Chapter 6
Biotechnological Aspects of Microbial Pretreatment of Lignocellulosic Biomass

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Abstract In several areas, products are obtained from lignocellulosic biomass, such as bioethanol and personal items. Notwithstanding, it features high recalcitrance, hence its use often demands pretreatment and hydrolysis stages to reach bio-based final products. Industrially, the most common method is the chemical pretreatment which, as the name implies, involves chemical components with potential environmental risks. This procedure is responsible to increase biomass accessibility and to enhance polysaccharides achieving in subsequent stages. Biological pretreatment presents a new perspective to replace or cooperate with its chemical counterpart, once microorganisms can modify the lignocellulosic structure and facilitate accessibility to macromolecules of interest. According to the above, this chapter covers the potential of biological pretreatment as well as the mechanisms of microbial degradation, their enzymes, and the impacts on the economy worldwide.

Keywords Microbial enzymes · Wood decay · Rot microorganisms · Recalcitrance · Biological delignification

Abbreviations

GHs Glycosyl hydrolases
LiP Lignin peroxidases

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6.1 Introduction

Recent technological, social, and environmental changes have brought new needs in both science and industry for developing alternative technologies that make it possible to achieve similar products, than those obtained from petroleum sources (Ruan et al. 2019). Since the last years of the nineteenth century, the world energy matrix has been based on fossil fuels (British Petroleum 2019). Among the possibilities to replace oil, biomass has become the most important resource, able to generate several products by different routes, with the great advantage of being environmentally friendly (Guedes et al. 2019). In this perspective, bio-based products are currently part of everyday life, with applications in sectors such as engines, packaging, medicines, and many others. With or without slight treatment/modifications, vegetal biomass like crops, vegetable oils, forest, agricultural waste, and also the municipal and industrial ones are used to produce bioproducts (Sorokina et al. 2017; Rosales-Calderon and Arantes 2019). However, turning vegetal biomass into bioproducts may become a challenge, since the raw material needs to be undergone to different types of stages during the conversion process until reaching suitable yields (Holwerda et al. 2019). Pretreatment has a huge importance in the steps of value-added products generated from biomass systems, where complex structure presented in plants must be conditioned for subsequent stages (Antunes et al. 2019).

The most used methods of biomass pretreatments, such as chemical and physical procedures, have in common the demand for plenty of chemical reagents and/or energy inputs in its process. Such chemicals are widely used in industries to separate biomass components in order to manufacture all kinds of (bio-) products, but in consequence, those reagents are found polluters for the environment. Nowadays, facing an economic and global warm crisis, it is essential and recommended looking for alternatives to low-cost, less oil-dependent, and non-polluting manufacturing methods.

Biological pretreatment of biomass is already known as an option to conventional methods used in industries. This method does not generate toxic and inhibitory compounds and need low quantity of chemical and energy input, which makes it an economically and eco-friendly feasible process. Biological pretreatment also can be used before a chemical or physical pretreatment: the biological stage can provide a better decrease of the recalcitrance while the chemical stage provides the separation of the macromolecules. This combination can reduce the costs and chemicals in the whole process (Sindhu et al. 2016; Singh 2018; Agbor et al. 2011; Felipuci 2020).

In this chapter will be discussed biological pretreatment characteristics, including the enzymes and microorganisms involved in the biomass structure modification. Moreover, the benefits and disadvantages of this method are discussed, as well as value-added and commodity products, mainly on large scale.

6.2 Biological Pretreatment

Biological pretreatment of lignocellulosic biomass became a fundamental research topic since it is clear that a near-term economy will depend on the supply of biomass to produce bioproducts and bioenergy. It is related to the use of microorganisms, aiming to degrade or modify vegetal biomass structure employing their special enzymatic complexes (Agbor et al. 2011; Sindhu et al. 2016). Among the vast variety of species in the world, fungi and bacteria are well known to produce specific enzymes for lignocellulose deconstruction, called cellulases, hemicellulases, and ligninases. These enzymes are capable to degrade natural macromolecules found in the plant cell wall, such as cellulose, hemicelluloses, and lignin. Cellulose and hemicelluloses, for instance, are hydrolyzed into smaller molecules (the monomeric sugars) (Sharma et al. 2019).

Among the numerous enzymes produced by fungi that degrade cellulose, hemicellulose and lignin, the most studied are: endoglucanases, exoglucanases, and β-glucosidases that hydrolyze cellulose; endoxylanases, β-xylosidases, acetyl xylan esterases and others that degrade xylan and laccases, manganese peroxidases and lignin peroxidases that degrade lignin (Pamidipati and Ahmed 2019; Gautam et al. 2019; Malgas et al. 2019).

The species of fungi that degrade lignin are known as white-rot. The ones that depolymerize cellulose and hemicelluloses are named brown-rot because the wood degraded takes a brownish appearance, due to the loss of polysaccharides (cellulose and hemicellulose) remaining high amounts of lignin (Hatakka and Hammel 2011).

Biological pretreatment does not generate toxic compound (degradation products, inhibitors) during its process and it is ecologically promising, which is an advantage comparing to other usual methods. Moreover, results can be optimized when the strains are pre-selected (Sindhu et al. 2016; Van Kuijk et al. 2015). In the biodegradation, variable microbial communities are important to the quality of the final results due to its vast amount of enzymes. However, in addition to the microorganism itself, biomass composition, temperature, humidity, pH, aeration rate, incubation time, and biomass particle size are elements that can also affect the result and the quality of the pretreatment (Sindhu et al. 2016; Fang et al. 2012; Li et al. 2012; Iqbal et al. 2013; Fatokun et al. 2016).

Usually, biological pretreatment needs long-time requirements (10–14 days), space, and careful growth conditions to work. In industrial scale it may be less attractive but the biological pretreatment can be used together with chemicals and physical pretreatment. The potential of delignification by microorganisms combining with chemical and physical methods is inviting because of the complete degradation of lignocellulosic biomass components, mainly lignin, that can take a long time to reach significant results (Agbor et al. 2011; Hatakka 1994; Hatakka et al. 1993).

Recalcitrance is the capacity of a biomass resist to a pretreatment or to enzyme action. The quantity and organization of the components into the cell wall such as cellulose crystallinity are factors that may change the recalcitrance level of biomass

(Naidu et al. 2018; Melati et al. 2019; Park et al. 2010). Lignin contributes to the material recalcitrance due to its resistance against pathogens and insects, and its removal influences the access to the polysaccharides (Shimizu et al. 2020; Schmatz et al. 2020; Zhao et al. 2012; Phitsuwan et al. 2013).

High recalcitrance is a challenge in the search for better methods of macromolecules isolation from biomass. Accordingly, different pretreatment methods have been developed, aspiring to circumvent this problem in order to separate its components. One method to work around the recalcitrance problem is to select varieties with low lignin content (Brienzo et al. 2015) or delignify biomass decreasing lignin content, considering that lignin is a barrier in carbohydrate extraction (Shimizu et al. 2020; Brienzo et al. 2017). A usual pretreatment focuses on improving the formation or capability to form fermentable sugars by hydrolysis; to prevent loss of carbohydrates; avoid by-product formation that may prevent subsequent processes and be a good cost-benefit ratio method (Melati et al. 2019). Thus, biological pretreatment is an option to replace or co-work with other methods of pretreatment by attending such ideal requirements.

Other way to degrade lignocellulosic biomass is using co-culture, which use more than one microorganism. This method is based in to use fungus or/and bacteria to degrade the lignocellulosic biomass. However, competition between microorganisms for the substrate is not recommended, and it can be used one after other. This technique is useful due to microorganisms encompass large quantities of enzymes, which can completely degrade the lignocellulosic material. This process can be used in different areas such as agronomy (degrade pesticides) and industry (carpet decolorization) (Yoon et al. 2014; Sariwati et al. 2017; Wang et al. 2017; Kumari and Naraian 2016).

6.2.1 Lignocellulosic Biomass Structure

Lignocellulosic biomass englobes all organic matter directly from plant sources. It is the largest source of carbohydrates in nature, with a great variety, abundance, and availability, involving wood, agro-industrial waste, municipal waste, and plants. What draws attention to these materials is that they are renewable resources with energy potential. This presents them as possible substitutes for fossil fuels, generating sustainable energy through bioethanol and co-generation of electric energy (by a burning process) (Nanda et al. 2015). Consequently, interest in research, both in scientific and industrial fields, grows constantly (Bilgili et al. 2017; Mao 2015; Aslan 2016; Toklu 2017; Sharma et al. 2019).

One of the most used lignocellulosic biomass is the sugarcane bagasse (*Saccharum* spp). Currently, the bagasse is used in the production of electrical and thermal energy through its combustion in high-pressure boilers in plants (Fernandes 2018). Another application aims to obtain second-generation ethanol (cellulosic ethanol), serving as an alternative to replace fossil fuels and charcoal.

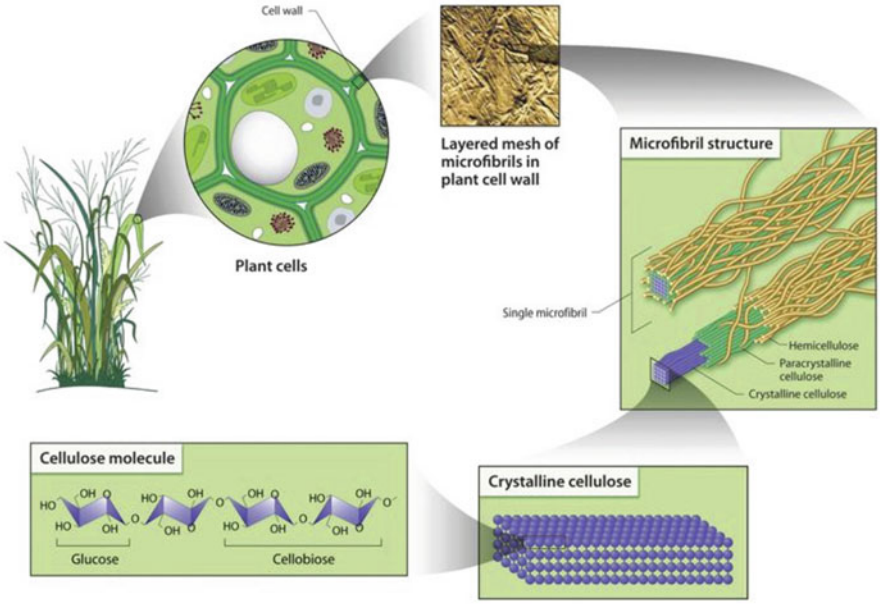

Fig. 6.1 Schematic representation of lignocellulosic biomass emphasizing the cellulose macromolecule (Jasmania and Thielemans 2018)

Lignocellulosic biomass is also used in the production of clothing, artificial skin, paper, and other products in common use (Mizuhashi et al. 2015; Kim et al. 2014). More specifically, in biotechnology and biomass conversion, it is possible to produce briquettes, carbon adsorbents, and biofilms. The production of these items depends on the treatment that those biomasses will be undergone. For separation of each macromolecule, there is one or a series of treatments to be based on biological routes.

The main characteristic of vegetal biomass is its lignocellulosic structure existing into the cell wall, presented in all plant forms. Its composition is mainly cellulose, hemicelluloses, and lignin, with less quantities pectins, proteins, and extractives (Naidu et al. 2018). Quantities of each component change according to biomass and soil types, geographic localization, and other factors (De Vasconcelos 2015). The three main components (cellulose, hemicelluloses, and lignin) in the cell wall are organized in a way that recalcitrance is increased, making its separation harder in biotechnological processes. Cellulose and hemicelluloses are strongly connected by hydrogen bonds. Hemicelluloses can be located between cellulose fibers, while lignin is connected to the carbohydrates forming a complex interaction network (Schmatz et al. 2020; Busse-Wicher et al. 2016).

Cellulose is the major macromolecule in the plant cell wall (Fig. 6.1). The quantity varies according to biomass type: rice toasts showed 28.7–34.7%; cotton presented around 95%, and sugarcane bagasse showed 25–45% (Naidu et al. 2018). It is also considered most abundant organic polymer found on the planet Cellulose is

an arrangement constituted by cellobiose unities (glucose dimers) joined by β-1,4 glycosidic chains. In the cellulose structure, there are amorphous regions which are organized regions demined crystalline and non-crystalline zones (Ioelovich 2016). Cellulose is widely sought in the industry as raw material for common use products, such as varnish, films, paper, among others. Due to several industrial interests, cellulose isolation from biomass is widely studied. Cellulose can be separated from other carbohydrates by alkaline treatment or broken by acid treatment. In the case of alkaline treatment, ester linkages break down, resulting in structural modification of the cell wall and facilitating separation from hemicelluloses (Galletti and Antonetti 2012).

Hemicelluloses, different from cellulose, are composed of more than one monosaccharide: pentoses, hexoses, and uronic acids. In pentoses group is found xylose and arabinose; in hexoses group is found mannose, glucose and galactose and in uronic acids is found glucuronic and galacturonic acids. Those monosaccharides can also be subdivided into three main groups: xyloglucans, xylans, and mannans, that are formed by subunits of mannose. The monosaccharides are connected by β and α glycosidic bonds and can have between 80 and 200 units. Hemicelluloses have amorphous characteristics and a lower degree of polymerization than cellulose. It makes up 15–35% of lignocellulosic biomass and it is associated to the integrity of the plant cell wall, having great importance in its shape and resistance. Hemicelluloses correspond to one-third of all renewable carbon on the planet. Hemicellulose has been studied for several applications, with a feature for oligomers such as xylooligosaccharides and manooligosaccharides (De Freitas et al. 2019; Chiyanzu 2014).

Lignin is a biomass macromolecule composed of phenylpropane units of p-hydroxyphenyl (H), syringyl (S), and guaiacyl (G). This polyphenolic structure is organized irregularly and has an amorphous structure. Depending on species, lignin comprehends between 10 and 20% of lignocellulosic biomass, being the third most abundant macromolecule in the plant cell wall. For plants, lignin helps in protection against insects and fungi and also contributes to growth development and mechanical strength. This protection is one of the reasons to the biosynthesis, once infections, metabolic stress, and disturbances in cell wall structure are starters to the plant initiate the process (Vanholme et al. 2010). It is arranged mainly on the secondary wall, making it rigid and waterproof. Lignin organization is to be linked with hemicelluloses, together with its irregular structure and a gigantic number of possibilities for connections between its forming units, which suggests that there is a low chance of existing two similar lignin molecules (Ralph et al. 2004). This favors the increasing recalcitrance of its biomass (Schmatz et al. 2020). Lignin is an obstacle for a process dedicated to macromolecule separations as it remains as residual content/contaminant (Felipuci 2020).

6.2.2 *Microorganisms in Biological Pretreatments*

Microorganisms are considered of key function in biological pretreatments of lignocellulosic biomass. Degradation capacity of microorganisms is widely known, mainly because of the degradative potential of its enzymes, which are produced during its growth. Biological pretreatment technology has generated results in several areas involving biotechnology, bioremediation, bio-pulping among others.

The most common microorganisms applied in biological pretreatment are white-rot, brown-rot, and soft-rot fungi, besides bacteria. These microorganisms are capable to consume all components in lignocellulosic biomass, mainly lignin, and the capacity to mineralize lignin into carbon dioxide and water. Brown-rot fungi are known to degrade polysaccharides more efficiently, and only slightly modifies the lignin, while white-rot fungi can degrade lignin with more facility (Kirk and Moore 1972; Kirk and Highley 1973). Holocelluloses/lignin ratio presented in biomass after degradation can be used to measure the fungal effect on the biomass decomposition. The effect on the biomass components can be classified at different ratios: Class 1 (corresponds to brown decomposition agents): ratio less than one; Class 2: whose process has a low amount of residual lignin; Class 3: holocelluloses content is two to five times higher than lignin content; both classes 2 and 3 correspond to white decomposition agents (Trojanowski 2001).

6.2.2.1 White-Rot Fungi

Industrially white-rot fungi are well known as lignin consumers, found in Basidiomycota phylum. Those comprehend over than 90% of all Basidiomycetes that rot woods. (Riley et al. 2014). This phylum has been studied in several areas, including medicine (Madhanraj et al. 2019), agriculture (Duplessis et al. 2011), and forestry (Martin et al. 2008). This phylum also includes mushrooms (Morin et al. 2012), and pathogens of plants, animals, and other fungi (Duplessis et al. 2011; Dawson and Thomas 2007).

White-rot fungi have great potential to degrade lignocellulosic biomass (Fig. 6.2). Although those fungi also can degrade polysaccharides, they are known as a well specific lignin degrader (Rudakiya and Gupte 2017). Syringyl (S) units of lignin usually are preferred instead of guaiacyl (G) units, due to its less resistance to degradation. In certain conditions, white-rot fungi are lignin-selective depending on several factors, like cultivation time, temperature, wood species, and other variables (Hatakka and Hammel 2011; Hakala et al. 2004). The degradation ability of these fungi has been quite studied not only in lignocellulosic biomass researches, but also in other areas, such as bioremediation, food, pharma, and other industries. These abilities allow the fungi grow in restrictive conditions, such as lignocellulosic wastes. In the last decade, several studies focused on these group showed results to degrade pesticides (Kaur et al. 2016; Gouma et al. 2019), to increase productivity,

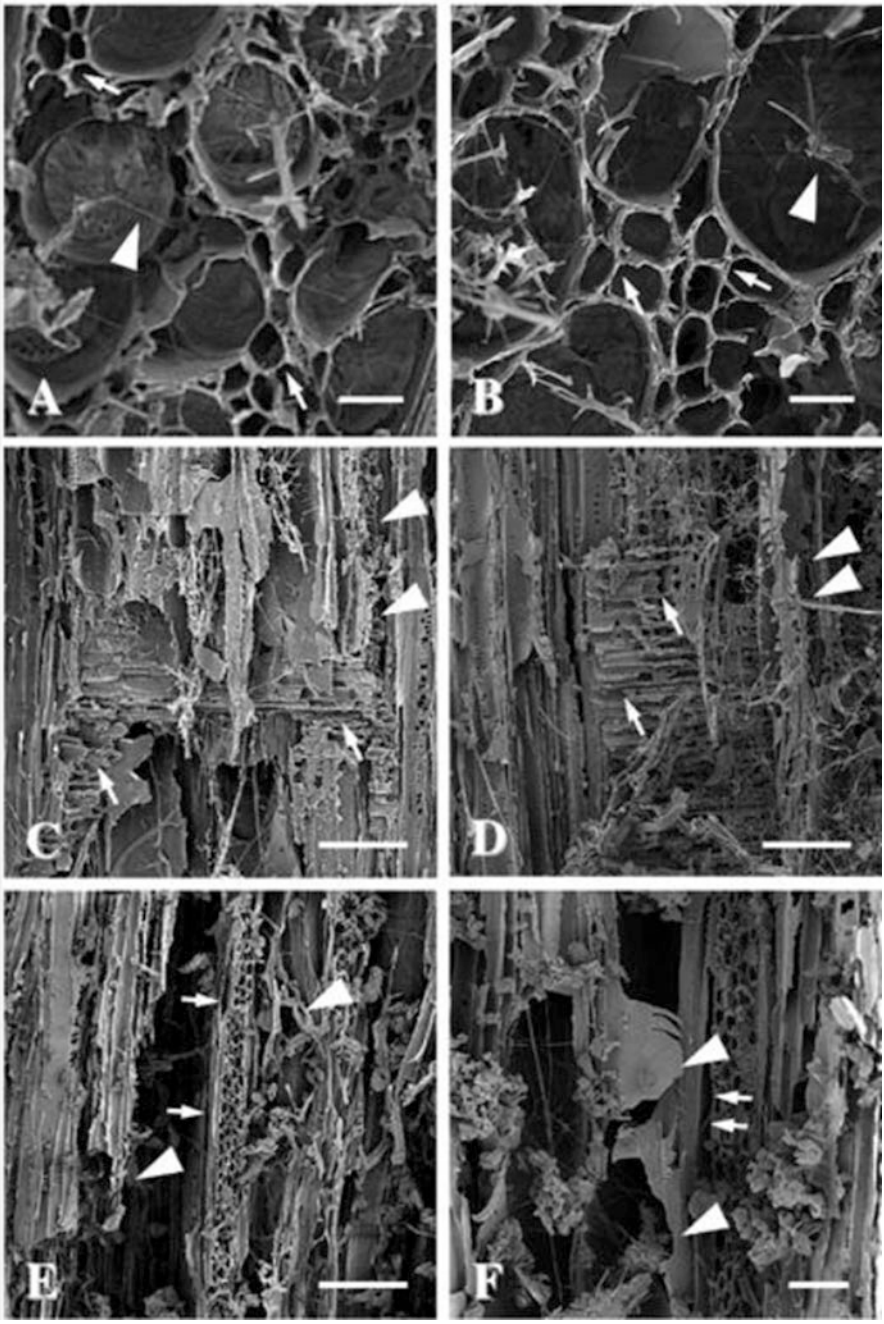

Fig. 6.2 Scanning electron micrographs of beech wood degradation by white-rot fungi after 120 days; (**a**, **c**, and **e**) *Pleurotus ostreatus*; (**b**, **d**, and **f**) *Trametes versicolor*. (**a**) and (**b**) show cross-sections (bar 20 μm): the arrows point cell walls already degraded and arrowheads point colonization of hyphae in the cell lumina; (**c**) and (**d**) show radial sections (bar 100 μm): the arrows point an entire decomposition of ray parenchyma and arrowheads point deconstruction of cell walls

efficiency, and quality of several products (Kushwaha et al. 2018) and applied in pulp and paper industry (Singh 2018).

6.2.2.2 Brown-Rot Fungi

Brown-rot fungi are also found in the Basidiomycota group, representing nearly 7% of this phylum (Hatakka and Hammel 2011; Goodell 2003). Evolutionarily, most of this group are derived from white-rot fungi, probably by losing of decay capability and biodegradative mechanisms (Hibbett and Thorn 2001). Otherwise, white-rot and brown-rot classification are discussed, since new genetic studies suggest continuum rather than a dichotomy between these two groups. In this case, authors suggest that the "white-rot fungi" term would be restricted to fungi that consume all the cell wall macromolecules through activity of lignin-degrading peroxidases (Riley et al. 2014).

The brown color of brown-rot fungi is due to residual lignin left after degradation. It is caused by fungi enzymatic arsenal that degrades polysaccharides: cellulose and hemicellulose contents decrease, and lignin percentage increases in the pretreated material (Felipuci 2020). Hemicellulose degradation is faster and polysaccharide depolymerization involves oxidative components and hydrolytic enzymes (Hatakka and Hammel 2011).

Degradation capacity is widely known in the bio-pulping area. Bio-pulping is a process where wood chips are treated by microorganisms to improve quality and make stronger paper produced. This method removes wood extractives and lignin, reducing toxicity and pitch content (Gupta 2019). Using some species of brown-rot fungi with worms to degrade paper mill sludge is a useful strategy to enhance cellulose decomposition (Negi and Suthar 2018).

6.2.2.3 Bacteria

Bacteria are known to produce cellulolytic, hemicellulolytic, and ligninolytic enzymes that can also be used in biological pretreatment (Sharma et al. 2019). An advantage in comparison to fungal pretreatment is that some bacteria can grow faster than fungi besides degrade lignin into small particles. Those small particles can be recovered to be used as value-added products as well being faster and low cost since it does not need high temperature and many processes after hydrolysis (Hatakka 2005; Kurakake et al. 2007).

Although bacteria can properly degrade lignocellulosic biomass, its sole use as biological pretreatment has not proved efficient. However, it can improve the enzymatic digestion of lignocellulose after applying another pretreatment, such as

Fig. 6.2 (continued) and vessels; (**e**) and (**f**) show tangential sections (bar 100 μm): the arrows point the separation of ray wall with vessels lumina, while arrowhead point disintegration of woody structure (Bari et al. 2018)

physicochemical method (Zhuo et al. 2018). Co-culture using bacteria and/or fungi can degrade lignocellulosic biomass almost completely due to high enzymatic activity. Selecting the best strains that can produce necessary enzymes is essential for an efficient biological pretreatment in order to produce biofuels and bioproducts (Sharma et al. 2019).

6.2.3 *Enzymes Involved in Biological Pretreatment*

The effectiveness of a biological pretreatment depends on enzymes ability to address biochemical and physical barriers to hydrolysis. Therefore, a mix of enzymes can co-work to increase biomass access by expanding small pores and open the cell wall matrix (Amin et al. 2017).

Lignocellulose degradation by microorganisms is mainly accomplished by a system of extracellular enzymes that hydrolyze and oxidize the biomass component (Fig. 6.3). Hydrolases (cellulases and hemicellulases) are produced by hydrolytic system to degrade polysaccharides and oxidative catalytic system to degrade lignin by the production of ligninases (Sajith et al. 2016).

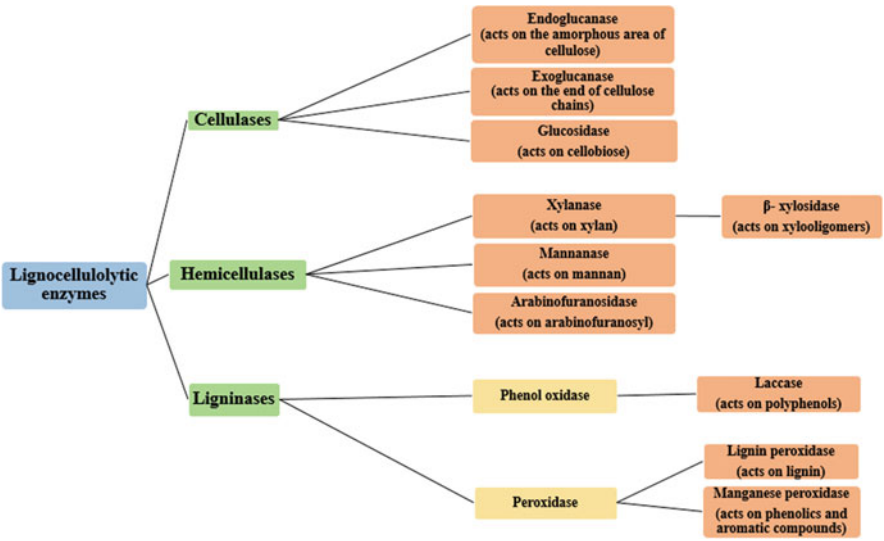

Fig. 6.3 Simplified representation of lignocellulolytic enzymes and their action mode (Sajith et al. 2016)

6.2.3.1 Cellulases

Cellulases are glycosyl hydrolases (GHs) produced by microorganisms while they grow on lignocellulosic materials. They hydrolyze cellulose into shorter chain polysaccharides by breaking down β-1,4-glycosidic bonds. In their structure, they usually have a catalytic domain at the N-terminal and a carbohydrate-binding module at the C-terminal. The catalytic domain cleaves the glycosidic linkage and the carbohydrate-binding module destiny the catalytic domain to the polysaccharide substrate (Jayasekara and Ratnayake 2019; Obeng et al. 2017).

Three main enzymes comprise cellulases enzyme system, endoglucanases (endo-β-1,4-D-glucanases; EC 3.2.1.4), exoglucanases (exo-β-1,4-D-glucanases; EC 3.2.1.91), and glucosidases (β-D-glucoside glucan hydrolases, EC 3.2.1.21). These enzymes are categorized as per their structure and function; however, their collaborative work is essential for complete hydrolysis of the complex cellulose fibers (Sajith et al. 2016).

Endoglucanases generate oligosaccharides with free chain ends by hydrolyzing internal β-1,4-glycosidic bonds and acting randomly on amorphous areas of cellulose. These enzymes can convert cellodextrin (intermediate product of cellulose hydrolysis) into cellobiose and glucose (Singh et al. 2016). Endoglucanases has rapid dissociation, can reduce chain length and viscosity by acting on cellulose but exhibit no activity against crystalline cellulose such as avicel (De Moraes Akamine et al. 2018; Obeng et al. 2017; Sajith et al. 2016).

Exoglucanases act on the crystalline region of cellulose and release cellobiose as product from reducing (EC 3.2.1.91) or non-reducing ends (EC 3.2.1.176). The oligosaccharide chain portion that each enzyme attacks are related to its classification. However, the actions of the enzymes are unidirectional in a long-chain oligomer (Obeng et al. 2017; Singh et al. 2016). These enzymes are more active against crystalline cellulose substrates such as avicel and cellooligosaccharides but do not hydrolyze soluble resultants of cellulose like carboxymethyl cellulose (Jayasekara and Ratnayake 2019; Sajith et al. 2016).

β-glucosidases present rigid structure with an active site that favors disaccharides entry, however, they also can hydrolyze low degree of polymerization soluble cellodextrins. These enzymes act on cellobiose to complete the hydrolysis process of cellulose. As result, glucose with a free hydroxyl group at C^4 from the non-reducing end of oligosaccharides are released (Obeng et al. 2017; Sajith et al. 2016).

Retention and reversion are catalytic mechanisms that lead to successful cellulose hydrolysis. This is performed by two catalytic amino acid residues of the enzymes, a proton donor and a nucleophile. Both of them stereochemically modifies the anomeric carbon configuration, facilitating enzymatic cleavage of the glycosidic bonds (Garvey et al. 2013).

Cellulolytic enzyme multisystem can suffer inhibition by its products. For this reason, β-glucosidases and exoglucanases are essential to alleviate exo- and endoglucanases, respectively, from feedback inhibition. In the same way,

β-glucosidase is also inhibited by glucose, therefore is necessary a search for glucose tolerant β-glucosidases (Obeng et al. 2017). Complementary action of these cellulases is crucial for efficient hydrolysis in order to obtain glucose residues, which can be used for several applications such as the production of biofuel and chemicals. Among microorganisms, fungi are responsible for approximately 80% of cellulose hydrolysis and therefore, considered great cellulase producers (Singh et al. 2016).

6.2.3.2 Hemicellulases

Efficient hemicellulose hydrolysis of lignocellulosic biomass improves hydrolysis yield and consequently reduces enzyme costs and dosages, which makes crucial the use of hemicellulases. They are most often glycoside hydrolases and are usually produced by microorganisms together with cellulases. The hemicellulose backbone of a lignocellulosic biomass can be composed by different polysaccharides, depending on the source (Sindhu et al. 2016; Singh et al. 2016).

Mannan and xylan are the most common hemicelluloses found in nature. Xylan is the main hemicellulose in lignocellulosic biomass from agriculture residues, comprised of xylose units in the backbone chain that are usually linked to acetyl and ferulic groups, arabinofuranosyl or glucuronic acid residues. Therefore, multiple enzymes are necessary to decompose xylan, including endoxylanase (EC 3.2.1.8), β-xylosidase (EC 3.2.1.37) that act on the main chain of xylan. The enzymes that work on the pending groups are α-arabinofuranosidase (EC 3.2.1.55) and α-glucuronidases (EC 3.2.1.139) (Ábrego et al. 2017). In addition, acetyl xylan esterases (EC 3.1.1.72), ferulic acid esterases (EC 3.1.1.73), and p-coumaric acid esterases (EC 3.1.1.x) are also requested for the complete deconstruction of xylan (Chadha et al. 2019). Hemicellulases structures are consisted by a catalytic domain to perform enzyme functions. They can be glycosyl hydrolases that cleave glycosidic bonds or can be carbohydrate esterases that hydrolyze ester bonds, between xylan and acetic acid or ferulic acid substitutions (Juturu and Wu 2013).

Xylanases hydrolyze β-1,4 linkages in xylan backbone chain, producing xylooligosaccharides. Most of them belong to glycoside hydrolase (GH) families 10 and 11, however, enzymes that are exclusively active on D-xylose-containing substrates, known as "true xylanases," are only on family 11 (Tyagi et al. 2019). β-xylosidases hydrolyze a low degree of polymerization xylooligomers, produced by xylan hydrolysis, into xylose. Xylanases action is inhibited by xylooligomers produced in the hydrolysis, therefore β-xylosidases action removes end-product inhibition increasing the efficiency of xylanases (Chadha et al. 2019).

β-mannanases hydrolyze mannan-based hemicelluloses. As result, short β-1,4-mannooligomers are released that can be hydrolyzed into mannose by β-mannosidases. Arabinofuranosidases catalyze the removal of arabinosyl substituents and facilitate an increase in access points of xylanase to xylan Both β-mannanases and arabinofuranosidases are required for mannan or arabinofuranosyl containing hemicelluloses (Terrone et al. 2020). The

α-1,2-glycosidic bond can be broken down by α-D-glucuronidases releasing glucuronic acid from the xylan chain (Chadha et al. 2019; Singh et al. 2016).

Acetyl xylan esterases are enzymes responsible to remove acetyl groups linked to β-D-xylopyranosyl residues by hydrolyzing the ester bonds. The accessibility of enzymes that break the backbone by steric hindrance can be interfered by acetyl side-groups, therefore their removal makes the xylanases action easier. Ferulic acid esterases and p-coumaric acid esterases also catalyze ester bonds on xylan. The first enzymes are recognized to break down ester linkages between ferulic acid and arabinose substitutions on xylan, and the second acts on the bond between arabinose and p-coumaric acid (Chadha et al. 2019; Bajpai 2014).

Hemicelluloses are chemical structure complex, its hydrolysis into its constituent monomers requires catalytic action of versatile enzymes that work synergistically. Hemicellulolytic enzymes can be produced by different fungi and bacteria, however, the source of most commercially important hemicellulases is fungi (Manju and Chadha 2011). They have biotechnological potential and several industrial applications, like hemicelluloses hydrolysis of lignocellulosic biomass, improving cellulose saccharification (Chadha et al. 2019).

6.2.3.3 Ligninases

Lignin is one of the main responsible for recalcitrance in lignocellulosic biomass because its complex structure, protecting polysaccharides (Schmatz et al. 2020). To break down the lignin structure, microorganisms developed some specific extracellular enzymes based on oxidative reactions. In nature, lignin degradation is important to the biogeochemical carbon cycle (Ruiz-Dueñas and Martínez 2009). Those enzymes are also used in the bioremediation process and its action is an important step for lignin removal in industries that work with cellulosic biomass (Jha 2019).

Ligninases are, generally, separated in two different types: phenol oxidases and peroxidases. Laccases are an example of phenol oxidases enzymes. Lignin degradation by laccases (EC 1.10.3.2) is normally by oxidation of phenolic compounds, yielding quinines and phenoxy radicals. Peroxidases make part of oxidoreductases family. This group of enzymes catalyzes lignin depolymerization utilizing H_2O_2 (Sajith et al. 2016).

Laccase enzymes are observed in plants, insects, bacteria, and fungi, mainly in the white-rot group. In fungi, these enzymes are involved not just in lignin degradation but also in sporulation, pigmentation of the fungus, detoxification, and fruiting body (Clutterbuck 1990; Thurston 1994). The molecular weight of laccase is around 50–100 kDa and they are classified as multicopper oxidases, which can be monomeric, dimeric, or tetrameric. Laccase use molecular oxygen to oxidize phenolic rings to phenolic radicals. Laccase can cleave Cα–Cβ cleavage, aryl-alkyl cleavage, and Cα-oxidation. Products may be submitted through non-enzymatic reaction, like polymerization, hydration, or dismutation, or a second enzyme-catalyzed oxidation (Madhavi and Lele 2009; Sajith et al. 2016). With a redox mediators present,

laccases can also catalyze the breakdown of non-phenolic lignin structures, and cleave β-O-4 linkages.

Lignin peroxidase (EC 1.11.10.14) is considered one of the key enzymes in plant cell wall degradation due to its ability to oxidize non-phenol lignin structures. This reaction can cleavage Cα–Cβ bonds, mediating ring-opening reactions. Lignin peroxidases are oxidized by hydrogen peroxide, and, this catalysis results in the creation of intermediate radicals such as phenoxy and veratryl alcohol (Wong 2009; Ruiz-Dueñas and Martínez 2009). Lignin peroxidase and laccase are considered "partners" enzymes in certain conditions, due to substrate provided by lignin peroxidase after lignin degradation (Boominathan and Reddy 1992).

Manganese peroxidase (EC 1.11.1.13) attacks both phenolic and non-phenolic lignin units. This enzyme works as a mediator in enzymatic activity, once it is converted from Mn^{2+} into Mn^{3+}. Several monomeric phenols are oxidized by Mn^{3+} cation, including dyes and phenolic lignin model compounds (Datta et al. 2017).

6.2.4 Enzymatic Hydrolysis of Biological Pretreated Material

In a biorefinery system, lignocellulosic biomass hydrolysis is an essential phase in the whole process, since through hydrolysis intermediate products are obtained by breaking up of macromolecules existent in pretreated biomass (Bichot et al. 2018; Pocan et al. 2018). The intermediate denomination is because these products will be used at a subsequent stage of conversion, the main intermediate products are monomers such as hexoses and pentoses coming from cellulose and hemicelluloses (Loow et al. 2016). Hydrolysis or saccharification can be performed by acid, enzymatic or combined procedures, among the aforementioned, the biological process is possibly the most researched in the last years (Pocan et al. 2018). Hydrolysis by biological routes shows benefits associated to mild temperature in operation, high ratio (quantitative) between obtained product and precursors (monomers), minimal corrosion problems and in enzymatic hydrolysis does not produce inhibitory chemicals that can modify enzymes activities (Amezcua-Allieri et al. 2017; Jahnavi et al. 2017).

The key to the biological hydrolysis of pretreated lignocellulosic biomass is the hydrolytic enzymes; cellulose saccharification happens by deed of cellulolytic enzymes (cellulases), and hemicelluloses splitting befalls by action of hemicellulolytic enzymes (hemicellulases) (Bhardwaj et al. 2019; Barbosa et al. 2020). These enzymes can be synthesized mainly by fungi, bacteria, yeast, or algae through its controlled growth in solid or submersed fermentations (Dotsenko et al. 2018; Aruwajoye et al. 2020). Instead of producing hydrolytic enzymes, there is the alternative to purchase commercial enzymes prepared by different industries dedicated to synthesize and purify enzymatic cocktails that act according to specific conditions in hydrolysis (Flores-Gómez et al. 2018). Table 6.1 shows a summary of some characteristics related to hydrolytic enzymes, their mode of action, product formation, and inhibitory aspects.

Table 6.1 Properties of cellulases and hemicellulases action on lignocellulosic biomass

Macromolecule	Enzyme	EC/Synonym	Act on	Product	Compounds that cause inhibition	References
Cellulose	Endoglycanases	3.2.1.4/ Carboxylmethylcellulases (CMCases)	β-(1 → 4) bonds at non-crystalline sections	Reducing and non-reducing new parts	Cellobiose	Murphy et al. (2013), Park et al. (2019)
	Exoglycanases	3.2.1.91/ Cellobiohydrolases (CBHs) or Avicelases	β-(1 → 4) bonds at cellulose ends and new reducing parts and non-reducing parts	Cellobiose and other glycooligomers	Glycose	Fry (2003), Vianna Bernardi et al. (2019)
	β-glycosidases	3.2.1.21/Cellobiases	β-(1 → 4) bonds at cellobiose	Glycose	Glycose, mannose and galactose	Teter et al. (2014), Hsieh et al. (2014)
Xylan	Endoxylanases	3.2.1.8	β-(1 → 4) bonds at xylan backbone	Xylobiose and other xylooligomers	Xylobiose and Xylotriose	Puchart et al. (2018), Fu et al. (2019)
	β-xylosidases	3.2.1.37	β-(1 → 4) bonds at xylobiose	Xylose	Xylose	Yeoman et al. (2010), Bosetto et al. (2016)
	α-arabinofuranosidases	3.2.1.55	α-(1 → 2), α-(1 → 3) and α-(1 → 5) bonds at xylose-arabinose linkages	Xylose and arabinose	Glycose and galactose	Numan and Bhosle (2006), Yeoman et al. (2010), Malgas et al. (2019)
	α-glucuronidases	3.2.1.139	α-(1 → 2) bonds at glucuronic acid-xylose linkages	Methyl glucuronic acid and xylose	–	Dashnyam et al. (2018), Malgas et al. (2019)
	β-galactosidases	3.2.1.23/lactases	β-(1 → 4) bonds at galactose-xylose linkages	Galactose and xylose	Galactose	Husain (2010) Khosravi et al.

(continued)

Table 6.1 (continued)

Macromolecule	Enzyme	EC/Synonym	Act on	Product	Compounds that cause inhibition	References
						(2015), Malgas et al. (2019)
	Acetyl xylan esterases	3.1.1.6	Acetyl groups located at xylan branches	Acetyl groups	[a]Organophosphate compounds	Montoro-García et al. (2011), Pawar et al. (2016), Razeq et al. (2018)
	Ferulic acid esterases	3.1.1.73	Ester bonds in arabinose-ferulic acid linkages	Arabinose, Ferulic acid and p-coumaric acid (phenolic acids[b])	–	Szwajgier et al. (2010), Lopes et al. (2018)
	p-coumaric acid esterases	3.1.1.73	Ester bonds in arabinose-p-coumaric acid linkages	Arabinose and p-coumaric acid (phenolic acid[b])	–	Lopes et al. (2018)
Linear mannan	Endomannanases	3.2.178	β-(1 → 4) bonds at mannan backbone	Non-reducing new parts and mannobiose and mannotriose	Glycose and galactose	Vries et al. (2005), Da Cruz (2013), Lopes et al. (2018)
	β-Mannosidases	3.2.1.25	Non-reducing new parts and other mannosaccharides	Mannose	Sucrose	McCabe et al. (1990), Da Cruz (2013), Lopes et al. (2018)
	α-Galactosidases	3.2.1.22	α-(1 → 6) bonds at galactose-mannose linkages	Galactose and mannose	[a]Ag^{2+} and Hg^{+}	Da Cruz (2013), Sirisha et al.

						(2015), Lopes et al. (2018)
Galactan	Endogalactanases	3.2.1.89	α-(1 → 3) bonds at galactanan backbone	Galacto-disaccharide Galacto-trisaccharide and Galcto-tetrasaccharide	–	González-Ayón et al. (2019)
	β-galactosidases	3.2.1.23/lactases	β-(1 → 4) bonds at galactose-xylose linkages	Galactose and xylose	Galactose	Husain (2010), Khosravi et al. (2015), Malgas et al. (2019)

[a]Product did not generate in pretreatment and/or hydrolysis of lignocellulosic biomass
[b]Cause inhibition in most of hydrolytic enzymes

Finally, it should be taken into account that hydrolytic enzymes can suffer deactivation by temperature, pH, reaction time, stirring intensity, enzymatic loads, and mixing modes (Balan 2014; Hu et al. 2016; Singhvi and Gokhale 2019). Substrate characteristics and modifications over the enzymatic hydrolysis can increase the material recalcitrance (Wallace et al. 2016). Therefore, it is recommended to develop new researches with new conditions that exploit novel tolerance levels for increasing pretreatment and hydrolysis yields.

6.2.5 *Mechanisms of Cell Wall Degradation by Microorganisms*

During periods of fungal growth, cell wall undergoes structural modifications that allow access to inside components (Riley et al. 2014). Although degrading enzymes are known and studied, degradation can occur in a different manner according to situations: chemical structure and composition of the cell wall are different among woody materials (or non-wood) and enzymatic arsenals of microorganisms are different among them (Fig. 6.4). These factors determine the degradation level of the material and make it difficult to fully understand how biomass is consumed and how the degradation process occurs. Thus enzymes involved in the degradation process must be suitable to each substrate. Furthermore, it is important to evaluate which microorganism and its respective strain are most adequate for each kind of substrate.

Degradation efficiency by microorganisms depends, in many cases, on the chemical structure of molecules and on the presence of efficient enzymes in degrading compounds, which are specific for most substrates (Pereira and De Freitas 2012). Biomass chemical structure can influence the metabolism of the microorganisms, especially regarding rates and extent of biodegradation. In the case of catabolic enzymes that have low specificity for its substrate, xenobiotics with a chemical structure similar to natural compounds can be recognized by an active enzyme system and, consequently, used by microorganisms as a source of nutrients and energy (Pereira and De Freitas 2012).

Carbon sources can influence fungi growth, which can affect growing patterns (Mannaa and Kim 2017). Hyphae development allows better colonization of lignocellulosic material and also penetrate easily to plant cell walls than bacteria, reaching macromolecules unavailable for those microorganisms (Pereira and De Freitas 2012). Enzymes are a crucial tool for the degradation of lignocellulosic biomass. Microorganisms release those enzymes which work in a synergistic and independently action, such as peroxidases, laccases, xylanases, and the other enzymes.

An example of cell wall degradation is proposed in Fig. 6.5 (Zeng et al. 2014). In this degradation proposal, the plant cell wall is degraded by *Phanerochaete chrysosporium*, which is capable to degrade all components of the lignocellulosic biomass. Fungal hyphae attach inside the cell wall, secreting enzymes. Manganese

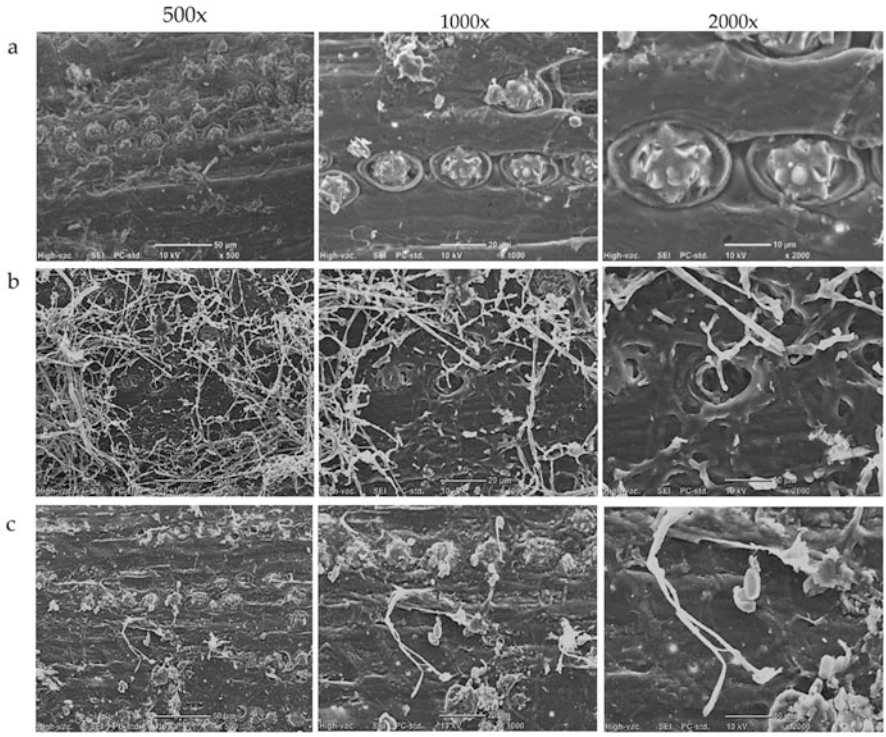

Fig. 6.4 Scanning electron microscope images on the surface of the Oil palm Empty Fruit Bunch. (**a**) Untreated; (**b**) biologically pretreated using *Schizophyllum commune* (ENN1); (**c**) biologically pretreated using *Phanerochaete chrysosporium* (Arbaain 2019)

peroxidases (MnP) oxidize Mn^{2+} to Mn^{3+} and break the phenolic and non-phenolic lignin units (Datta et al. 2017; Wong 2009). Lignin peroxidases (LiP) oxidize non-phenolic structures to mineralized lignin, cleaving Cα–Cβ bonds, mediating ring-opening reactions (Wong 2009; Ruiz-Dueñas and Martínez 2009). This process occurs in the secondary cell wall, in which are located structural carbohydrates as well as aromatic backbone. Cellulases hydrolyze β-1,4-glycosidic bonds and act on the microcrystalline region in cellulose chain to break the cellulose into monomers of cellobiose and D-glucose. Cellobiose dehydrogenases co-work with cellulases to break cellulose chains into small saccharides, generating hydroxyl radicals, H_2O_2, and Fe^{3+}.

Although the process of degradation could be different from all microorganisms, the enzymes work similarly but secreted at a different amount, and one characteristic that can be noticed is the variety of the lignocellulosic structure/composition. In wheat lignin degradation using analytical pyrolysis was revealed that Cα–Cβ bonds and free phenolic units are preferred than non-phenolic units by *Pleurotus eryngii* and *Phanerochaete chrysosporium*. This preferential is due to the redox potential that is lower in comparison with the etherified ones, permitting easier oxidation by

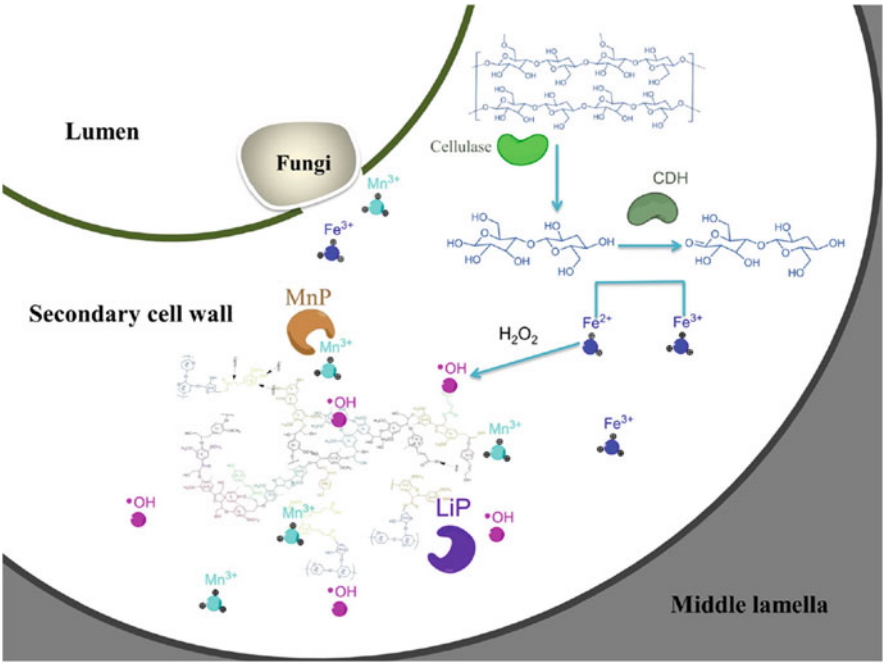

Fig. 6.5 Proposed process of degradation of the wheat straw cell wall by *Phanerochaete chrysosporium* (Zeng et al. 2014)

ligninolytic peroxidases and laccases produced by the fungi. In vitro, applying enzyme in lignocellulosic biomass, *P. eryngii* is capable to reduce the phenolic content of lignin, evidencing its capacity of modifying lignocellulosic materials (Martínez et al. 2001; Camarero et al. 2001). Another example of lignocellulosic biomass deconstruction is with the brown-rot fungi *Penicillium echinulatum*. In this case, using different carbon sources was grown wild-type (2HH) and a mutant strain (S1M29). It was realized that the mutant was more capable to produce cellulases and hemicellulases, showing that the variety of microorganisms can differentiate by the quantity of enzymes produced (Schneider et al. 2016).

6.3 Economic Impacts and Challenges on Industrial Scale Involving Biological Pretreatment

Studies involving biological pretreatments are needed today for several reasons, including environmental friendly process, chemical reduction, and energy savings. There is a growing number of items produced from fossil derivatives such as plastics and tires that are not renewable, in addition to remaining in nature indefinitely. Nevertheless, it is important to mention that a biotechnological route should concern

about energy and chemical reagents applied, aiming to be more advantageous than traditional processes.

For biofuels, specifically, greenhouse gases bring concern and it is on the part of governments. Gas derived from fossil is already being replaced by biofuels, which draws attention to new processes of production and ways to reduce costs. The type of biomass, process complexity, and value of by-product influence the choice of pretreatment (Bajpai 2016). Despite chemical pretreatments holding the main focus on these procedures, biological pretreatments are able to optimize those processes in several levels, for instance: reduce the water, chemicals, and energy spent, generate less inhibitor and toxic compounds, reduce the costs, and improve performance and yield.

In the food industry, one of the most worrying problems is waste since all economic classes in society have a certain degree of waste generation (McCarthy and Liu 2017). This food that is not used can be turned into energy by the biological or thermochemical process. Biological pretreatment in food waste has advantages in comparison with conventional methods of pretreatment such as low cost and simplicity (Pham et al. 2015). Lignocellulosic biomass products can be a source of material and energy in order to support a more sustainable society. Products of direct consumption or second value-added are already present in human life such as paper, fibers and textiles, nanocellulose, organic acids, furfural, and others (Zamani 2015). Food and biofuels are examples where biological pretreatment can be used to improve the productivity and reduce costs. Moreover, several million tons of lignocellulosic are produced annually, and the biological pretreatment can makes this biomass even more useful.

Biological pretreatment can be economical. The extensive number of products that can be produced with lignocellulosic biomass after a biological pretreatment makes harder this count, considering the production cost and sell value of each one. An example, the xylan extraction using biological pretreatment before chemical (H_2O_2) pretreatment reduced the need for the chemical reagent to reach the same results, which means less cost in the process (Felipuci 2020). On the other hand, the production of fermentable sugar by biological pretreatment of corn stover using posterior enzymatic hydrolysis showed to be more expensive (1.41 $/kg) than steam explosion (0.43 $/kg), dilute sulfuric acid (0.42 $/kg), and ammonia fiber explosion (0.65 $/kg) methods (Baral and Shah 2017). In this case, there was no need of detoxification using biological pretreatment. However, this method investigated required reactors, mainly due to long pretreatment time. Biological pretreatment could considerer an option of process outside not using any reactor, but face other problems such as contamination.

Although the advantages of an experimental scale, the use of biological pretreatment in the industry is still a challenge. Recent studies showed the potential of microorganisms in biofuels productions using biological pretreatment (Yahmed et al. 2017; Zabed et al. 2019). However, it is a common view of all the difficulties involved in biological pretreatment on a large scale. Microorganism utilization in biotechnological processes requires certain precautions, which needs to add one or

more steps in the process: contamination and sterilization of growth site are some examples. Furthermore, microorganism growth is slow, while sugars are fundamental as an energy source (Vasco-Correa et al. 2016; Ummalyma et al. 2019). An option to improve the process and pass through those problems is the genetic engineering as well as co-culture of suitable microbial consortium (Sharma et al. 2019).

6.4 Concluding Remarks

Biological pretreatment has several advantages over traditional biomass separation methods. Application of microorganisms and their enzymes, in addition to enhancing the breakdown of lignocellulosic structure, makes the process cheaper and less aggressive to nature. An important advantage is no by-products generation, improving the fermentable sugars production by enzymatic hydrolysis of cellulose, with appreciable cost-benefit, among other benefits.

Microorganisms present great potential for industrial use. Employment of microorganisms in pretreatments, or just their enzymes, can provide a reduction of energy and chemical reagents consumption in the separation process of lignocellulosic biomass macromolecules. Microorganism co-cultivation is a valid technique option with biotechnological potential, once the enzymes produced by the microorganisms can complement each other, achieving a greater degree of degradation. Mechanism degradation of plant cell wall depends on the microorganism in question and, mainly, on its enzyme production and action on lignocellulosic biomass. Even though the use of the micro in the industrial scale requires greater cultivation assistance, it still offers important advantages: there are cost reduction and yield improvement for the biorefinery area and also less chemical residues in the environment.

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