WU; HAN, 2014; RAMAGE et al., 2017).

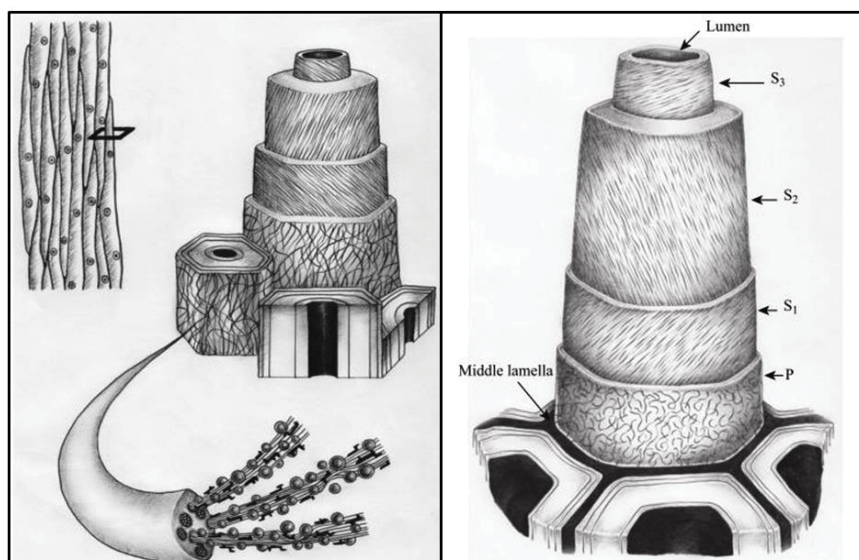
FIGURE 1.6 – TRANSVERSAL SECTION OF SOFTWOOD (a) AND HARDWOOD (b).



SOURCE: Daniel (2005).

Regarding to cell wall, softwood composition is an aggregate of microfibrils oriented in a specific way with the long axis of the cell itself. FIGURE 1.7 presents a diagram of this organized structure. From outer to inner there is the middle lamella that binds adjacent cells together due to its high lignin content, following by primary cell wall (P), which is a thin layer of cellulosic microfibrils with approximately $0.1 \mu\text{m}$ in thickness. The secondary cell wall is made up by three layers from outside to inside called S1, S2 and S3, respectively (STOKKE; WU; HAN, 2014; JONG, 2015).

FIGURE 1.7 – LAYERED CELL WALL STRUCTURE OF A SOFTWOOD LONGITUDINAL TRACHEID.



SOURCE: Stokke; Wu; Han (2013).

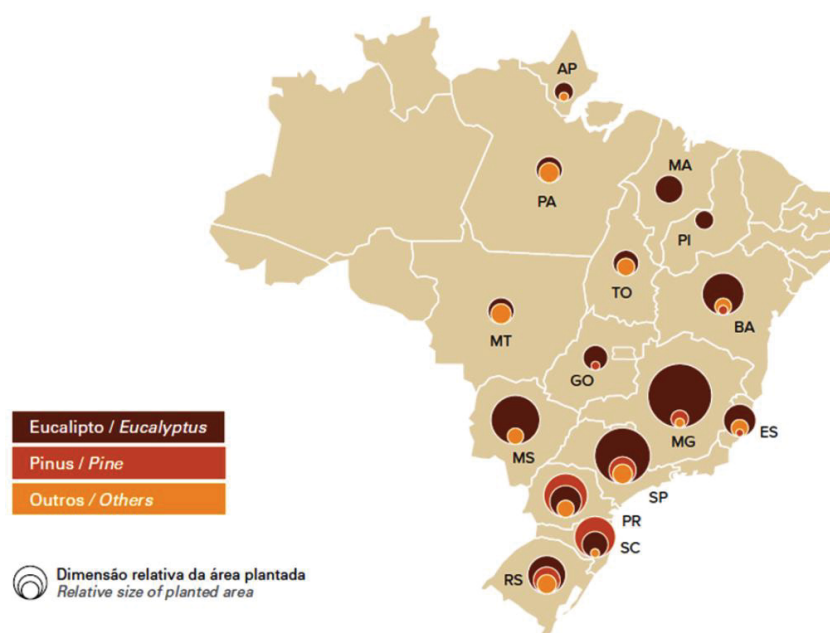
In the wood from a mature coniferous tree S1 and S3 have a similar thickness (0.1 – 0.3 μm), whereas S2 is the thickest layer, ranging from a few micrometers to 20 μm or more. The open space in the center of the cell is named lumen and there may be a bumpy surface called “warty layer” (STOKKE; WU; HAN, 2014).

1.3.1 PINE WOOD (*Pinus* spp.)

The trees belonging to the genus *Pinus* in the family Pinaceae are called pine and there are about 115 species. They are native from the Northern Hemisphere and are cultivated in subtropical and temperate regions of the world. Pines are coniferous (softwoods), evergreen and resinous trees; mostly, their heights range between 15 to 45 meters tall and are long-lived organisms, reaching ages of 100 to 1,000 years. Besides, pines are commercially important because of their value in wood pulp and timber worldwide (AMERICAN CONIFER SOCIETY, 2018).

In Brazil, according to data of Brazilian Institute of Geography and Statistics (IBGE), the total planted area of pine in 2017 was approximately 2.0 million hectares. The states of Paraná, Santa Catarina e Rio Grande do Sul are the largest contributors to national forestry production (36.1%); additionally, in Paraná and Santa Catarina there is a predominance of the genus *Pinus*, as depicted in FIGURE 1.8.

FIGURE 1.8 – AREA OF TREES PLANTED IN BRAZIL BY STATE AND SPECIES (2016).



SOURCE: Brazilian Industry of Trees (2017).

Furthermore, the planted area of pine has remained constant over the last five years in the south region of Brazil because of the good conditions of the weather and soil. Of the total area of planted trees 34% is for pulp and paper industry, 29% is from independent producers, 14% is for charcoal fired steelworks, 10% is from financial investors, 6% is for wood panels and laminate flooring, 4% is for solid wood products and the remaining comprises other usages. In relation to sawn wood, Brazil produced 8.6 million m³ in 2016 and exported 74% of that amount (BRAZILIAN INDUSTRY OF TREES, 2017).

1.4 AGROINDUSTRIAL RESIDUES AND BIOREFINERY

Residues and byproducts are generated by all human activities and their quantity, quality and polluting potential are different from one to another. A material can be classified as a residue, a byproduct or a feedstock according to its use in other process due to its characteristics. The use of residues as a feedstock promotes an environment solution, since otherwise they would be a problem, demanding suitable treatments and disposal. Besides, residues applications are convenient because they generally have cheaper prices and become the process less expensive (WOICIECHOWSKI et al., 2013).

Within the category of agroindustrial residues are the lignocellulosic ones. They comprise, among others, straws, stover, cobs and husks in the group of crop residues and treetops, branches, stumps, leaves, sawdust, cutter shavings, scrap wood, wood pulp and wood chips in the group of forest residues (CORATO et al., 2018). Moreover, according to Jong e Jungmeier (2015), the most source of biomass in the future is expected to be lignocellulosic because it is widely available at moderate cost and does not compete with food and feed production. Forests, for example, are a great source of lignocellulosic biomass since they are responsible for 42.9% of the total biomass production every year worldwide and 89.3% of the total standing biomass (NIZAMI et al., 2017).

In this context biorefinery concept shows up, focusing on industries which use biomass as raw materials. The aim of biorefinery is to separate the biomass fractions by different technologies and convert them in products with higher added value promoting the byproducts valuation. Thus, biorefinery can be seen as an upstream, midstream and downstream processing of biomass (CHERUBINI; STROMMAN,

2011; JONG; JUNGMEIER, 2015; BHOWMICK; SARMAH; SEN, 2018). Therefore, to overcome some drawbacks in biorefinery implementation, the concept can be integrated with existing industrial processes such as pulp and paper industry, which would be able to produce fuels, chemicals or electric power along with their conventional products (HASSAN; WILLIAMS; JAISWAL, 2018). However, residues coming from other existing industrial processes must be assessed as a new potential for biorefinery approach as well.

1.4.1 WOOD WASTES

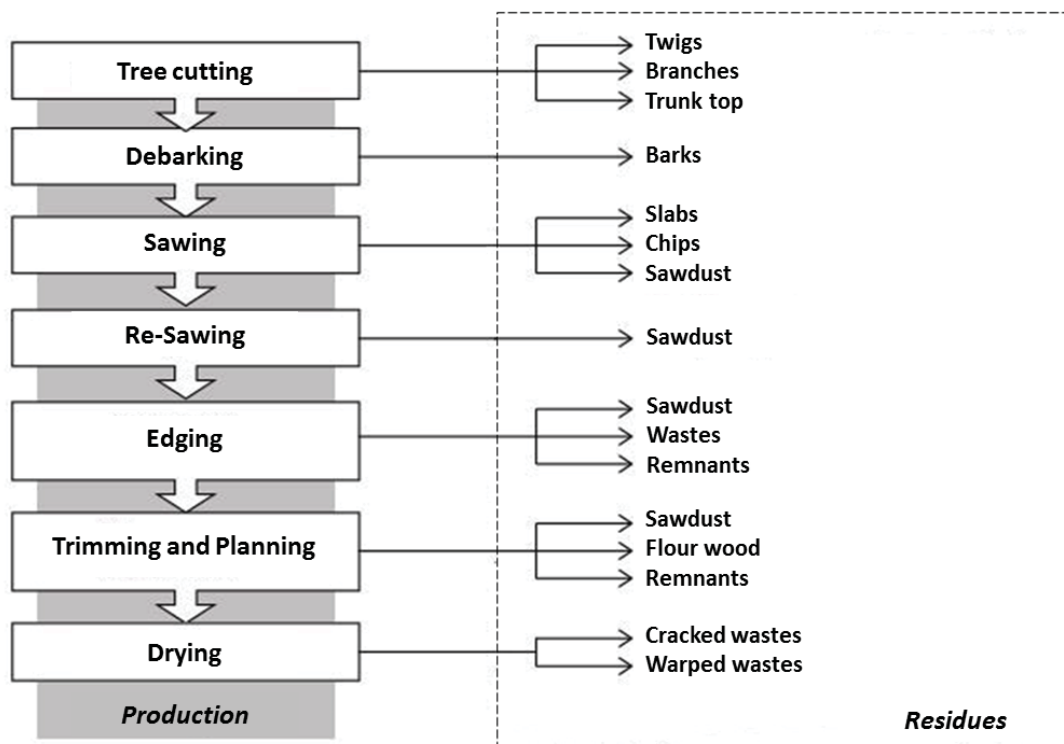
The demand for wood as a raw material is connected to demand for related products since there is an increase request for wood-products as well as for wood energy purpose. On the other hand, these processes generate wood-based residues during the different stages of wood processing that are available for other usages. Besides, biotechnological purposes and biorefinery of wood are also promoting the increase utilization of these residues in chemical industry (SAAL; WEIMAR; MANTAU, 2017).

The generation of large amounts of wastes during wood processing is inevitable in logging industry. Sawmill residues, for example, accumulate in sawmill industries as a byproduct during processing of sawn wood and their main components are chips, slabs and sawdust (SAAL; WEIMAR; MANTAU, 2017). Sawdust, whose characteristics are similar to wood, is a residue of small particles generated in the timber industry, commonly considered an environment pollutant. Outdoor burning of sawdust causes atmospheric pollution due to the emission of carbon oxide, a greenhouse gas, and it also contributes to the problem of acid rain. Moreover, if sawdust is disposed on soil it can promote negative effects such as reduction of hydrogen when used as mulch or phosphorous decline when incorporated; in addition, sawdust can increase soil acidity and pollute it with phenol compounds. In this regard, there are some applications in order to add value for this residue such as briquetting, oxygen gasification, production of oil and manufacturing for production of structural panels (ROMINIYI et al., 2017).

As shown in FIGURE 1.9, each stage during the production line in sawmills provides various types of residues as byproduct and it is worth pointing that sawdust is generated in several steps. In the processing of logs, for instance, 45% of loss is

estimated, i.e., almost half of the raw material becomes waste. Sawdust, which comes from the operation of saws in wood processing, is a significant portion of the residual amount because the losses range from 20 to 40%. Brazilian Southern states due to large production of wood are responsible for the greater production of wastes coming from mechanical wood processing ($21,051,848.70 \text{ m}^3 \cdot \text{year}^{-1}$), representing 44% of the national generation ($48,110,133.60 \text{ m}^3 \cdot \text{year}^{-1}$) of this type of residue (SCHNEIDER et al., 2012).

FIGURE 1.9 – WOOD WASTES GENERATED BY SAWMILLS.



SOURCE: Schneider et al. (2012).

In 2016 the planted forest sector generated 47.8 million tonnes of solid residues due to forests and industrial activities; the former contributing with 70.5% and the latter 29.5%. Of all portions industrially produced, 66% (chips, sawdust and black liquor) are utilized in power generation by burning in boilers, which does not allow a suitable valuation of this wastes (BRAZILIAN INDUSTRY OF TREES, 2017). Thence, pine sawdust has been evaluated to many applications by several studies in order to add value to this biomass instead of burning it (BRAVO et al., 2017; STOFFEL et al., 2017; TARRÉS et al., 2017; BALLINAS-CASARRUBIAS et al., 2015; STOFFEL et al., 2014; WANG; LEITCH; XU, 2009).

1.5 DILUTE ACID PRETREATMENT OF BIOMASS

Recalcitrance is a natural characteristic of the lignocellulosic materials which needs to be overcome so that their fractions can be isolated. For that purpose there are several pretreatments and according to their methods they can be classified in four categories: physical, chemical, physicochemical and biological (SILVEIRA et al., 2015).

Regarding to chemical, acid pretreatment can be used in concentrated or diluted form. The latter is a process in which concentration is lower than 5% (wt·v⁻¹) and both temperature and pressure are maintained in mild conditions. In this procedure the acid acts as a catalyst and, by attacking the intermolecular and intramolecular bonds between cellulose, hemicellulose and lignin, it hydrolyzes the carbohydrates (KANDHOLA et al., 2017; MUSSATTO, 2016). However, dilute acid hydrolysis is complex because the catalyst is in a liquid phase while substrate is solid. For this reason, there are many factors that influence this type of pretreatment such as temperature, acid concentration, reaction time, substrate composition and substrate concentration (LENIHAN et al., 2010).

In this reaction, the diffusion of H₃O⁺ through lignocellulosic material results in the breakdown of the ether bonds between monosaccharides. During this cleavage a carbocation is formed, which, after solvation with water, allows proton release so that it can act again. Hence, monomers, oligomers or sugar polymers are generated depending on the position at which the hydrolysis takes place and those products are subsequently diffused into the liquid medium (AGUILAR et al., 2002).

The first fraction degraded in this form of hydrolysis is hemicellulose, since it possesses a shorter structure when compared to cellulose and has lateral branches; the amorphous characteristic of this polysaccharide favors its own degradation. Thus, moderate temperatures along with a controlled reaction time and a low acid concentration can selectively hydrolyze the hemicellulosic fraction and a small portion of lignin, without significantly decomposing the cellulose. Therefore, solid fraction that remains after extraction of hemicellulose is composed of cellulose and lignin (BRAVO et al., 2017; BRANDT et al., 2013; KILPELAINEN et al., 2012; MÄKI-ARVELA et al., 2011).

Thereby, parameters involved in the process such as temperature, acid concentration, and reaction time needs to be optimized so that a condition with

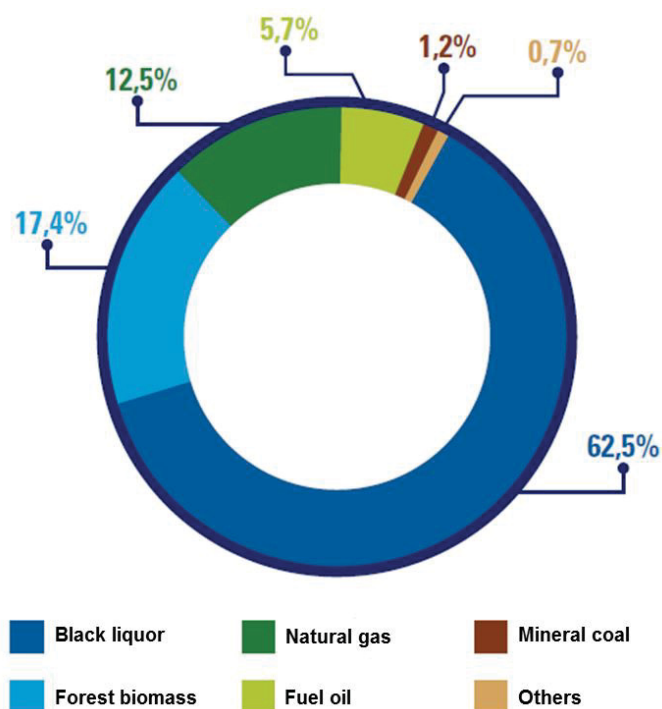
convenient extraction of the hemicellulosic carbohydrates is achieved. In addition to mannose, xylose, arabinose and galactose, which are present in softwood hemicellulose, formation of acetic acid can also occur due to the cleavage of the acetyl groups also present in this heteropolysaccharide. Lignin is modified because it is bounded to hemicellulose and when the latter is degraded the redistribution of the former into the cell wall is evident (CHEN; ZHAO; LIU, 2016; SILVEIRA et al., 2015; CHUNDAWAT et al., 2011; FREDERICK et al., 2008).

Dilute acid (organic or minerals) is an attractive way to pretreat lignocellulosic materials due to its low cost and high sugar yields and it is one of the most common explored methods to hydrolyze hemicellulose (ARORA; CARRIER, 2015; CHANDEL et al., 2012). Moreover, dilute acid pretreatment has been widely studied to hydrolyze pine sawdust (SANNIGRAHI; RAGAUSKAS; MILLER, 2008; MARZIALETTI et al., 2008; JEON; XUN; ROGERS, 2010; STOFFEL et al., 2014; BRAVO et al., 2017).

1.6 LIGNIN – BIOSYNTHESIS, GENERATION AND SOME APPLICATIONS

Lignin is intermittently produced by plants, making this source of organic compounds a renewable resource. At industrial level, pulp and paper production generates large amounts of lignin as a byproduct which is generally burned as a fuel and its usage is still restricted. In Brazil, as shown in FIGURE 1.10, the sector uses its byproducts such as black liquor and forestry biomass, two lignin-rich wastes, for almost 80% of energy sources (thermal and electric) utilized. However, the lignin from those byproducts could be used as new source of renewable organic substances for more rentable applications (BRAZILIAN INDUSTRY OF TRESS, 2017; PATIL; TANGUY; YAN, 2016).

FIGURE 1.10 – ENERGY SOURCES USED BY THE TREE INDUSTRY.



SOURCE: Brazilian Industry of Trees (2017).

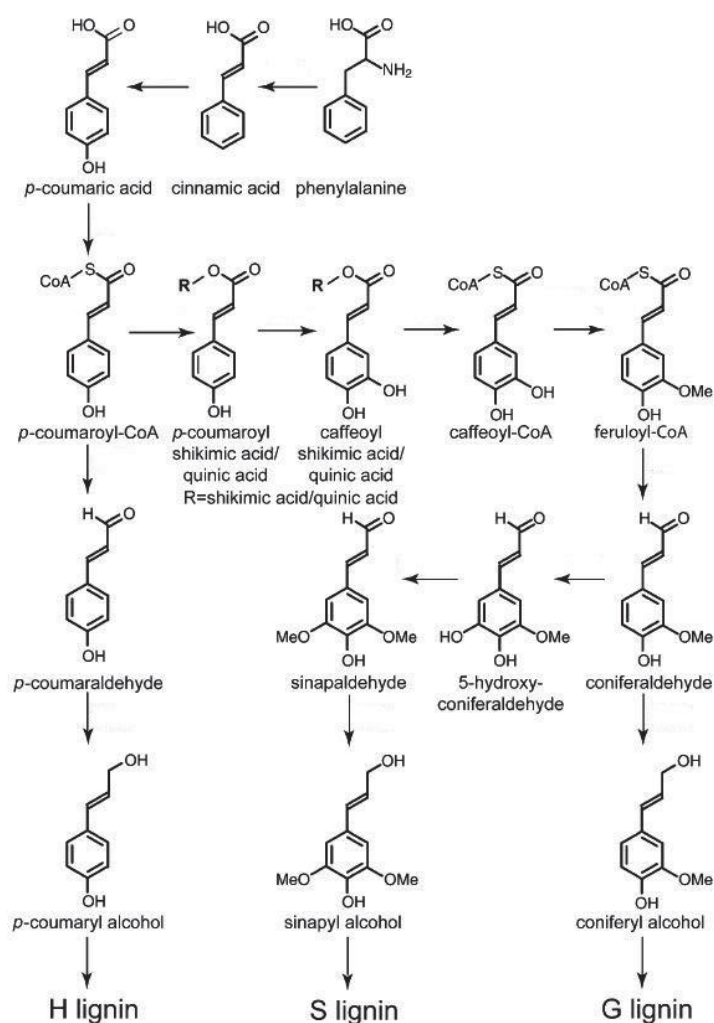
1.6.1 LIGNIN BIOSYNTHESIS

Large plants acquired the capacity of living in terrestrial habitat due to lignification development. Lignification is a biochemical process that includes monolignols biosynthesis, their transportation and polymerization in the cell wall. In simple terms, the deamination of phenylalanine following a sequence of reactions catalyzed by enzymes results in the three main lignin monomers: *p*-coumaryl, coniferyl and sinapyl alcohols. Nevertheless, there are also other uncommon monolignols present in lignin composition (ZHAO, 2016; LIU; MIAO; ZHANG, 2011; BONAWITZ; CHAPPLE, 2010; BOUDET, 2000).

Plants, inside their plastids, perform the shikimic pathway which starts with condensation of phosphoenolpyruvate and erythrose-4-phosphate that are metabolites from glycolysis. These reactions lead to shikimate production and shortly thereafter to chorismate. The latter, catalyzed by chorismate mutase, generates prephenate that consists the first step of both phenylalanine and tyrosine biosynthesis; in the next phases prephenate undergoes an amination by prephenate aminotransferase generating aroenate that forms the aforementioned amino acids (FRASER; CHAPPLE, 2011; LIU, 2012).

From phenylalanine to monolignols production inside the cytoplasm are necessary deamination, hydroxylation and/or methylation reactions as shown in FIGURE 1.11. Hydroxylation can occur at one, two or three positions of the aromatic ring whereas methylation happens either at one or two of the hydroxyl groups and it is what differs one monomer from another. Monolignol side chain is still reduced twice, first to an aldehyde and then to *p*-coumaryl, coniferyl or sinapyl alcohol. Once monolignols are synthesized, their transportation occurs to cell wall where they compose the matrix of the secondary cell wall by oxidation reactions. However, even though a lot of studies debate the issue, lignin biosynthesis and polymerization are complex processes that is not yet complete understood (VOXEUR; WANG; SIBOUT, 2015; LIU, 2012; BONAWITZ; CHAPPLE, 2010).

FIGURE 1.11 – PATHWAY OF MONOLIGNOLS BIOSYNTHESIS FROM PHENYLALANINE.



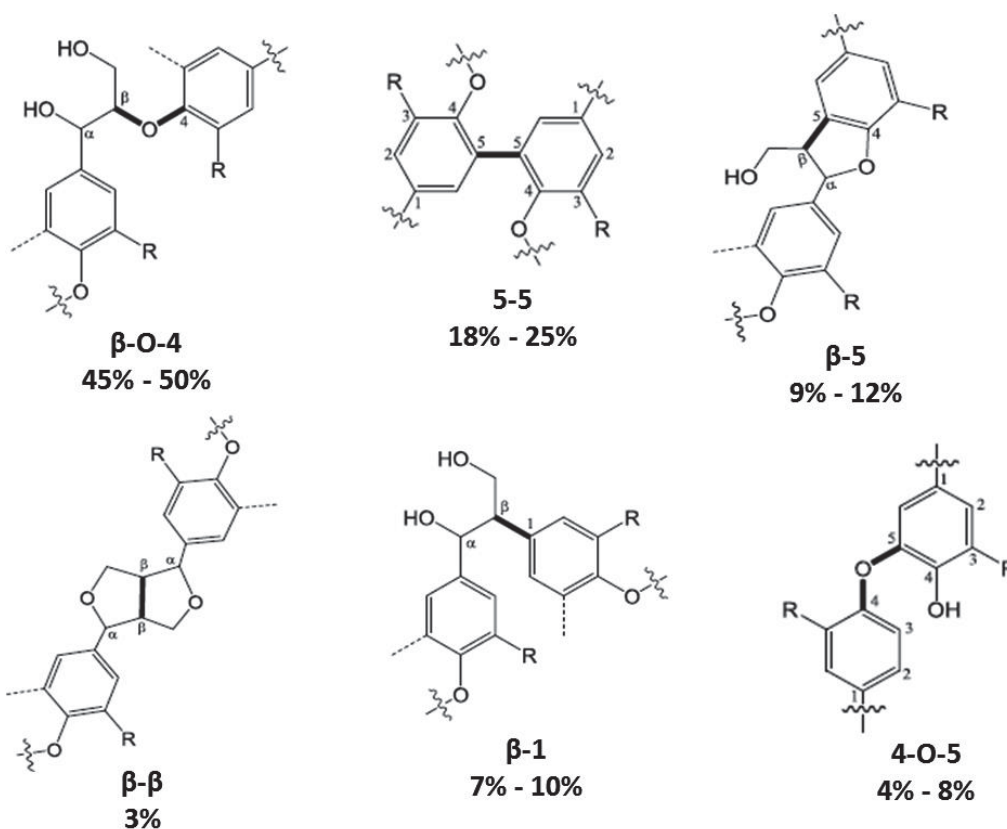
SOURCE: Vanholme et al. (2010).

Lignification of the xylem cells is a final step that occurs during thickening of the secondary cell wall (S1, S2 and S3 layers). After carbohydrates, lignin distribution starts at the middle lamella and primary cell wall, following to the secondary cell wall when polysaccharides in the S2 layer had already been completed. As a phase-process, complete cell lignification takes place after disposition of hemicellulose and cellulose in the last layer (S3). Since the secondary cell wall comprises a larger fraction of the wall, the highest lignin content is found there (BOERJAN; RALPH; BAUCHER, 2003; VANHOLME et al., 2010; WAGNER; DONALDSON; RALPH, 2012; VOXEUR; WANG; SIBOUT, 2015).

1.6.2 ALKALINE DELIGNIFICATION

The most common linkages in lignin structure are β -O-4, 5-5, β -5, 4-O-5, β -1 and β - β . The content of each linkage depends on biomass source and vary according to the technique used to recover lignin. Generally, β -O-4 is prominent among all other linkages, comprising more than 50% in most plant species (PATIL; TANGUY; YAN, 2016). Softwoods have higher lignin content than hardwoods which present more lignin than grasses. Still, softwoods contain 1.5 times less β -O-4 linkages compared to hardwoods, although this linkage makes up 45 to 50%, as shown in FIGURE 1.12 (AZADI et al., 2013).

FIGURE 1.12 – LINKAGES IN SOFTWOOD LIGNIN.



SOURCE: Adapted from Patil; Tanguy; Yan (2016).

The lignin recalcitrance is because of its aromatic composition, and the monomers are held together by strong C-C and C-O linkages. Additionally, depolymerization strategies focus on breakage of β -O-4 linkages due to their high content (SUN et al., 2018). Depolymerization of lignin includes cleavage of α and β ether bonds, which start in phenolic units and, in a latter phase of delignification, in nonphenolic units, as well as saponification of intermolecular ester bonds that links hemicellulose and lignin; the lignin fragments are insoluble in the alkaline medium (CALVO-FLORES et al., 2015; LORA, 2008).

In alkaline depolymerization fibers become swelled and the reagent first interacts with lignin promoting its removal. The main reactions involved in this process comprise dissolution of lignin and saponification of the intermolecular ester bonds. Furthermore, each component of lignocellulosic biomass has its degree of polymerization modified, and physical changes happen, affecting the surface area, crystallinity (removal of amorphous region – hemicellulose and lignin) and porosity (KIM; LEE; KIM, 2016; LEHTO; ALÉN, 2014; KIM, 2013).

When sodium hydroxide (NaOH) is used as alkaline agent it attacks the lignin-carbohydrate complex, breaking the ester and ether bonds. Moreover, NaOH might also be efficient for cleaving the ester and C-C bonds in lignin molecules. The hydrolysis rate increases as the hydroxide ion (OH⁻) concentration rises due to NaOH dissociation in the medium (KIM; LEE; KIM, 2016; LEE et al., 2014).

1.6.3 TECHNICAL LIGNINS

Fibers present in lignocellulosic materials such as wood can be separated by a process called pulping which is carried out chemically, mechanically or by a combination of both treatments. (SIXTA; POTTHAST; KROTSCHEK, 2006). Since cellulose is the desired product in the paper and pulp industry, large amounts of lignin is generated and it is denominated commercial-grade lignin (CHUNG; WASHBURN, 2016). Total lignin produced at these facilities is estimated at about 50 million tons per year, making pulping waste streams a great source of lignin (HU; ZHANG; LEE, 2018). Therefore, in order to separate lignin from lignocellulosic matrix, there are some methods applied; the most common industrial processes are Kraft, sulfite, soda and organosolv (FIGUEIREDO et al., 2018; CHUNG; WASHBURN, 2016).

The aim of the Kraft process is to isolate cellulose from wood by chemical reactions at temperatures ranging between 155 to 175°C using sodium hydroxide and sodium sulfide (CALVO-FLORES et al., 2015; CHUNG; WASHBURN, 2016). Lignin is then dispersed into the liquor (denoted as black liquor) and depolymerized because its β -O-4 linkages are cleaved by sulfide and bisulfide ions while fibers are released, targeting a low degradation of the carbohydrates (HU; ZHANG; LEE, 2018).

Sulfite or lignosulfonated process comprises the digestion of wood in an aqueous solution of a sulfite or bisulfite salt of sodium, calcium, magnesium or ammonium; according to the salt used, the media can be alkaline, neutral or acidic (CALVO-FLORES et al., 2015). This takes place at temperatures ranging from 140 to 170°C and includes the break of linkages between lignin and carbohydrates, cleavage of carbon-oxygen bonds that interconnect lignin units and the sulfonation of aliphatic chain at α -carbon position, which confers to sulfite lignin its main characteristic (LORA, 2008). The sulfonates groups are responsible to produce a

water-soluble lignin and to prevent its recondensation (DESHPANDE et al., 2018; CHUNG; WASHBURN, 2016).

Soda procedure has this denomination due to sodium hydroxide (NaOH) concentration used which is around 1.0 M (CHUNG; WASHBURN, 2016). It is predominant in pulping of non-wood materials such as sisal, kenaf, bagasse, hemp and wheat straw. The lignin obtained from this process is called “soda lignin” which, due to no sulfur and little hemicellulose content, has a great potential to be used in high value product (DOHERTY; MOUSAVIOUN; FELLOWS, 2011).

Lignin from organosolv process is obtained after the treatment of the biomass with a mixture of water and organic solvents catalyzed by either an acid or a base; the acid catalyst is common used and enables applying lower temperatures (CHUNG; WASHBURN, 2016). The organic solvent solubilizes and removes the lignin fraction that is a sulfur-free, low molecular weight and with high purity (LØHRE; KLEINERT; BARTH, 2017). This process is a good alternative compared to conventional methods of pulping since it is relatively clean, less aggressive and produces a more similar lignin to the native one (FIGUEIREDO et al., 2018).

1.6.4 LIGNIN APPLICATIONS

In 2015 the global lignin market volume surpassed 1,100,000 tons and will grow further by 2025, raising this market that has greatly expanded and is expected to reach 913.1 million dollars by the same year. It is the response to global demand of aromatics, which was recorded over 350,000 tons in 2015 due to the high requirements for bio-based raw materials. Low purity, lignosulfonates and Kraft lignin markets are predicted to exceed 800, 95 and 15 million dollars, respectively, by 2024. Low purity lignin has superior characteristics such as sulfur free and low molecular weight and it is used as catalyst in biorefinery. Lignosulfonates are applied as binders, emulsifiers and dispersants, whereas Kraft lignin is an intermediate in production of various compounds like vanillin, phenolic resins, activated carbon and cement additives (AHUJA; DEB, 2018). Additionally, lignin can also be used as antioxidant agent and in the synthesis of nanoparticles since these areas have been recently received a lot of attention due to their promising market (SANTOS et al., 2014; SYAFIYUDDIN et al., 2017).

1.6.4.1 Antioxidant activity of lignin

A substance whose low concentrations decrease or prevent the oxidative damages in a molecule is named antioxidant. The molecular oxygen (O_2), the final electron acceptor in aerobic life for energy production, is not toxic but it can be converted to oxygen-centered free radicals, which are reactive oxygen species (ROS). Superoxide anion (O_2^-), hydroxyl (HO^\cdot), peroxy (ROO^\cdot), alkoxy (RO^\cdot) and nitric oxide (NO^\cdot) are example of ROS. Moreover, hydroxyl and alkoxy readily attack the molecules in nearby cells since they are very reactive oxygen free radicals. Therefore, in order to avoid that phenomenon, antioxidants are capable of capturing and neutralizing free radicals, preventing the adverse effects of ROS. Hence, antioxidants are widely applied to chemical industry, food and medicine (GÜLÇİN, 2011; AN et al., 2017; POPA, 2013).

There are many synthetic compounds derived from petroleum commercially available to prevent or slow oxidative degradation of useful materials. However, there has been an increase interest for natural or renewable substances as antioxidant agents (LARSON et al., 2017). Lignin, for example, with diverse functional groups (phenolic and aliphatic hydroxyls, carbonyls, carboxyls, etc.) and a phenylpropanoic structure, can serve as an inhibitor or neutralizer in oxidation processes by stabilizing reactions induced by oxygen radicals and their derived species. In addition, the source of lignin as well as the treatment used in its isolation and purification has a strong influence on its antiradical activity (SANTOS et al., 2014).

A higher quantity of methoxy groups and phenolic hydroxyl along with a narrow polydispersity, lower content of aliphatic hydroxyl groups and low molecular weight are requirements of lignin for a higher antioxidant activity. Additionally, the phenol content in lignin is the main factor on antioxidative efficiency and the presence of methyl groups increases antioxidant capacity of phenolic compounds. (PONOMARENKO et al., 2015; KAI et al., 2016; AN et al., 2017).

Although the mechanism by which lignin acts like antioxidant is still not clear, it is presumed that the phenolic structures present in lignin work as a scavenger of free radicals. Some hypotheses have been raised such as lignin acting as a chelation agent that scavenges metals (Fe^{2+} and Mn^{2+}) of Fenton's reagent; as a receptor of the hydroxyl radicals attack, preventing the target molecules from being oxidized; or

as an inhibitor of those enzymes present in the metabolic pathway responsible for generating free radicals (POPA, 2013).

Peroxyl radicals are scavenged by phenols due to the presence of hydroxyl groups containing mobile hydrogens. In addition, the capability to reduce or to chelate necessary divalent ions for some reactions is also a phenol characteristic (CAZACU; CAPRARU; POPA, 2013). Generally, there are two well-known mechanisms by which a phenolic antioxidant (ArOH) inhibits the oxidation process: (a) hydrogen atom transfer and (b) single-electron transfer followed by proton release since a cation phenoxy is formed and fast deprotonated generating a phenoxy radical (GÜLÇİN, 2011).



Although the antioxidant pathway of lignin is not well-defined, there are some methodologies to evaluate its capability on scavenging free radicals. The most common assays are 2,2-diphenyl-1-picrylhydrazyl (DPPH \cdot) and 2,2-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS), which have been applied on several researches (GARCÍA et al., 2010; MA; GAO; ZHAI, 2013; MEDINA et al., 2016; AN et al., 2017; GARCÍA; SPIGNO; LABIDI, 2017; AMINZADEH et al., 2018).

As a stable radical, DPPH \cdot has violet color with adsorption band at 517 nm when it is not reduced. In the presence of an antioxidant, DPPH \cdot receives H $^+$ and the absorbance decreases, presenting a color change to yellow. This alteration enables determining the scavenging capability of the molecule of interest with a simple absorbance method (AN et al., 2017). Analogously, ABTS assay has the same principle as DPPH \cdot but while the latter is a stable radical the former must first react with a strong oxidizing agent such as potassium persulfate (K $_2$ S $_2$ O $_8$) to obtain ABTS $^+$ (blue-green color). The free radical will then react with the antioxidant and will be reduced, alternating the medium color, which is measured by absorbance at 734 nm (JIANG et al., 2018; GARCÍA et al., 2012).

In this regard, following the aforementioned procedures, a lot of researches have tested different sources of lignin for evaluating it as a natural antioxidant. Apple

tree pruning residues (GARCÍA; SPIGNO; LABIDI, 2017), rice straw (JIANG et al., 2018), oil palm empty fruit bunches (CORAL MEDINA et al., 2016), wheat straw (MA et al., 2013), sugarcane bagasse (KAUR; UPPAL; SHARMA, 2017) and enzymatic hydrolysis residue of corn straw (AN et al., 2017) are a few examples of lignins tested for antioxidant purposes due to promising potential of this biopolymer.

1.6.4.2 Lignin for synthesizing silver nanoparticles and their antimicrobial potential

General awareness of using nontoxic chemicals, renewable materials and environmentally harmless solvents has also addressed the green synthetic strategies in the nanotechnology field. In order to synthesize nanoparticles in agreement with those principles of green chemistry, some requirements must be followed such as the choice of an environment-friendly solvent, a benign reducing agent and a nontoxic material for nanoparticle stability (RAVEENDRAN; FU; WALLEN, 2003).

The synthesis of metal nanoparticles can be performed by physical, chemical or biologic methods. While physical approach deals with evaporation/condensation, laser ablation and thermal decomposition processes, chemical and biological procedures apply reducing agents and stabilizers. Regarding to the biological route, reducing agents may be plants, bacteria, fungi or algae. Therefore, it is necessary two reactants for synthesizing metal nanoparticles chemically or biologically: a compound to reduce the metal ions to a zero-valent state, which then agglomerate into oligomeric clusters and a stabilizing agent to prevent the aggregation of the nanoparticles formed to micro-sized ones. In some cases, however, a single compound might serve for both functions (MILCZAREK; REBIS; FABIANSKA, 2013; IRAVANI et al., 2014; SYAFI UDDIN et al., 2017).

According to the definition, nanoparticles are classified by their sizes. Thus, bulk materials (500 nm) are formed due to aggregation of large nanoparticles (greater than 100 nm) which in turn are a product of small nanoparticles (1 – 100 nm). These small nanoparticles come from clusters (approximately 1 nm) that result from atoms (less than 0.1 nm) agglomeration. The physicochemical properties are distinct for each particle as a consequence of its size (SINGH, 2016).

Recently, metal nanoparticles have been explored for many applications in areas like cosmetology and dermatology (NISKA et al., 2018), catalysis (AKBARI et al., 2018), food packaging (GARCIA; SHIN; KIM, 2018) and environment remedy

(SAIF; TAHIR; CHEN, 2016; YAO et al., 2018). Silver nanoparticles, for example, have received enormous interest from the past decade due to their special physical, chemical and biological properties, which boost their utilization in several areas like chemistry, materials science, physics and astronomy, engineering, biochemistry, medicine, environmental, pharmacology, among others (SYAFI UDDIN et al., 2017).

Thereby, as a result of those large applications, current researches are focused on silver nanoparticles synthesized by green routes in which reducing agent of silver and their respective stabilizer are biopolymers such as polysaccharides and lignin. Polysaccharides act as capping and supporting agents, while lignin, due to its functional groups, readily complex the silver cations, reducing them to atomic level and stabilizing the silver nanoparticles formed (BEYENE et al., 2017; MARULASIDDESHWARA et al., 2017). In this regard, plant biomass and plant extracts are very suitable for biosynthesis of nanoparticle since their use is an effective and rapid method besides being nontoxic. Compared to other biosynthesis procedures, the kinetics of nanoparticle synthesis with those plant components is higher and occasionally equivalent to chemical route (DHAND et al., 2015). These advantages have then boosted the researches on lignin silver nanoparticles as presented by several studies (MILCZAREK; REBIS; FABIANSKA, 2013; AADIL et al., 2016; MARULASIDDESHWARA et al., 2017; MODRZEJEWSKA-SIKORSKA et al., 2017; XUE et al., 2018).

Another important factor on silver nanoparticles is the economic aspect because the market has increased widely. It was valued at over 1.3 billion dollars in 2017 with the estimation of surpassing three billion by 2024. In 2017, healthcare and life sciences sector, which will be valued over a billion by 2024, shared 30% of this market due to increasing utilization of silver nanoparticle in antibacterial and antifungal products whereas textile sector accounted for over 25% of the total demand. Food and beverages along with electronic and electricals are other important segments with strong participation in the silver nanoparticle market (VERMA; IQBAL, 2018).

Hence, according to statistics, silver nanoparticles for antibacterial applications present a promising future. In a world where antibiotic resistance is considered a constant threat to health, antimicrobial agents which overcome the bacterial evolution are desired. Thus, as known before the pharmaceutical antibiotic revolution, metals such as silver, copper, magnesium and zinc have been used for

treating bacterial diseases, which brings about the potential of silver nanoparticles as an alternative against antibiotic resistance (ZHENG et al., 2018).

Silver nanoparticles act as antimicrobial because they release silver cations (Ag^+), which attach to the bacterial cell wall as a result of an electrostatic interactions or penetrate inside the microorganism. For these reasons, the biocidal effect of silver nanoparticle on bacteria can be attributed either to damages on the membrane cell wall (carbohydrates, proteins and fatty acid are degraded) or in the subcellular structures (Ag^+ ions interact with DNA, enzymes and proteins damaging them or they might generate ROS, which also destroys those molecules by oxidation). Therefore, size, shape and surface must be well-designed since these parameters have a significant effect in the action of the silver nanoparticle both on the membrane and inside the bacterial cell (ZHENG et al., 2018; AJITHA et al., 2018).

1.7 CONCLUSION

The searching for products from renewable sources is a consequence of the fossil fuels usage, which are well-known to be environmentally harmful and by causing serious losses. Regarding to that, renewable raw materials are required in order to achieve this goal and the agroindustrial chain has an important role, since it is an available source of those feedstocks due to the large generation of several residues. Lignocellulosic wastes are attractive because consist of a matrix of cellulose, hemicellulose and lignin, which is able to be fractionated for using in many processes according to the biorefinery concept. Woody residues are a great supplier of those lignocellulosic components due to intensive wood production. For instance, softwoods, generally pine wood, have a great economic value in timber and pulp and paper sectors. In sawmills that deal with the aforementioned wood there is an abundant generation of pine sawdust as byproduct that is readily able for high-valued applications. That residue may be submitted to a fractionation process by convenient methods such as diluted acid pretreatment and alkaline treatment for hemicellulose and lignin recovering, respectively, still remaining cellulose. The lignin has a heterogeneous structure made up of phenolic compounds available for potential usages such as natural antioxidant and in the synthesis of silver nanoparticles. Regarding to that, researches concerning this topic are important both to treat and

add value to wastes as well as to contribute to the development of the bio-based economy.

**2 LIGNIN CHARACTERIZATION AND HEMICELLULOSIC CARBOHYDRATES
RECUPERATION FROM PINE (*Pinus* spp.) RESIDUAL SAWDUST BY
SEQUENTIAL ACID-ALKALINE TREATMENT**

Lignin characterization and hemicellulosic carbohydrates recuperation from pine (*Pinus* spp.) residual sawdust (PRS) by sequential acid-alkaline treatment

Lignin is aplenty produced by plants and it is made of phenolic structures able to be processed according to the biorefinery concept. Lignocellulosic wastes can be an interesting source of lignin due to their abundant availability; they also are renewable raw material presenting many advantages over fossil resources. Sawdust is an example of lignocellulosic waste generated in the timber industry as a byproduct in the mechanical processing of wood. This residue can be better utilized if its fractions, lignin, hemicellulose and cellulose, are suitable used for convenient applications. Within the group of gymnosperm, the genus *Pinus* is widely used worldwide since these trees present a high economic value both in timber industry and paper production. Regarding to that, this section described the recovering of carbohydrates from pine residual sawdust (PRS) by dilute acid pretreatment and lignin by alkaline treatment. First PRS was characterized for determining its content of carbohydrates (cellulose and hemicellulose), acid soluble and insoluble lignin, extractives and ashes. The dilute acid pretreatment was evaluated according to a 2³ experimental design and the factors assessed were temperature, time and acid concentration. After pretreatment, PRS was submitted to lignin recovery, and three temperatures were tested in this step to achieve convenient yields. The lignins from PRS (PRSL) obtained at each temperature had their residual carbohydrate and inorganic matter contents determined and they were also characterized by thermogravimetric analysis, Nuclear Magnetic Resonance (NMR) and Fourier-Transform Infrared Spectroscopy (F-TIR). The detailed methodology applied and the results comprehensively discussed with the conclusions achieved are restricted to the publication of the paper*.

*The paper related to this section with a similar title will be available after publication and it will be able to be found by the keywords "lignocellulosic biomass", "softwood", "pretreatment" and "biorefinery".

3 LIGNIN FROM PINE (*Pinus* spp.) RESIDUAL SAWDUST: ANTIOXIDANT ACTIVITY AND ITS APPLICATION IN THE SYNTHESIS OF SILVER NANOPARTICLES AS A POTENTIAL ANTIMICROBIAL AGENT

Lignin from pine (*Pinus* spp.) residual sawdust: antioxidant activities and application in the synthesis of silver nanoparticles as a potential antimicrobial agent

After cellulose, lignin is the most plentiful biopolymer in nature, and it has several functional groups in its composition that can mitigate or prevent the oxidation process caused by oxygen radical or their derived species. Besides to have the potential of being a natural antioxidant, lignin can also be utilized to synthesize silver nanoparticles since this biopolymer is proposed as a reducing and stabilizing agent. Pine residual sawdust (PRS) is a great source of lignin because this lignocellulosic residue is abundantly generated in sawmills as a byproduct. Moreover, lignin from PRS (PRSL) has not been extensively assessed as antioxidant and in the synthesis of silver nanoparticles. According to that, PRSL was recovered from dilute-acid-pretreated PRS by an alkaline treatment performed at three temperatures as reported in the preceding section. Thus, the three lignins obtained in that sequential acid-alkaline treatment had their phenolic content estimated previously to have their antioxidant activities evaluated by 1,1-diphenyl-2-picrylhydrazyl (DPPH·) and 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) tests. Silver nanoparticles were then synthesized using lignin (LAgNPs) and their diameter was measured by dynamic light scattering (DLS) and transmission electron microscopy (TEM), which also allows verifying their morphology. In addition, LAgNPs were analyzed by Fourier-transform infrared spectroscopy (FTIR) as well. Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative (*Escherichia coli* and *Salmonella typhimurium*) bacteria were used to assess the potential of PRSL and LAgNPs as antimicrobial agent. The detailed methodology applied and the results comprehensively discussed with the conclusions achieved are restricted to the publication of the paper*.

*The paper related to this section with a similar title will be available after publication and it will be able to be found by the keywords "lignocellulosic biomass", "softwood", "nanotechnology" and "silver nanoparticles".

4 SUGGESTIONS FOR FUTURE STUDIES

- 1) Evaluating other methods for lignin recovery from pine residual sawdust such as organosolv and establishing suitable conditions;
- 2) Proposing convenient applications of the hemicellulosic carbohydrates as well as assessing the cellulose obtained at the end of the process for saccharification or in the nanocomposites production;
- 3) Optimizing the synthesis of silver nanoparticles with pine residual sawdust lignin in order to obtain a standardized diameter as well as stabilized nanoparticles;
- 4) Understanding the interaction between lignin silver nanoparticles and microorganisms as well as the influence of the silver-lignin combination on the mechanism of antimicrobial action at the molecular level;
- 5) Estimating the impacts of silver nanoparticles on aquatic and soil environment for defining safe tolerance limits.
- 6) Utilizing the pine residual sawdust lignin for synthesizing nanolignins and their application on environmental remediation of metal-contaminated sites;
- 7) Elaborating an economic analysis of pine residual sawdust biorefinery for comparing to the current uses of this residue.

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