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*Review*

# Plant cell wall composition and enzymatic deconstruction

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**Abstract:** Cellulosic ethanol is one the most prominent technologies capable of replacing the use of fossil fuels in an observable horizon of technological development. The complexity of plant biomass, however, continues to challenge our ability to convert it into biofuels efficiently. Highly complex and cross-linked polysaccharides, hydrophobic and protein adsorbent polymers, and crystalline supramolecular structures comprise some of the structures that shield the plant cell contents (and the shield structures themselves) against predators. In response, a sophisticated enzymatic weaponry, with its associated chemical and physical mechanisms, is necessary to overcome this recalcitrance. Here we describe basic information about chemical composition of lignocellulosic biomass and the enzymatic arsenal for lignocellulose deconstruction into fermentable sugars.

**Keywords:** biomass; cellulose; enzymatic hydrolysis; hemicellulose; lignin; lignocellulose; saccharification

**Abbreviations:** Ara: arabinose; FA: ferulic acid; Fuc: fucose; Gal: galactose; Glc: glucose; GlcA: glucuronic acid; Man: mannose; Xyl: xylose

## 1. Introduction

Currently, our energy is mainly derived from oil reserves. These fossil resources are finite and therefore our economy is unsustainable in the long term. Besides, the intensive and increasing burning of fossil reserves since the industrial revolution has introduced an excessive amount of $CO_2$

into the atmosphere and increased the temperature of the planet. These factors demand the development of technologies that allow us to exploit sustainable energy sources to ensure sustainable economic development [1,2]. Lignocellulosic biomass is the most abundant renewable raw material in nature. The production of plant biomass in the world is about $200 \times 10^9$ tons per year and over 90% of this biomass is lignocellulose [3,4] and has the potential to replace oil in a reasonable scenario of technological development [5]. Currently, sugarcane and maize are the main crops used in the production of ethanol [6] starting from soluble carbohydrates as sucrose and starch [7].

Due to its long history of sugarcane production, Brazil is prominent in the use of biomass to produce ethanol [8]. Bioethanol can be an alternative to gasoline [9]. The United States is currently the main producer of ethanol in the world, primarily using corn starch, while Europe uses wheat starch and sugar beet. In 2013, the total production of ethanol by the United States was 50.3 billion liters [9]. The global production of biofuels was 18.2 billion liters in 2000, 60.6 billion liters in 2007 and 85 billion liters in 2011 [3]. Therefore, almost all ethanol produced in the world today comes from soluble carbohydrates such as sucrose and starch [7].

The global demand for biofuels quadrupled between 2000 and 2008. In 2000, the production of biofuel was 400 petajoule (PJ) per year and in 2008 was nearly 1800 PJ per year [10], justifying investments in the development of technologies to increase ethanol production [11,12,13]. The bioethanol production from sugar feedstock is called "first generation ethanol". Second generation ethanol is made by saccharification of lignocellulosic feedstock as agricultural wastes [3].

In sugarcane plants, after extraction of the soluble carbohydrates, the residual biomass is burned to sustain the energy demands of the industry [14]. Surplus of biomass is usually converted into electricity and sold to distributors or, less commonly, used as cattle feed [15]. As this residual biomass is essentially composed of carbohydrates, it could be partially converted into ethanol, contributing to increased productivity, without competing with food production [16]. Therefore, different sources of lignocellulosic biomass have high potential for bioenergy, mainly monocots plants—rice, wheat, sorghum, tall fescue, giant reed and elephant grass; and some eudicots—poplar, eucalyptus and rapeseed [17].

However, in contrast to the processing of sucrose and starch, degradation of lignocellulosic biomass demands a sophisticated set of enzymes. The complexity of the carbohydrate polymers and their cross-linkages with lignin demands a complex set of enzymes in order to allow the access of polysaccharidases and release fermentable sugars [18]. Lignocellulose is basically composed of plant cell wall components. The recalcitrance of cell walls to enzyme digestion is the result of long-range co-evolution among plants and their predators [19].

Microorganisms and herbivores promote the enzymatic degradation of lignocellulose via multiple carbohydrate-active, lignin-active and accessory enzymes, which typically act together with complementary and synergistic activities [20]. The industrial conversion of lignocellulosic materials into ethanol typically involves: (i) physical or chemical pretreatments to disrupt polymer interactions and make cellulose and hemicellulose more accessible for enzymatic hydrolysis; (ii) saccharification of pretreated biomass by enzyme complexes including cellulases, hemicellulases and accessory enzymes; (iii) fermentation of monosaccharides to produce ethanol or other platform chemicals [21].

However, the technology to produce cellulosic ethanol is still under development and to make the process competitive in terms of cost, it is necessary to improve the efficiency of lignocellulosic degradation [22]. We therefore need to enhance our knowledge about cell wall organization and its enzymatic breakdown. The review describes the basic information about chemical

composition of lignocellulosic biomass and the enzymatic arsenal for lignocellulose deconstruction into fermentable sugars.

## 2. Structure of lignocellulose

Lignocellulose biomass can be divided into polysaccharide—cellulose, hemicellulose and pectin—and non-polysaccharide fractions—lignin, phenolic compounds and proteins [23]. Plant tissues vary widely in structure and composition. The composition and architecture of cell walls vary according to species, cell type, tissue, developmental stage and cell wall layer [24,25]. During plant growth and cell elongation, plant cells produce a primary cell wall, which typically contains cellulose, hemicellulose, pectin and proteins [26]. The primary cell walls of grasses and eudicots share some similarities (i.e. a cellulose fraction embedded in a non-cellulosic fraction) with differences in the abundance and type of different components (Figure 1). After cell elongation, some tissues produce a secondary cell wall, which is deposited inside the primary cell wall, displacing it outwards. The secondary cell wall is a prominent feature of fibers, such as xylem and sclerenchyma. Secondary cell walls are composed of cellulose, hemicellulose and lignin [27,28].

### *2.1. Cellulose*

Cellulose, the most abundant biopolymer, consists of D-glucose units connected to each other by glycoside β-1,4 linkages, with cellobiose as the fundamental repeating unit (Figure 1a), synthesized by cellulose synthase complex [29]. Cellulose chains show an exceptionally high degree of polymerization, with lengths of 2,000 to 25,000 glucose residues [16,30]. These cellulose molecules are interconnected in parallel by hydrogen bonds, generating microfibrils comprising 30 to 36 linear chains, which have a high degree of mechanical resistance and recalcitrance against enzyme attack [31].

### *2.2. Hemicellulose*

The cellulose microfibrils are cross-linked by hemicellulose molecules (also known as cross-linking glycans; Figure 1b–1e). Hemicellulose also impedes the collapse of cellulose microfibrils, preventing the microfibrils from sliding over each other [32]. Finally, the cellulose-hemicellulose network is embedded in a matrix of pectin that may contain lignin [29]. Hemicelluloses are the second major polysaccharide fraction of the cell wall [33].

Compared with cellulose, hemicelluloses are of lower molecular weight, comprising 100 to 200 monomeric units. The backbone of hemicellulose is mainly composed of hexoses (such as D-glucose and D-mannose) or pentoses (such as D-xylose) connected to each other by β-1,4 linkages. Except for β-1,3; β-1,4 mixed linkage glucans found exclusively in grasses, hemicelluloses are heteropolysaccharides presenting different monosaccharides (such as D-galactose, D-fucose, arabinose and D-glucuronic acid) attached to the backbone core [28].

Xyloglucan is the main hemicellulose in eudicots and non-commelinid monocots. It consists of a β-1,4-D-glucose backbone regularly branched by α-(1,6)-linked xylosyl residues, which may be further connected to galactosyl, arabinosyl and fucosyl residues, formally named fucogalactoxyloglucans (Figure 1b) [34].

The main hemicelluloses in eudicots are xyloglucans, xylans and mannans [16]. Xylan is a major hemicellulosic component in grasses, consisting of a β-1,4-linked D-xylose backbone exhibiting different patterns of branching with arabinose and glucuronic acid (Figure 1c). Glucuronoarabinoxylan (GAX) may present hydroxycinnamic acids such as ferulic acid and *p*-coumaric acid, ester-linked to arabinosyl residues of the GAX structure [35].

Mixed-linkage glucans, also simply called β-glucans, are unbranched homopolymers of glucose, alternating short sequences of β-1,4-glucan with single β-1,3-glucans (Figure 1d). β-Glucans are unique to the cell walls of grasses (family Poaceae) and a few related families from the order Poales [28]. The content of β-glucans in vegetative cells is highly correlated with cell growth and expansion, suggesting that β-glucan plays a role in this phase [36].

Mannan is the third most important kind of hemicellulose. Mannans and glucomannans are the main hemicelluloses in charophytes. Their backbones consist of β-1,4-linked mannose, e.g. mannans and galactomannans; or include both mannose and glucose in a non-repeating pattern, as in glucomannans and galactoglucomannans (Figure 1e) [37].

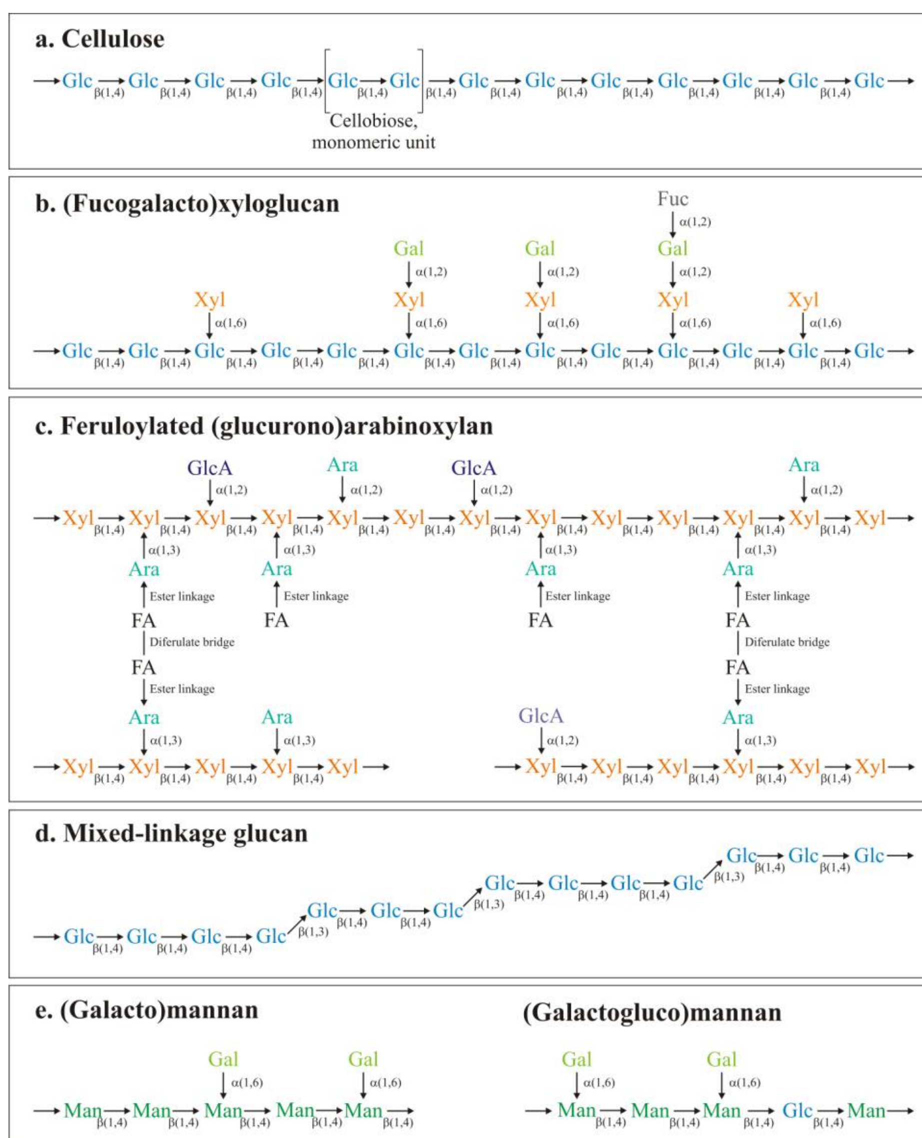


**Figure 1.** Schematic structures of cellulose and hemicelluloses.

### 2.3. Pectin

Pectin is the most complex class of structural polysaccharides, consisting of branched heteropolysaccharides presenting acidic sugars (galacturonic and glucuronic acid) and neutral sugars (rhamnose, galactose and arabinose). Abundant in the middle lamella and in primary plant cell walls [38], it is involved in intercellular adhesion, confers charge and preserves the water content of plant cell walls. Pectin also contributes to the integrity and rigidity of plant tissues and is important in defense mechanisms against pathogens [39]. Pectin is used in the food, cosmetic and drugs industries, e.g. in paper substitutes and biodegradable films [40]. Plant primary cell walls contain approximately 30% pectin in dicotyledonous and non-commelinid monocot plants, while lower levels (2%–10%) are found in grasses and other commelinid plants [39,40].

Pectin contains different monosaccharides, the most abundant being galacturonic acid [38]. Homogalacturonan (HG) is the most abundant pectic polysaccharide. It consists of a linear homogeneous polymer of α-1,4 linked galacturonic acid [40]. Other abundant types of pectin are xylogalacturonan, apiogalacturonan, rhamnogalacturonan I and rhamnogalacturonan II [39].

### 2.4. Lignin

Lignin is the most abundant non-polysaccharide fraction of lignocellulose and the second most abundant biopolymer, after cellulose. It consists of a complex phenolic polymer linked to cellulose and hemicellulose [41]. Corresponding to 15% - 40% of dry weight [42], lignin is present in the plant secondary cell walls of specialized tissues (fibers, vessel, cortex and so on), where it interacts with cellulosic microfibrils, interrupting cell growth and providing mechanical strength to the plant and chemical resistance against pathogens, herbivores and abiotic stresses [43,44].

Lignin is produced by the phenylpropanoid pathway [45], which begins in the cytosol with the deamination of L-phenylalanine to produce cinnamic acid, a reaction catalyzed by phenylalanine ammonia-lyase [46,47]. Afterwards, hydroxylation of the aromatic ring produces *p*-coumaric acid, the first phenylpropanoid in the pathway. Following further hydroxylations and methoxylations at C-3 and C-5 of the aromatic ring, and reduction of the carboxylic acid to an alcohol, these intermediates are converted to three different hydroxycinnamyl alcohols: *p*-coumaryl, coniferyl and sinapyl alcohols, see Figure 2 [48–50].

Specific cell wall peroxidases promote an oxidative polymerization of monolignols resulting in a highly hydrophobic matrix of C-C and C-O-C. The monolignol residues in lignin polymers may be identified by their ring decoration, and are referred to as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively [51,52]. The incorporation of monolignols H, G and S in a growing lignin polymer occur via mutual coupling and cross-coupling of monolignols by inter-linkage β-O-4 (β-ether), β-5 phenylcoumaran, β-β resinol and 4-O-5 biphenyl ether [48].

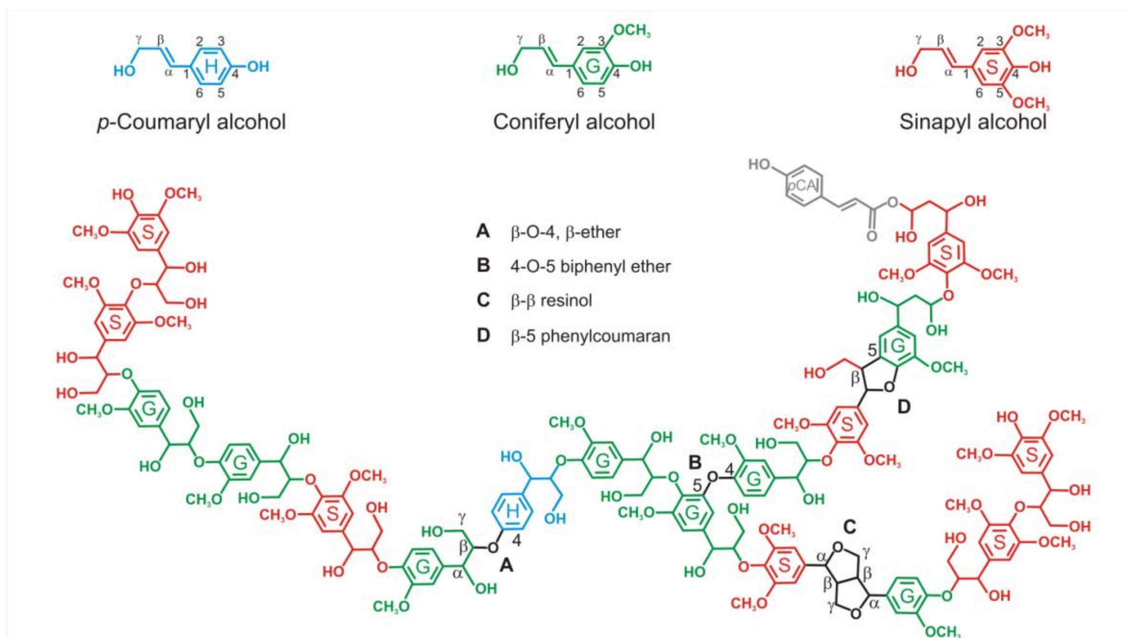


**Figure 2.** Structural components of lignin polymers. The biosynthetic precursors, coniferyl (blue), coniferyl (green) and sinapyl (red) alcohols are shown, as well as *p*-coumarate ester conjugated lignin (gray). The linkages specifically formed by radical coupling reactions are shown in bold and labeled with the type of unit produced in the polymer.

## 3. Enzymatic breakdown of lignocellulose

Different types and large quantities of enzymes are necessary to release fermentable sugars from cell wall components. Table 1 presents different types of enzymes used for the breakdown of cellulose and hemicellulose [53]. Enzymes that modify complex carbohydrates are known as Carbohydrate-Active EnZymes (CAZymes). Collectively they are organized into families: Glycoside hydrolases (GHs), glycosyl transferases (GT), polysaccharide lyases (PL), carbohydrate esterases (CE), and auxiliary activities (AA). The latter group includes oxidative enzymes, such as cellobiose dehydrogenase (CDH) and lytic polysaccharide monooxygenase (LPMO) that are involved in polysaccharide degradation [54,55]. Many CAZymes are modular proteins, consisting of catalytic modules and non-catalytic carbohydrate-binding modules (CBMs) [56,57]. CBMs have an important role in crystalline cellulose degradation and are also found in enzymes that act on glucans, xylans, mannans and glucomannans [57]. CBMs promote the association of enzymes with substrates, potentiating the action of cellulolytic enzymes on insoluble substrates [58–60].

### *3.1. Cellulases*

Cellulases are the primary enzymes used for cellulose hydrolysis. Deconstruction of cellulose is achieved by three predominant activities: Cellobiohydrolase (also called exoglucanase), endoglucanase and β-glucosidase. They act synergistically in the hydrolysis of the cellulose, which reduces problems of product inhibition [21]. Endoglucanases (EC 3.2.1.4) cleave the glycosidic internal bonds of the non-crystalline cellulose portion [61]. Cellobiohydrolases and exoglucanases (EC 3.2.1.91 and EC 3.2.1.176) remove glucose dimers (cellobiose) from the reducing and non-reducing

ends of cellulose chains, respectively [62]. The main distinction between cellobiohydrolase and exoglucanase is that cellobiohydrolase releases cellobiose from crystalline cellulose [63]. Finally, β-glucosidases (EC 3.2.1.21) cleave cellobiose into two glucose molecules [64].

### *3.2. Hemicellulases*

The β-1-4-D-glucose backbone of xyloglucans can be hydrolyzed by the cellulases described above, after elimination of the branches containing xylose, galactose and fucose. Enzymes responsible for the hydrolysis of the xyloglucan backbone are xyloglucan endo-β-1,4-glucanases, EC 3.2.1.151 [65]. Different classes of xyloglucanases present affinities for xyloglucans with different degrees of branching [62].

Degradation of xylan backbones requires at least two different enzymes: 1) endoxylanases (EC 3.2.1.8) hydrolyze glycoside linkages from the xylan chain releasing xylooligosaccharides; 2) β-xylosidases (EC 3.2.1.37) hydrolyze xylobiose and xylooligosaccharides from the non-reducing end. The xylanase group of enzymes have different specificities for xylan backbones depending on the kind and degree of branching [66]. α-Arabinofuranosidases (EC 3.2.1.55) act on α-glycosidic bonds of arabinofuranoses (Araf) branching from the xylan backbone [67,68], while α-glucuronidases (EC 3.2.1.139) hydrolyze xylan linked with glucuronic acid [69]. Acetyl xylan esterases (EC 3.1.1.72) remove acetyl groups [70,71], and feruloyl esterases (EC 3.1.1.73) hydrolyze ester-linked ferulic and *p*-coumaric acids attached to Araf branches in xylan chains and pectin [72,73]. Feruloyl esterases present synergistic actions with xylanase, β-glucosidase, arabinofuranosidase and other accessory enzymes in the degradation of cell walls [74,75]. These synergies may reduce the quantity of enzyme necessary for saccharification and reduce the costs of bioethanol production from lignocellulosic biomass [76,77]. The enzymatic saccharification system using feruloyl esterase combined with accessory enzymes could contribute to the production of fermentable sugars for bioethanol production [35].

The structurally heterogeneous nature of mannans requires associations and synergistic actions among a variety of cleaving enzymes such as endo-β-mannanase (EC 3.2.1.78), exo-β-mannosidase (EC 3.2.1.25), β-glucosidase (EC 3.2.1.21), acetyl mannan esterases (EC 3.1.1.6), and α-galactosidase (EC 3.2.1.22) for efficient enzymatic hydrolysis [37]. Endo-β-mannanases, also referred to simply as mannanases, hydrolyze the endo-β-(1,4)-glucose-mannose backbone of galacto(gluco)mannans, releasing predominantly mannobiose and mannotriose. β-Mannosidases hydrolyze β-(1,4)-glucose-mannose, releasing mannose from the non-reducing end of manno-oligosaccharides [37].

Degradation of mixed linked β-glucans is catalyzed by linkage specific β-glucanases. Depending on the type of glycosidic linkage they cleave, β-glucanase is grouped into four main categories, namely β-1,3;1,4-glucanases (lichenases; EC 3.2.1.73), endoglucanases (cellulases; EC 3.2.1.4), β-1,3-glucanases (laminarinases, EC 3.2.1.39) and β-1,3(4)-glucanases (EC 3.2.1.6) [62].

### *3.3. Pectinases*

Pectinases or polygalacturonases (pectin depolymerases) form a heterogeneous group of enzymes with the capacity to hydrolyze α-1,4-glycosidic linkages of pectate present in plant cell walls [78]. Pectins are extremely important for cell wall growth and extension [79]. Pectinases have a potential application in improving ethanol production from various feedstocks, as pectinase treatment requires less energy and produces no inhibitory factors [80–82].

**Table 1.** The main enzymes required to degrade cellulose and hemicellulose to monomers.

| Group of enzymes | Enzymes | Linkages breakdown |
|---|---|---|
| Cellulases | Cellobiohydrolase | β-(1,4)-Glc |
| | Endoglucanase | Endo-β-(1,4)-Glc |
| | β-Glucosidase | β-(1,4)-Glc |
| Hemicellulases | Endoxylanase | Endo-β-(1,4)-Xyl |
| | β-Xylosidase | β-(1,4)-Xyl |
| | β-Glucanase/lichenase | β(1,3)-Glc, β(1,4)-Glc |
| | Feruloyl esterase | Ester linkage FA-Ara |
| | *p*-Coumaroyl esterase | Ester linkage *p*CA-Ara |
| | Arabinofuranosidase | α-(1,2)-Ara, α-(1,3)-Ara |
| | Glucuronidase | α(1,2)-GlcA |
| | 4-O-Glucuronoyl methylesterase | α-(1,2)-4-O-metil-α-glucuronic |
| | Xyloglucanase | Endo-α-(1,4)-Glc |
| | Fucosidase | α-(1,2)-Fuc |
| | α-Galactosidase | α-(1,3)-Gal, α-(1,6)-Gal |
| | Mannanase | Endo-β-(1,4)-Glc-Man |
| | β-Mannosidase | β-(1,4)-Glc-Man |
| | Acetyl xylan esterase | α-(1,2)-Xyl |

### *3.4. Ligninases*

Ligninases are laccase, lignin peroxidase and manganese peroxidase. These enzymes are able to hydrolyze the lignin fraction, improving polysaccharide degradation by glycosyl hydrolases, and reducing the recalcitrance of lignocellulosic biomass, as well as decreasing the adsorption of lignin to enzymes [83].

Laccases (EC 1.10.3.2) are copper-containing enzymes with four copper atoms in the catalytic center [84]. They catalyze the oxidative cleavage of phenolic compounds, producing radicals [12]. Lignin peroxidase (EC 1.11.1.7) and manganese peroxidase (EC 1.11.1.7) are the two largest classes of glycoproteins in the peroxidase group. They present a heme group that requires hydrogen peroxide as an oxidant [12]. Laccases play an important role in lignin biosynthesis. Plant cells secrete peroxidases and laccases into the apoplast for the polymerization of monolignols by radicals [85], while fungi and bacteria secrete them for lignin depolymerization [86].

## 4. Pretreatments of lignocellulosic biomass

Lignocellulosic biomass presents several features that confer recalcitrance, such as crystalline cellulose which precludes decomposition by enzymes [87]; highly complex hemicelluloses and pectin, which demands a huge number of enzymes; the high degree of lignin adsorption to proteins

that inhibits enzymatic activity [88]; and the complex cross-linkages between phenolic and polysaccharide components [35,89]. Biological, chemical and physical pretreatments can reduce the crystallinity of lignocellulose and break various linkages, drastically reducing its complexity [17].

Biological pretreatments have been widely studied and have demonstrated some advantages over chemical and physical pretreatments such as a low demand for energy, environmental friendliness and low levels of toxic products [90]. Biological pretreatments include in vivo application of microorganisms [91], for example, brown, white and soft rot fungi that produce hydrolytic enzymes such as laccase and manganese peroxidase that degrade lignin [92].

Chemical pretreatments strongly improve the biodegradability of cellulose [93]. In alkali pretreatments, biomass is mixed with bases such as sodium or potassium hydroxides. These pretreatments promote modifications in the cell wall structure and increase enzyme accessibility for saccharification [94]. Acid hydrolysis mostly employs sulfuric acid, but phosphoric acid, hydrochloric acid and nitric acid are also used to remove lignin [95]. In addition, microwave energy has been applied to facilitate alkaline and acid pretreatments [96]. Pretreatments that use organic solvents are known as organosolv and utilize aliphatic alcohols, polyols (e.g. glycerol), acetone or phenol as solvents to promote delignification. Organic solvents improve removal of lignin content and reduce the viscosity of the pretreatment medium [97].

Physical pretreatments are used to enhance lignocellulosic porosity. Milling procedures are the most traditional physical pretreatment used in laboratories [98]. Although effective, milling is energy intensive and only mild milling procedures have been shown to be industrially viable. Ultrasonic pretreatment induces mechanical vibrations and cavitations that help to disrupt tissues [99]. One of the most promising pretreatment methods is steam explosion. It consists of compression and fast decompression of the biomass to increase the porosity of the lignocellulosic material and facilitate the access of hydrolytic enzymes. The process has been demonstrated to be efficient for biomasses containing low amounts of lignin [7,94].

The extraction of lignin by pretreatments improves saccharification [100]. Although in principle these treatments are feasible, they still require a substantial technological development to become cost and energy efficient enough for industrial application [7,101].

## 5. Conclusions

Lignocellulose has a complex and varied composition that, although reasonably well known, is still a challenge for efficient conversion in biorefineries. Development of technologies that improve the efficiency of generation of biofuels and platform chemicals from lignocellulose has been the focus vigorous scientific efforts. While bioethanol has real potential as an oil replacement, considerable technological advances are necessary to reduce financial and energetic costs and make the biochemical conversion of lignocellulose into biofuels a commercial reality.

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## Conflict of interest

All authors declare no conflicts of interest in this paper.

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