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Characterization of Lignocellulolytic Enzymes from White-Rot Fungi

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Abstract The development of alternative energy sources by applying lignocellulose-based biofuel technology is critically important because of the depletion of fossil fuel resources, rising fossil fuel prices, security issues regarding the fossil fuel supply, and environmental issues. White-rot fungi have received much attention in recent years for their valuable enzyme systems that effectively degrade lignocellulosic biomasses. These fungi have powerful extracellular oxidative and hydrolytic enzymes that degrade lignin and cellulose biopolymers, respectively. Lignocellulosic biomasses from either agricultural or forestry wastes are abundant, low-cost feedstock alternatives in nature but require hydrolysis into simple sugars for biofuel production. This review provides a complete overview of the different lignocellulose biomasses and their chemical compositions. In addition, a complete list of the white-rot fungi-derived lignocellulolytic enzymes that have been identified and their molecular structures, mechanism of action in lignocellulose hydrolysis, and biochemical properties is summarized in detail. These enzymes include ligninolytic enzymes (laccase, manganese peroxidase, lignin peroxidase, and versatile peroxidase) and cellulolytic enzymes (endo-glucanase, cellobiohydrolase, and beta-glucosidase). The use of these fungi for low-cost lignocellulolytic enzyme production might be attractive for biofuel production.

Abbreviations

AAO	Aryl-alcohol oxidase
BGL	Beta-glucosidase
CMC	Carboxy methyl cellulose
CMCase	Carboxymethyl cellulase
Cpd-I	Compound I
Cpd-II	Compound I
DTT	Dithiothreitol
EG	Endo-glucanase
CBH	Cellobiohydrolase
CBQ	Cellobiose:quinone oxidoreductase
CDH	Cellobiose dehydrogenase
FDH	NAD-dependent formate dehydrogenase
GLO	Glyoxal oxidase
LiP	Lignin peroxidase
MnP	Manganese peroxidase
ODC	Oxalate decarboxylase
*p*I	Isoelectric point
pNPC	*p*-Nitrophenyl-beta-D-cellobioside
pNPG	*para*-Nitrophenyl beta-D-glucopyranoside
pNPL	*p*-Nitrophenyl-beta-D-lactoside
SDS-PAGE	Sodium dodecyl sulfate polyacrylamide gel electrophoresis
VA	Veratryl alcohol
VP	Versatile peroxidase

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Introduction

In 2011, global CO_2 emission from fossil fuel combustion reached 31.6 gigatonnes, which accounted for 35 % of the global CO_2 emission, while coal and natural gas accounted for 45 and 20 % of the global CO_2 emission [48]. Rising energy consumption levels, the depletion of fossil fuels, and environmental concerns have spurred the search for alternative energy generation methods for biofuel utilization. Based on World Energy Council calculations, the worldwide primary energy consumption is approximately 12 billion tons of coal equivalent per year. The world's population is projected to increase from 6.4 billion in 2005 to 9.3 billion in 2050; proportionally, global primary energy consumption could double from 11.4 billion tons (2005) to 22.3 billion tons (2050) coal equivalent per year depending on economic, social, and political developments [100].

In Brazil and the United States of America, ethanol is usually produced from cane juice and starch crops [97], which depletes our food supply and poses ethical and economic problems. These concerns have become a driving force in the generation of new biofuel research using lignocellulosic biomasses as a major source of biofuel production, as the annual production of this type of biomass has been estimated at approximately 10–50 billion tons worldwide [98]. Lignocellulose biomass is a complex biopolymer consisting of cellulose, hemicellulose, pectin, and lignin. Hardwood stems contain 18–25 % lignin, 40–55 % cellulose, and 24–40 % hemicellulose, while softwood stems contain 25–35 % lignin, 45–50 % cellulose, and 25–35 % hemicellulose [97]. However, the current bottleneck for lignocellulosic biofuel production is the high cost of lignocellulolytic enzyme production for the efficient hydrolysis of biomass to sugar. Lignocellulosic biomass residue-mediated biofuels could provide environmental benefits (reduced greenhouse gas emissions and air pollution levels, which could slow global warming), would be economically feasible, and could be produced in large quantities, without competing with food supplies, for biofuel production. Such biofuels would also be free of public health and social conflict issues.

A highly degradation-resistant lignin polymer is part of a complex matrix into which cellulose microfibrils are embedded. This type of lignin polymer reduces the accessibility of efficient saccharification of the cellulose microfibrils. Moreover, a current constraint to chemical and physical strategies, such as treatment with acid, alkali and steam, to remove lignin from lignocellulose biomass is the formation of lignin-derived compounds. These compounds can inhibit the downstream processes of saccharification and fermentation, which can be partially overcome by treatment with lignocellulolytic enzymes [54]. Several microbes, including bacteria and fungi, have evolved to degrade lignocellulose biomass by producing synergistic ligninolytic enzymes [e.g., laccase, manganese peroxidase (MnP), lignin peroxidase (LiP), and versatile peroxidase (VP)] and cellulolytic enzymes [endo-glucanase (EG), cellobiohydrolase (exo-glucanase or CBH), and beta-glucosidase (BGL)]. However, only a few groups of fungi, such as white-rot fungi, brown-rot fungi, and soft-rot fungi, can degrade lignocellulose biomass effectively. Among these, white-rot fungi, such as *Auricularia polytricha*, *Coriolus versicolor*, *Flammalina velutipes*, *Ganoderma lucidum*, *G. applanatum*, *G. australe*, *G. capense*, *G. carnosum*, *G. fornicatum*, *G. gibbasum*, *G. resinaceum*, *G. stipitatum*, *G. trabeum*, *Irpex lacteus*, *Phanerochaete chrysosporium*, *Pleurotus sajor-caju*, *Pleurotus ostreatus*, *Pleurotus dryinus*, *Pleurotus tuberregium*, *Lentinus edodes*, *Trametes hirsuta*, and *Trametes versicolor* [5, 7, 26–28, 30–32, 59, 74, 90, 96, 105], have the ability to degrade both lignin and cellulose biopolymers in lignocellulose biomass. Other lignocellulose-degrading fungi include brown-rot and soft-rot fungi, which can also effectively depolymerize cellulose biopolymers into simple sugars; however, lignin can only be partially degraded [97]. Compared to fungi, the metabolism of lignin by bacteria is less well characterized, and based on the differences in the resulting product profile, bacteria are known to exhibit different actions in this process [13].

The identification of lignocellulolytic enzymes in a complex secretome has several disadvantages, such as reagent cross-reactivity, limits in detection sensitivity, a lack of Ribonucleic acid stability, and the choice of primer sets; additionally, these types of gene expression methods cause high numbers of false-positive/false-negative results. A false-positive result means the detection of an effect that is not present, while a false-negative result fails to detect an effect that is present [63]. However, to overcome these issues, in recent years, sensitive, quantitative proteomics technologies have been developed that offer the opportunity to study the entire secretome of a sample in a single experiment, enabling the identification of a diverse set of proteins from a complex biological sample [72].

In recent years, white-rot fungi-derived lignocellulolytic enzymes have been employed in various industrial applications, especially in the pre-treatment and hydrolysis stages of biorefinery systems [127]. Accordingly, the following review discusses lignocellulose biomass degradation systems and provides an overview of the specific enzymes involved in these processes. In this review, the chemical compositions of different lignocellulose biomasses are summarized. Additionally, this review summarizes the list of identified lignocellulolytic enzymes from white-rot fungi and their physicochemical properties.

Structure and Chemical Composition of Lignocellulosic Residues

Lignocellulose consists of lignin (an aromatic polymer), carbohydrates (such as cellulose and hemicellulose), pectin (a heteropolysaccharide), proteins, ash, salt, and minerals, and the compositions (Supplemental Table 1) and proportions of these compounds vary among various plants. Each layer of a plant cell wall contains cellulose, hemicellulose, and lignin, but the S2-layer of the secondary wall is particularly rich in cellulose, while the middle lamella has the highest percentage of lignin [102]. A representative scheme of lignocellulosic biomass is illustrated in Fig. 1.

Lignocellulose Degradation by Fungi

Lignocellulose biomass is highly resistant to microbial degradation. This is due to the presence of lignin, the degree of crystallinity of the cellulose, the degree of polymerization of the polysaccharides, the available surface area, and the moisture content [97]. The organisms predominantly responsible for lignocellulose degradation are fungi (Supplemental Table 2), which are classified by the type of degradation, namely, white-rot fungi, brown-rot fungi, and soft-rot fungi. White-rot fungi break down the lignin in wood, leaving lighter colored (white) cellulose behind; some of these fungi break down both lignin and cellulose by producing powerful extracellular oxidative and hydrolytic enzymes. Brown-rot fungi degrade wood polysaccharides (cellulose and hemicellulose), while partially modifying lignin. As a result of this type of decay, the wood shrinks, shows a brown discoloration due to oxidized lignin, and cracks into rough cubical pieces. Soft-rot fungi secrete cellulase, an enzyme that breaks down cellulose but not lignin in wood, from their hyphae, which leads to the formation of microscopic cavities inside the wood and sometimes to a discoloration and cracking pattern similar to that of brown-rot fungi. In addition, soft-rot fungi need fixed nitrogen to synthesize enzymes, which they obtain either from the wood or from the environment. Soft-rot fungi can usually be found in dry environments but are mostly known to occur where brown-rot and white-rot fungi are inhibited by factors such as high moisture, low aeration, the presence of preservatives, or high temperatures [1, 76].

White-Rot Fungi Lignin-Degrading Enzyme Systems

LiP (EC1.11.1.14), MnP (EC 1.11.1.13), VP (EC 1.11.1.16), and laccase (EC 1.10.3.2) are the major lignin-degrading enzyme systems of white-rot fungi [20, 26, 27,

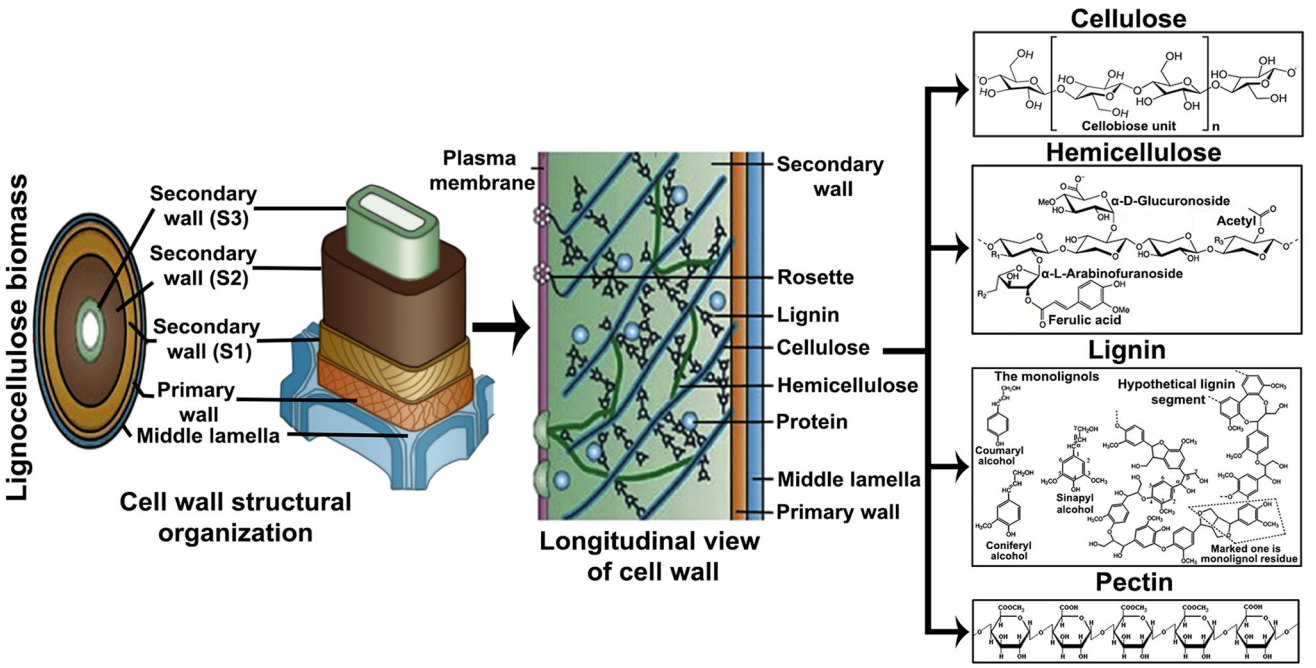

Fig. 1 Diagrammatic structure and chemical composition of lignocellulose residues. The plant cell wall contains three major layers, namely, the middle lamella (which is the first layer formed during cell division and is rich in pectic compounds and protein), the primary wall (which is formed after the middle lamella and consists of a rigid skeleton of cellulose microfibrils embedded in a gel-like matrix composed of pectic compounds, hemicellulose, and glycoproteins), and the secondary wall (which is a thick layer made of cellulose, hemicellulose, and lignin that is formed inside the primary cell wall after the cell is completely grown and is extremely rigid and provides compression strength; it is often layered)

29, 69, 73, 90]. Additionally, some accessory enzymes, such as cellobiose dehydrogenase (CDH), glyoxal oxidase (GLO), aryl-alcohol oxidase (AAO), oxalate decarboxylase (ODC), NAD-dependent formate dehydrogenase (FDH), P450 monooxygenase, glutathione reductase, copper radical oxidase, isoamyl alcohol oxidase, peroxiredoxins, benzoquinone reductase, pyranose 2-oxidase, multicopper oxidase, glutathione *S*-transferase, glucose oxidase, and manganese superoxide dismutase, have been isolated from white-rot fungi [3, 4, 20, 26, 29, 69, 73, 87] (Supplemental Table 3). Recently, Chen et al. (2012) reported that the ligninolytic enzyme-encoded genome of *G. lucidum* contains a set of 36 ligninolytic oxidoreductases, including 13 laccases, eight class-II peroxidases, one cellobiose dehydrogenase, three aryl-alcohol oxidases, nine copper radical oxidases, one benzoquinone reductase, and one alcohol oxidase [20].

LiPs (EC1.11.1.14)

Fungal LiPs are globular in structure and are mostly helical glycoproteins of approximately 30–50 kDa with an isoelectric point (*p*I) of 3.2–4.0 [7, 43, 91]. LiP was initially reported from the white-rot fungus *P. chrysosporium* [61]. LiPs are capable of mineralizing lignin, dyes, and a variety of recalcitrant pollutants [106]. The optimum pH and temperature for LiPs from different sources may vary significantly with optimum activities observed between pH 2–5 and a temperature of 35–55 °C, respectively [6]. Xerogel matrix-entrapped and mesoporous silica-immobilized LiPs have a broad range of temperature and pH conditions and inactivating agents, respectively [7, 46]. LiPs catalyze the oxidation of veratryl alcohol (VA) using H_2O_2 in aqueous solution in three intermediate stages (Fig. 2). The enzyme LiP contains iron (Fe^{3+}) in its active site, which oxidizes H_2O_2 while forming an intermediate compound I (Cpd-I) known as LiP oxyferryl ([LiP]$P^{\bullet+}$–Fe^{4+}=O). Cpd-I is then reduced by VA via one-electron transfer and forms another intermediate, compound II (Cpd-II) ([LiP]P–Fe^{4+}=O). Finally, Cpd-II is reduced again to its initial form [LiP]P–Fe^{3+} via another electron transfer [45, 68]. Inhibitors, such as acetone, dioxane, diethylether, acetonitrile, dimethylformamide, cationic surfactant cetyltrimethylammonium bromide, and H_2O_2 (higher concentration), were reported as LiP inhibitors from different fungi [19, 68, 122].

MnPs (EC 1.11.1.13)

MnPs are extracellular glycoproteins with an iron protoporphyrin IX (heme) prosthetic group and are secreted as multiple isoforms with molecular weights varying between 32 and 62.5 kDa, at an optimum pH of 4–7 and an optimum temperature of 40–60 °C [6, 70, 114]. However, a MnP from *Bjerkandera adusta* with an optimum pH as low as 3.0 has been reported [38]. MnP was first discovered in *P. chrysosporium* [35, 88]. The catalytic mechanism of MnP is depicted in Fig. 3, and it is similar to that of LiP but differs in utilizing Mn^{2+} as the electron donor. The reaction of MnP is initiated by the native ferric enzyme and H_2O_2 to form a MnP Cpd-I, which is a Fe^{4+}-oxo-porphyrin-radical complex. A monochelated Mn^{2+} ion donates one electron to the porphyrin intermediate to form Cpd-II and is oxidized to Mn^{3+}. The native enzyme is generated from Cpd-II in a similar way through the donation of one electron from Mn^{2+} to form Mn^{3+}. The chelated Mn^{3+} ion generated by MnP acts as a diffusible charge-transfer mediator, allowing for the oxidation of various phenolic substrates, such as simple phenols, amines, dyes, and phenolic lignin model compounds [45]. The activity of the MnP is completely inhibited by Hg^{2+}, Pb^{2+}, Ag^{+}, lactate, NaN_3, ascorbic acid, beta-mercaptoethanol, and dithreitol [6, 57].

VPs (EC 1.11.1.16)

VP (EC 1.11.1.16) is a heme-containing ligninolytic peroxidase with a hybrid molecular architecture combining MnPs and LiPs. VP was first described from the white-rot fungus *Pleurotus eryngii* [77] as having a molecular weight

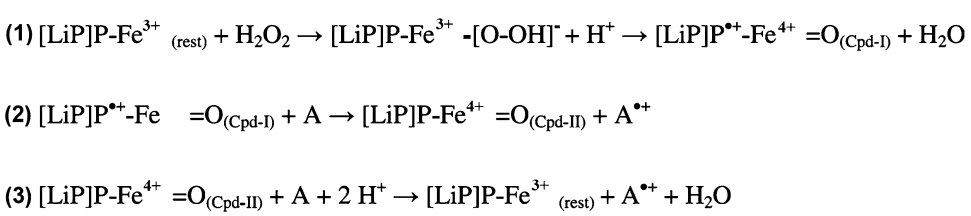

Fig. 2 Catalytic cycle of lignin peroxidase (LiP) (adapted from [45, 68]). *P* porphyrin ring system; *rest* resting state; *Cpd-I* compound I; *Cpd-II* compound II; *A* nonphenolic aromatic substrate (e.g., a nonphenolic beta-*O*-4 lignin model compound or VA (veratryl alcohol)); $A^{\bullet+}$ aryl cation radical of A. The LiP co-factor iron (Fe^{3+}) oxidizes H_2O_2 and forms an intermediate Cpd-I called LiP oxyferryl ([LiP]$P^{\bullet+}$–Fe^{4+}=O). Cpd-I is then reduced by VA via one-electron transfer, and it forms another intermediate called Cpd-II ([LiP]P–Fe^{4+}=O). Finally, Cpd-II is reduced again to its initial form, [LiP]P–Fe^{3+}, via another electron transfer

(1) $[MnP]P\text{-}Fe^{3+}{}_{(rest)} + H_2O_2 \rightarrow [MnP]P\text{-}Fe^{3+}\text{-}[O\text{-}OH]^- + H^+ \rightarrow [MnP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + H_2O$

(2) $[MnP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + Mn^{2+} \rightarrow [MnP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + [Mn^{3+}\ chelate]$

(3) $[MnP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + Mn^{2+} + 2\ H^+ \rightarrow [MnP]P\text{-}Fe^{3+}{}_{(rest)} + [Mn^{3+}\ chelate] + H_2O$

(4) $[Mn^{3+}\ chelate] + Phe\text{-}OH \rightarrow Mn^{2+} + PheO^{\bullet} + H^+$

Fig. 3 The MnP catalytic cycle (adapted from [45]). *P* porphyrin ring system; *rest* resting state; *Cpd-I* compound I; *Cpd-II* compound II; *[Mn^{3+} chelate]* chelate complex of organic acids (e.g., oxalate) and reactive Mn^{3+}; *Phe–OH* phenolic compound; *Phe–O*$^{\bullet}$ phenoxyl radical. The MnP reaction is initiated by the native ferric enzyme MnP and H_2O_2 to form a MnP Cpd-I ([MnP]$P^{\bullet+}$–Fe^{4+}=O). A monochelated Mn^{2+} ion donates one electron to the porphyrin intermediate to form Cpd-II ([MnP]P–Fe^{4+}=O) and is oxidized to Mn^{3+}. The native enzyme is generated from Cpd-II in a similar way through the donation of one electron from Mn^{2+} to form Mn^{3+}. The chelated Mn^{3+} ion generated by MnP acts as a diffusible charge-transfer mediator, allowing for the oxidation of various phenolic substrates, such as simple phenols, amines, dyes, and phenolic lignin model compounds

(1) $[VP]P\text{-}Fe^{3+}{}_{(rest)} + H_2O_2 \rightarrow [VP]P\text{-}Fe^{3+}\text{-}[O\text{-}OH]^- + H^+ \rightarrow [VP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + H_2O$

(2a) $[VP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + Mn^{2+} \rightarrow [VP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + [Mn^{3+}\ chelate]$

(3b) $[VP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + A \rightarrow [VP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + A^{\bullet+}$

(4c) $[VP]P^{\bullet+}\text{-}Fe^{4+}{=}O_{(Cpd\text{-}I)} + Phe\text{-}OH \rightarrow [VP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + PheO^{\bullet} + H^+$

(5abc) $[VP]P\text{-}Fe^{4+}{=}O_{(Cpd\text{-}II)} + Mn^{2+}\ or\ A\ or\ Phe\text{-}OH + 2\ H^+ \rightarrow [VP]P\text{-}Fe^{3+}{}_{(rest)} + [Mn^{3+}\ chelate]\ or\ A^{\bullet+}\ or\ PheO^{\bullet} + H_2O$

Fig. 4 Catalytic cycle of VP adopted from [45]. Porphyrin (P), nonphenolic high-redox potential aromatic substrates (A) such as VP or a nonphenolic beta-O-4 lignin model, aryl cation radical ($A^{\bullet+}$) of A, phenolic compound (Phe–OH), phenoxyl radical ($PheO^{\bullet}$). The VP co-factor iron (Fe^{3+}) oxidizes H_2O_2 and forms an intermediate Cpd-I called oxyferryl VP ([VP]$P^{\bullet+}$–Fe^{4+}=O) and H_2O. Cpd-I is then reduced by VA via one-electron transfer and forms another intermediate called Cpd-II ([VP]P–Fe^{4+}=O). A monochelated Mn^{2+} ion donates one electron to Cpd-I ([VP]$P^{\bullet+}$–Fe^{4+}=O) to form Cpd-II ([VP]P–Fe^{4+}=O) and is oxidized to Mn^{3+}. The phenolic compound (Phe–OH) donates one electron to Cpd-I ([VP]$P^{\bullet+}$–Fe^{4+}=O) to form Cpd-II ([VP]P-Fe^{4+}=O), phenoxyl radical ($PheO^{\bullet}$) and H^+ ion. Finally, Cpd-II is reduced again to its initial form [VP]P–Fe^{3+} via another electron transfer by Mn^{2+}, A, or Phe–OH

of 38–45 kDa and a *p*I of 3.7 [18, 81]. The VP enzyme has the same catalytic activity as LiP and MnP and is able to catalyze the oxidation of Mn^{2+}, VA, dyes, and phenolic and nonphenolic aromatic compounds [45]. The catalytic cycle of VP combines both LiP and MnP, but this cycle differs from the classical MnPs by catalyzing the Mn^{2+}-independent oxidation of simple amines and phenolic monomers [89]. The catalytic versatility of VP permits its application in Mn^{3+}-mediated or Mn-independent reactions in both low- and high-redox potential aromatic substrates (Fig. 4). Although VP from *P. eryngii* catalyzes the oxidation of Mn^{2+} to Mn^{3+} with H_2O_2, it differs from classical MnPs in its manganese-independent activity, thereby enabling it to oxidize substituted phenols and synthetic dyes as well as the LiP substrate, VA [17]. VP genes were first cloned and sequenced from *P. eryngii* [16] and also recently from *Antrodia cinnamomea* [47]. The activity of VP can be inhibited by NaN_3, Tween-80, anthracene, and fluorene, whereas *p*-aminobenzoic acid is able to enhance the activity of VP [92].

Laccases (EC 1.10.3.2)

Laccases are extracellular N-glycosylated multicopper blue oxidases with a molecular weight that varies from 38 to 150 kDa, although some laccases from *P. eryngii* and *Podospora anserine* have been reported with molecular weights of 34 and 383 kDa, respectively [82, 118]. A laccase was first reported from *Toxicodendron vernicifluum* (*Rhus vernicifera*), a Japanese lacquer tree [125]. Laccases have also been found in plants, fungi, and bacteria [22, 34, 79] and are particularly widely distributed in wood-degrading fungi, such as *T. versicolor*, *G. lucidum*, *P. chrysosporium*, and *P. eryngii* [8, 20, 74]. Purified laccases from *G. lucidum* have been reported to consist of 7–10 % N-linked carbohydrates [62]. The optimal pH and temperature of laccases from different white-rot fungi vary from 2 to 10 and from 30 to 70 °C, respectively [74, 84, 110, 117, 118]. Recently, a laccase from *Coltricia perennis* has been reported as having optimal activity at 75 °C [56]. Interestingly, four laccase isozymes (Glac 1, 2, 3, and 4) could be identified in *G. lucidum* [74].

Laccases catalyze a one-electron oxidation with a concomitant four-electron reduction of molecular oxygen to water (Fig. 5). Laccase catalysis requires four copper atoms arranged at two sites: a blue type-1 (T1) mononuclear copper center and a trinuclear copper cluster consisting of one type-2 (T2, or normal copper) center and two type-3 (T3, or coupled binuclear copper) centers. The four copper atoms are held in place at the catalytic center of the enzyme by four histidine-rich, copper-binding regions [23]. The copper atoms each differ in their spectroscopic and paramagnetic properties. The T1 copper is characterized by a strong absorption approximately 600 nm, which gives the enzyme its blue color, whereas the T2 copper exhibits only weak absorption in the visible region. The T2 site is electron paramagnetic resonance (EPR)-active, whereas the two copper ions at the T3 site are EPR-silent due to an antiferromagnetic coupling mediated by a bridging ligand. The mononuclear T1 copper is the primary electron acceptor site at which the enzyme catalyzes four 1-electron oxidations of the substrate. The electrons extracted from the reducing substrate are transferred to the T2/T3 trinuclear center where oxygen is reduced to water [80]. Yellow laccase has been reported from *Panus tigrinus* [66], which lacks a characteristic absorption band at approximately 600 nm; hence, it is called yellow laccase or untrue laccase.

In most cases, the addition of Cu^{2+}, Cd^{2+}, Ni^{2+}, Mo^{2+}, or Mn^{2+} ions increases the activity of white-rot fungus laccases, whereas Ag^{+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, NaN_3, NaCl, and H_2O_2 inhibit their activity [84, 113]. Immobilization of laccase on alginate beads increases its stability and enhances the catalytic activity of the enzyme to allow for repeated use in dye decolorization applications [99].

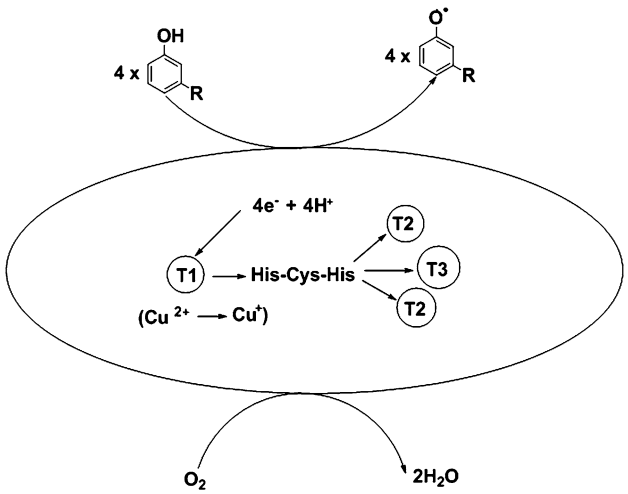

Fig. 5 Catalytic mechanism of laccase (adopted from [80]). T1, type 1 copper ion; T2, type 2 copper ion; and T3, type 3 copper ion. The substrates (phenolic compounds) are oxidized by T1 copper, and the extracted electrons are transferred via a strongly conserved His–Cys–His tripeptide motif to the T2/T3 site, where molecular oxygen is reduced to water. For further details, see the main text

White-Rot Fungi Cellulose-Degrading Enzyme Systems

The structural integrity of cellulose is one of the main obstacles to the enzymatic hydrolysis of cellulose [36]. The cellulose hydrolyzing enzymes from various white-rot fungi are divided into three major groups, namely, EG, CBH, and BGL [20, 27, 52, 53, 69, 73, 124] (Supplemental Table 3). Recently, Chen et al. (2012), identified 417 genes from *G. lucidum* that encode carbohydrate-active enzymes, including 288 with glycoside hydrolase domains, 70 with glycosyltransferase domains, 30 with carbohydrate esterase domains, 10 with polysaccharide lyase domains, and 53 with carbohydrate-binding modules [20].

EGs (EC 3.2.1.4)

The EGs catalyze the random cleavage of internal bonds in the cellulose chain by releasing cellobiose or cello-oligosaccharides, as depicted in Fig. 6. EGs were isolated from several white-rot fungi, namely, *G. lucidum*, *G. applanatum*, *Ganoderma boninense*, *Ganoderma neo-japonicum*, *G. australe*, *P. chrysosporium*, *P. ostreatus*, *Pleurotus gibbosa*, *T. hirsuta*, *Trametes ochracea*, *Trametes pubescens*, *T. versicolor*, and *Fomes fomentarius* [26, 27, 29, 53, 72, 73, 124]. Recently, an EG from *G. lucidum* with a molecular weight of 42.67 kDa and a *p*I of 4.67 was reported [73]. EGs with molecular weights of 18 and 28 kDa were isolated from the culture filtrates of the K3 strain of *P. chrysosporium* [41, 49]. An EG characterized from *I. lacteus* possessed a molecular weight of 15.5 kDa [58]. EG I from *Volvariella volvacea* was shown to have a molecular weight of 42 kDa, as determined by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) [25]. Three carboxymethyl cellulases (CMCases) from *Polyporus arcularius* were purified and were estimated to have molecular weights of 39.1, 36.3, and 24.3 kDa [50]. An *Armillaria gemina* EG with a molecular weight of 65 kDa has been purified using single-step purification by gel filtration [51]. Most of the *p*I values for the fungal cellulolytic enzymes are typically acidic in nature, between 2.0 and 6.0 [2, 72, 73], but the EGs isolated from *V. volvacea* and *Rhodotorula glutinis* exhibit a *p*I of 7.7 and 8.57, respectively [25, 86].

The EGs of white-rot fungi and other types of fungi have a maximal catalytic activity at a pH between 4.0 and 6.0 [9, 51, 58, 60]. However, an unusually acidic pH of 3.1 and even a slightly alkaline pH of 7.5 have been reported from *Trametes trogii* and *V. volvacea*, respectively [25, 67]. Optimal temperatures for EGs from white-rot fungi are

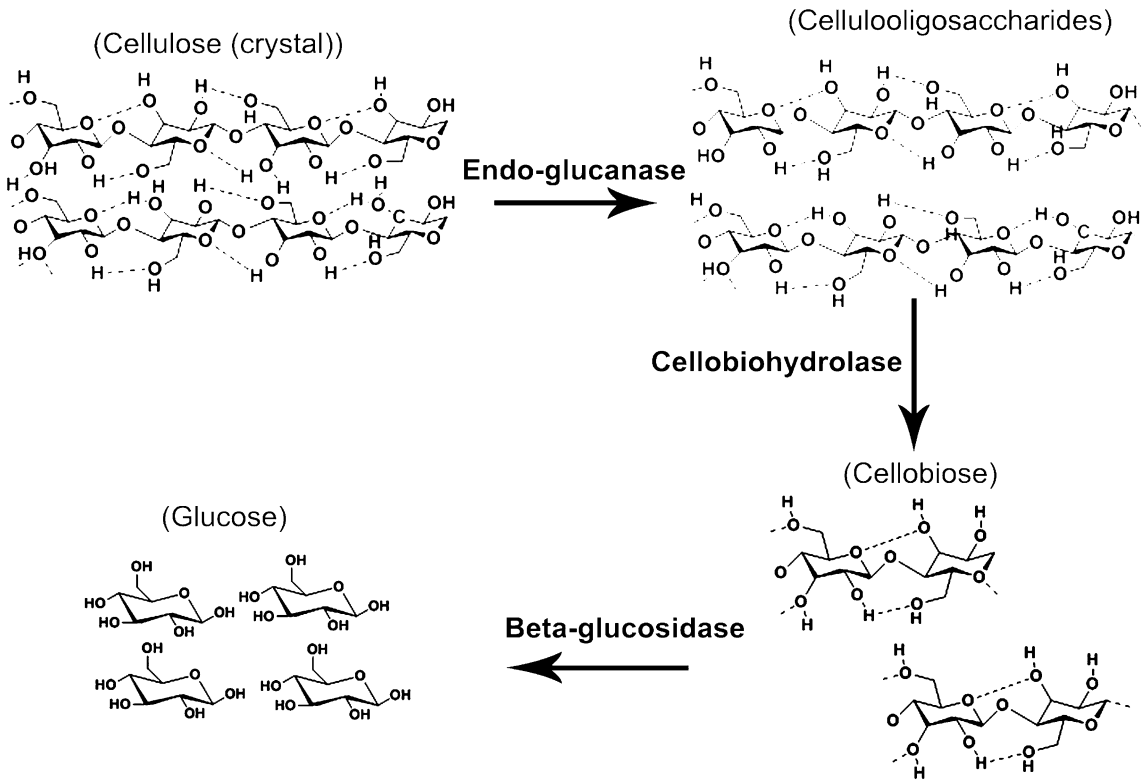

Fig. 6 Schematic representation of the enzymatic hydrolysis of cellulose. Endo-cellulase catalyzes the random cleavage of internal bonds in the cellulose chain by releasing cellobiose or cello-oligosaccharides. Cellobiohydralase cleaves cellulose chains at their terminal ends to release cellobiose or cellulo-oligosaccharides. Beta-glucosidase acts on cellobiose or gluco-oligosaccharides to release glucose molecules

between 45 and 70 °C [9, 50, 51, 67]. The optimal temperatures for purified EG during CMC hydrolysis are approximately 50 and 60 °C, as previously reported for *I. lacteus* and *A. gemina*, respectively [51, 58]. The optimal temperature for *P. arcularius*-derived CMCase I and II activities, as determined by viscometric analysis, was 68 °C; whereas CMCase IIIa exhibited maximum activity at 52 °C [50]. Purified EG from *Trametes trogii*, *V. volvacea*, and *A. gemina* exhibited optimal activity at temperatures of 45, 55, and 60 °C, respectively [25, 51, 67].

CMC, amorphous cellulose, crystalline cellulose, and cello-oligomers (cellotetraose and cellotriose) are all good substrates for most of the EGs reported from *P. arcularius*, *Fomitopsis palustris*, and *Piptoporus betulinus* [50, 115]. The apparent colorimetric K_m values of CMCase I, II, and IIIa against CMC were 0.35, 0.26, and 0.26 mg/ml, respectively [50]. The K_m values for barley-beta-glucan are 2 and 6.66 mg/ml for EG I and EG II, respectively, and for CMC, the K_m values are 20 mg/ml for EG I and 13.3 mg/ml for EG II [60]. The K_m values for *p*-nitrophenyl-beta-D-cellobioside (pNPC) are between 7 and 16 mM [41, 75, 115]. The *A. gemina*-derived and purified EG had the highest catalytic efficiencies with CMC (k_{cat}/K_m = 3,590 mg/ml/s) than reported for any other fungal EG, thus highlighting the significance of this study [51]. The effect of metal ions and chemical activity has been reported for EGs derived from *Melanocarpus* sp. (strain MTCC 3922) [60]. The presence of beta-mercaptoethanol, SDS, and dithiothreitol (DTT) inhibits the activity of EG I, while no negative effect could be observed on EG II. It was further observed that the presence of $CaCl_2$ and $ZnSO_4$ decreased EG I activity by 20 and 40 %, respectively. However, $FeSO_4$ and $MnSO_4$ had a significant negative effect on EG II [60]. The cellobiose and palladium complex has been reported to be a strong inhibitor of EG [107, 128, 130].

CBHs (EC 3.2.1.91)

CBHs are monomeric proteins with little or no glycosylation, and these enzymes cleave cellulose chains at their terminal ends to release cellobiose or cellulo-oligosaccharides, as depicted in Fig. 6 [24]. CBHs have been characterized from several white-rot basidiomycetes, namely *G. lucidum*, *G. applanatum*, *Ganoderma boninense*, *Ganoderma neo-japonicum*, *G. australe*, *I. lacteus*, *Dichomitus squalens*, *Schizophyllum commune*, *P. chrysosporium*, *Auricularia fuscosuccinea*, *Pleurotus giganteus*, *P. gibbosa*,

P. eryngii, *P. ostreatus*, and *P. sajor-caju* [3, 4, 21, 37, 73, 94, 112].

The CBH enzymes are usually monomeric with a molecular weight typically ranging between 39 and 65 kDa, although *D. squalens*-derived CBH is smaller with a CBH II molecular weight of 36 kDa (*D. squalens*-derived CBH I is 39 kDa) [37, 65, 94]. In contrast, a dimeric form CBH has been isolated from *Agaricus arvensis* with a relative molecular weight of the monomer of 65 kDa, as determined by SDS-PAGE, and of 130 kDa, as characterized by size-exclusion chromatography, thus indicating that the native enzyme acts as a dimer [65]. Secretome analysis of *P. chrysosporium* revealed five CBH proteins using liquid chromatography–tandem mass spectrometry (LC–MS/MS) when cultivated in minimal media containing lignin, cellulose, and micronutrients [72]. Two CBHs have been reported for *Coniophora puteana* with molecular weights of 52 kDa for CBH I and 50 kDa for CBH II estimated by SDS-PAGE; however, the molecular weights were slightly higher (65 and 60 kDa, respectively) when determined by fast protein liquid chromatography and gel filtration. Both enzymes were glycosylated, and treatment with endoglycosidase H gave rise to two distinct polypeptides for which the molecular weights decreased to only 6.5 kDa for CBH I and to 2.5 kDa for CBH II [101]. The molecular weights and carbohydrate contents of two CBHs from *I. lacteus* were also different, namely, CBH I (53 kDa, 2.0 %) and CBH II (56 kDa, 4.0 %) [37]. The *p*I values for CBHs are acidic, typically between 3.6 and 4.9 [37, 101], whereas in *F. palustris*, the *p*I has been reported to be as low as 2.3 [44].

The optimum catalytic activity of most CBHs from basidiomycetes occurs in a narrow pH range between 4.0 and 5.0 [37, 67, 94]. The optimal temperatures of CBHs are usually between 37 and 60 °C, depending on the specific isoenzyme and its substrate [37, 94], but optimum temperature as high as 70 °C has been reported from *D. squalens* [94]. CBH I and CBH II from *C. puteana* are both active on amorphous cellulose [101]. Only enzymes acting from the reducing ends are able to liberate cellobiose from *p*-nitrophenyl-beta-D-cellobioside (pNPC) or *p*-nitrophenyl-beta-D-lactoside (pNPL), and the K_m values are between 2 and 7 mM [9, 65]. Some CBHs are also active on cellotriose, cellotetraose, or higher cellodextrins [9, 44, 101]. Palladium complexes and cellobiose have been reported as strong inhibitors of CBH I [107, 128].

BGLs (EC 3.2.1.21)

BGLs are monomeric, dimeric, or even trimeric proteins that act on cellobiose or gluco-oligosaccharides and release glucose molecules, as depicted in Fig. 6 [24]. BGLs have been reported from many basidiomycetes, namely, *G. lucidum*, *Ganoderma neo-japonicum*, *P. chrysosporium*, *Ceriporiopsis subvermispora*, *S. commune*, *A. fuscosuccinea*, *P. ostreatus*, *Trametes gibbosa*, and *T. versicolor* [3, 4, 12, 33, 53, 71, 73, 83, 119].

The molecular weights of BGLs typically vary between 35 and 640 kDa [9]. BGLs reported from *T. versicolor* are glycosylated up to 90 % with molecular weights of approximately 300 kDa [24]. Recently, a BGL form *G. lucidum* has been reported with a molecular weight of 45.78 kDa and a *p*I of 4.96 [73]. An intracellular BGL has been reported from *P. chrysosporium* with a molecular weight of 410 kDa [108]. Similarly, two intracellular BGLs have been identified from *V. volvacea* with molecular weights of 158 kDa (BGL I) and 256 kDa (BGL II) [14]. The cellular localization of BGLs from *V. volvacea* has been described as 10 % extracellular, 26 % cell wall-associated, and 64 % intracellular [15]. The *p*I values of extracellular BGLs are acidic, typically between 3.5 and 5.2, but a near neutral *p*I value of 6.7 has been reported for extracellular BGLs from *F. fomentarius* [116]. However, intracellular BGL enzymes usually have *p*Is, ranging between 6.2 and 7.0 [9].

The optimum pH values of BGLs are usually in a range from 3.5 to 5.5 [9, 67]. However, a neutral pH of 7.0 has also been reported from *V. volvacea* for the isoform BGL I [15], and the intracellular BGL enzyme from *P. chrysosporium* also has a neutral optimum pH of 7.0 [108]. The optimum pH values of BGL, when acting with *p*-nitrophenyl-xyloside, *p*-nitrophenyl-cellobioside, *p*-nitrophenyl-galactoside, and *p*-nitrophenyl-mannoside, were 6.0, 3.5, 5.0, and 4.0–6.0, respectively [116]. The optimal temperatures are between 45 and 75 °C [9, 67], although an optimum temperature of 40 °C has been reported from *T. gibbosa* [12]. The activities of BGL are typically measured using artificial substrates such as pNPG, cellobiose, and sophorose. Cello-oligosaccharides are usually good substrates, but the enzymes are inactive on crystalline cellulose and exhibit only low activity on amorphous high molecular weight cellulose [9]. The K_m value of BGL from *F. fomentarius* was 0.062 μM when pNPG was used as a substrate [116]. Palladium complexes, Hg^{2+}, Fe^{3+}, Cu^{2+}, and glucose (competitive inhibitor) have been reported as strong inhibitors of BGL [12, 107].

CDHs (EC 1.1.99.18)

CDH is an extracellular enzyme produced by basidiomycetes and ascomycetes. It efficiently oxidizes cellobiose, as well as soluble cellodextrins, mannodextrins, and lactose, to their corresponding lactones using a wide spectrum of electron acceptors, including quinones, phenoxy radicals, Fe^{3+}, Cu^{2+} cytochrome *c*, or triiodide ions [42, 129].

CDHs reported from basidiomycetes are monomeric proteins with molecular weights of 90–110 kDa and

glycosylation of approximately 10–20 % [9, 109]. Recently, CDHs have been identified from *G. lucidum* and *Grifola frondosa* with molecular weights of 82.09 and 79.6 kDa, respectively, as well as with *p*I values of 5.06 and 4.32, respectively [73, 126]. The *p*I values of CDHs are typically between 4.0 and 5.0 [9, 73, 85, 109]. CDHs possess K_m values of 10–200 mM when cellobiose is used as the substrate, and the optimum pH levels for quinone reduction are between 4 and 5 [9, 85]. Optimal temperatures are typically between 30 and 55 °C [10, 39] but can be as high as 60–75 °C as reported from *T. hirsuta*, *Phlebia lidnteri*, *Pichia pastoris*, and *Pycnoporus cinnabarinus*, respectively [11, 85, 109, 111].

CDH is an extracellular redox enzyme of a so-called 'ping-pong' type that generates hydroxyl radicals by reducing Fe^{3+} to Fe^{2+} (Fig. 7) and O_2 to H_2O_2, which plays an important role in both lignin and cellulose hydrolysis by (i) breaking beta-ethers, (ii) demethoxylating aromatic structures in lignin, and (iii) introducing hydroxyl groups in nonphenolic lignin [40, 42, 78]. Furthermore, CDH can be converted into a lignin-degrading cellobiose:quinone oxidoreductase (CBQ) via proteolytic cleavage [120]. However, detailed research on the CDH protein is required to elucidate its exact role in the lignin degradation mechanism to tailor its potential industrial CDH-mediated lignin degradation applications; information about the CDH gene, identified in *G. lucidum* by Liu et al. (2012), might also be useful [69].

White-Rot Fungi Hemicellulose-Degrading Enzyme Systems

Various enzymes are responsible for the degradation of hemicelluloses (Fig. 8). For instance, in xylan degradation, endo-xylanase (EC 3.2.1.8), beta-xylosidase (EC 3.2.1.37),

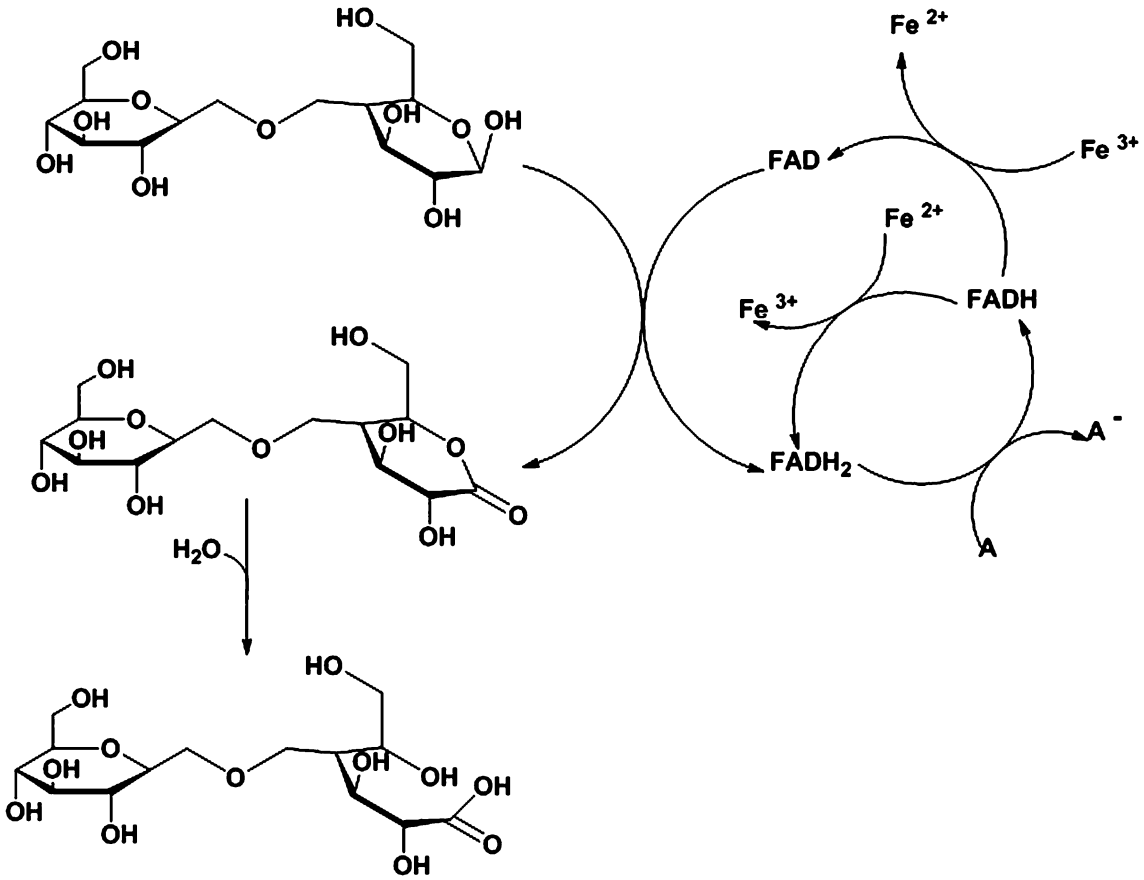

Fig. 7 Catalytic mechanism of cellobiose dehydrogenase (adopted from [9, 40]). $Fe^{2+/3+}$ represents the heme ion, and A/A^- represents the one-electron acceptor. In the electron sink model, the electron acceptor reacts directly with the reduced flavin, $FADH_2$. This model is based on the assumption that the FADH created reacts more slowly with the electron acceptor than does the fully reduced enzyme. Electron exchange between the flavin radical and the heme, which works here as an electron sink, will increase the time that the flavin is in the fully reduced and oxidized stage, thereby increasing the overall k_{cat}. In the electron chain model, the electrons are transported individually to the heme and eventually to the electron acceptor. The electron sink model is supported by the fact that all known electron acceptors, including cytochrome *c*, are reduced by the FAD-containing fragment of CDH

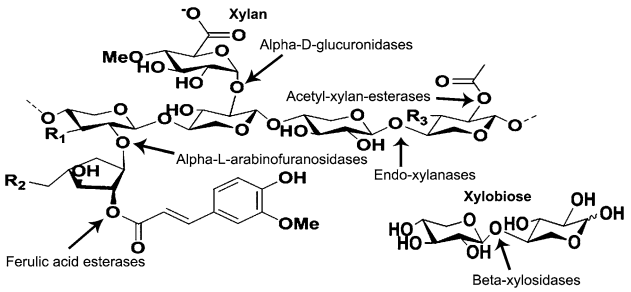

Fig. 8 Schematic representation of the enzymatic hydrolysis of hemicelluloses (adopted from [103]). Alpha-L-arabinofuranosidase hydrolyzes the terminal nonreducing alpha-L-arabinofuranoside residues in alpha-L-arabinosides. Alpha-D-glucuronidase hydrolyzes the alpha-1,2 glycosidic bond between either D-glucuronic acid or its ether 4-*O*-methyl-D-glucuronic acid and D-xylose residues of xylo-oligosaccharides (aldouronic acids) from xylan. Acetyl xylan esterase catalyzes the deacetylation of xylans and xylo-oligosaccharides. Beta-xylosidase hydrolyzes xylobiose into D-xylose molecule. Endo-xylanase hydrolyzes beta-1,4-xylan into xylose. Ferulic acid esterase acts on carboxylic ester bonds of feruloyl-polysaccharide with H_2O and releases ferulate and polysaccharide

alpha-glucuronidase (E.C. 3.2.1.131), alpha-L-arabinofuranosidase (EC 3.2.1.55), acetyl xylan esterase (EC 3.1.1.72), and ferulic acid esterase (EC 3.1.1.73) all act on different hetero-polymers available in nature [95, 103]. In glucomannan degradation, beta-mannanase (EC 3.2.1.78) and beta-mannosidase (EC 3.2.1.25) cleave the polymer backbone [55, 95, 103].

Endo-xylanase, alpha-galactosidase, and endo-mannanase have been identified from *G. lucidum* with molecular weights of 30.8, 48.99, and 49.12 kDa, respectively [73]. The relative molecular weight of *Coprinus cinereus*-derived xylanase was determined to be 20.1 kDa by SDS-PAGE, indicating that the enzyme is a monomer [64]. The *p*I values of endo-xylanase, alpha-galactosidase, and endo-mannanase from *G. lucidum* are 5.43, 4.59, and 4.24, respectively [73]. The hydrolytic activity of the xylanase had an optimum pH of 7.0 and an optimum temperature of 60 °C [64] (Supplemental Table 3).

White-Rot Fungi-Derived Pectin-Degrading Enzyme Systems

The complex and heterogeneous structure of pectin requires degradation by the combined action of different enzymes that are classified according to their mode of action and by the substrate upon which they act. These enzymes include polygalacturonases, which degrade homogalacturonan through the hydrolysis of glycosidic bonds and are classified as endo-polygalacturonase (E.C. 3.2.1.15) and exo-polygalacturonase (E.C. 3.2.1.67). Additionally, the other subclass of homogalacturonan-degrading enzymes are broadly termed depolymerases, which break α-1,4-linkages via a trans elimination mechanism, namely, pectate lyases (E.C. 4.2.2.2) and pectin lyases (E.C. 4.2.2.10). The acetyl, methyl, and feruloyl residues of pectin are removed by pectin methylesterases (E.C. 3.1.1.11), pectin acetylesterases (E.C. 3.1.1.6), and pectin feruloyl esterases (EC 3.1.1.73). The main role that pectinases play is to degrade pectin found as structural polysaccharides in the middle lamella and primary cell wall of young plant cells [123].

Thus far, pectinolytic enzymes from different white-rot fungi, namely, *Lentinus* sp., *Trametes* sp., *Pycnoporus sanguineus*, *P. chrysosporium*, and *S. commune,* have been identified [121]. Exo-polygalacturonase from *P. sanguineus* and endo-polygalacturonase from *P. chrysosporium* have been purified and found to have molecular masses of 42 and 41.7 kDa, respectively [93, 104]. The optimum temperature and pH of endo-polygalacturonase from *P. chrysosporium* were reported as 66 °C and 4.7, respectively [104], while exo-polygalacturonase from *P. sanguineus* acts at 50–60 °C and at a pH of 4.8 [93]. The *p*I values of the endo-polygalacturonase isoenzymes were 4.26, 4.46, and 4.64 from *P. chrysosporium* [104].

Conclusion

The production of fungal enzymes for lignocellulose degradation and biofuel production still requires comprehensive research on thermo-stable protein identification, gene mutation, and engineering to make the enzymes more readily available at lower costs. In recent years, white-rot fungi have received much attention due to their potential lignocellulolytic enzyme-mediated bioconversion of lignocellulose biomasses into simple sugars. However, the characterization of white-rot fungi-derived lignocellulolytic enzymes requires further studies to identify novel enzymes with industrial application potential in lignocellulose degradation technologies. Recent advances in sensitive proteomic technologies offer opportunities to study the entire fungal proteome of any sample in a single experiment to identify a diverse set of proteins from such a complex biological sample.

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